

NATIONAL CHEMICAL LABORATORY

Half-yearly report

April/September 1966

NATIONAL CHEMICAL LABORATORY

Poona-8

HALF-YEARLY REPORT

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S.No.	page
SPONSORED PROJECTS	
1. Calcium silicate ... ..	1
2. Utilization of longifolene ... ..	1
3. Utilization of $\Delta^3$ -carene ... ..	1
4. Utilization of terpene-G ... ..	2
5. Sodium cyclamate ... ..	2
6. Isolation of emetine from ipecac roots ... ..	2
7. Carbimazole (New-marcazole) ... ..	2
8. Sulphacetamide and its sodium salt ... ..	3
9. Sorbide nitrate ... ..	3
10. Nonyl phenol ... ..	3
11. Industrial chemicals from diketene ... ..	4
12. Vanillin and ethyl vanillin ... ..	4
13. Chlorinated copper phthalocyanines ... ..	4
14. Radio opaque dyes (like urografin and biligrafin)	5
15. Aminotriazole ... ..	5
16. Improvements in the process for the manufacture of 1-menthol from dementholised peppermint oil	6
17. Investigation of a fermentation problem ... ..	6
18. Development of manufacturing processes for rayon grade pulp from some species of wood ... ..	7
19. Benzoic acid ... ..	7
20. Calcium hypophosphite ... ..	7
21. Fabrication of electron diffraction camera	8
22. Composite drug research scheme on Indian medicinal plants ... ..	8
23. Constitution of lac ... ..	10
24. Lac dye ... ..	11
25. Titanium tetrachloride from ilmenite ... ..	13
26. Popularisation of commercial uses of costus roots (Kuth) in India ... ..	14
27. Work on investigations on the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporationx to extend the industrial utilisation of cotton seed oil	14

28.	Chemical and thermodynamic properties of refractory materials at high temperatures	16
29.	Investigation of the effect of heat on Tung oil and derivatives of Tung oil and the characterization and identification of compounds resulting from heat treatment to extend the utilisation of Tung oil	16
30.	Wood phenolics with special reference to their use in chemotaxonomy and their biosynthesis by tissue culture studies	17

PILOT PLANTS

1.	Dissolving pulp	19
2.	Chlorination and hydrochlorination of ethylene	20
3.	Aniline	20
4.	Phthalates and other plasticizers	21
5.	Carbonation of phenols	21
6.	Fine chemicals project	21
7.	Design cell for industrial projects	22

APPLIED TIME TARGETTED PROJECTS

1.	Thermoelectric semiconductors	23
2.	Preparation and studies of physico-chemical properties of mixed copper-nickel-carbonate type catalysts	23
3.	Silicon tetrachloride	24
4.	New ferrite composition with high figure of merit	24
5.	Silicone and silicone intermediates	25
6.	Chromatographic adsorbents	25
7.	Synthetic inorganic chemicals	26
8.	Utilization of by-product fluorosilicic acid	26
9.	Vitamin B <sub>6</sub>	26
10.	Diethyl-m-toluamide	27
11.	Sorbic acid	27
12.	Synthetic glycosides	27
13.	Cellulose caprate	28
14.	Modification of indigenous gums for use as substitutes for gum arabic	28
15.	Dithranol	28

16.	Saponex (o-toulylbiguanide)	...	29
17.	Reactive dyes based on cyanuric chloride		29
18.	Dyes for synthetic fibres	...	29
19.	Macrocyclic musk compounds	...	30
20.	Inulin from costus roots and its conversion to fructose	... ..	30
21.	Bacterial diastase	... ..	30
22.	Ion-exchange resins	... ..	31
23.	Expandable polystyrene	... ..	33
24.	Rubberised cork sheets	... ..	33
25.	Surface coatings from styrenated alkyd resins		33
26.	Modification of lac	... ..	34
27.	Binder for composite propellants	... ..	34
28.	Coatings for nylon fabric	... ..	34
29.	Rubber base adhesives	... ..	34
30.	Isocyanate base adhesives	... ..	35
31.	Typewriter rollers	... ..	35
32.	Rubber reclaiming agents	... ..	35
33.	Recovery of light and heavy pyridine bases from their aqueous solutions	... ..	35
34.	Vitamin C and sorbitol	... ..	35
35.	Monoethylaniline	... ..	36
36.	Aliphatic amines - methylamines	... ..	36
37.	Dimethylaniline	... ..	36
38.	Construction of a precision ultrasonic interferometer		37
39.	Foundry chemicals	... ..	37
APPLIED BASIC PROJECTS			
1.	New ferrite compositions	... ..	38
2.	Manganites	... ..	38
3.	Development of some ferroelectric materials and studies in their structural and dielectric properties	... ..	39
4.	Studies of dielectric and ferroelectric properties of materials having a general formula $ABO_3$		39
5.	Studies of semiconducting barium titanate materials (Perovskite type)	... ..	39

6.	Studies in photoconducting and electric properties of sulphides and selenides of lead and cadmium	40
7.	Metal-insulator-metal junctions ...	40
8.	Oxidic semiconductors ...	41
9.	Laser materials ...	42
10.	Spectrochemical studies ...	42
11.	Studies in catalysis ...	43
12.	Semi-conductivity properties of thin films (i) resistivities and thermoelectric power measurements (ii) studies on Hall effect ...	44
13.	Physico-chemical studies of proteins with particular reference to Indian silks ...	45
14.	Synthesis and study of new titanium organics	45
15.	Fluorine chemicals ...	46
16.	New methods of analysis ...	47
17.	Studies on the chemical structure of the gum from Terminalia tomentosa ...	48
18.	Cyclic acetals and ketals of monosaccharides	48
19.	The chemical investigation of the plant Balanophora Indica ...	49
20.	Transformation products of citral ...	49
21.	Polyesters as stationary phases in GLC analysis	49
22.	Transformation of Kurchi alkaloids ...	50
23.	Antioxidants, anti-ozonants, accelerators and blowing agents for rubber ...	50
24.	Polymerization of turpentine fractions ...	50
25.	Mass transfer characteristics of rotary sieve contactor ...	51
26.	Reaction models and reactor design ...	51
27.	Studies in fluidization ...	52
28.	Studies in mass transfer ...	52
29.	Estimation of the thermodynamic and transport properties ...	52

SERVICE PROJECTS

1. National collection of industrial microorganisms	54
2. Physico-analytical chemistry	54
3. Mass spectroscopy	55
4. Microanalysis	55
5. Spectroscopic work	55
6. V.P.C. analysis	56
7. X-ray patterns	56
8. Instrumentation	56
9. Workshop	57
10. Glass blowing section	57
11. Technical services	58

BASIC PROJECTS

1. Theoretical investigations on solid state and molecular physics	60
2. Experimental studies in molecular physics	63
3. Radiation and nuclear chemistry	66
4. Thin films	68
5. Synthetic inorganic chemistry	69
6. Natural organic products	70
7. Synthetic organic chemistry	75
8. Physical organic chemistry	86
9. Microbiological studies	89
10. Microbiological transformations of terpenes	90
11. Growth of plant cells	92
12. Enzymes	93
13. Physico-chemical studies in polymers	96
14. Urethane rubber from castor oil	97
15. Grafting of cellulose	98
16. Chemical engineering studies	98
APPENDICES	99

## INTRODUCTION - SUMMARY OF THE MAIN ACHIEVEMENTS

### Sponsored Projects:

During the period under review, the total number of sponsored projects increased to 30 from 24 in the last period. Five old schemes were successfully completed during the last period and work on 11 new schemes (10 private and 1 PL-480) has been initiated.

In attempting to find suitable industrial outlets for  $\Delta^3$ -carene, a compound has been prepared and the firm is likely to produce this item soon. A chlorinated product of terpene-G has been prepared and is being evaluated as a potential insecticide. Nonyl phenol has been prepared from propylene trimer in high yields. Conditions for the conversion of acetic acid to ketene, the preparation of chlorinated copper phthalocyanine pigment, liquid phase catalytic oxidation of toluene to benzoic acid on a bench scale, and a preparation of vanillin from guaiacol obtained from ortho-anisidine have been standardized. Suggestions to improve the yields of l-menthol from dementholised peppermint oil have been offered. The sample of calcium hypophosphite prepared was found to conform to B.P. specifications.

Fabrication of one unit of electron diffraction camera for Gauhati University has been completed. Few more compounds have been isolated from the medicinal plants under investigation and these have been sent for pharmacological testing. On the basis of the pilot plant work, a complete design for the proposed semi-commercial plant for 500 kg. of  $TiCl_4$ /day has been supplied to the sponsor. The structure of 14.1 cyclic monomer accessible by sulphur catalysed thermal cyclisation of methyl -eleostearate has been unequivocally proved to be methyl 5-butyl-1,3-cyclohexadiene 6-caprylate. A new PL-480 scheme on 'Wood Phenolics' to isolate and study the phenolic constituents of certain Indian woods has been initiated.



Pilot Plant Projects:

In the dissolving pulp project, eucalyptus hybrid was investigated by the acid prehydrolysis sulphate process. Equipment for the hydrochlorination of ethylene to ethyl chloride has been set up. A new 6 kg./hour pilot plant for catalytic hydrogenation of nitrobenzene to aniline was successfully operated. Pilot plant studies for dimethyl phthalate and bench scale runs for diethyl phthalate were undertaken. A process for sorbic acid from calcium malonate has been worked out in Fine Chemicals Project. Chemical engineering designs for plants to produce aniline, dibutyl and dioctyl phthalates, dimethyl and diethyl phthalates, were prepared.

Applied Time-targetted Projects:

Silicon tetrachloride produced in the small unit was sold through FCP. The silicon tetrachloride obtained has also been purified to give a starting material for the preparation of semiconductor grade silicon. A new ferrite (hard) composition, which gives an improved energy product for unoriented sample and a nickel free, high frequency ferrite, which could be cheaper than known compositions, have been prepared. A method of upgrading ferro-silicon by acid extraction to silicon of over 98% purity has been worked out.

The conditions for the condensation of ketene and crotonaldehyde which is the first step for the preparation of sorbic acid, has been standardized. A new process for the synthesis of difficultly accessible  $\alpha$ -aryl-glycosides has been developed and two galactosides worth \$400 were exported to USA. The bench scale process development for dithranol has been completed. The preparative conditions for 4 reactive dyes, the method of converting anionic acid dyes into water insoluble disperse dyes, and the process for extracting inulin from deoiled costus roots, have been standardized. Active start-up help was rendered to M/s Chemaux Ltd.,

who have set up the plant to produce bacterial diastase, based on the NCL process.

Modification in the amination technique for the preparation of the styrene DVB-base anion exchange resin, have resulted in the reduction of the cost of production and time of amination. Preparation of high grade pectin from citrus peel was successfully carried out using NCL styrene-DVB base cation and anion exchange resins. Typewriter rollers were moulded from a new castor oil - isocyanate type composition and the rollers are being evaluated.

The process for the production of sorbitol from glucose has been standardized on 10 kg./batch scale. Experimental studies on the preparation of monoethylaniline has been completed and the design is in progress.

A design report for a plant to produce 500 tonnes/annum of dimethylaniline has been prepared.

A precision ultrasonic interferometer has been fabricated and tested.

#### Applied Basic Projects:

Studies have been continued on the properties of new ferrite compositions synthesized earlier. The electric conductivity measurements of some of the manganites synthesized have indicated their suitability for low temperature thermistors. Thin film thermistors of manganite type have been prepared. Two of the doped lead titanate ferroelectric samples are being evaluated for use as transducers similar to P-Z-T type. A special impedance bridge has been constructed to study dispersion of conductivity. The properties of vacuum deposited CdSe films and effect of internal oxidant on properties of chemically deposited PbS films are being investigated. Highly sensitive CdS photoresistors have been prepared. Al-CdS-Al indium sandwiches were studied in detail. Studies on the plate-type zinc oxide single crystals were continued. A number of

new europium and samarium chelates have been prepared for their possible application as laser materials. Spectrochemical studies of substituted ureas, nicotinic acid, isonicotinic acid, three forms of anthranilic acid and para-aminobenzoic acid were carried out. The properties of Ni-Zn,  $V_2O_5$  and evaporated copper film were studied with a view to use them as catalysts. Investigations on the Hall coefficient and various semiconducting parameters of thin films have been carried out to study the effects of substrate temperature during deposition and of thickness of the films. A Bruce Phoenix photometer has been set up for characterization studies of the proteins of Indian silks and a method for removal of sericin and fibroin has been standardized.

New derivatives of cyclohexanol were synthesized and are being used for the synthesis of complex titanium organics. The properties of newly synthesized titanium organics are being studied. Amongst fluorine chemicals,  $(NH_4)_2MnF_6$  has been prepared by electrolytic oxidation process and attempts are being made to employ this reaction for fluorination.

All the four chromatographically pure aldobiouronic acids isolated from the gum from Terminalia tomentosa have now been assigned structures. The earlier structure assigned to one of the new di-o-isopropylidene derivative of L-sorbose has been revised. A convenient method for conversion of citral to citral epoxide in high yields has been developed. Studies of the preparation and properties of polyesters used as stationary phases in GLC analysis were continued. In the studies on transformation of Kurchi alkaloids to steroidal intermediates, an intermediate 18-amino progesterone has been isolated and a compound having IR spectra of ketoxime has been prepared and its final conversion to aldosterone has been undertaken. From CNSL, compounds were prepared for use as rubber antioxidants, anti-ozonants and blowing agents.

The mass transfer characteristics of rotary sieve contactors are being investigated. Reaction models have been developed for oxidation of benzene and toluene and a rate equation has been determined for hydrogenation of anacardol to tetrahydroanacardol. The performance of a semi-fluidized reactor has been studied and a new reactor utilizing this principle has been proposed. Computation has been carried out for proposing a generalised equation for liquid-liquid extraction. Improved methods have been developed for estimating diffusion coefficients in liquids and latent heats of vaporisation.

#### Basic Projects:

A possible mechanism of resistance minimum in dilute alloys with transition element impurities which do not show localized magnetic moment has been formulated. Thermal studies on diamagnetic  $KZnF_3$ ,  $SrMo_{1/2}CO_{1/2}O_3$  and  $SrW_{1/2}Ni_{1/2}O_3$  have been completed. Crystal and molecular structures of p-nitrobenzaldehyde, nickel-imidazole nitrate and dichloroanthranilic acid have been determined with the help of X-ray diffraction methods. Mossbauer spectra of the inverse spinels containing  $Fe^{+3}$  have been obtained. Data is being collected on use of gamma radiation in promoting oxidation and amination of naphthalene and benzene. The recording microphotometer (Livcpho-2) has been installed. Electron transport properties of various compounds are being correlated with their surface structures.

A number of metal  $\beta$ -dicarbonylchelates have been synthesized and their quasi-aromaticity is being studied through different chemical reactions.

Geranylgeraniol, the biogenic precursor of diterpenoids and carotenoids, has been identified as one of the compounds of Cedrella toona. Naturally occurring anthraquinone pigments from Cassia siamea have been isolated, characterized and synthesized. From the leaves of Viola odorata, the isolation of a triterpene friterpene has been reported for the first time. A number of optically

active indanes of known absolute configurations were prepared starting from ar-turmerone. The major volatile components of the solvent extracted sandalwood oil have been identified as  $\alpha$ - and  $\beta$ -santalenes and  $\alpha$ - and  $\beta$ -santalols. Alantolactone and iso-alantolactone which are the major constituents of the oil of Inula racemosa have been converted into many interesting new products. A newly developed method for liquid phase catalytic oxidation of m-xylene has been extended to mixed xylenes. The new process developed for the synthesis of hitherto unknown 4-(o-hydroxyphenyl)-cinnolines has been proved to be general method for the synthesis of 4-arylcinnolines. A simple method for the synthesis of proto-berberine alkaloids has been developed. Several new cationic sulphur heterocyclic compounds, having potential biological activity are being synthesized. Lithio-ethylene diamine has been found to be very useful reagent for isomerization and dehydrogenation of terpenoids. Acidic portion of sandalwood oil was found to be a mixture of eight to nine compounds; three of these have been identified.

In the scheme of identifying different cultures which can grow on hydrocarbon media, 6 cultures of ustilaginales were isolated and are being sponsored for the production of amino acids; 30-40 mutants which require certain amino acids have been isolated. A 25-fold purification of citraconase has been achieved. Bacterial fermentation studies are in progress on limonene, l-p-menthene and camphene. Callus cultures have been obtained from wheat, its viability and nutritional requirements are being investigated. Study of the kinetics of the purified brain enzyme was continued. Interesting data have been obtained on the nature of the enzyme citrase-oxaloacetate complex. Preliminary data obtained indicate that nitrite reductase from A.fischeri consists of several sub-units.

New catalyst systems have been successfully tried for the polymerization of styrene. Rubbery formulations using castor oil and di-isocyanates have been prepared.

## ORGANIZATIONAL SET UP ( as on 30th September 1966 )

DIRECTOR											
DEPUTY DIRECTOR											
ADMINISTRATION			DIVISIONS					AUXILIARY TECHNICAL			
Admn. Officer			Sanctioned strength (Regular + pilot plants )								
Accounts Officer											
Section Officers (4)											
(E.I, II, III and											
Purchase Officer )											
Medical Unit											
Maintenance & Security staff											
Civil Engineering staff											
	PHYSICAL CHEM.	INORGANIC CHEMISTRY	ORGANIC CHEM.	ESSENTIAL OILS	BIOCHEM.	POLYMER CHEM.	CHEM. ENGG.	O.I.D.	DTS	FINE CHEM.	ENGG. SER.
Sc.E.	3	1	1	1	1	1	1	1	1	-	1
Sc.C.	5 + 1	3	4+1	1	3+1	1	3	2	-	-	-
Sc.B.	14	5	7	7	6	5	10+2	2	3	1	1
Sc.A.	1	1	5	3	1	3	3+1	1	1	-	-
S.S.A.	13	14	16	8	14	12	3+2	2+4	5	9	-
J.S.A .	20	10	9	10	2	3	3+5	2+1	2	3	-
Aux. Tech.	17	8	14	6	10	7	5+1	6+9	8	13	62

RESEARCH STAFF : DIVISION-WISE AND CATEGORY-WISE ( as on 30th September 1966 )

Working staff

Category	Physical chem.	Inorganic Chemistry.	Organic Chem.	Essential oils.	Biochem.	Polymer Chem.	Chem, Engg.	O.I.D.	Fine Chem.	D.T.S.	Engg. Ser.
Sc. E.	3	1	1	-	1	1	1	1	-	1	1
Sc. C.	3	3	5	1	3	1	3	2	-	-	-
Sc. B.	13	5	7	6	6	5	10+2	2	1	3	1 (STO)
Sc. A.	1	1	4	3	1	2	3+1	-	-	-	-
S.S.A.	11	13+1	13	8	13	10	8+1	2+3	8	5	-
J.S.A.	19	19	8	8	-	3	3+5	2+1	8	1	-
Aux. Tech.	15	7	16	6	8	7	5+1	6+5	12	8	58
Pool Officers.	3	2	4	-	2	1	-	-	-	-	-
S.R.F.	3	1	9	2	-	-	-	-	-	-	-
J.R.F.	7	8	25	6	4	1	-	-	-	-	-

Private parties :

1. Calcium silicate :

Calcium silicate is an industrially important insulation material used for the preparation of moulded insulation products. The aim of the project is to arrive at the optimum conditions for the technical preparation of low bulk type calcium silicate from indigenous raw materials. Investigations will also be undertaken for finding out uses of calcium silicate other than for thermal insulation.

Experiments were conducted, with raw materials available with us, to get a clear picture regarding the nature, composition and other properties of calcium silicate. Several factors are being studied, for instance, rate of stirring, the rate of addition of the reactants, time of mixing, ageing of the precipitate, drying of the precipitate, etc. Preliminary experiments have shown encouraging results.

2. Utilization of longifolene :

Longifolene is one of the major components of Indian turpentine oil. Attempts are being made to find out suitable industrial outlets utilizing longifolene.

A number of products from longifolene were prepared and sent to the sponsor for their evaluation.

3. Utilization of  $\Delta^3$ -carene :

$\Delta^2$ -Carene is another major component of Indian turpentine oil. Attempts are being made to find suitable industrial outlets for the utilization of  $\Delta^3$ -carene.

A number of reactions of carene were investigated, and several products sent to the sponsor for evaluation. One compound has been approved by the firm and hence its method of preparation has been standardized. The firm is likely to go into the production of this item.



4. Utilization of terpene-G:

Terpene-G is a by product in the manufacture of camphor from turpentine oil. Work has been undertaken to prepare useful products from this component.

Chlorinated product of camphene, known as Toxaphene, is a good insecticide. Terpene-G which consists of mostly dihydrocamphene and camphene was therefore chlorinated. The chlorinated product is being evaluated.

5. Sodium cyclamate :

Sodium cyclohexylsulfamate or sodium cyclamate is used as a non-nutritive sweetening agent in different types of food and beverage preparations. It is about 50 times as sweet as sucrose.

On the basis of laboratory experiments, optimum conditions have been standardized on 250 g. scale of the final product.

6. Isolation of emetine from ipecac roots :

The principle therapeutic use of emetine is in the treatment of amoebiasis. At present emetine is imported. Work has been undertaken to optimise the conditions for the isolation of emetine from ipecac roots and the conversion of cephaeline ( which is also present in the roots), to emetine.

Laboratory scale extraction experiments were carried out on the roots supplied by the sponsor. Along with emetine cephaeline was obtained. Conditions have also been worked out for the conversion of cephaeline to emetine.

7. Carbimazole ( Neo-marcazole ):

Carbimazole is an anti-thyroid substance. It is reputed to cause less triperplasia and vascularity of the gland, than other anti-thyroid agents.

Starting from vinyl acetate the synthesis consists of in all four steps. Preliminary work on the first step, i.e. vinyl acetate to bromoacetal, has been completed on 1 kg. scale.

8. Sulphacetamide and its sodium salt :

Sulphacetamide sodium is used in the treatment of acute conjunctivitis, infections after injuries or burns in the form of solution or ointment, for eyes.

Starting from sulphanilamide, the diacetyl derivative is hydrolysed to yield sulphacetamide. Laboratory conditions for the preparation of sulphacetamide and its sodium salt have been standardized on 3 kilo/scale of the final product.

9. Sorbide nitrate :

This is a pharmaceutical chemical which when taken orally relieves pain in the heart.

Sorbitol is dehydrated to isosorbide which on nitration gives sorbide nitrate. Conditions for the technical preparation of the final product have been established on 1 kg./scale.

10. Nonyl phenol :

Nonyl phenol is a starting material for the preparation of ethylene oxide condensates which are used as non-ionic surfactants. It is also used for the preparation of anionic surfactants, and additives and anti-oxidants for lubricating oils. Nonyl phenol can be used as protective coatings, plasticizers, solvents etc.

Using p-toluene sulphonic acid as a catalyst, experimental conditions on laboratory scale for the condensation of propylene trimer and phenol have been standardized. Overall yield of more than 85% ( based on phenol ) is realised.

11. Industrial chemicals from diketene :

Diketene is an established raw material for variety of industrial chemicals acetoacetarilides including naphthol AS-G, acetoacetic ester, acetoacetamide and pyrazolones. The work has been undertaken under the following three steps:  
(1) acetic acid  $\rightarrow$  ketene (2) ketene  $\rightarrow$  diketene  
(3) diketene  $\rightarrow$  industrial chemicals mentioned above.

Experimental conditions for the dehydration of acetic acid to ketene have been standardized on laboratory scale. Yields upto 60-70% based on acetic acid have been realised in an experimental glass reactor.

12. Vanillin and ethyl vanillin :

Vanillin is an established flavouring agent for different food preparations. It is obtained either from vanilla pods and beans or is synthesized from lignosulphonic acid available from sulphite liquor in paper mills or from eugenol. Attempts are being made to synthesize vanillin from o-anisidine through guaiacol, as o-anisidine is likely to be available in the country in near future. Similar attempts will be made to synthesize ethyl vanillin from o-phenetidine. At present nearly 5000 kg. of ethyl vanillin valued at Rs. 2 lakhs and 23,000 kg. of vanillin valued at Rs. 6.5 lakhs are imported per annum.

Laboratory scale experiments were conducted for the preparation of guaiacol from o-anisidine. 75-80% yields have been realized. Preparation of vanillin from guaiacol was also tried wherein yields upto 60% have been realized.

13. Chlorinated copper phthalocyanines :

Chlorinated copper phthalocyanines are bright green pigments which possess excellent tinctorial and fastness properties. They are widely used in paints, plastics and printing inks etc. Present imports of these type of pigments are of the order of Rs. 2 lakhs/annum. The object of the scheme is to work out the chlorination conditions to produce a material equivalent to Heliogen Green G. shade and fastness properties.

Few runs on 0.5 kilo ( final product ) scale have been successfully carried out in a glass reactor and shades have been approved by the sponsor. At present a cast iron reactor is being used for the runs on the same scale. Shades of the final product obtained in this reactor are being examined.

14. Radio opaque dyes ( like urografin and biligrafin ) :

Radio opaque dyes are of great importance in X-ray diagnostic studies. At present these are imported. Work has been undertaken to develop indigenous know-how for some of these preparations.

The optimum conditions of certain steps in the preparation of sodium diatrizoate ( for urografin ) were established. The preparation of sodium diatrizoate was repeated on a scale of 20 gms.

15. Aminotriazole :

Aminotriazole is an useful herbicide having a potential market in the country. Work has been undertaken to develop an economical process for the manufacture of aminoguanidine and aminotriazole. Aminoguanidine is the penultimate intermediate in the manufacture of aminotriazole.

A literature survey of the methods available for the production of aminotriazole starting from a basic raw material such as calcium cyanamide was made. Nitroguanidine is ; in production at present by the Defence Department, from whom a small quantity was obtained for our experiments. Attempts were made to prepare aminoguanidine by electrolytic reduction of nitroguanidine in which 50% yield could be obtained. Aminoguanidine can further be converted to aminotriazole in practically quantitative yields by a known method.

16. Improvements in the process for the manufacture of l-menthol from dementholised peppermint oil :

The sponsor is producing l-menthol from imported dementholised peppermint oil. The object of the work is to simplify the process at present followed by the party.

A stereospecific method of reduction of l-menthone to l-menthol has been worked out.

Optimum conditions have been standardized to get the maximum conversion of l-menthol from l-menthone. It has been found that pure l-menthol can be separated from the mixture of menthol isomers (neo-menthol, iso-menthol etc.) by decomposing its crystalline chloroacetate derivative. It has been established that the maximum yield of l-menthol from dementholised peppermint oil depends upon the following factors : (1) conversion of menthyl acetate to menthol (2) efficient fractionation of the dementholised peppermint oil to achieve the separation of l-menthol by natural cycle (3) suitable method of reduction for conversion of menthone to menthol, preferentially stereospecific in nature, and (4) the method to separate l-menthol from the mixture of menthol isomers formed during reduction.

17. Investigation of a fermentation problem :

In the preparation of some of the Ayurvedic pharmaceuticals preparations ( such as Asavas and Arishtas ), it was observed by the sponsor that there was some percentage of spoilage of the final products during storage, for reasons not easily detected in their manufacturing processes. The present work has been initiated to investigate the causes of the above mentioned spoilage and to suggest remedial measures for the same.

The causes of spoilage of the pharmaceutical preparations required by the sponsor were determined and the contaminating organisms were studied in detail. Methods for destroying and/or preventing the growth of this spoilage organisms are being standardized.

18. Development of manufacturing processes for rayon grade pulp from some species of wood :

Under this scheme samples of woods supplied by the sponsor are being investigated for chemical analysis. Bleached pulps are made by acid, water prehydrolysis sulfate and T.S. alkali processes and their properties studied.

During the period under report, work on three such species of woods have been started.

19. Benzoic acid :

Benzoic acid is an important industrial aromatic fine chemical which is mainly used as a food preservative. It has a variety of uses in pharmaceuticals and fine chemicals. The scheme has been undertaken to follow up the laboratory scale experiments carried out by the sponsor and to optimise the operating conditions for the liquid phase catalytic oxidation of toluene to benzoic acid.

The optimum conditions of temperature, pressure, catalyst concentration and time of reaction have been established on a laboratory scale unit of 2 litres capacity. Under the optimum conditions the bench scale unit was run continuously to collect data for a continuous pilot plant. On the basis of the bench scale data a pilot plant of 120 litres of toluene per batch was commissioned and it will subsequently be run as a continuous plant. The pilot plant will be run continuously to collect the design data for a 500 tonnes/annum benzoic acid plant.

20. Calcium hypophosphite :

Calcium hypophosphite used in pharmaceutical industry is at present imported to the tune of 50 tonnes/year valued at Rs. 5 lakhs. Work has been undertaken to develop a process for the production of calcium hypophosphite from yellow phosphorous. On the basis of the laboratory trials, a 30 kg./day plant will be designed.

The reaction conditions to treat 1 kg. of phosphorous per batch have been standardized. Attempts were made to improve the recovery of the by-product phosphoric acid.

Trial runs were held up due to the inability of the sponsor to supply yellow phosphorous. One of the samples prepared in the previous trials was tested by a private analytical laboratory. It was found that the sample conforms to B.P. specifications.

Central and State Government Institutes :

21. Fabrication of electron diffraction camera :

The technical know-how for the fabrication of this costly equipment has been developed. One such unit is being used at present in NCL and two more are in actual use at Atomic Energy Establishment, Bombay, and National Metallurgical Laboratory, Jamshedpur.

The project includes designing and fabrication of electron diffraction equipment and associated accessories; to assist outside parties in connection with installation of high tension unit and training of personnel in this field.

Three more parties (1) Gauhati University, Assam (2) Fertilizer Corporation of India, Sindri (3) Defence Science Laboratory, New Delhi, have already advanced money for the fabrication of the equipment. During the period under report, fabrication of one unit for Gauhati University has been completed and the final testing is in progress.

22. Composite drug research scheme on Indian medicinal plants :  
( Ministry of Health, Govt. of India )

22.1. Chemical investigation of Caesalpinia bounducella Flem  
(Putikaranja) Leguminosae family :

This work has been undertaken to study the chemistry of some of the Indian medicinal plants.

The individual isolated components will be tested for their pharmacological properties, by another unit organized elsewhere.

A number of pure crystalline compounds which were different from the previously reported  $\alpha$ ,  $\beta$  and  $\gamma$ -caesalpins, were isolated.

The preliminary reports received from the Pharmacology unit show that the various extracts are devoid of any useful activity. From the chloroform extract of the defatted seed kernels, seven closely related fatty acid esters of long chain alcohols and six closely related diterpenoids other than the reported caesalpins have been isolated. On the basis of spectral evidences two of the diterpenoids compounds E<sub>3</sub> (m.p. 122-23°) and compounds E<sub>4</sub> (m.p. 253-54°) have been assigned the tentative structures I and II respectively. ( Fig. I and II, at the end)

22.2. Chemical investigation of Asparagus Racemosus Willd  
(Shatavari) Liliaceae family :

From n-hexane extract a crystalline compound m.p. 153-56° was isolated which is most probably  $\Delta^2$ -sitosterol. Two crystalline compounds were obtained from ether extract. The ethyl acetate extract and ethanol extract consisted mostly glycosides and carbohydrates.

Pharmacological testing indicated three extracts (i.e. alcohol, ethyl acetate and acetone ) to contain an active substance that blocks uterine activity, both spontaneous and induced by acetylcholine and oxytocin. In view of this, efforts were directed on the ethylacetate and alcohol extract.

Ethylacetate Extract : This extract, which responds to saponins foam test, on acid hydrolysis furnished a mixture of steroidal sapogenins. This on column chromatography (SiO<sub>2</sub>/II ) gave two pure crystalline sapogenins (A and B). Sapogenin A has been identified as sarsasapogenin. Work on sapogenin B is in progress.



Ethanol extract: This also responds to saponins foam test and has been separated into glycosidic and non-glycosidic portions. The glycosidic portion shows eight spots on TLC; three of these components have been isolated in a somewhat impure state for further screening.

22.3. Chemical investigation of Boerhavia diffusa Linn  
(Punarnava) Nyctaginaceae family :

Air-dried powdered roots were subjected to successive extraction with different solvents. Thin layer chromatography of these extracts showed them to be complex mixtures. One crystalline compound m.p. 136-7° isolated from petroleum ether extract was identified as 3-sitosterol.

As the pharmacology unit reported useful diuretic activity for the petroleum ether extract and other extracts were pharmacologically uninteresting, efforts were mostly expended on the petroleum ether extract.

It was separated into acidic (~59%) and neutral (~41%) fractions by 5% Na<sub>2</sub>CO<sub>3</sub> aqueous and the following compounds have been isolated from neutral fractions.

- i) 3-Sitosterol - m.p. 136-37;  $\alpha$  D-34° (CHCl<sub>3</sub>)
- ii) Saturated fatty ether - IR spec. 1750, 1180, 730 cm<sup>-1</sup>.
- iii) Mixture of hydroxy esters - IR spec. 3400, 1750 cm<sup>-1</sup>.

23. Constitution of lac : (Indian Lac Research Institute, Ranchi)

Very little is known about the chemical constitution of the resin molecule of lac. The present study has been undertaken with a view to open new fields for lac utilisation.

Number of acids arising from the hydrolysis of lac, namely jalaric, shellolic, epishelloic, laksholic, epilaksholic, butelic and aleuritic have been isolated. The structures of jalaric, laksholic and epilaksholic were established for the first time. Results obtained strongly suggest that the chief building blocks of lac resin are aleuritic acid and jalaric acid. The isolation of the pure fraction of the resin using repeated precipitations has been successfully completed.

In order to obtain a partially hydrolysed lac molecule containing only two or three acid units, methanolysis of hard resin was undertaken. The methanolysed product was fractionally precipitated. The fractions are under investigation. Methyl aleuritate was methylated using methyl iodide in dimethyl sulphoxide in the presence of calcium oxide. The products of the reaction were separated and their spectral properties studied. Esterification of the oxidized pure fraction using diazomethane and methanol-sulphuric acid showed that the latter reagent has some added advantages in that lesser number of products are formed. This would considerably simplify the esterification of these dehydration products.

24. Lac dye : ( Indian Lac Cess Committee, Ranchi )

The colouring matter of lac is under investigation. There are possibilities of using lac dye in various fields. The object of the scheme is to find uses for the colouring matters of lac.

The complete structure of one laccaic acid containing nitrogen has been determined. Work on the isolation and characterisation of non-nitrogen containing lac pigments has been undertaken.

When the crude laccaic acid ( the isolation of which was described in the earlier reports ) was dissolved in n-butanol saturated with 0.3 N hydrochloric acid and chromatographed on polycaprolactam powder using the same solvent system for development and elution, a minor fast-moving fraction was

followed successively by two main fractions. Extraction of each with saturated aqueous sodium acetate and acidification with hydrochloric acid yielded laccaic acid A & B respectively. Laccaic acid A separated as bright red needles and could be recrystallised from water or methanol.

The molecular formula of laccaic acid A is  $C_{26}H_{19}NO_{12}$ . The colour reactions and its absorption spectrum indicate that it is an anthraquinone derivative. Methylation with dimethyl sulphate and potassium carbonate in acetone gave a methyl ether identical with MLA III (methylated laccaic acid III; obtained earlier as one of the products of prolonged methylation of lac dye). Similarly laccaic acid A underwent the purpurin  $\rightarrow$  xanthopurpurin reaction, and the product on methylation with methyl iodide and silver oxide in DMF gave methylated xantholaccaic acid corresponding in all properties to MXLA III.

MXLA III - The molecular formula is  $C_{32}H_{31}NO_{11}$ . It shows in its NMR spectrum a  $\underline{C}$ -methyl group at 8.08 and a single-proton broad triplet at about 4.2 corresponding to an NF proton. In addition it shows an  $ArCH_2CH_2-$  group, 6-methoxyl groups and 5 aromatic protons. The nature of the NF and the methylene groups indicate the presence of a  $PhCH_2CH_2NHCOC_2H_5$  group. The available evidence leads to structure I for MXLA III. ( Figure I at the end )

MLA III - The molecular formula  $C_{31}H_{27}NO_{11}$  is in agreement with the NMR spectrum. It has five methoxyl groups which exhibit two features of great significance and in which it differs from MXLA III; one is the absence of the high field signal at 6.48 and the other is the signal at 5.68, unusually low for a methoxyl group. In the conversion of purpurin to xanthopurpurin a hydroxyl group is lost; and in the methylation products, the change should therefore result in the loss of a methoxyl group and the appearance of an aromatic proton. However, although MLA III and MXLA III are

both derived from the same purpurin, derivative, MXLA III contains one methoxyl group more than MLA III and not one less as expected. Consequently there can be little doubt that the methylation of laccaic acid A by the prolonged action of dimethyl sulphate and potassium carbonate in acetone is accompanied by cyclisation in which a molecule of water or methanol is lost. On this basis, laccaic acid A can be constituted as II and its methyl ether as III. ( Figure II, page )

25. Titanium tetrachloride from ilmenite :  
(M/s Travancore Titanium Products Ltd., Trivendrum )

At present the sponsors are manufacturing titanium dioxide pigment from Indian ilmenite by the conventional sulphate process. The titania obtained by this process is not very pure and is of anatase form and besides, the process requires substantial quantities of imported sulphur. To obtain rutile grade titania in the above process, rutile seeds prepared from titanium tetrachloride are employed during the hydrolysis of sulphate liquor. The total requirement of the titanium tetrachloride is being imported (50 tons/year value Rs. 1.5 lakhs )

Under the present scheme, the work carried out earlier at NCL on CSIR sponsored pilot plant scheme on chlorination of ilmenite ( 2 kg  $TiCl_4$ /hour) was further scaled up. The data obtained would be utilized for the installation of a plant, to meet the total requirement of titanium tetrachloride for the titania factory, at Trivendrum.

Based on the earlier work at NCL, a 10 kg titanium tetrachloride/hour unit was fabricated, and run successfully, with a view to understand the design and fabrication problems involved in the pilot plant to be installed at Travancore Titanium Products factory at Trivandrum. On the basis of the data obtained, a complete design for the proposed pilot-plant producing 500 kg/day of titanium tetrachloride has been supplied to sponsors.

The iron chloride by-product obtained in the benefication step of the process was successfully converted to the pigment grade iron oxide, on laboratory scale.

26. Popularisation of commercial uses of costus roots (Kuth) in India : ( Govt. of Punjab )

Costus plant is widely cultivated in Punjab and Kashmir. Formerly these roots were exported to China. The export has now been stopped. A new process for the extraction of oil from costus roots at room temperature has been developed. The object of the scheme is to assess the commercial uses of these roots.

A large number of samples of roots grown under various manurial and irrigational trials supplied by the Govt. of Punjab have been examined for yield of oil and lactones.

Five more samples of roots grown under different manurial conditions by the Punjab Government were extracted by petroleum ether and yields of oil and lactones and properties of the oil were determined. Hexahydrocostunolide was prepared. Dimethylamine adduct of dehydrocostus lactone was reduced to the tetrahydro compound. Since petroleum ether 40-60° is not available indigenously, solvents like methanol and benzene were tried for extraction of the oil.

PL-480 schemes :

27. Work on investigations on the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation to extend the industrial utilisation of cotton seed oil :

Work is divided into two aspects : (1) preparation of cetosteryl alcohol mixtures by the hydro-genolysis of cotton seed oil, and (2) collection of basic data on monolayer properties of long-chain alcohols including alcohol mixtures obtained from cotton seed oil and alkoxy ethanols.

More than 90% yields have been obtained in the hydrogenolysis of cotton seed and other oils. The cetostearyl alcohol mixtures obtained as above showed better water evaporation retardation as compared to pure cetyl and stearyl alcohols. Measurements of specific resistance to evaporation of C<sub>16</sub> to C<sub>22</sub> alcohols showed that the ethylene oxide monocondensates exhibit higher values than the di- and tri-substituents.

Pure C<sub>16</sub>- C<sub>18</sub> (99.9%) alkoxy ethanols were synthesised by the Williamson's method. C<sub>20</sub> and C<sub>22</sub> alkoxy ethanols are being prepared. The monolayer properties of alkoxy propanols are also being investigated and compared with alkoxy ethanols.

The surface viscosity measurements ( of C<sub>16</sub> to C<sub>22</sub> alcohols) were continued at various temperatures and pressures, which revealed two dimensional phase changes at temperatures in 15°- 30° regions.

To elucidate the characteristic behaviour of odd and even chain alcohols in monolayer on water surface the following properties were measured (i) pressure-area ( $\pi$ -A) isotherms, (ii) collapse pressure, (iii) equilibrium spreading pressure.

$\pi$ -A isotherms of the odd chain alcohols (C<sub>17</sub>-OH, C<sub>19</sub>-OH) were found to lie in between those of the adjacent even chain ones.

The collapse pressure increases from C<sub>16</sub>-OH to C<sub>18</sub>-OH whereas it decreases in the case of C<sub>20</sub>-OH and C<sub>22</sub>-OH indicating the influence of chain length on the anchorage.

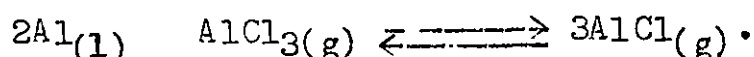
The equilibrium film pressures of C<sub>17</sub>-OH and C<sub>19</sub>-OH are higher than those of C<sub>16</sub>-OH and C<sub>18</sub>-OH respectively.

$\pi$ -A isotherms of C<sub>18</sub>-OH was studied for different pH of the substrate water and at different temperatures. The results indicate the expansion of the monolayer above pH 10 and no distinct variation in the  $\pi$ -A isotherms between pH 2.5 to 9.

28. Chemical and thermodynamic properties of refractory materials at high temperatures : ( National Bureau of Standards, Washington )

The chemistry of refractory oxides, sulphides and nitrides of Al, Ce, La etc., at high temperatures is of interest to several important fields like ceramics, materials for rocketry, atomic energy. Thermodynamic properties of some of the above materials are being investigated employing techniques such as transpiration, Langmuir free evaporation and Knudsen cell effusion.

The following equilibrium reactions were studied at temperatures 1125° to 1425°K and the results have been published.



The reaction of  $\text{AlCl}(g)$  and  $\text{MgO}(c)$  between 1298°K and 1465°K was found to yield a spinel of magnesium oxide and  $\text{Al}_2\text{O}_3$  and the results have been sent for publication.

Oxygen absorption capacities of rare earth sulphides ( of Ce, Pr, Nd and Sm ) between 400-600° have been studied and the results communicated.

The reaction  $\text{AlCl}(g)$  with  $\text{BeO}(s)$  between 1150°-1350°K was studied and was found to yield a spinel of Beo and  $\text{Al}_2\text{O}_3$  together with gaseous product  $\text{BeCl}(g)$ .

Aluminium oxychloride has been prepared by reacting  $\gamma$ -alumina with anhydrous  $\text{AlCl}_3$  in a sealed tube kept at 300°. The sample of aluminium oxychloride thus prepared was found to be stable in a flow system in which the carrier gas nitrogen was saturated with  $\text{AlCl}_3$  vapour.

29. Investigation of the effect of heat on Tung oil and derivatives of Tung Oil and the characterisation and identification of compounds resulting from heat treatment to extend the utilisation of Tung oil : ( U.S. Department of Agriculture, Washington ).

The investigation deals with the thermal treatment of tung oil and its derivatives with a view to extend the utilisation of this drying oil by the development of new industrial chemicals.

Methanolysis of tung oil was found simple and convenient for the large scale preparation of methyleleostearate. Mild thermal treatment of methyleleostearate in presence of catalyst resulted in a 30% conversion to the cyclic monomer. It was found that the monomer is formed via the initial isomerised ~~isomer~~ with the 11-double bond dis-configured. Isolation of this unique isomer of eleostearate has been reported for the first time.

The structure of the 14.1 cyclic monomer ( readily accessible by sulphur catalysed thermal cyclisation of methyl  $\gamma$ -eleostearate ) has been unequivocally proved to be methyl, 5-butyl, 1,3-cyclohexadiene 6-caprylate on the basis of spectral (UV, IR and NMP ) and incisive chemical evidence ( retro Diels-Alder reaction with acetylene dicarboxylic acid, photolysis to the acyclic triene, ozonolysis, maleic anhydride adduction etc. ).

30. Wood phenolics with special reference to their use in the preparation of their biosynthesis by tissue culture studies : ( U.S. Department of Agricultural Research Service, USA ).

The phenolic constituents of wood play an important part in the technical utilisation of wood. The object of the project is to isolate the phenolic constituents of certain woods, to determine their structures, study the relation between the phenolics in leaves, cambium, pith, and xylem, investigate the toxic problems concerning woods, and to examine the possibility of growing callus tissues of the plants under investigation and of using them for following the biosynthesis of the phenolic constituents.

Salix tetrasperma: Work has been initiated on the extractives of Salix tetrasperma ( Indian willow ) and three crystalline compounds were obtained. Two of them have been identified as 3-sitosterol and friedelin. The third crystalline compound,  $C_{30}H_{50}O$ , which is isomeric with friedelin, has been obtained in very low yield. Work is in progress to isolate more of this compound for further investigation.



Artocarpus heterophyllus: From the examination of the stem bark it has been found that it does not contain the flavonoids found in the heartwood. Earlier work on the heartwood of the species showed the presence of several new flavones and a flavanone. Besides cycloartocarpin, artocarpin, artocarpanone, artocarpesin, artocarpetin, norartocarpetin, morin and cyanomaclurin, a new flavonoid occurs in the heartwood. Work is in progress to isolate more of this material for further investigation.

Tissue culture : Conditions for obtaining callus cultures from Artocarpus heterophyllus and Tectona grandis (teak) are being investigated. Studies on the viability and nutritional requirements of these tissues on sub-culture are in progress.

PILOT PLANT PROJECTS

1. Dissolving pulp :

Investigations on different cellulosic raw materials available in India have been undertaken and their suitability for the production of dissolving pulp is being studied. Similar work on certain other woods has been undertaken on behalf of a private firm, on sponsored basis.

The indigenous production of dissolving pulps is of the order of 60,000 tonnes/annum. Licensed capacity is 1,85,000 tonnes/annum, while the imports of dissolving grade chemical wood pulps are of the order of 11,228 tonnes/annum valued at Rs. 1.27 crores ( 1965-66 ).

Number of bamboo species ( Ochelendra travancorica; Melocanna bambusoides ) have been processed by two stage alkaline pulping process. Groundnut shells were investigated by number of pulping processes and pulp suitable for carboxy methyl cellulose was prepared by water prehydrolysis sulfate process with suitable modification, in the CMC process.

Investigations have been carried out on eucalyptus hybrid. This specie was investigated by acid prehydrolysis sulfate process. The effects of varying acid concentrations, time and temperature in prehydrolysis, were studied.

Acid prehydrolysis sulfate and two stage alkaline pulping processes were found suitable for pulp preparation, in a comparative study on pulping, of Shorea-robusta. Filterability evaluation by varying percentages of carbon disulfide in xanthation and varying percentage of cellulose and alkali in viscose preparation were undertaken on different commercial pulps like soft wood sulfite, hard wood sulfite, hard wood sulfate, 'NCL' acid prehydrolysis sulfate and two stage alkali process pulps.

Detailed design and drawing data for continuous digester was prepared and sent to Mr. Ranga ( as directed by the 2nd Cellulose Advisory Panel ), and report is obtained.

Fractionation of dissolving pulp from EWNN solution for polydispersity was carried out for commercial pulps in order to standardise the process.

2. Chlorination and hydrochlorination of ethylene :

Attempts are being made to optimise conditions for the preparation of tetrachloroethylene and trichloroethylene by chlorination and ethyl chloride by hydrochlorination of ethylene. By-products such as dichloroethane, ethylene dichloride, pentachloroethane and tetrachloro-ethane are obtained in these reactions.

At present trichloro and tetrachloroethylene are not produced in the country and are imported to the tune of 2000 tonnes/year valued at Rs. 25-30 lakhs. The estimated demand by 1970 is of the order of 15,000 tonnes/year. Ethyl chloride is being manufactured in India in small quantities and the demand is estimated at 300 tonnes/year.

After a series of experiments on direct chlorination of ethylene in 2" glass reactors, bench scale investigations are being carried out at 100-150 g./hour of chloro compounds.

Equipment for the hydrochlorination of ethylene to ethyl chloride has been set up and a few preliminary experiments carried out.

3. Aniline :

More than 1300 tonnes/annum (valued at Rs. 25 lakhs ) of this important organic intermediate is being imported at present. The demand in 1970 is estimated to the tune of 6000 tonnes/annum.

A pilot plant for the vapour phase catalytic hydrogenation of nitrobenzene to aniline is being developed and design data for a commercial plant is being collected.

The original 2 kg./hr. pilot plant has been considerably modified and a new pilot plant of 6 kg./hr. with necessary improvements has been installed. The new unit is found to operate satisfactorily. Chemical engineering designs for a 600 tonnes/annum were prepared. A project engineering firm has been contacted to provide an estimate for the commercial plant.

4. Phthalates and other plasticizers :

On the basis of the pilot plant experiments, design data for the manufacture of dioctyl and dibutyl phthalates has been collected.

Process development work on the manufacture of dimethyl and diethyl phthalates has been undertaken.

Several bench scale runs ( 1 to 1.5 kg./batch) for the preparation of dimethyl phthalate have been carried out to establish the process conditions. On the basis of these bench scale trials pilot plant operations were carried out on 25 kg./batch.

Process conditions for the preparation of diethyl phthalate are being standardised on a bench scale unit.

5. Carbonation of phenols :

Process developmental work on the carbonation of 3-naphthol for the manufacture of BON acid has been undertaken on 2-3 kg./batch pilot plant.

Several trials on a scale of 3 kg./batch were made by re-using the recovered 3-naphthol in subsequent batches, so as to check whether there is any lowering in the conversion or yield of the final product. It was found that the recovered 3-naphthol can be re-used up to 10 successive batches without affecting the yield and conversion considerably. Some preliminary work on the process development for salicylic acid was carried out starting from phenol.

6. Fine Chemicals project :

The catalogue of FCP has been reduced only to those 300 chemicals which have been prepared in the project some time or the other. The new catalogue has been distributed to various institutions.

A new process starting from calcium malonate for the

preparation of sorbic acid has been worked out. The process is being standardized.

In the process developed earlier for the extraction of costus root oil, imported petroleum ether was used. As this solvent is not available in the country due to import restrictions indigenous solvents like n-hexane, acetone etc. are being tried.

Value of production during April/September 1966 ...	...	1,17,083 = 65
Sabs during April/Sept. 1966	...	87,189 = 57.

7. Design cell for industrial projects :

The design cell is the outcome of several designs prepared by different groups. It has been created with the object of preparing chemical engineering designs ( wherever necessary) for processes offered by the laboratory for commercial exploitation.

Chemical engineering designs for the following have been prepared :

1. Semi-commercial aniline plant of 600 tonnes/annum.
2. Dibutyl and dioctyl phthalates plant of 10,000 tonnes/annum.
3. Dimethyl and diethyl phthalates of 1,500 tonnes/annum.

In addition, design drawings prepared by the project engineering firms for the opium alkaloids plant were checked and several modifications suggested. The design cell is also in continuous contact with the project engineering firms to whom the acetanilide process has been given and several design points raised by the firm have been answered.

APPLIED TIME TARGETTED PROJECTS

1. Thermoelectric semiconductors :

The thermoelectric figure of merit (Z) of a material is given by  $\frac{\alpha^2 T}{k\rho}$  where  $\alpha$  is the thermoelectric power, k is the thermal conductivity and  $\rho$  is the resistivity. In order to increase the efficiency of the system, some physical agencies which will increase  $\alpha$  and decrease k and  $\rho$  have been introduced.

Measurement of  $\text{Bi}_2\text{Te}_3$ , PbTe and their solid solutions have been carried out, and in many cases good thermoelectric properties have been observed. The work was submitted in the form of a thesis.

2. Preparation and studies of physico-chemical properties of mixed copper-nickel-carbonate type catalysts :

Nickel formate is a well known material for the preparation of catalysts specially for hydrogenation of fatty oils. Previous work has shown that nickel-copper mixed carbonate could be employed for this purpose yielding a catalyst which was found to possess activities comparable to the commercially used catalysts. Although small quantities of nickel catalysts are being produced in the country, these are still largely imported.

The optimum preparative conditions for the copper promoted nickel catalyst determined earlier were tried on 0.5 kg. scale ( of final catalyst ) by the wet reduction of coprecipitated nickel copper carbonates in groundnut oil. The conditions best suited to this wet reduction were studied in detail. The catalyst prepared on this scale was found to have activity comparable with that obtained earlier on small scale ( 25 g. scale ). These catalysts will be sent to hydrogenation factories for evaluation on their pilot plants.



3. Silicon tetrachloride :

Silicon tetrachloride is of primary importance in the preparation of semi-conductor grade silicon. A small unit of 0.5 kg. of silicon tetrachloride per hour from ferrosilicon was fabricated and run successfully. The object is to prepare pure silicon tetrachloride to be sold through FCP and to obtain pure poly-crystalline silicon.

The unit was run at 1 kg.  $\text{SiCl}_4$ /hr. and the product was sold through FCP. Purification of this silicon tetra-chloride has been achieved to give a starting material for the preparation of semi-conductor grade silicon. Silicon deposits on silicon and on ruby substrates have been studied.

4. New ferrite composition with high figure of merit :

By proper choice of compositions, preparation conditions and doping agents, it was possible to get products of high figure of merit. A number of ferrites (hard and soft) of the following type have been prepared and their properties studied : Ag-La, Th-La, Ni-Zn, Mg-Zn, Mg-Mn, Pb-La etc. The magnetic properties of these compounds were studied.

A new ferrite (hard) composition which gives an improved energy product for unoriented sample, has been prepared and samples have been distributed to various parties. Soft ferrite compositions for medium wave applications with  $\mu = 38000$  (at 1Mc/Sec) has been prepared. High frequency ferrite having a cut off frequency greater than 20 mega cycles/second and a  $\mu$  product of about 5000 has also been prepared. This does not contain any nickel and is substantially cheaper than other compositions known in this field.

Attempts are being made for the commercial exploitation of these compositions.

5. Silicone and silicone intermediates :

In the Get-to-Gether of Research & Industry held in December 1965, a programme of research on silicone fluids, greases and rubber was suggested. It was later agreed that the developmental work on the preparation of the monomers and intermediates will be undertaken at NCL. There are two generally accepted methods for the synthesis of silicone intermediates: (1) alkylation of elemental silicon with alkyl chlorides, and (2) reaction of a silicon halide with Grignard reagents. A study on the reaction of alkyl chlorides on silicon or silicon tetrachloride to yield alkyl chloro-silanes, tetra-alkyl silanes or other intermediates has been undertaken in the first instance.

The common silicone fluid (dimethyl silicone) is obtained from hydrolysis of dimethyl dichlorosilane. Direct action of methyl chloride on silicon to produce crude dimethyl dichlorosilane is being studied. Since pure silicon is not produced in the country, a method of upgrading ferrosilicon (85-90% Si) by acid extraction to silicon of over 98% purity has been worked out.

Experiments on the standard Rochow procedure have shown three important variables, (i) nature of coating of copper on silicon (ii) rate of flow of methyl chloride, and (iii) reaction temperature, influencing yield and composition of the liquid product. Some alternative ways of chloromethylation of the silicon are also being tried.

6. Chromatographic adsorbents :

Conditions for the preparation and activation of silica gel and alumina and also for the preparation of other less frequently used materials such as the oxides of calcium and magnesium, the carbonate and silicate of magnesium, calcium hydrogen phosphate and bone meal, have been standardized. These were supplied to outside parties through FCP.

7. Synthetic inorganic chemicals :

The object is to develop methods for the preparation of important inorganic chemicals which are not readily available in the country.

At the instance of microanalytical section and RRL, Jorhat, some samples of drierite and ascarite were prepared and are under tests. On request from Defence Research Establishment, Kanpur, one kg. of zinc sulphide phosphor was prepared.

8. Utilization of by-product fluorosilicic acid :

The material is available as an effluent. ( 6-10% solution ) in the superphosphate industry. On the anhydrous basis the availability is estimated around 2000-3000 tonnes/year.

Preliminary exploratory experiments were conducted and a reaction of the effluent was tried at room temperature with mineral rock phosphate. The results indicated that phosphoric acid can be obtained. The yields were comparatively low; however, efforts are being made to optimize the conditions for maximum conversion and separation of phosphoric acid from  $\text{CaSiF}_6$ .

9. Vitamin B<sub>6</sub> :

The process for the preparation of vitamin B<sub>6</sub> has been earlier worked out on laboratory scale as well as on bench scale in Organic Chemistry Division. The process consists of ten main steps starting from chloroacetic acid.

The first three steps in the synthesis has been reinvestigated on laboratory scale and improvements resulting in the avoidance of the use of sodium have been effected.

10. Diethyl-m-toluanide :

The compound is a useful insect repellent and is not produced in the country.

Conditions for the preparation of diethyl-m-toluanide have been standardized on 0.5 kg./day scale in a continuous reactor using m-toluic acid and diethylamine.

Several lots of mixed toluic acids were condensed with diethylamine to give mixed anides containing approx. 60% of the m-isomer. The samples were supplied to AFMC for testing.

11. Sorbic acid :

The chemical is used as a preservative for food, bakery products, chapatis etc. Arrangements have been made with a private party for carrying out the first stage of synthesis viz. preparation of the polyester. The acid catalysed conversion of this ketene crotonaldehyde polyester into sorbic acid is being worked out.

The conditions for the condensation of ketene and crotonaldehyde which is the first step for the preparation of sorbic acid, has been standardized. The results of this condensation could not be reproduced by the private firm. A scientist from the laboratory was then deputed to demonstrate this reaction to the party at their factory. The demonstration was successful and the party is now preparing the condensate on their own.

12. Synthetic glycosides :

The object of the scheme is to prepare some of the glycosides which are used in studies in genetics and other research purposes in India and abroad. Phenyl-3-D galactoside was prepared and supplied to Salk Institute for Biological Studies, California, USA.

The know-how for the preparation of two galactosides and one thio-galactoside was established. A new process for the synthesis of difficultly accessible  $\alpha$ -aryl - glycosides has been developed. Two galactosides worth \$ 400 were exported to USA.

13. Cellulose caprate :

Cellulose caprate with requisite degree of substitution is the main ingredient of an optical cement composition. This is imported at present. Work was undertaken at the instance of the Defence Department.

Work for the preparation of the optical cement could not be completed as the two plasticizers required could not be procured from the Defence Department or from other sources.

14. Modification of indigenous gums for use as substitutes for gum arabic:

At the instance of the Indian Posts & Telegraphs Board, easily available indigenous gums are being modified for use as substitutes for gum arabic. Indigenous gums such as ghatti, jeol, karaya, babul and cashew were examined. Two new methods for modifications were developed and employed for these gums.

Some of the modified gums prepared in this laboratory were approved by the P & T Board and larger samples were prepared and supplied to them for trials in different parts of the country.

15. Dithranol :

Dithranol is an anti-dermatatic agent and work has been initiated by Defence Dept. At present defence need is met by imports.

The bench scale process development work on dithranol has been completed in an overall yield of 53% by a two-step process starting with the potassium salt of 1,8-disulphonic acid of anthraquinone ( available as 40% paste ).

16. Saponex (o-toulylbiguanide ):

This chemical is widely used as antioxidant for soaps and detergents. Reported annual requirement of M/s Tata Oil Mills, Bombay, alone is 2.3 tonnes. At present 'Saponex' is imported and demand is likely to increase.

Starting from o-toludine and dicyanamide, few experiments have been carried out on 0.5 kg. scale and 80% yields based on o-toludine have been realized.

17. Reactive dyes based on cyanuric chloride :

Reactive dyes are at present produced in the country, only by a few firms and their output is not enough to meet the indigenous demand.

Exploratory work for the preparation of Procion Reactive Red 5 BS type dyes has been undertaken.

Preparative conditions for 4 dyes in this series have been standardized and their dyeing and fastness assessments are being examined.

18. Dyes for synthetic fibres :

Disperse dyes specially suitable for synthetic fibres such as nylons and/or terylene etc. are not at present manufactured in the country. A new method for the preparation of water insoluble dyes has been developed.

The purpose of this investigation is to explore the possibility of making dyes for synthetic fibres with raw materials easily available in the country.

Starting from different easily available anionic acid dyes, number of water insoluble, disperse dyes have been prepared on laboratory scale by suitably modifying their structures. The method of converting anionic acid dyes into water insoluble dyes has been standardized. <sup>e</sup>Dyeing and fastness assessments of these dyestuffs are in progress.

19. Macrocyclic must compounds :

Syntheses of macrocyclic ketones and lactones such as exaltone, exaltolide, civetone, dihydrocivetone, ambrettolide, isoambrettolide are important as they are valuable perfumery materials.

New methods for the syntheses of these compounds from cheap raw materials have been developed and standardized.

During the period, about 100 g. of exaltolide and 880 g. of exaltone were prepared for sale through FCP.

20. Inulin from costus roots and its conversion to fructose :

Costus roots contain a high percentage (about 25%) of inulin and no other indigenous source, so rich in inulin, is available. Although the existence of inulin in costus roots was reported in 1929, a process for its economic extraction from the roots has not so far been developed. Inulin on hydrolysis is converted to fructose, which is used in medicine and is a sugar, tolerated by the diabetic patients. The demand for fructose is, at present, met by imports.

A process has been standardized for extracting inulin from costus roots as well as from the powder remaining after the oil has been extracted. Inulin has been obtained to the extent of 25% on the weight of roots. It has been converted into fructose (solid and syrup). During this period an experimental batch using 20 kg. of costus roots was processed and 5 kg. of crude inulin was obtained. Hydrolysis of inulin to fructose was studied on a 200 gm. batch scale.

21. Bacterial diastase :

Stock cultures specially developed for the process are regularly maintained.

Tests on the stability and performance of the culture used for the bacterial diastase process have been carried out.

Members of the staff paid several visits to the factory which is being set up by the firm and assistance was rendered to them in the preliminary trials on their equipment.

## 22. Ion-exchange resins :

### 22.1. Acrylic-base cation exchange resins :

Cation exchange resins used in pharmaceutical and antibiotic industry are at present imported.

Based on the recommendations made in CSIR and Research and Industry Get-to-Gether (1965), preliminary work has been undertaken on available acrylic monomers.

Conditions were standardized for the preparation of methacrylic acid from methyl methacrylate by saponification followed by neutralisation and fractional distillation. As the monomer was soluble in water, suspension polymerization was carried out in concentrated salt solution. The experiments were carried out on 50 gms. scale, and the copolymer was obtained in bead form. Further work on the standardization of the process conditions is in progress.

### 22.2. Styrene-DVB base cation exchange resin :

Attempts are in progress to improve properties of the resin and introduce modifications in the processing conditions to reduce cost of the final product.

Use of a catalyst for the sulphonation reaction was found promising. This will reduce the period of sulphonation and amount of sulphuric acid required, considerably. Washing of the



sulphonated copolymer has been modified to a speedy and simpler procedure. In the initial washing of sulphonated copolymer p-chlorobenzene sulphonic acid is obtained as a by-product which has been recovered as its sodium salt. Attempts are being made to find suitable applications for the by-product sodium salt. This may further reduce the cost of the final product.

### 22.3. Styrene DVB-base anion exchange resin:

Optimum conditions for the chloromethylation of styrene-DVB copolymer, having different degree of cross linking have been established and the capacities of the resins so produced were determined.

65 litres of chloromethyl ether was prepared in the bench scale unit (3 lit/day). Column studies were conducted with the resin in hydroxyl form and using N/10 hydrochloric acid and sodium chloride as effluents.

Modifications in the amination technique with trimethylamine have effected reduction in cost of production and time of amination.

For the preparation of another grade of resin, investigations were carried out to increase the extent of amination using dimethylaminoethanol as aminating agent. Use of different swelling agents and their mixtures prior to amination was also tried.

### 22.4. Cation exchange resin from phenol formaldehyde scrap:

Phenol formaldehyde scrap available from the plastic industry do not find any use at present.

Preliminary experiments to prepare cation exchange resin from this material have been carried out and a low capacity resin with 1.2 to 1.6 meq/gm. has been obtained.

### 22.5. Application of ion-exchange resins:

Attempts have been made to separate lac dye components by ion exchange chromatography using strongly basic ion-exchange resins. It was found that lac dye forms some kind of irreversible complex with it which cannot be eluted out. The use of weak base ion-exchange resin also led to no useful results.

Preparation of high grade pectin from citrus peel was successfully carried out using NCL styrene-DVB base cation and anion exchange resins. The use of these resins was demonstrated in CFTRI, Mysore, and they propose to extend this technique for pilot plant trials.

23. Expandable polystyrene:

Preparation of free flowing expandable polystyrene beads has been standardized in a 2 gallon kettle.

By adjustment of suspending agent it was possible to obtain 60% beads in the required size range. Moulding conditions have been standardized to reduce the mould shrinkage and foamed sheets with a density of 1.5 lb/cuft. have been prepared. A semi-automatic pre-foaming unit has been designed and fabricated.

24. Rubberised cork sheets:

Systematic study on the incorporation of cork granules into natural and synthetic rubbers so as to obtain sheets with good tensile strength, compression set, age resistance, resistance to shrinkage and with standard hardness number was carried out.

Rubberised cork sheets prepared by our process proved equivalent to the imported ones and a satisfactory process demonstration of the same was given to the firm licensed to utilize the process.

25. Surface coatings from styrenated alkyd resins:

A satisfactory composition of the alkyd resins based on high and medium oil length has been found to meet the requirements of a good surface coating in all respects. About 10 kg. of the modified styrenated alkyd resin was prepared and sent to few interested parties for evaluation.

A detailed project report on the basis of data obtained on the preparation of styrenated alkyd resin based coating on a 6 kg per batch scale, has been prepared.

26. Modification of lac:

Film properties of few compositions based on the reactions of different polyisocyanate products with shellac have been studied.

At present use of castor oil in place of polyols is being worked out.

Castor oil and glycerol were reacted with toluene-diisocyanate and reaction product was then reacted with phenol to block isocyanate group, thereby making the composition quite stable. Requisite quantity of shellac was then combined with this blocked isocyanate intermediate in the ratio of NCO:OH::1.2:1. Baked film of this composition was found to possess excellent adhesion, hardness, flexibility and showed good chemical resistance. These compositions could be useful as insulating varnishes for metal wires.

29. Binder for composite propellants:

A castor oil based formulation for making composite propellants was developed and samples were sent for testing.

As per the suggestions received few more compositions were tried and samples have been sent to Thumba Research Station for evaluation.

28. Coatings for nylon fabric:

At the instance of SASMIRA, Bombay, polyester polyisocyanate based coating compositions have been developed. Many formulations were tried. Two of the promising samples have been sent for evaluation.

29. Rubber base adhesives:

Many rubber base adhesive formulations are used for binding metal or metal to rubber joints. One such adhesive required by HAL, Bangalore has been successfully prepared. The adhesive is now being prepared in larger quantities for actual trials.

30. Isocyanate base adhesives:

Adhesive formulations based on cashewnut shell liquid and phosgene have been prepared and their properties are being studied. These adhesives find a variety of domestic and industrial applications.

31. Typewriter rollers:

A new castor oil-isocyanate type composition has been developed and rollers were moulded. These rollers are first being tested for their specific properties. Few more samples will be prepared and sent for consumer acceptance.

32. Rubber reclaiming agents:

Technical preparation of the rubber reclaiming agent of the 'Renacit' type is being attempted.

One such sample has been prepared and sent to a commercial firm for evaluation.

33. Recovery of light and heavy pyridine bases from their aqueous solutions:

In many industries pyridine bases are recovered from their dilute solutions using salting out technique without or with azeotropic distillation.

The following three methods: (a) Binary azeotropic distillation followed by benzene azeotropic distillation, (b) combination of biphasic separation, solvent extraction and benzene azeotropic distillation, and (c) combination of hot solvent extraction and benzene azeotropic distillation have been worked out on laboratory scale.

34. Vitamin C and sorbitol:

The process for the production of vitamin C from sorbitol was worked out on the pilot plant scale. Based on the data collected a project report for a 50 tonnes/annum plant was prepared. The process was demonstrated to Hindustan Antibiotics Ltd., Pimpri. Assistance in the form of equipment and staff was rendered to HAL for their pilot plant trials.

The process for the production of sorbitol from glucose was worked out on pilot plant scale of 10 kg/batch and conditions have been standardized. The final report on the project is being prepared.

35. Monoethylaniline:

Monoethylaniline is an important intermediate required in the manufacture of carbamate type explosives. The estimated total demand of this chemical is around 100 tonnes/year. Based on bench scale experiments, optimum conditions have been arrived at for a continuous process (3 to 4 kg/hr).

The experimental part of the project is completed. Process design is under preparation and demonstrations will be given to interested parties.

36. Aliphatic amines - methylamines:

Methylamines are widely used as intermediates in the manufacture of herbicides, fungicides, detergents, pharmaceuticals, photographic developers, etc., and are not presently manufactured in India. The estimated requirement is around 3-4 thousand tonnes/year.

Ammonia and methanol (both are now available in India) are reacted over a catalyst to form a mixture of methylamines. A bench scale reactor of mild steel of 45 mm dia. has been set up with suitable instruments and accessories. Preliminary runs have been carried out at atmospheric pressures using an indigenous catalyst. Work on the identification and separation of different amines formed is presently in progress.

37. Dimethylaniline:

Pilot plant trials on the batch process (9 kg/batch) were completed with an overall yield of 95% for a 99.5% pure product.

A design report for 500 tonnes/annum was prepared. Work on the development of a continuous process is being continued.

38. Construction of a precision ultrasonic interferometer:

Above instrument is useful in studying thermodynamical data of solutions such as adiabatic compressibility, specific heat at constant value and apparent molal properties.

A complete unit according to our design has been fabricated and tested. The instrument mainly consists of a 5-MC crystal oscillator with a stabilized frequency and power supply, a ratio-bridge consisting of a three matched 52-Ohm resistors and the ultrasonic cell as the fourth arm, a DC-difference amplifier to compare the off balance signal of the ratio bridge with the bridge input voltage and a detector. The velocity in water has been determined with this instrument at 25° as  $(1496.05 \pm 0.08)^m/sec.$  which is comparable with recently published values.

39. Foundry chemicals

39.1. Shell moulding resins: Different compositions using cashew phenol, formaldehyde, hexamine and some industrial wastes like sulphite liquor etc. were prepared and tested for their baking and physical properties of sand cores.

39.2. Sinol core binder: Different trial runs were conducted to standardize the conditions and products tested for their baking and physical characteristics.

39.3. Dry core binder resin: Different compositions were prepared based on sulphite lye etc. and tested.

39.4. Linseed oil - substitute for foundries: The process conditions and the compositions were evolved and standardized. Trial runs on 5 kg/batch have been conducted. On the basis of the bench scale unit, 100 kg/batch pilot plant scale work is being carried out.

39.5. Barrier cream: Modifications in the compositions to bring down the cost and also to improve the qualities and general acceptability of the product were carried out.

39.6. Starch - Dextrin substitute: Samples were prepared and evaluated with regard to their green strength of sand cores, and other physical and baking characteristics.

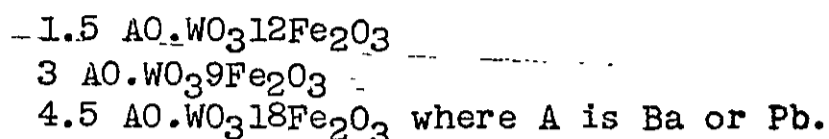
39.7. Starch phosphate: The phosphorous contents of the different compositions prepared are being analysed.

APPLIED BASIC PROJECTS



1. New ferrite compositions:

New ferrimagnetic compounds of the general formula  $La^{3+}Me^{2+}Fe^{3+}_{11}O_{21}$  where Me represents Ni, Co, Mg, Cd, Cu, Zn etc., have been synthesized by solid state reactions between respective oxides. Attempts were made to synthesize magnetic materials of ferroxplane structure having the following general formulae



On all these new compounds, studies in saturation magnetisation, curie temperatures, X-ray powder patterns, electrical conductivity and permeability (initial and complex) have been carried out.

2. Manganites:

New type of manganites having interesting semi-conducting properties have been synthesized earlier which find applications as thermistor materials. Recent studies have established that ZnLi manganites show a new type of magnetic interaction under certain conditions.

On the basis of crystallographic and electrical studies of  $FeCuMnO_4$ ,  $CuCrMnO_4$  and  $NiMnCrO_4$ , it was found that these compounds exhibit the cubic spinel structure and  $Mn^{4+}$  and  $Cu^{1+}$  ions coexist in Cu-Mn spinels. Structural, magnetic and electrical studies of number of compounds having a general formula  $Cu_xMe_{1-x}Mn_{2x}Fe_{2-2x}$  (where Me = Cu, Co, Ni, Mn and Zn) have enabled to establish the site preference energies of the various transition metal ions for the octahedral and tetrahedral sites in the manganites containing Cu. The electrical conductivity measurements indicated that some of the compositions may be suitable for low temperature thermistors.

Similar studies were carried out on  $ZnMn_{2-x}Ni_xO_4$  systems. The paramagnetic susceptibility of these compounds confirmed our earlier observation regarding a new type of magnetic interaction in compounds containing  $Mn^{3+}$   $Mn^{4+}$ .

Thin film thermistors of manganites were prepared by chemical decomposition on glass substrate. Compositions with high

temperature coefficient of conductivity (4 per cent/degree) and small time constant have been found.

3. Development of some ferroelectric materials and studies in their structural and dielectric properties:

The investigation is aimed at preparation of newer potential ferroelectric materials and to study their structural and other characteristics in relation to their ferroelectric and allied properties. Six different samples of doped lead titanate of the general formula  $Pb (La_{\frac{1}{2}} V_{\frac{1}{2}})_x Ti_{1-x}O_3$  were prepared.

Study of above types of doped lead titanate samples was continued. It has been observed that only two compositions with  $X = 0.15$  and  $0.20$  show sharp curie temperatures at  $170^\circ$  and  $100^\circ$  respectively. Further studies also revealed that the dielectric loss for these two compositions are comparatively low. Results for these two compositions are encouraging and further studies to evaluate the suitability of using these materials as transducers similar to the conventional P-Z-T materials are being carried out. Studies are also in progress on systems substituting vanadium with niobium in the compositions.

4. Studies of dielectric and ferroelectric properties of materials having a general formula  $ABO_3$ .

These are ceramic materials, known as Piezoelectric, and have a formula  $Ba_x Pb_{1-x-y/2} Nb_y Zr_{1-y} O_3$ . Similar system can be obtained by replacing 'B' ions. They are widely employed as transducers for vibrations, for the generation of sonic and ultrasonic waves, in electroacoustic pick ups, etc. These materials are not yet made in India and a detailed study of their properties was undertaken. Piezoelectric coupling coefficients of polarised samples were measured and the observed values of certain compositions were found to be higher than the conventional PZ-T materials.

Work carried out so far was submitted in the form of a thesis for a Ph.D. degree.

5. Studies of semiconducting Barium titanate materials (Perovskite type)

These recently developed materials show very high temperature coefficient of resistance and are very

important for making temperature sensors, automatic temperature controllers, safety cut outs, transistor current stabilizers etc. A number of samples were prepared and their dielectric and conductivity properties were studied.

A special impedance bridge capable of simultaneous measurement of capacitance and conductance has been constructed to study the dispersion of conductivity.

6. Studies in photoconducting and electric properties of sulphides and selenides of lead and cadmium

Above compounds find extensive use in visible and infrared spectroscopy, exposure meters, temperature controllers, television and night vision cameras. Attempts are being made to develop and fabricate photoconducting devices using internal oxidants and having optimum properties. Preliminary investigations on the effect of the internal oxidants on the chemically deposited PbS films were found encouraging. The photosensitive layers of CdSe were prepared by vacuum deposition techniques.

The effect of internal oxidant on the various properties of chemically deposited PbS films is being systematically studied. The properties of vacuum deposited CdSe films are being systematically investigated. A recording D.C. field effect bridge of a new design has been developed and constructed. It enables the study of changes in surface states of thin film semiconducting samples and the measurement of time constants of surface relaxation phenomenon. A study of the field effect conductance and time constant changes as a function of oxidation is being carried out for PbS. films. Highly sensitive CdS photoresistors have been prepared by a condensation process. The photoresistors show a change of four to five orders of magnitude in resistivity on illumination.

7. Metal-insulator-metal junctions:

The metal-insulator-metal sandwiches using Al, Bi, Cd, Zn, Au, In etc., as electrode metal films and their oxide or sulphide films as insulators have been studied. The ohmic contact (In-CdS) generally gave space charge limited current in thick films. The non-ohmic contact to perfect insulator (Al-Al<sub>2</sub>O<sub>3</sub>) gives tunneling in very

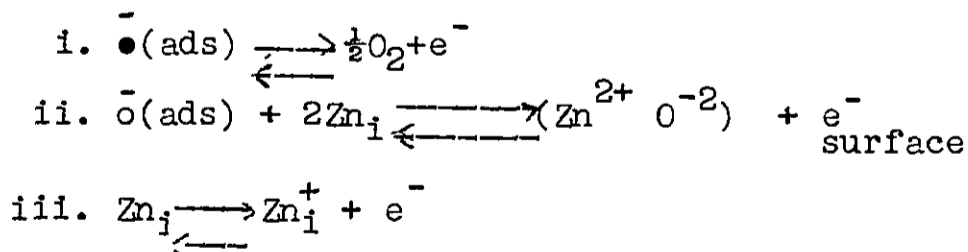
thin films ( $< 100 \text{ \AA}$ ) and in thicker films Schottky-type conduction is predominant.

Al-CdS-Al- Indium sandwiches were studied in detail. It was found that after an irreversible break-down the I-V curve shows an interesting dual negative resistance phenomenon. When the upper electrode is positive the curve first follows a low conductivity path from which it switches over to a high conductivity state through a current controlled negative resistance. On decreasing voltage the high conductivity path is maintained till a critical voltage in the opposite direction is reached where the structure switches back to the low conductivity state through a voltage controlled negative resistance.

#### 8. Oxidic semiconductors:

Studies on plate type and rod type zinc oxide single crystals have been completed. It was found that zinc oxide changes from n- to p-type at  $200^\circ$  which was attributed to ionization of vacant sites. Similar transformation was also observed when zinc oxide was irradiated by  $\gamma$  rays. Resistivity of zinc oxide was found to be sensitive to ambient atmosphere and increases with oxygen pressure.

In plate-type crystals a resistance minimum and maximum was found at  $325^\circ$  and  $370^\circ$  respectively in air. The values shift to  $300^\circ$  and  $390^\circ$  in case of thin films doped with Indium. This behaviour has been explained as due to interplay of the following three reactions:



During the studies of D.C. conductivity of transition metal oxides, a persistent polarization was observed which was present even after the field was switched off. The polarization decayed according to the equation:  $I_0 = I_0 + I \exp -t/T$ . Further T is found to be temperature dependant and follows the equation

$T = I_0 \exp - \Delta E / KT$  where  $\Delta E = 6$  Kcal. A phenomenological theory has been developed for this behaviour which gives the relationship:

$$I = I_0 \exp -t/\tau \quad \text{where } \tau = \epsilon / 2\pi\delta$$

The observed exponential dependance of  $\tau$  on  $T$  suggests that  $\delta$  varies as  $\delta = \delta_0 \exp - \Delta E / KT$  indicating an activated mechanism of conduction. Hence this method can therefore be used to determine the value of  $\Delta E$

#### 9. Laser materials:

It is proposed to synthesize a number of rare earth chelates which may have a possible application as laser materials.

A number of new Europium and Samarium chelates viz. (a) mixed ligand complexes containing  $\beta$ -diketone and the acetate anion, (b)  $\beta$ -diketonates complexed with nitrogen donors and (c)  $\beta$ -diketonates complexed with lewis bases have been prepared for their possible applications as laser materials. Absorption and fluorescence spectra of these compounds have been studied from room temperature down to liquid nitrogen temperature in various solvents.

Properties such as quantum yield, radiative life time, spectral band width of these materials are being studied.

#### 10. Spectrochemical studies:

Infra-red and electronic spectral studies are used in the elucidation of molecular structural problems as well as in the quantitative analysis of compounds. The spectral data collected are interpreted to characterize the compounds and correlate with their physical and chemical properties.

In continuation of our studies on urea derivatives infra-red spectra of a series of substituted ureas of the type  $R \cdot NH \cdot CONH_2$  and  $R \cdot NHCONH \cdot R_1$  where  $R =$  alkyl and  $R_1 =$  Aryl or alkyl were investigated. It has been shown that the coupling between the carbonyl and amino group in the secondary amide is much

larger than in the primary amide group.

Dimer equilibrium in carbon tetrachloride solutions of compounds  $C_2H_5OCH_2CH_2OH$ ,  $CH_3(CH_2)_{17}OCH_2CH_2OH$ ,  $C_2H_5OCH_2CH_2OCH_2CH_2OH$  and  $CH_3(CH_2)_{17}OCH_2CH_2OCH_2CH_2OH$ , were studied by the I.R.-Spectra in the hydroxy stretching region. These compounds were found to form only dimers at higher concentrations in contrast to normal alcohols which form polymers at similar concentrations. In the case of compounds with two  $(OCH_2CH_2O)$  groups two types of intramolecularly bonded monomers having five and eight membered rings were found to be in equilibrium with the cyclic dimer.

Infra-red spectra of nicotinic and isonicotinic acids were analysed and the frequencies due to  $NH^+$  and  $COOH$  groups have been characterized.

A comparative spectral study of the three forms of anthranilic acid showed that while forms I and III are similar and probably form dimers in the solid, form II could have molecules which are dipolar. Further, with the help of a variable temperature cell, it was found that the form II changes over to form I at  $82^\circ C$ , and it is irreversible.

I.R. spectrum of paraminobenzoic acid was investigated and the assignments for the various bands were given.

#### 11. Studies in catalysis:

Transition metals and their compounds are used as catalyst for industrial reactions. The object of the project is to prepare such catalysts for oxidation and other reactions, to study their physico-chemical properties and to correlate them with their activity.

Ni-Zn catalyst was prepared in the form of mixed oxalate by co-precipitation. The decomposition temperatures and surface activities of the catalyst were studied by thermogravimetric analysis and surface area determinations.

Vanadium pentoxide was prepared by thermal decomposition of ammonium vanadate. Thermogravimetric analysis revealed that the decomposition proceeds in four well defined stages. Analysis of the various intermediates and their surface area measurement showed that they possess low surface areas ranging from  $2\text{m}^2/\text{g}$  to about  $12\text{m}^2/\text{g}$ . Supported  $\text{V}_2\text{O}_5$  catalyst was sintered at temperatures from  $100-500^\circ$  and with the increase in temperature surface area decreased from  $114\text{m}^2/\text{g}$  to  $74\text{m}^2/\text{g}$ . Surface area of the support decreased from  $200\text{m}^2/\text{g}$  to  $114\text{m}^2/\text{g}$ .

In experiments with evaporated copper film, it was found that copper film does not adsorb molecular hydrogen at low temperatures. However, atomic hydrogen is taken up rapidly at liquid air temperatures. On raising the temperature the hydrogen atoms recombine and desorb as molecular hydrogen.

12. Semi conductivity properties of thin films (i) Resistivities and thermoelectric power measurements (ii) Studies on Hall effect:

The basic knowledge of electron transport and study of thermoelectric power and Hall co-efficient are useful in technical applications of semi-conductors. A systematic study of semi conducting properties of thin films of PbS, PbSe, PbTe,  $\text{Bi}_2\text{S}_3$ ,  $\text{Bi}_2\text{T}_3$  and InSb have been made.

Investigations on the Hall coefficient of thin films of  $\text{Tl}_2\text{T}_e$ ,  $\text{Tl}_2\text{Se}$ , HgTe, HgSe and InSb was carried out especially to see the effect of substrate temperature during the deposition on the various semiconducting parameters such as Hall coefficient ( $R_H$ ), conductivity ( $\sigma$ ), Hall mobility ( $\mu_H$ ), carrier concentration ( $\mu$ ), and mean free path ( $l_0$ ). Increase in the values of  $R_H$ ,  $\sigma$ ,  $\mu_H$  and  $l_0$  of the deposited films formed at higher substrate temperature is explained on the basis of the decrease of the growth defects of films with the rise in substrate temperature. Indium antimonide films deposited at  $360^\circ$ . Substrate temperature exhibited high Hall mobilities up to about  $3200\text{ cm}^2/\text{v-sec}$ . A comparison of the different semiconducting parameters of single crystal films formed on mica was made with those of polycrystalline

films and results indicated that  $R_H$ ,  $\rho$ ,  $\mu$  H and  $l_0$  increased considerably for single crystal films, even though these values were much less than those for the bulk. A set up for the measurement of Hall coefficient of the thin films of above compounds upto liquid air temperature is made and the investigation is in progress. A detailed study has also been made on the semiconducting parameters especially conductivity, thermoelectric power, mean free path etc. of thin films, with thickness varying from 1500  $\text{Å}$  to 6000  $\text{Å}$  of selenide and telluride of thallium which are often used as photoconductors. Though the selenide is a semiconductor, the telluride films behaved more or less as metalloids as previously observed by us in case of  $\text{Bi}_2\text{Te}_3$ .

13. Physico-Chemical studies of proteins with particular reference to Indian silks:

Although extensive work has been carried out on the characterization and study of the composition on Bombyx Mori, precious little is known about more common Indian silks. The characterization of various Indian silk proteins for their composition and to study the physical characteristics like tensile strength, ageing etc., and their comparison with the standard variety is the object of the study. Some work on solution behaviour of silk in different salt solutions and study of the amino composition of some Indian varieties was carried out.

Brice-Phoenix Photometer was repaired, calibrated and set up for characterization studies. Removal of sericin from fibroin, is necessary for any further fundamental studies. A process has been standardized to achieve this separation without least damage to protein. A technique has been standardized for the dissolution of silk fibroin in LiBr solution without drastic heat treatment. The solubilities of some of the fibroins in salt solutions of varying concentrations have also been determined spectrophotometrically.

14. Synthesis and study of new titanium organics:

Organic titanium compounds are used in heat resistant coatings, water-proofing agents, and in modifying polymers. They also catalyse some polymerization reactions. Basic research on the synthesis and study



of new titanium organics in which the organic moieties are linked to the titanium non-ionogenically through oxygen or other atoms has been undertaken.

Starting from the commercially available titanium tetrachloride, a number of organoxy titanium compounds and their aliphatic and aromatic derivatives have been prepared and their chemical properties studied.

The primary products (halogeno-derivatives) obtained from partial substitution of titanium tetrachloride with aliphatic and aromatic oxy-compounds as well as with the sulphate esters were used as intermediates for the introduction of further substitution of the remaining chlorine atoms. New derivatives of cyclohexanol were synthesized and are being used as intermediates for the synthesis of more complex titanium organics. Partly substituted organoxy-titanium chlorides were used in attempts to introduce direct Ti-C bonds. Some successes have been recorded.

In view of the recent applications of organic titanium compounds in many fields, the physical properties of the newly synthesized compounds are being studied.

#### 15. Fluorine chemicals:

Attempts are being made to prepare fluorine chemicals with the help of readily available fluorinating agents.

All the fluorinating agents so far tried, especially  $\text{KSbF}_6$ ,  $\text{Na}_2\text{SiF}_6$ ,  $\text{AsF}_3$  (dry state reactions)  $\text{KF}$  (in dry and solvent state) are found effective in replacing activated chlorine by fluorine; however, yields of the final products are not promising.

During fluorination of aromatic chlorine compounds by using  $\text{KF}$  in solvent medium along with catalyst,  $\text{CaF}_2$  was found to be rather inert towards carbon plus chlorine at about  $800^\circ$ .  $(\text{NH}_4)_2\text{MnF}_6$  has been prepared by electrolytic oxidation of divalent manganese in  $\text{HF}$  acid. Attempts are in progress to employ this electrolytic reaction for fluorination purposes. A compound believed to be  $\text{CF}_3$  substituted dithizone has been prepared.

Following preparations were also attempted. Anhydrous mercuric silicofluoride (by the reaction of  $\text{HgCl}_2$  and anilinium

silicofluoride in alcohol), anhydrous magnesium fluoberyllate and  $\text{Ag}_2\text{TiF}_6$ .

16. New methods of analysis:

16.1. Direct reduction of insoluble vat dyes in the solid state at the dropping mercury electrode

Identification of vat dyes by direct reduction in a suspension form at the dropping mercury electrode give rise to maxima shaped peaks. It was concluded that the peak currents depend on several parameters such as particle size, rate of stirring etc.

Comparison of half-wave potentials of certain vat dyes with their respective peak potentials do not show any simple thermodynamic relationship. Nevertheless the respective peak potentials can be used for the quantitative identification of such vat dyes which are polarographically active in the solid form. The work is completed.

16.2. Separation and electro-depositions of Ni and Co:

Accurate determination of Ni and Co from their mixtures by using conventional gravimetric or titrimetric procedures involve the prior separation of one from the other. Besides, even the so-called best method for Co which is electrodeposition at the cathode suffer from serious defects. From no electrolytic bath a pure bright and adherent deposit is obtained.

The objective is (i) to develop rapid method for separation, and (ii) a satisfactory method for electrodeposition.

Preliminary experiments indicate that using malonic acid or its derivatives both these objectives could be obtained. Separation of Co from Ni as well as their electrodeposition could be achieved.

16.3. Mechanism of molybdate catalysed dimethyl glyoxime reduction

The catalytic reduction of dimethyl glyoxime with stannous chloride in presence of molybdate has been investigated.

It has now been established that  $\text{MO}^{+3}$  and  $\text{MO}^{+4}$  are the catalytically active species responsible for reduction of dimethyl glyoxime to Ammonia and Acetoin via diacetyl. The study on the mechanism of reaction has been completed.

17. Studies on the chemical structure of the gum from Terminalia tomentosa (Mar - Ain)

Chemical investigations on the structure of this indigenous gum have been undertaken with a view to suggest its proper utilization. The gum was found to consist mainly of D-galactose, D-xylose and L-arabinose units. The minor components are L-rhamnose and D-glucuronic acid. Out of the four chromatographically pure aldobiouronic acids isolated by partial degradation of the gum, two were assigned structures.

The remaining two chromatographically pure aldobiouronic acids which were isolated by the partial degradation of the gum were assigned the following structures:

- (a) 3- O - (  $\beta$ -D - glucopyranosyluronic acid)
- (b) 4- O - (  $\beta$ -D - glucopyranosyluronic acid)

18. Cyclic acetals and ketals of monosaccharides

This problem was taken up in connection with attempts to improve the yields of 2,3 : 4,6 - di-O-isopropylidene L-sorbofuranose, which is a key-intermediate for the synthesis of vitamin C. New TLC techniques were developed and using these techniques many hitherto unknown cyclic acetals and ketals of various sugars were isolated and characterized.

On the basis of mass spectral studies, the structure of one of the new di-O-isopropylidene derivatives of L-sorbose which was earlier assigned the structure of 2,3 : 4,5-di-O-isopropylidene- $\alpha$ -L-sorbofuranose (I) was revised to 1, 2:3, 4-di-O-isopropylidene-3-L-sorbofuranose (II) (Figures at the end )

19. The chemical investigation of the plant Balanophora Indica:

This plant is a root parasite and causes destruction of coffee plantation. Tubers of the plant are being investigated for the chemical constituents and for suggesting possible remedies against these infections.

Isolation of active principles responsible for the root parasites was tried.

20. Transformation products of citral:

The object of the project is to find new ways of utilization of citral, obtained from lemon grass oil. Transformation of citral to perfumery materials such as linalool, citronellal, citronellol, geraniol will be studied.

A convenient method for the conversion of citral to citral epoxide (25 g. of starting material) in high yields has been developed. This method can be adopted for large-scale production. A process for the preparation of methyl heptenone involving retro-aldolization of citral under mild conditions has been developed.

21. Polyesters as stationary phases in GLC analysis:

The spacing of methylene groups in glycolic fragment has been critically examined and the relation found to be linear. The molar proportions of the polyesters have also been investigated.

Study of the self-polymerisation of the hydroxy acids was continued. The effect of temperature and other experimental conditions on the nature of the polymer, was studied. The temperature of the ester formation was found to be a governing factor and it controlled the nature of the polyester. Simultaneously, a novel method was developed for the impregnation of the polyesters synthesised from hydroxy acids. Indian fire-brick supports were used throughout these experiments. For this purpose, supporting material from Indian fire-bricks - was carefully processed. For direct comparison, columns were prepared by using (a) 'celite' and (b) Indian fire-brick powder as supporting material and these two types of columns are being compared and

necessary treatments will be carried out in the case of Indian fire-bricks.

22. Transformation of Kurchi alkaloids:

Work has been undertaken with a view to converting some of the 'Kurchi' alkaloids to steroidal intermediates. Apart from their significance enroute to aldosterone they may constitute a new class by themselves having some pharmacological properties. The work which was started in 1959 June involved the standardization of the methods of isolation of alkaloids and stepwise conversion of conessine, isoconessmine and conessimine and holarrhimine to 18-hydroxy-progesterone or its derivatives.

The present work involves the reinvestigation of the reaction (conessine  $\longrightarrow$  Schiff's base) on account of the poor yields. One of the intermediates, 18-amino-progesterone has been isolated. Further studies on the characterization of this compound are in progress. Secondly, as indicated from the studies of the model compound, isoquinoline, the Schiff's base on treatment with perbenzoic acid and sodium meta-periodate yields a crystalline compound having the desired IR spectra of the ketoxime. Further confirmation of this compound and its final conversion to aldosterone have been undertaken. The work will be continued.

23. Antioxidants, anti-ozonants, accelerators and blowing agents for rubber:

Attempts are being made to develop various types of rubber chemicals from indigenous raw material such as cashew shell oil.

Sulphides of tetrahydroanacardol have been synthesized. Antiozonants based on tetrahydroanacardol possessing urea linkages are also prepared. Sulphides of anacardol have been synthesized which are expected to find use as reclaiming agents for rubber. Two types of antioxidants have been prepared and evaluated for their properties.

24. Polymerization of turpentine fractions:

Indian turpentine oil contains a large proportion of

$\Delta^3$  carene and with a view to find useful applications of carene, some studies on its polymerization have been initiated.

Polymerization of  $\Delta^3$  carene using  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{SnCl}_4$  and  $\text{TiCl}_4$  as catalysts gave a very small proportion of a polymeric material. The major portion of the resultant product was found to be a dimer. The dimeric products were not found much useful as plasticizer for PVC and although they were compatible with natural rubber, no useful properties could be imparted to rubber mix. No useful products were obtained in the attempts of making copolymers of  $\Delta^3$ -carene with styrene and 3-pinene. Work on this problem has been discontinued.

25. Mass transfer characteristics of rotary sieve contactor:

The object is to study the characteristics of rotary screen contactor (RSC) for liquid-liquid extraction. This is in continuation of work done on perforated rotary disc contactor (PRDC).

Use of soldered-edge rotary sieve plates, instead of the plain discs is being investigated. The flooding performance was determined using water-kerosene and water-benzene systems. The mass transfer characteristics are being studied with benzene-acetic acid-water system.

26. Reaction models and reactor design:

A knowledge of the controlling mechanism in different reactions is a necessary prerequisite for the design of industrial reactors. Furthermore the basic aspects involved in the development of models can lead to generalised conclusions. It is hoped eventually to formulate a unified approach for different reacting systems and develop basically sound and rational methods for the design, optimisation and stability of industrial reactions.

Work has so far been carried out on certain fluid-solid and gas-liquid systems. In particular, models have been proposed for the chlorination of ethylene to ethylene dichloride, formation of BON acid, chlorination of ilmenite, and a few other vapour phase catalytic reactions.

Models have been developed for the oxidation of benzene and

toluene and a rate equation has been determined for the hydrogenation of anacardol to tetrahydrocardol.

#### 27. Studies in fluidization:

Fluidization is one of the very important operations in the chemical industry, but several aspects of fluidization still require theoretical and experimental examination.

A new type of fluidized bed operation termed as semi-fluidization has been studied in detail and suitable equations have been developed. A new and completely generalised method for the prediction of the onset of fluidization has been proposed.

The performance of a semi-fluidized reactor has been studied and a new reactor utilising this principle has been proposed. The superiority of this reactor over the other types of reactor for exothermal reactions has been experimentally established. Further, a fluidized bed reactor from plastic sheets and tubes has been designed for examining the use of fluidization for heating industrial reactors. A theoretical analysis of the uniformity of fluidization has been made.

#### 28. Studies in mass transfer:

Several operations in chemical engineering involves mass transfer. Theoretical and experimental studies have been carried out to elucidate certain aspects of mass transfer.

Investigations have been carried out on the use of pulsed extraction columns for improving the efficiency of extraction by pulsation.

Considerable computation has been carried out for proposing a generalised equation for liquid-liquid extraction. Experimental work on mass transfer during drop formation has been completed.

#### 29. Estimation of the thermodynamic and transport properties:

Often it is not possible to experimentally determine some of the properties required in process design and hence these have to be estimated. Work on the development of improved estimation procedures for different transport and thermodynamic properties has been undertaken. These will also be determined experimentally.

An improved method has been developed for diffusion coefficient in liquids and also for estimating the latent heat of vaporisation. The method for latent heat estimation is being further improved. A beginning has been made for setting up an apparatus for determining the more important properties.



SERVICE PROJECTS

1. National collection of industrial microorganisms:

NCL maintains a number of non-pathogenic microorganisms such as yeast bacteria and fungi which are of importance in research and industry. Cultures are supplied free of charge on request, to scientific institutions and industries.

90 cultures have been received from CFTRI, Mysore for their maintenance in the national collection. The number of the microorganisms now maintained is nearing 1300.

253 cultures have been despatched to various industries and institutions.

Different Agar samples from CMCRI, Bhavnagar were tested for their suitability for growth of microorganisms.

2. Physico-analytical chemistry: (Service project)

Work done for outside parties:

Ash from sulphur burners - M/s. Travancore Titanium Products Ltd., Trivendrum.

Indium metal from M/s. Semiconductors Ltd., Poona.

Cutlery alloy from All India Handicrafts Board, Bombay.

Preparation of standard samples for analysis in collaboration with NML - 2 brass samples.

Metallic lead from National Peroxide, Bombay.

Work done for other groups in NCL:

Work relating to colour standards for the following was done.

Butyl phthalate (OID)

Silica gel (FCP)

Calcium halophosphate (Dr. Sinha)

Sodium diethyl dithiocarbonate (FCP)

Phenoxyacetic acid (FCP)

Soda meta per iodate (FCP)

3-5-Dinitrobenzoyl chloride (FCP)

ZnO for trace impurities (Dr. Gupta)

Silver foil for trace impurities (RTL)

Lac dye ash (DRL)

### 3. Mass spectroscopy:

Installation of a double focussing mass spectrometer CEC-21-110B was completed.

In collaboration with scientists in the NCL about 200 samples were analysed and the mass spectra interpreted to get mass spectral evidence on the structure of sesquiterpenes, triterpenes, carbohydrates and a few other oxygen heterocycles. Extensive deuteration studies were also carried out on some samples to support the proposed structures. A limited number of samples were also analysed for outsiders.

### 4. Microanalysis:

Microanalysis of organic compounds for various elements and functional groups e.g. C and H, N, halogen, S, Methoxyl, Acyl, C-methyl, N-methyl, Active hydrogen, Molecular weight is conducted. During the period 1490 analyses for elements and 112 analyses for various functional groups were carried out, the calculated charges for which would be Rs.9,810/- according to the present charges for microanalysis. Of these analyses 61 were carried out for outside institutions and the charges for the same were Rs.352/-.

Modifications of the existing microanalytical methods for their wider applicability were also studied and a rapid micro-Dumas method is being standardised for the estimation of Nitrogen in Organic Compounds.

### 5. Spectroscopic work

Analytical and structure elucidation work is carried out by various physico organic techniques such as NMR, IR, UV, and visible spectra. Samples studied during the period are as follows.

	NCL workers	Outsiders	Total
I.R.	3354	131	3485
U.V.	781	66	847
Visible	168	-	168
N.M.R.	954	22	976

6. V.P.C. Analysis:

Samples analysed for NCL workers	-	3020
Samples analysed for outsiders	-	180

7. X-ray patterns:

90-X-ray powder patterns have been obtained for various groups in NCL.

8. Instrumentation:

Servicing and maintenance work of the following special equipments in the NCL is routinely done.

NMR, Mass spectrometer, IR, UV and visible spectrophotometers x-ray machine, pH meters, colorimeters, potentiometers, gas chromatographs, electron diffraction camera, electron microscope, ultrasonic generator, Sova recorders and nuclear instruments.

Running and maintenance of the liquid air plant and supply of liquid air to various groups in NCL is carried out.

Work done for outside parties

1. Reconditioning of three Mercury pulse delay units (IAF Radar).
2. Servicing of Electronic stimulator (B.J.Medical College).
3. Servicing of pH meters (CPHERI field station, Poona).

Total number of jobs completed	184
Test reports	69
	253

9. Workshop:

Total number of jobs completed by Workshop is 1306. The roughly worked out cost for this work is estimated <sup>at</sup> /about Rs.91,388.

1. General maintenance	- 987	Approx. cost Rs.62,723.00
2. Fabrication of equipments	- 81	Approx. cost Rs. 4,520.00
3. Project jobs including fabrication of equipment and general maintenance	- 238	Approx. cost Rs.24,145.00

10. Glass Blowing Section:

Number of repair-jobs for NCL workers		2000 App. value Rs.50,000
Number of jobs for sponsored schemes in NCL		662 App. value Rs.20,000
Production of Standard Ground Glass joints		2800 App. value Rs.30,000

Special Fabrications for NCL

		<u>App. cost Rs.</u>
(a) Mercury diffusion pump for Mass Spectrometer	-	1500/-
(b) Mercury diffusion pump for T.R.L.		1500/-
(c) Continuous cyclone film evaporator unit for DRL	-	2000/-
(d) Reactor for general utility for OID 6 Nos.	-	3000/-

Work done for outside parties

		<u>Cost Rs.</u>
(1) Extractor with condenser, adopter, aspirator bottle and soxhlet unit with cold finger (B.J.Medical College, Poona)	-	200/-
(2) Fabrication of jacketed columns (Maharashtra Association for the Cultivation of Science, Poona 4)	-	136/-
(3) Preparation of cells as per sketch (Dept. of Chem., University of Saugar, Saugar,MP)	-	250/-
(4) Fabrication of Pyrex Glass distiller-double stage (Institute of Tropical Meteorology, Poona 5)	-	400/-
(5) Repairing of one number of rotameter glass pipe (Sandvik Asia Ltd., Poona 12)		

## Training

- (1) Shri S. Vishwanathan, Glass Blower, from College of Nagpur, has undergone training in this Section for detailed operational know-how of Glass Blowing Lathe for making standard ground glass joints, for a period of six weeks from 23rd May 1966.
- (2) Shri M.V.Gole, STA, from Central Salt and Marine Chemicals Research Institute, Bhavnagar 2, has undergone training in the technology of assembling and checking high-vacuum of B.E.A. apparatus for studying nitrogen absorption methods, from 6 July 1966 for one week.

## 11. Technical Services:

Feasibility reports were prepared on the following projects.

Anion exchange resins, Hard ferrites, Rayon grade pulp, Carbon tetrachloride, Chlorination of ethylene, Vapour phase chromatograph.

Feasibility reports on the following projects are in progress

$\beta$ -Ionone, l-menthol,  $\omega$ -chloroacetophenone, theophylline, Costus root oil, Ambrettolide.

Price fixation for chemicals made in FCP is carried out.

More than 200 enquiries of industrial importance were attended and about 58 non-technical notes on various processes were supplied to private parties and Govt. organizations.

Negotiations were conducted for the release of vapour, phase chromatograph, Acetanilide, and Phthalates. Draft agreement for the release were finalised and the last two have already been executed.

Annual Report for (1965-66) was compiled and published.

A report on the various projects in NCL giving its background, actual work, market potential etc. was compiled for estimates committee.

A summary of the position on the various processes released through NRDC was prepared.

About 24 exhibits on NCL developed processes were prepared and sent to various exhibitions.

Dr. S. K. Subramanian and Dr. N.L.Dutta visited M/s. Sarabhai Merck, Baroda and Bombay in connection with FCP work (17th to 19th May) and submitted a report of their visit.

Terms and conditions for release. of processes in various CSIR Laboratories and other research institutions was studied.

Study of technical and economic aspect involved in foreign collaboration and collection of data on compressors is in progress.

In addition to the above work, routine work like sending Research Utilization Data, CSIR News, attending visitors, technical advice, project follow up, collection of information for answering parliamentary questions etc. was carried out.

## BASIC PROJECTS



## 1. Theoretical investigations on solid state and molecular physics

### 1.1. Interactions involving conduction electrons in magnetic metals and alloys

Earlier the interaction between conduction electrons and impurity states were studied taking into account s-d mixing and exchange interactions.

The possible mechanism of resistance minimum in dilute alloys with transition element impurities which do not show localised magnetic moment has been formulated. The interaction consists of a combination of potential scattering of conduction electrons by impurity coupled with exchange interaction of the conduction electrons with the electrons of the impurity atoms. In the formulation the role of both empty and occupied impurity states is taken into account. The resulting expression has the form

$$\rho(\text{Total}) = aT^{-1} + C\rho_r - C\rho_s^{(0)}T$$

where  $C$  = concentration of impurity and  $a, \rho_r, \rho_s^{(0)}$  are appropriate coefficients and  $T$  is the temperature. Actual comparison shows that in titanium containing transition element impurity a resistance minimum does occur at around  $20^\circ\text{K}$ . This is in agreement with the available experimental results.

### 1.2. Superconductivity in metals and alloys:

Various physical factors which influence the transition temperature of superconductors are being studied since superconductors with high transition temperatures will open up numerous avenues for practical application. The effect of pressure and impurities were studied and a theoretical mechanism was developed to explain the increase or decrease of superconducting transition temperatures.

The occurrence of high transition temperatures in certain superconducting systems has been examined in relation to their structures and other physical factors. For this purpose the effect of one-body spin independent interactions involving

conduction and localised electrons states taken in conjunction with phonon induced attractive electron-electron interaction was analysed. The method of double time Green's function was followed in the formulation. It has been found that there is a definite enhancement in the transition temperature by a factor.

$$\exp \left[ C^2 M^4 \rho(\omega) / \langle \Delta^2 + \pi^2 C^2 M^4 \rho^2(\omega) \rangle \right]$$

which 'C' is the concentration of sites carrying nonmagnetic localised states, M is the one-body interaction parameter ( $\kappa \omega_D$ ) Debye energy and  $\Delta$  is the parameter related to the energy of the localised level. Thus the one-body interaction terms which arise from structure effects seem to be responsible for enhancement of transition temperature in superconductors. This is very promising for development of high transition temperature superconductors.

### 1.3. Phonon - magnon interactions in magnetically ordered solids:

The object is to find out the basic mechanism of interactions involving phonon and magnon excitations in magnetic solids. Atomistic theory of interaction processes involving accoustical phonons and magnons in ferro, antiferro and ferri-magnetic systems have been completed and the rate processes determined. Study of thermal conductivity and magnetisations of manganese ferrite and magnetic garrets was also completed.

Taking into account the above interactions the renormalization of the energy spectrum of the phonon and magnon modes was carried out. The renormalized phonon modes show that there will be change in the Debye temperature at the Curie point of the magnetic systems. The renormalised spin wave frequency shows that instability in the acoustic mode may develop in the high temperature region. In order to formulate the co-existence of magnetic and ferroelectric phases the interactions between polarisation waves and spin waves were studied in magnetodielectrics. For this purpose the role of optical phonons and magnons was taken into account. Relaxation frequencies for such processes in antiferro and ferrimagnetic systems were calculated at various temperatures. It was found that the contribution of optical phonon-magnon

interaction becomes quite appreciable at 25°K.

1.4. Exchange interaction in magnetic solids:

In the last few years indirect exchange process in magnetic compounds were studied.

Taking cognisance of mixing and exchange interactions between impurities and its neighbours in dilute alloys (Fe in Pb) the origin of giant magnetic moment has been studied. A method of treating spin waves in linear ferro-antiferro chains using semi-classical approximation has been developed.

1.5. Electronic structure of molecules:

The electronic structures of conjugated organic molecules and the electron densities are extremely difficult to calculate by rigorous quantum mechanical methods. For molecules containing mobile electrons the electron gas approximation was found more suitable. This method and its variations have been used to calculate the above mentioned properties of a large number of quinone molecules.

The matter was prepared for presentation of the work in the form of a thesis.

1.6. Mobility in polar semiconductors:

The transport properties of semiconductors are governed by the interaction of carriers of current (electrons and holes) with various other physical factors in the system such as phonons and static perturbing potentials. A general theory of mobility in compound semiconductors has been completed and a new concept of multi-band conduction has been introduced. The high and low temperature mobilities in compound semiconductors have been explained.

The behaviour of carriers in semiconductors in high electric fields has been studied. In the perturbation the role of the electric field causing intervalley transition has been taken into consideration.

1.7. State of atoms in the presence of crystal and radiation fields:

The object is to study the spin and electronic states

of paramagnetic atoms in crystals in the presence of the static and oscillating fields. By a suitable canonical transformation it was possible to get spin-spin interaction in some paramagnetic system.

An expression has been derived for the temperature dependent exchange integral for a pair of interacting shallow donors substituted, in a dielectric material. This has been achieved by taking into account the phonon induced mixing of excited orbital states with the ground orbital states of the impurity centres. The results have been used to explain the temperature narrowing of the EPR line width observed by some workers in phosphorous doped germanium at low temperatures. Good agreement between theory and experimental results seems to favour the proposed mechanism in preference to one of motional narrowing due to hopping.

#### 1.8. Magnetic break-down in solids:

The behaviour of matter in the presence of very high magnetic field has been studied to investigate the electron trajectories and the criteria of the magnetic break-down under various conditions.

The Schrodinger equation for certain typical electron orbits in metals was set up and the solutions of this equation were obtained. The probability that the adiabatic part is not followed, that is, the criteria for the magnetic break-down was obtained by using the method of analytical continuation. It is found that high magnetic field low energy gap between two electronic states and a large bend in the adiabatic path, favours the phenomenon of magnetic break-down. Work on the problem has been completed.

## 2. Experimental studies in molecular physics:

### 2.1. Studies in thermodynamic properties of solids:

Variations of specific heat characteristics with temperature would provide an insight into the details of molecular structure, electronic energy level pattern, and mechanism of various transitions and phase transformations occurring in solids and also provides

basic data for evaluating thermodynamic functions and to control or predict chemical behaviour. Studies of heat capacities of the compounds of the type  $KMF_3$  where  $M = Mn, Co, Ni$  and  $Cu$  have been undertaken.

Low temperature calorimetry: Heat capacity measurements on the diamagnetic  $KZnF_3$  have been completed and the detailed calculations of the entropy changes are in progress. This will give a detailed picture of the entropy and enthalpy changes associated with the anti-ferromagnetic ordering in compounds of  $KMF_3$ , referred to above. Since the magnetic interaction is by super exchange, the random replacement of the transition metal ion by zinc may be expected to weaken the interaction resulting in a lowering of the Neel temperature. The study of such an effect on  $KNiF_3$  has been undertaken. Two compounds with compositions  $Ni_{0.85}Zn_{0.15}F_3$  and  $KNi_{0.69}Zn_{0.31}F_3$  have been prepared. The heat capacity measurements of the first compound have been completed and its Neel temperature was found to be  $239^\circ K$  as compared to  $253^\circ K$  for  $KNiF_3$  reported earlier.

High temperature calorimetry: The thermal studies  $SrMo_{\frac{1}{2}}Co_{\frac{1}{2}}O_3$  have been completed. A transition observed at  $489^\circ K$  has been attributed to be due to crystallographic change from tetragonal to cubic structure of the compound. Work on the compound  $SrW_{\frac{1}{2}}Ni_{\frac{1}{2}}O_3$  is in progress. In continuation of the work on telluride systems a compound with the formula  $Fe_{1.1}Te$  has been prepared and its heat capacity measurements revealed a peak at  $478^\circ K$  which was ascribed to be due to a change of direction of the moments in the ferromagnetic state of the compound. The excess entropy due to magnetic and crystal structural transitions have been calculated. The thermodynamic functions such as entropy, enthalpy etc, have been tabulated at regular intervals of temperature in the respective ranges.

## 2.2. Studies in crystal and molecular structure of organic compounds with the help of x-ray diffraction methods:

X-ray diffraction studies provide valuable data to understand the electronic structure of the molecules which would explain the mechanism of the physico-chemical behaviour of the material system. At NCL studies of

the structure of simple aliphatic and aromatic compounds are being made and the crystal and molecular structures of a number of compounds have been determined.

The structure analysis of ortho-nitrobenzoic acid,  $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$  was completed and the structure discussed on the basis of electronic theories. The approximate structure of p-nitrobenzaldehyde has been determined, refinement is in progress. The approximate structures of nickel-imidazole nitrate and di-chloroanthranilic acid have also been determined. These structures are being refined. A study of disorder and polytypism in sodium 2-oxocaproate was also made.

Potassium benzilate,  $\text{C}_{14}\text{H}_{11}\text{O}_3\text{K}$  was crystallized from aqueous solution in monoclinic form with space group  $\text{P}2_1/a$  and cell dimensions as

$$a = 10.34; b = 9.02; c = 14.08 \text{ \AA} \text{ and } \beta = 111.4^\circ$$

The observed density at  $25^\circ\text{C}$ , obtained by the flotation method is  $1.441 \text{ g.cm}^{-3}$  and that calculated on the basis of 4 molecules per unit cell is  $1.446 \text{ g.cm}^{-3}$ .

Work on the determination of the structure is in progress. Three dimensional refinement of the structures of

- (1) Sodium pyruvate
- (2) Sodium 2-oxovalerate
- (3) Sodium 2-oxocaproate
- (4) Sodium 2-oxoheptanoate

.. was completed.

### 2.3. Measurement of adiabatic compressibility, specific heat at constant volume and apparent molal properties of some solutions

Ultrasonics is a powerful method for studying the characteristics of solutions. Sound velocity measurements in the polyelectrolyte solutions are expected to give interesting results.

A precision ultrasonic interferometer has been developed

to measure accurately the velocity in dilute solutions. The adiabatic compressibilities of dilute solutions of carboxy methyl cellulose has been determined from sound velocity and density data. Assuming solvent molecules concerned in solvation to be effectively incompressible, the degree of solvation has been estimated from the adiabatic compressibilities of the solution and solvents.

#### 2.4. Degradation of low chain molecules by ultrasonics:

The ultrasonic degradation has some resemblance to mechanical degradation i.e. mastication and the process is investigated on different industrially useful polymers. Studies are being made on degradation of butyl rubber.

Four samples of butyl rubber having molecular weights in the range  $0.6 \times 10^6$  to  $1.66 \times 10^6$  have been used and the degradation has been studied both by DPPH estimation and solution viscosity methods. It has been observed that both the rate parameters  $K$  and the final value,  $(\overline{DP})_{\infty}$  of the degree of polymerization are influenced by  $(\overline{DP})_0$  values. It is reasonable that molecules with larger chain length will encounter a greater rupturing stress and would degrade more drastically than molecules having comparatively shorter chain length. The plot of  $K$  and  $(\overline{DP})_{\infty}$  versus  $(\overline{DP})_0$  shows a linear relationship indicating that the rate constant  $K$  and  $(\overline{DP})_{\infty}$  are directly proportional to  $(\overline{DP})_0$  in the system studied.

### 3. Radiation and nuclear chemistry

#### 3.1. Mössbauer spectra of spinel type compounds:

The object of the project is to study the use of M. effect and its application to magnetism and the nature of chemical bonding.

M.S. of  $Fe^{2+} [Cr_2^{3+}]O_4$ ,  $Ge^{4+} [Fe_2^{3+}]O_4$ ,  $Zn^{2+} [Fe^{3+}]O_4$  and  $Cd^{2+} [Fe^{3+}]O_4$  were studied.

Table

S.No.	Absorber	Absorber temp. °C.	Isomer shift w.r.t. stainless steel. (mm./sec.)	Quadrupole splitting (mm./sec.)
1.	Fe(CoNi)O <sub>4</sub>	465°	0.18 ± 0.04	0.4 ± 0.04
2.	Fe(MnCu)O <sub>4</sub>	454°	0.19 ± 0.04	0.5 ± 0.01

The M.S. of the inverse spinels containing Fe<sup>+3</sup> at the A sites (referred in the table above) in the paramagnetic state, show a pronounced quadrupole splitting which may be attributed to the asymmetric charge distribution associated with the random distribution of the trivalent and divalent ions on the neighbouring 12B sites which surround each A-site.

### 3.2. Effect of radiation on chemical reactions:

The possibility of use of gamma radiation in promoting chemical reactions is of industrial importance. In this project data is being collected on the oxidation and amination of naphthalene and benzene. Radiolysis of naphthalene to yield naphthol and radiolytic amination of benzene were studied and G values determined.

New methods of estimation of  $\alpha$ ,  $\beta$  naphthols produced in the oxidation of naphthalene and for the estimation of three phenylene-diamines produced in the amination of benzene were developed using p-nitrobenzenediazonium chloride as a coupling compound. For the final quantitative estimation of the products IR and visible spectrophotometers were used. The amination of benzene was tried in the region of 300°. In a flow system aniline is formed from benzene and ammonia with a G value of nearly 1000. In the case of benzene and water system improvements in the yields have been found. Final analysis is being done.

### 3.3. Mössbauer studies on the nature of chemical bonding in Fe<sup>III</sup> (Acetylacetonate) Cl and Fe<sup>II</sup> (Acetylacetonate) Cl<sub>2</sub>:



Mössbauer effect is used to explain the nature of chemical bonding of some organometallic compounds as mentioned above. M.S. of ferrous and ferric compounds of cysteine were studied.

Mössbauer Spectrum of  $\text{Fe}(\text{Ac Ac}) \text{Cl}$  shows no evidence of quadrupole splitting while the Mössbauer spectrum of  $\text{Fe}(\text{Ac Ac}) \text{Cl}_2$  shows a quadrupole splitting of 0.44 mm/sec at  $-194^\circ$ . The unsplit resonance line in the spectrum of  $\text{Fe}(\text{Ac Ac})_2 \text{Cl}$  indicates that  $\text{Fe}^{+3}$  ion is at the centre of a tetrahedron of four nearest oxygen atoms from the two acetylacetonate ions and that the Cl-ion is outside the coordination sphere. The isomer shifts of both these compounds show that the iron-oxygen bonds are predominantly ionic. This result is in agreement with the observed magnetic moment of 6 Bohr Magnetons for the above two compounds.

#### 4. Thin films

##### 4.1. Detailed structure analysis of thin films:

A saw tooth wave generator has been designed which would make the diffraction lines or spots of crystalline materials amenable to microphotometry. The instrument will now be used for detailed structural analysis of crystalline materials.

The recording microphotometer (Livepho-2) recently received has been installed and tested. Intensity of various electron diffraction plates has been measured and results are being processed. The facilities of this apparatus are being given to others from the laboratory and also to universities.

##### 4.2. Studies on oxidation mechanism of metal films:

Oxidation studies on thin films have been undertaken to understand crystal growth process and to have a comparative idea of mechanism of oxidation in thin film state.

Studies have been made on the epitaxial growth of metal films such as Sb and Bi on (100), (110) and (111) faces of rock salt as well as (0001) face of mica at different substrate

temperature and subsequent oxidation of these films under different air pressure and temperatures with a view to find the orientation relationship between the oxide films with the epitaxially grown layers of the metal film on the single crystal substrates. Even though the substrates intermediate metal films and the top oxide layers had different types of structures, epitaxial growth of the metal film layers and the oxide layers over them could still be observed.

#### 4.3. Structure and crystal growth process studies of thin films by electron diffraction technique:

The object of the project is to study various compounds having semi-conducting properties with a view to correlate their electron transport properties with their surface structure and face changes during deposition. Vapour phase deposits of chalcogenide type compounds have been studied.

A detailed study has been made on the crystal growth process of the compounds  $Tl_2Se$ ,  $Tl_2Te$ ,  $HgSe$ ,  $HgTe$ ,  $In_2Te_3$ ,  $In_2Te$ ,  $In_2Se$ , and  $InSb$  on different faces of rock-salt and cleavage face of mica at different substrate temperatures, also on collodion and glass substrates.  $HgSe$ ,  $HgTe$ ,  $In_2Te_3$  and  $InSb$  showed phase transition along with twinning on (111) plane, whereas  $Tl_2Se$  and  $Tl_2Te$  both tetragonal showed twinning on (310) plane. Lattice parameters of  $Tl_2Te$  determined and the cell type was found to be tetragonal.  $In_2Se$  and  $In_2Te$  both having orthorhombic type structure showed epitaxial growth inspite of large misfit with the substrate structure.  $InSb$  grew epitaxially over  $200^\circ C$  substrate temperature sharing extensive (111) twinning.

#### 5. Synthetic Inorganic Chemistry:

##### Cordination compounds:

The objectives of this work are (i) to study the quasi-aromaticity of metal chelates which may lead to new synthetic routes and novel reactions and may furnish useful results of both academic and applied interest. (ii) To investigate the preparative techniques of inorganic co-ordination polymers and study their properties. (iii) To investigate the

structures of metal complex through their infra-red spectra.

A number of metal  $\beta$ -dicarbonyl chelates have been synthesized and the quasi-aromaticity of some of them has been studied through nitration, halogenation and thiocyanation. The cis-trans isomerisms of chromium acetoacetanilides and colour isomerism of salicylaldoximato copper (II) chelates have been studied. Structural informations for a number of complexes, particularly cobalt amines, have been gained through infra-red spectral studies.

In an attempt to "mercurate"  $\beta$ -dicarbonyl chelates, the corresponding di-mercurated ligands were obtained and were fully characterized. Aromatic pendant groups present in some of these chelates were unaffected. Substitution occurred only at the reactive methyl group of the ligands. Mono-bromo and mono-iodo acetoacetanilide chelates of titanium were prepared and studied. These involved the preparation of titanium tetrabromide and tetraiodide.

Diethoxy, dibutoxy and diisopropoxy bis (8-quinoloxo)-titanium (iv) compounds were prepared. These were hydrolysed to obtain polymers having Ti-o-Ti bond.

Infra-red spectra of these compounds were recorded and studied. The results obtained call for further intensive research in these fields.

## 6. Natural Organic Products

### 6.1. To study the chemistry of the extractives from Cedrella toona:

The work has been undertaken to study the chemistry of extractives from commercially important Indian timbers. From the non-volatile portion a new degraded triterpene similar to cedrolone was isolated.

Geranylgeraniol, the biogenetic precursor of diterpenoids and carotenoids has been identified as one of the components. Isolation of this precursor from a natural source is being reported for the first time. Geranylgeraniol has been found to occur both in the free states as well as esterified

with long chain fatty acids.

6.2. The Chemical examination of the resin of *Ailanthus malabarica* (mal : Mattipal)

Work on this indigenous forest product was initiated with a view to study its chemistry for assessing its commercial utility. The resin was found to be a mixture of triterpenes possibly of dammarane group. Eight new compounds were isolated.

Systematic degradation of the main triterpene was undertaken. Chromic acid oxidation, oxidation with ruthenium oxide and catalytic hydrogenation were studied.

6.3. Chemical investigations of the gum of *Boswellia serrata* (Hindi - Salai)

Salai gum is a regular products of Madhya Pradesh and its annual potential is around 3500-4000 quintals/year. Work on this gum was initiated with a view to study its chemistry for assessing its commercial utility. The gum was separated into acidic and neutral components and the former was found to consist of  $\beta$ -Boswellic acid.

The neutral part of the resin was examined and three new triterpenes isolated. Work on their identification is in progress. A quantity of essential oil has also been collected for further studies.

6.4. Naturally occurring anthraquinone pigments

A series of naturally occurring anthraquinone pigments are being isolated, characterized and synthesized. It was shown that cassiamin, an anthraquinonoid pigment from *Cassia siamea* Lam, is 1,6,8,1',8'-pentahydroxy-3,3'-dimethyl-2,2'-bianthraquinonyl. A second bianthraquinonyl accompanying cassiamin in the root bark of *Cassia siamea* has been isolated, and work on its structure is nearing completion. Attempts are being made to isolate a third pigment which is also present. The synthesis of several naturally occurring anthraquinone pigments has been undertaken.

6.5. Flavonoids and other plant pigments:

Systematic work on the isolation and characterisation of the pigments of Garcinia species has been undertaken. Attempts are being made to synthesize several naturally occurring flavones. Work on the structure of munetone, the infrared spectra of flavones and isoflavones, and the synthesis of a few flavones derived from iretol has been completed and submitted in the form of a thesis.

6.6. Chemical investigation of the plant of Melia azadirachata (Hindi - Neem)

The structure and stereochemistry of the main crystalline bitter principle from neem viz. nimbin has been elucidated.

The absolute stereochemistry of nimbin was determined by measuring the ORD of a diene derivative.

6.7. Chemical investigation of the leaves of viola odorata:

The plant is of medicinal value and the study is of basic interest.

From the leaves of the plant, the isolation of a triterpene - friedeline, has been reported for the first time. Besides the  $\beta$ -sitosterol, a straight chain alcohol of triacetone amine has been isolated.

6.8. Chemical investigation of the plant of Astercantha longifolia (Hindi - Talimkhana)

The plant is of medicinal value and the work is of basic importance.

The extraction of whole plant was done and it revealed the presence of stigmaterol to the extent of 0.1%, Lupeol 0.3%, a straight chain ketone and a mixture of hydrocarbons.

6.9. Chemical examination of Cyperus scariosus (Mar : Nagarmutha)

A new crystalline sesquiterpenic ketone,

isopatchoulenone, has been isolated from the ketonic fraction of the essential oil, obtained from the tubers of Cyperus scariosus.

Ether fraction of Cyperus scariosus oil has been repeatedly chromatographed over alumina, silica gel and silica gel impregnated with 15% AgNO<sub>3</sub>. Two primary alcohols have been isolated and the structural investigations of these alcohols are in progress.

#### 6.10. Chemical examination of vetiveria zizanioides (Hindi :Khus)

The structure of tricyclic sesquiterpene primary alcohol, khusimol, C<sub>15</sub>H<sub>24</sub>O, was elucidated. The structure and stereochemistry of khusinoloxide and khusinoldiol was established, and four more alcohols, l-cadinene and six acids were isolated from the various fractions of the North Indian vetiver oil.

A new tricyclic sesquiterpene primary alcohol khusimol C<sub>15</sub>H<sub>24</sub>O has been isolated from South Indian vetiver oil. It has been assigned structure I. Further examination of the alcohol fraction of the oil has led to the isolation of another primary alcohol, C<sub>15</sub>H<sub>24</sub>O, having the same carbon skeleton as in Khusimol. We propose to name it as isokhusimol and the probable structure of which will be II. Ketone fraction (isolated in the form of semi-carbazone derivatives) was found to contain a mixture of about six ketones from which a solid ketone and α-vetivone have been isolated. (Figures at the end)

#### 6.11. Chemical examination of Nardostachys Jatamansi DC:

Several hydrocarbons along with calarene, aristolene, an α-3 unsaturated aldehyde and two alcohols have been isolated. One of the alcohols, nardol, has been assigned the structure.

The following compounds are characterized: (1) Valeranal (2) n-hexacosane (3) n-hexacosanol (4) n-hexacosanyl-arachidate (5) n-hexacosanyl-isovalerate (6) β-sitosterol (7) valeranone. Two new sesquiterpenic constituents have been isolated and the structure elucidation of these compounds is in progress.

6.12. To study the volatile compounds of curcuma longa (turmeric oil):

Turmeric oil consists of turmerone and ar-turmerone. The evaluation of the odour of ar-turmerone is being carried out by a leading firm. Our object is to study the volatile constituents of turmeric oil and to study conversion of turmerone to ar-turmerone.

A convenient process of preparing ar-turmerone from turmerone was developed. A number of optically active indanes of known absolute configurations were prepared starting from (+) ar-turmerone.

6.13. Analysis of solvent-extracted sandalwood oil:

CFTRI, Mysore have developed a process for the extraction of sandalwood oil by solvent extraction. The oil, so obtained, is dark in colour and contains a number of constituents other than santalols. In certain aspects of chemical analysis of this oil NCL is assisting CFTRI. The work aims at understanding the components and improving the quality of solvent extracted oil.

The major volatile components of the solvent extracted oil have been identified as a mixture of  $\alpha$ - and  $\beta$ -santalenes and  $\alpha$ - and  $\beta$ -santalols. During the course of investigations it was possible to obtain the mixture of  $\alpha$ - and  $\beta$ -santalols free from hydrocarbons and colouring material.

6.14. Chemical examination of Inula racemosa (Kashmir - Pecky)

Alantalactone, iso-alantalactone and dihydroisoalantalactone have been isolated from the oil obtained from the above roots.

Alantalactone (I) and isoalantalactone (II), the major constituents of the oil, have been converted into many interesting new products. Starting from tetrahydroalantalactone (III), a synthesis of 9-keto eudesman (dihydrocanarone) (IV) and tetrahydrocotic acid (V) has been achieved through a series of steps. The intermediate products have been properly characterised and their stereochemistry established. Tetrahydrocotic acid has been previously converted to dihydroeudesmol, and this decides the stereochemistry of

tetrahydroalantolactone (III) at all the centres except at C-11 centre. On similar lines, transformation reactions of dihydroalantolactone have been carried out. (Figures at the end).

#### 6.15. Chemical examination of Valeria Wallichii (Hindi:Tagar):

The valerian root oil (concrete) from adjoining areas in the Himalayan regions has been subjected to steam distillation and the distillate separated into acidic and neutral parts. The acidic portion contains isovaleric and caproic acids. The neutral portion contains calarene,  $\beta$ -bergamotene,  $\alpha$ -curcumene and valeranone.

Some transformation products of valeranone have been prepared and were investigated for their pharmacological properties.

### 7. Synthetic Organic Chemistry

#### 7.1. Oxidation of alkyl side chains in aromatic compounds:

The liquid-phase catalytic oxidation of m-xylene has been studied in detail and a complete analysis of reaction product has been carried out.

The liquid phase, catalytic oxidation method, was next successfully used for mixed xylenes. Extension of this method to oxidation of tetralin and indan, could not be achieved, either under the standardised conditions or several other variations.

#### 7.2. New analogues of warfarin:

The object of the project is to investigate on the structures of some new analogues of warfarin and to study their anticoagulant and rodenticidal properties.

Studies have been made on the structure of new products obtained by condensation of warfarin with benzaldehyde and optimum conditions for the isolation of the unstable major product were established.

#### 7.3. Meerwin arylation of 4-hydroxy coumarins:

The object of the study is to prepare 3-aryl-4-hydroxycoumarins from the appropriate 4-hydroxycoumarins



by the Meerwein arylation method and study their possible anticoagulant and oestrogenic properties.

During the course of Meerwin arylation of 4-hydroxycoumarins a new group of compounds was obtained as by-product. These compounds have now been established to be the hitherto unknown ammonium salts of o-hydroxyphenylglyoxalic acids (II) and this has been confirmed by synthesis. They are formed from another by-product of this reaction, namely, 2,3,4-triketochroman-3-oximes (I) possibly through an exceptional self-catalysed Beckmann type of transformation followed by hydrolysis and rearrangement of the resulting amide. (Figures at the end).

#### 7.4. Synthetic studies on 4-arylcinnolines:

A new route has been developed for the synthesis of hitherto unknown 4-(o-hydroxyphenyl)-cinnolines (II) of possible therapeutic value. The cinnolines were obtained by cyclisation of (I) with fused  $AlCl_3$ . Its N-oxide (III) was also prepared for screening against cancer.

The new process developed, has been extended to a general method for the synthesis of 4-arylcinnolines (V) from the cis isomers of phenylglyoxal-2-phenylhydrozones (IV). (Figures at the end).

#### 7.5. 4-Acetomethylcoumarins:

The object of the study is to confirm the structures assigned to the Kostanecki-Robinson acylation products of 3-oreacetophenone and its derivatives. An unambiguous synthesis of 4-acetomethyl-5-methyl-7-methoxycoumarin (I) was carried out and the product was found to be different from the Kostanecki-Robinson acetylation product of 3-oreacetophenone monomethyl ether to which the same structure (I) was assigned by the earlier workers.

3-Acetyl-4,5-dimethyl-7-hydroxycoumarin (II) was synthesized by a new route as a possible alternative structure for the Kostanecki-Robinson acetylation product of 3-oreacetophenone but was found to be different from it. (Figures at the end).

#### 7.6. Synthetic studies towards proto-berberine alkaloids:

These alkaloids are reported to be of medicinal value and this study is of basic interest.

A simple and unambiguous method for the synthesis of proto-berberine alkaloids has been developed.

#### 7.7. Conformational studies of West phalene's diacetate:

The conformation of west phalenes diacetate has been shown to be A/B quasi trans, B/C quasi cis, and C/D trans chair forms with the  $C_6$ B-substitute equatorial, by IR and NMR studies of this and model compounds.

Ring B being trans-fused to C-ring on one side and fused to the A-ring on the other side, is very rigid in the usual steroids and is generally taken as an example of the rigid chair form of the cyclohexane ring. However, in West phalenes Diacetate it is found that when a  $C_6$ -substituent is  $\beta$ -oriented, the ring systems are A/B quasi trans, B/C quasi cis and when the  $C_6$ -substituent is  $\alpha$ -oriented, the ring systems are A/B quasi cis, B/C quasi trans. This is, thus a very rare instance in the steroids, wherein the B-ring flips from one half-chair conformation to another, by a change of configuration of the  $C_6$ -substituent. ORD and C.D. measurements of the  $C_6$ -ketone and further reactions with it show that it exists as a mixture of both the conformations mentioned above. The centrally located B-ring thus shows an unusual conformational mobility in this type of steroids.

#### 7.8. Synthetic dyes:

NMR spectral methods were applied to the study of azophenol-quinone hydrazone tautomerism. This is of general interest in connection with the structures of azo and azoic dyes. The structures of three new azoic coupling components have been determined. The points of attachment of reactive dyes to the cellulose macromolecule are being investigated with the aid of NMR

spectra; model derivatives of glucose are being prepared in this connection.

Orientation problems concerning benzanthrone and viclanthrone derivatives are under study, mainly using NMR spectra. For the separation and purification of anthraquinonoid vat dyes it is convenient to convert them to the products of reductive methylation or acetylation. Solubility in organic solvents is thus greatly increased, and the products also become amenable to mass spectroscopy.

### 7.9 Synthesis of cyanine dyes:

The cyclodehydration of 3-aryl mercapto ethyl methyl ketones with polyphosphoric acid yielded a mixture of thiachromens and thianaphthalenium salts (which subsequently change in suitable cases, to thiacyanine dyes). A mechanism involving an acid catalysed intermolecular hydride shift from  $\Delta^3$ -thiachromene has been proposed.

The ketosulphide (II) was prepared from Mannich base (I) obtained from 2-methylcyclohexanone, formaldehyde and dimethylamine hydrochloride in 30% yield the remaining being the isomer (Ia). (II) was reduced to (III) by  $\text{LiAlH}_4$ . The cyclisation of ketosulphide (IV) gives the thiachroman (V) and the perchlorate (VI) by  $\text{H}^+$  transfer. (See reaction A at the end). The ketosulphide (IV) was prepared by condensing m-methoxy phenol with 2-dimethylamino-methyl cyclohexanone. Treatment of alcohol (III) with  $\text{HClO}_4$  gave the perchlorate (VII) (see reaction B at the end). Its structure has been proved by NMR, UV and analysis. The  $\text{NaBH}_4$  reduction of this perchlorate gives (VIII), the structure of which has also been proved by NMR and analysis. The stereochemistry of the thiachromone (V) at ring junction 3,4 was studied by preparing an authentic cis-thiochroman (see reaction C at the end). Sulphones obtained from both (V) and (Va) showed that (V) is not an entirely pure cis-compound like (Va). VPC done on these showed (V) to be a mixture of 75% cis- and 25% trans-isomer; also the VPC was done

on the di-sulphurisation products (IX). (Figures and reactions A, B and C at the end).

#### 7.10 Hydride transfer studies in dyes and N-heterocyclics:

These are fundamental studies in nitrogen heterocyclics. The Mannich base (5-N-Morpholino 2-methyl-pentanone) was prepared according to the usual Mannich reaction and amine exchange with aniline was done to get (II). The cyclodehydration and subsequent hydride shift/transfer reactions on this product was carried out. Attempts to isolate the leucobase of Meldola's blue was undertaken, but this appeared to be quite unstable and got easily converted to the dye. In the formation of Meldola's blue from p-nitroso dimethylaniline and 3-naphthol this intermediate leuco-base is presumed to lose hydride giving the cationoid dye. Incorporation of trityl chloride found to give triphenyl methane in this reaction.

The leuco-base of Methylene blue was prepared and its reaction with trityl chloride to give the dye by hydride abstraction was studied. The usual Mannich reaction gave only very poor yield of the required product, the major product being its isomer (Ia). The dimethylamine Mannich base (I) was prepared in good yields (see reaction A at the end). The ketone (II) obtained by amine exchange with (I) was reduced to the alcohol by LAH and its acid catalysed transformation is under study (see figures at the end).

#### 7.11 Biologically active heterocyclic compounds:

These compounds are of potential interest as far as their biological activity in general and carcinostatic activity in specific is concerned. Synthesis of hitherto unreported cationic heterocyclic compounds containing sulphur where the charge can move from the one hetero atom to another within the heterocyclic frame-work of the molecule. 1-phenyl  $\alpha,3$ -thienopyrylium perchlorate was prepared and the results indicate that the thiophene sulphur does participate in the resonance.

In the synthesis of 10-N-methyl, 9,10-dihydro 3,4-benz-phenanthridine-9-mercapto acetic acid which is of interest as a carcinostatic compound, condensation of 2-dimethyl-amino-methyl cyclohexanone with 2-naphthylamine yielded 2-(3-naphthylamino)-methyl cyclohexanone. This was further cyclised with polyphosphoric acid to 3,4-benzo-5,6,7,8-tetrahydro-phenanthridine.

Work on the synthesis of sulphur heterocyclic compounds has been continued.  $\alpha$ ,3 -thieno-thiopyrylium perchlorate has been prepared. Work on the synthesis of  $\gamma$ -ethyl, $\alpha$ , 3-thieno-thiopyrylium perchlorate and  $\alpha$ , 3-(2-ethylthiopheno) thiopyrylium perchlorate is in progress. Disproportionation reaction of 4-phenyl mercapto butane-2-ol in 60% perchloric acid has been studied. Results obtained so far indicate that disproportionation reaction does not take place; however, 4-phenylmercaptobutane-2-ol yields phenyl thiochroman in minute quantities. The synthesis of 10-N-methyl 9,10-dihydro-3,4-benzo-phenanthridine-9-mercapto acetic acid was continued. It was realised that cyclization of 2-(3-naphthylamino)-methyl cyclohexanone with polyphosphoric acid and tritylchloride gave a mixture of 3,4-benzo-5,6,7,8-tetrahydro-phenanthridine (I) and triphenylcarbinol (II) in the form of a loose complex which behaved as a single compound. Later (I) was isolated in the pure form through its hydrochloride and aromatised to give 3,4-benzophenanthridine. Similarly benzophenanthridine is being synthesized starting from  $\alpha$ -naphthylamine. Synthesis of 4-phenyl, 7-methoxy quinolinium methiodide (III), 4-phenyl quinolinium methiodide (IV), 4-thienyl, 7-methoxy quinolinium methiodide (V) and 4-thienyl quinolinium methiodide (VI) are under progress. Compounds (III) and (IV) are already synthesized. The above compounds and their dihydro derivatives are to be tested as potent analgesics. (Figures at the end).

7.12 Transformation products of tricycloekasantalic and bicycloekasantalic acid:

Tricycloekasantalic acid was converted into optically pure  $\alpha$ -santalene,  $\alpha$ -santallic acid and  $\alpha$ -santalol.

Purification of bicycloekasantalic acid from a mixture of bicycloekasantalic acid and isobicycloekasantalic acid is in progress. Synthesis of  $\beta$ -santalol and  $\beta$ -santalene will be carried out starting from pure bicycloekasantalic acid.

7.13 Base catalysed reaction of lithioethylene diamine:

The reagent is very useful for isomerisation and dehydrogenation of terpenoids. It is useful in synthesis of compounds which cannot be synthesized by conventional routes. The study of this reaction was extended to compounds like steroids and medium-sized ring compounds.

Humulene on treatment with this reagent furnished a mixture of two isomeric hydrocarbons presumably with the formation of bicyclic products. Characterization of these products is in progress. Zerumbone was polymerized during the base-catalysed reaction. Zerumbol (I) gave the bicyclic ketone (II) (2-keto-3,6,9,9-tetramethyl  $\Delta^{5:6, 4:11}$ -bicyclo (6:3:0) undecane) which has been characterized. The isomerized product of stigmasterol was oxidized by Oppenauer method to get the mixture of isomeric  $\alpha,3$ -unsaturated ketones which on selective ozonolysis furnished a mixture of essentially two ketones. These were identified as androstenedione and progesterone. Androstenedione was separated in a pure form and identified. Progesterone could not be obtained in completely pure form (figures at the end).

7.14 Perfumery chemicals from longifolene and camphene (condensation with phenol):

This work has been undertaken with a view to develop new types of aromatic compounds.

The structure of the novel lactone, isolongifolanolide, prepared by the lead tetracetate oxidation of isolongifolol, was confirmed by converting it by a series of reactions to isolongifolane diol, keto-isolongifolic acid, keto-isolongifolol, isolongifolanol and isolongifolanone. Finally the ketone, isolongifolanone was converted into the known hydrocarbon, isolongifolane, and compared with the standard sample. The condensation of longifolene with the phenol in the presence of catalytic quantity of boron trifluoride etherate at 0° afforded a mixture of two ethers. The structures of these as well as that of the isobornylphenyl ether, obtained by a similar reaction of camphene with phenol, have been proved by spectral data and their stereospecific cleavage to the known alcohols with Li-liquid ammonia reduction. The separation of this alcohol mixture was achieved by converting it into a ketone mixture and separating one of them via semicarbazone formation. The condensation at an elevated temperature (100°) led to the formation of a complex mixture of o- and p-terpenyl phenols. The characterization was done by the spectral evidences.

#### 7.15 Studies on chemical transformations of dehydrocostus lactone:

The object of the study is to establish the structure and stereochemistry of dehydrocostus lactone. A ketocarboxylic acid obtained during CrO<sub>3</sub> oxidation of the monol (I) obtained from dehydrocostus lactone (II) was assigned structure (III) on the basis of bromination and dehydrobromination experiments.

Additional evidence has now been obtained by showing the presence of cyclopentanone absorption in (III) by initially converting its ethylene ketal into the corresponding alcohol by LAH and regenerating the ketol (IV) from it. The ketol has also been converted into the ketone (V). This conclusively proved the structure of the keto acid (III) and also established the presence of a cyclopentane ring in dehydrocostus lactone (figures at the end).

7.16 Acidic constituents of costus root oil:

The object of the scheme is to convert costic acid into other naturally occurring eudesmane type compounds. Costic acid was isolated and its structure and stereochemistry were established.

Methyl ester (I) of costic acid has been converted into its monoepoxide which has been reduced to the diol (II) by  $\text{AlH}_3$ . The diol was oxidized by Jones reagent to the corresponding conjugated aldehyde and subsequently to the acid (III). The latter is under examination (figures at the end).

7.17 Conversion of costunolide into eudesmane type compounds:

Various transformations of costunolide and its derivatives resulting in eudesmane type compounds have been studied. The object of this study is to convert costunolide into  $\alpha$ - and  $\beta$ -tetrahydrosantonins and also to santonin.

$\alpha$ -Cyclo-dihydrocostunolide (I) obtainable from costunolide (II), and also from solid dihydrocostunolide (III) was converted into its epoxide (IV) and the latter subjected to acetolysis to give a ring contracted compound (V) and presumably a hydroxy lactone (VI), characterization and structure determination of (VI) are in progress (figures at the end).

7.18 Transformation products of costunolide:

The object of the project is the conversion of a ten-membered carbocyclic ring into a guaiane-type compound and thereby synthesize compounds belonging to the latter type. Thermal rearrangement of cyclodeca-1:6 diene system to a guaiane system was studied.

The thermal rearrangement of the ester (I), alcohol (II) and hydrocarbon (III) as such and also in presence of diethylene glycol and alkali has been studied. They rearrange to the



corresponding guaiane type of compounds (IV), (V), (VI), for which chemical evidence has been obtained. The compounds containing exocyclic double bonds have been observed to undergo rearrangement to bulnesol (VII) type of compounds on treatment with an acid (figures at the end).

#### 7.19 Synthesis of compounds related to selinane and elemene:

A systematic study of the synthesis and reactions of these compounds has been undertaken. Junenol, dihydrojunenol, tetrahydro-saussurea lactone, 4-epi-dihydroeudesmol, tetrahydroelemol and a number of 1-oxo-eudesmanes have been synthesized. The stereochemistry of a hydroxylactone obtained in 70% yield from the hydrogenation of santonin has been established.

Tauremisin (I), a constituent of Artemisia taurica Willd . and Artemisia vulgaris L., has been synthesized starting from the keto-oxide (II). It has also been synthesized by a different approach in which the key reaction is the allylic oxidation of the santanolide (III). 1-Ketosantanolide (IV) and Saussurea lactone (V) have been synthesized starting from the keto-oxide (II). On the basis of this synthesis, a convenient route for the preparation of 2,3-seco steroidal 1,3-dienes has been developed. 3-Ketocholestane has been transformed to 2,3-seco-cholesta 1,3-diene (figures at the end).

#### 7.20 Synthetic approach in santalene-longifolene series:

The synthesis of isobicycloekasantalic acid was established, starting from camphene.

Acidic portion of sandalwood oil was isolated and was found to be a mixture of eight to nine compounds. From these, three were identified as (a) teresantalic acid (b) nortricycloekasantalic acid, and (c) tricycloekasantalic acid. One more new ester has been isolated in the pure form and was found to be a ketoester for which

the tentative structure as (I) has been proposed. It is a saturated ketoester having molecular formula  $C_{16}H_{24}O_3$  and molecular weight 264 (mass spectrum) suggesting tricyclic nature. The presence of cyclopropane ring was proved by NMR and IR studies. The position of the ketone in the side chain was proved by reducing the keto- group to alcohol which immediately gives  $\gamma$ -lactone. When W.K. reaction was carried out to reduce the keto function, it was observed that the product was a lactum which also proves the position of the keto- and the acid-groups with respect to each other in the side chain. A synthesis of this keto ester is being attempted (figure at the end).

7.21 Transformation products in carvone series (a) hydroboration (b) epoxidation and  $BF_3$  etherate reactions (c) synthesis of canarone:

The work originated in connection with the work on the synthesis of a naturally occurring compound canarone.

Carvone was reduced with LAH to obtain carveol, the acetate of which was hydrogenated by Raney nickel to dihydrocarveolactate. Hydroboration of this compound with disiamyldiborane and diborane gas was studied. Similarly the epoxidation of dihydrocarveolactate was done and its treatment with  $BF_3$ -etherate studied. The main object of this was to isolate the ketoacetate (I) which was later found to be unsuitable for the synthesis of canarone. An alternative method obtaining from the diketone (II) was therefore initiated (figures at the end).

7.22 Synthesis of bergamotenes:

The key intermediate cis-norbergamotinic acid was synthesized. 3-Bergamotene, a pinene analogue was obtained in the valerian root oil. The synthesis of 3-bergamolene is the main object of the work.

The cyclization of ester of the keto carboxylic acid was attempted using potassium t-butoxide in butanol as well as in benzene, without success. Nopinone (I) was condensed with methyl lithium to obtain the tertiary alcohol (II) which was treated with HgO and Br<sub>2</sub> followed by exposure to U.V. light. The reaction product was an oxide (III) which was subjected to chromic acid oxidation to obtain the lactone. The lactone on LAH reduction gave the diol which on reaction with p-toluene sulphonyl chloride gave the mono-tosyl derivative (IV) (reaction and figures at the end).

### 7.23 Transformation product of eudesmol and elemol:

Eudesmol and elemol have been converted into eudesman-6-one and eudesman-8-one, eleman-6-one and eleman-8-one and their stereochemistry established.

Eudesman-8-one was reduced with LiAlH<sub>4</sub> and Na and isopropyl alcohol. The NMR spectrum indicated them to be α- and β-alcohols respectively. The β-alcohol on reaction with lead tetracetate gave a mixture of two oxides which on oxidation with chromic acid in acetic acid gave a mixture of two lactones separated by TLC, one of which was found to be identical with tetrahydroalantalactone. The other lactone was shown to be the lactone of 8 β-hydroxy-eudesman-15-oic acid. Eudesman-6-one has been equilibrated with alkali and pure dihydrojunenone was separated by chromatography, which was reduced to dihydrojunenol (reaction at the end).

## 8: Physical Organic Chemistry:

### 8.1. Electron impact studies of organic molecules :

Although mass spectrometry is widely used as an analytical and structural tool in organic chemistry very little information is available on the actual mechanism of the fragmentation of organic molecules induced by electrons.

Exploratory work on the behaviour of simple organic compounds under electron impact has been studied and following compounds were examined : amides, amidines, hydrazones, phenyl-hydrazones, semicarbazones and semithiocarbazones. Labelling experiments were carried out to support the observations. Additional information was obtained on skeletal rearrangements. The data obtained will help correct interpretation of the mass spectra of unknown organic natural products. Use of spectral methods and stable isotopes in biogenetic studies ( of Afalotoxin ) is in progress.

## 8.2 Stereochemical studies by PMR spectroscopy:

Using diterpene acids as model compounds and utilizing solvent effect on spectral signals, methods have been evolved to find (a) whether a carbon bearing a carboxyl group also holds a methyl group on it, (b) if so, what is the conformation of this methyl group, and (c) the type of fusion of the ring holding the carboxyl with adjacent ring.

Using model compounds, several  $\gamma$ -lactones fused, cis and trans, angularly as well as linearly to rigid cyclohexane rings, a method has now been evolved by utilizing solvent shifts in PMR spectroscopy, to find the stereochemistry of the side chain in these lactones.

## 8.3 Application of NMR spectroscopy:

These are structural and physico-chemical studies of the fundamental type.

Aromatic compounds: The methyl band widths of the isomeric toluic esters and nitrotoluenes were found to be in agreement with the reported lengthening of the C<sub>2</sub>-C<sub>3</sub> and C<sub>5</sub>-C<sub>6</sub> bonds on substitution (at C<sub>1</sub>) of NO<sub>2</sub> and CO<sub>2</sub> R groups in the benzene ring. However, some difference between the two systems was observed which suggested that there may be interaction between the methyl and nitro groups when they are para to each other in an aromatic ring. The interaction can be of the hyperconjugative or inductomesomeric type. The chemical shift data, obtained by the examination of the NMR spectra of the methyl esters of 2-nitro-4-methyl-, 2-nitro-5-methyl-, 2-nitro-4-t-butyl- and 2-nitro-5-t-butyl- benzoic acids have shown that the interaction of the nitro group with the methyl group is stronger than its interaction with t-butyl group. Thus, unambiguous evidence for the controversial concept of hyperconjugation (of the sacrificial type) in the ground state has been obtained for the first time. The spectra of a large number of systems, related to

those mentioned above, have also been examined in this connection.

Solvent-solute interactions: Supplementary data on NMR solvent shifts have been obtained, which supports earlier conclusions.

Structural applications: The stereochemistry of cyanomaclurin has been reconsidered in the light of additional NMR data and it has been shown that inversion of the configuration suggested earlier for the 3-position is necessary. Synthetic work has been found to support the basis for this conclusion.

The application of NMR spectroscopy in the study of the azophenol-quinone hydrazone tautomerism has been examined using a number of compounds.

#### 8.4 Studies on the Mills-Nixon effect:

A recent NMR spectroscopic study from the laboratory has shown that the mobile bond order of the C<sub>4</sub>-C<sub>5</sub> bond of indane is larger than that of the C<sub>5</sub>-C<sub>6</sub> bond indicating localization of  $\pi$ -bonds in a sense opposite to that suggested by Mills and Nixon.

The reactivity of the ethylene thioketals of 5- and 6-bromoindan-1-ones towards lithium diethylamide has been examined. The latter compound does not react with the reagent while the former gives a complex product mixture that has not yet been analysed. The lack of reactivity of the 6-bromo derivative gives some measure of support to the earlier conclusion regarding bond fixation in this system.

#### 8.5 Carbonium ions:

In connection with the measurement of barriers to rotation in carbonium ions that can be generated from aromatic aldehydes, we have undertaken an exploratory study on the preparation of stable carbonium salts from p-substituted benzaldehydes. These have so far been regarded as being too unstable to be isolated.

A method has been worked out for the preparation of a series of p-substituted  $\alpha$ -acetoxybenzyl perchlorates by the action of acetic anhydride and perchloric acid on benzaldehydes. The compounds can be obtained pure either as crystalline solids or as viscid masses that do not crystallize readily. The stability of these salts varies with the nature of the p-substituent. Some of them are stable over a period of several days. All of them are highly sensitive to moisture in contact with which decomposition to the aldehydes proceeds with extreme ease.

## 9. Microbiological studies:

### 9.1 Screening of microorganisms for industrially useful chemicals:

Several microorganisms which can grow on hydrocarbons such as kerosene have been reported in recent years. The selected cultures of them can be utilized for the production of industrially useful chemicals such as aminoacids.

The objective is to isolate and identify different cultures which can grow on hydrocarbon media and to explore the possibility of producing aminoacids with the help of these microorganisms.

6 Cultures of Ustilaginales (Smut fungi) were isolated and are being sponsored for the production of aminoacids. This group of microorganisms has not been hitherto extensively screened for its utility.

### 9.2 Isolation of mutants for the estimation and production of useful food chemicals such as aminoacids:

30-40 Mutants which require certain aminoacids have been isolated. Some of them will be used for screening aminoacid producing mutants. Study of the biosynthetic control mechanism of the above mutants has been undertaken.

### 9.3 Metabolism of C<sub>5</sub>- and un-natural C<sub>4</sub>-dicarboxylic acids:

The aim is to study the mechanism of the hydration of citraconate and maleate and to purify the concerned enzymes.

Citraconate was found to be hydrated to leavorotatory citramalate by a new enzyme called citraconase.

The purification of citraconase has been continued and a 25-fold purification has been achieved.

The enzyme malease has also been found to be present in the citraconate-cells. It has been purified 10-fold. It converts maleate into dextrorotatory (un-natural) malic acid. This is distinct from citraconase.

## 10. Microbiological Transformations of Terpenes:

### 10.1 Degradation of p-cymene by bacteria, particularly the studies on the enzymatic ring cleavage and aldol type reaction:

This work is undertaken with a view to elucidate the biochemical mechanism underlying the transformations of easily available terpene hydrocarbon into oxygenated products of potential industrial interest. p-Cymene degradation has been studied and a degradative pathway has been suggested. This is based on isolation of a number of compounds which could be regarded as intermediates.

2,3-Dihydroxycumic acid has been prepared in quantities from the fermentation bath. Another possible intermediate, which on aldol cleavage gives rise to isopropylpyruvic acid  $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{CO}.\text{COOH}$  and acetaldehyde  $\text{CH}_3\text{CHO}$ , is being synthesized chemically. This will provide more information regarding the degradative pathway. Studies on hydroxylation and cleavage of p-cymene and other aromatic acids by PL strains show that the enzyme hydroxylase carrying out the conversion of cumic acid to 3-hydroxy cumic acid is present in 15,000 x g supernatant and requires NADH preferably as cofactor. The latter is further



hydroxylated to give 2,3-dihydroxycuminic acid. The model studies with 2,3-dihydroxybenzoic acid support this observation. Also 2,3-dihydroxycuminic acid is further degraded to isopropylpyruvic acid and acetaldehyde by the 15,000 x g. supernatant.

## .10.2 Bacterial fermentations :

This work is undertaken with a view of  
(i) converting easily available terpenic hydrocarbons into oxygenated products of potential interest to perfumery, and  
(ii) elucidating the biochemical mechanisms underlying these transformations.

### 10.2.1. Limonene :

Limonene on fermentation with a pseudomonad strain has been found to undergo chemical changes of different nature and accumulate many transformation products.

Starting from carvone, which is one of the transformation products of limonene, a synthesis of 2-9 dihydroxy p-menth-1-ene has been completed.

### 10.2.2. 1-p-menthene :

A major pathway of degradation of  $\alpha$ - and  $\beta$ -pinene by PL strain involved a p-menth-1-ene intermediate, and hence its fermentation study was undertaken. Tetrahydrocarvone, phellandrol, p-menth-1-ol, phellandric acid, 2-hydroxy-p-menth-7-oic acid, and 3-isopropylpimelic acid were isolated from the medium.

The products have been identified and characterized. Similar studies have been undertaken using 3-p-menthene as a substrate to compare the earlier observation of the pathway of degradation.

### 10.2.3. Camphene :

It has been established that the PL strain converts camphene to isoborneol by a prototropic rearrangement. Isoborneol is then dehydrogenated to camphor which is metabolised by a closely similar pathway followed by the camphor metabolising pseudomonad C<sub>1</sub> and C<sub>5</sub>. For the comparative studies our strains have been sent to University of Illinois ( USA ),

### 10.3. Fungal hydroxylations :

Fermentation of 1-methyl-1-cyclohexene and 1-methyl-3-cyclohexene by *Aspergillus niger* has been shown to yield products such as 2-hydroxy-1-methyl-1-cyclohexene and 2-hydroxy-1-methyl-3-cyclohexene. This failure of stereospecificity has been explained on the basis of 'hot' carbonium ion mechanism. Studies are undertaken to establish whether the hydroxy oxygen is derived from the atmosphere or from the medium using H<sub>2</sub>O<sup>18</sup>.

## 11. Growth of plant cells :

The study of growth and metabolism of different plant cells is of interest to examine the formation of useful plant products. The objectives of this project at present are (i) to determine the requirements for rapid growth of different plant cells especially of chulai bean cells, and (ii) to study the growth of monocotyledonous cells and other plant tissues which have hitherto been investigated only to a limited extent. These studies on different agricultural plant tissues are of very great agricultural importance.

The requirements for the continuous growth in vitro of cells from different plants such as opium, chulai, digitalis etc., were determined. Twenty five plant cells cultures are being maintained at present of which some were isolated and established for the first time in this laboratory. Viable maize callus and root culture was also established.

Callus cultures have also been obtained from a second monocotyledonous tissue-wheat, Its viability and nutritional requirements are being investigated. Crown gall and normal tissue of parthenocissus showed no significant difference in their ubiquinone content. Work on the establishment of viable cultures of normal and tumour tissues from other plants is in progress. Work on the determination of the conditions for obtaining single cell cultures from different plant tissues is also being continued with different supplements added to the medium.

## 12. Enzymes:

Study of enzymes is closely related to the study of intermediary metabolism. The work on enzymes is directed towards the isolation of enzymes and the study of regulatory mechanisms which control metabolism.

### 12.1 Hexokinase:

Animal tissue hexokinases have not hitherto been obtained in pure form. A new method for the solubilization of the particulate hexokinase of brain was discovered and the enzyme was purified till it was 85 per cent pure as shown by ultracentrifugal studies.

Study of the kinetics of the purified brain enzyme was continued. Using pyruvic kinase and lactic dehydrogenase for the estimation of ADP formed in the hexokinase reaction and with mannose as substrate it was found that the enzyme was inhibited 50 per cent at about  $10^{-5}M$  glucose-6-phosphate and that the inhibition was reversible by inorganic phosphate. Work on the mechanism of action of the enzyme using labelled phosphorous and glucose is in progress. Methods for the solubilization and stabilisation of heart and rabbit muscle hexokinases were studied and both the enzymes were purified about 5 to 10-fold. The purification of the muscle tissue hexokinase which is present in relatively smaller amounts than in brain is in progress.

### 12.2 Phytase:

A bacterial enzyme which specifically hydrolyses inositol hexaphosphate was discovered. Partial purification of the enzyme and the study of its specificity has been undertaken.

Several methods of purification which were tried resulted in the inactivation of the enzyme. This was traced to the removal of calcium, which was found to be essential both for the stability as well as the activity of the enzyme. The enzyme was partially purified by fractionation on IRC-50 resin and by alcohol fractionation.

### 12.3 DPNase:

The isonicotinic acid hydrazide-insensitive DPNase have been purified from different animal tissues but the isonicotinic acid hydrazide sensitive enzyme from brain has not hitherto been obtained in soluble form. A new method was found for preparing the enzyme in soluble form from ox brain.

The enzyme was partially purified (about 10-fold) by ammonium sulphate fractionation and anion exchange resin chromatography. It was found to be very stable to acid and alkali (pH 2 to 12) as well as to heat treatment but on acid treatment the enzyme was found to become insoluble. Work on the purification of the enzyme is in progress.

### 12.4 Acetylcholinesterase:

Acetylcholinesterase plays an important role in the metabolism of brain and nerve and has been obtained in soluble form and purified to a considerable extent from electric organs of some fish. A new method has been worked out for the preparation of soluble acetylcholinesterase from ox brain. Most of the work was carried out with caudate nucleus and the enzyme was purified about 40-fold by DEAE chromatography.

The enzyme was further purified by ammonium sulphate fractionation. It was, however, not possible to chromatograph the purified enzyme on anion exchangers since it was found to be rapidly denatured. Several different compounds were tested for their effect on stabilizing the enzyme and are being tested for their suitability for use in further purification work. A simple spectrophotometric method with phenylacetate as the substrate was standardized for rapid assay of the enzyme.

#### 12.5 Citrate-oxaloacetate lyase:

Two aspects of the enzyme are being studied:  
(i) active sites of citrase, and (ii) citrase induction.

The induction of citrase, the enzyme which cleaves citrate to oxaloacetate and acetate, takes place in cells of Aerobacter aerogenes grown on citrate. The enzyme requires divalent metal ions for its activity and is inhibited by oxaloacetate. Citrase has been purified and the application of the pure preparation to a rapid, accurate and sensitive spectrophotometric assay of citrate has been developed. In studies on the location of the active sites on the enzyme molecule involved in binding of the inhibitor, oxaloacetate, the conditions for the formation of an enzyme inhibitor complex have been established.

Interesting data have been obtained on the nature of the enzyme-oxaloacetate complex. One of the sites of attachment appears (on the basis of sodium borohydride reduction) to be an amino group present on the enzyme molecule which probably reacts with oxaloacetate to form a Schiff base.

#### 12.6 Nitrate and nitrite reductase:

Microorganisms play an important role in maintaining the nitrogen cycle. The activity of denitrifying bacteria accounts for substantial losses of nitrate-containing fertilizers. Biochemical investigations undertaken with whole cells and isolated enzymes will help understand the basic mechanisms involved in these denitrifications. The problem has a bearing on understanding the soil fertility.

The isolation of A.fischeri nitrite reductase in an ultracentrifugally homogeneous form has permitted the elucidation of certain of its physico-chemical properties. The enzyme was characterized as a c-type cytochrome and is autooxidizable. It has so far been believed that A.fischeri can form inducible nitrate reductase but no nitrite reductase. The formation of nitrite reductase by A.fischeri was demonstrated for the first time in this laboratory.

15 mg. of ultracentrifugally homogeneous nitrite reductase was prepared and its molecular weight and spectral characteristics on reaction with CO and cyanide determined.

The molecular weight of the enzyme as determined by Archibald's method was found to be of the order of 100,000. Spectral properties also indicated that nitrite and oxygen have greater affinity for the enzyme than CO and cyanide. Nitrite reductase activity of the enzyme was inhibited by CO and cyanide but its reaction with oxygen was not inhibited by these reagents. The enzyme probably mediates the cyanide-resistant respiration in A.fischeri.

Preliminary data obtained indicate that nitrite reductase from A.fischeri consists of several sub-units. The kinetics of the reformation of the enzyme and the regulatory mechanism of its formation are being studied.

### 13. Physico-chemical studies in polymers:

#### 13.1 Stereospecific polymerizations:

Polymerization of different monomers was studied with  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)$  catalyst system.

Polymerization of styrene with  $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$  catalyst system at  $40^\circ$  in presence of n-hexane has been carried out. It has been found that rate of polymerization decreased with increase in Al/V molar ratio. Kinetic studies showed that the new catalyst system behaved exactly in the same manner as the previous one

$\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$ .  $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$  gave much better stereospecificity than  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$  presumably due to stronger  $\pi$ -bonding of the monomer.

A fall in rate of polymerization was observed above the catalyst concentrations  $1.6 \times 10^{-2}$  moles/l with  $\text{ZrCl}_4$ -organo-metallic catalyst system. A similar effect is also observed in case of isoprene. This effect is attributed to the agglomeration of catalyst at higher concentrations.

### 13.2 Solution properties of polymers:

By the single parameter method of determination of M.W. of polymers from their solution viscosities following, polymers have already been studied. Polystyrene, polymethyl acrylate, polyvinyl acetate, poly-p-chlorostyrene and azeotropic copolymer of p-chlorostyrene. The studies have been extended to polymethyl methacrylate.

The value of  $[\eta]_R$  correlate well with the square root of the M.W., but the constant of proportionability is more than twice the value obtained by Flory-Schaeffgen method. It has been inferred that the unperturbed dimensions of polymethyl methacrylate are higher in solid or concentrated solutions in comparison with those obtained from studies of dilute solutions.

### 14. Urethane rubber from castor oil:

Rubbery formulations using castor oil and di-isocyanates have been prepared. Different vulcanization techniques have been tried. The rubbery products obtained are being tested for their properties and will be evaluated for their possible applications.

15. Grafting of cellulose:

Studies have been initiated to improve certain properties such as resistance to microorganisms and mold, and to impart anti-crease characteristics to naturally occurring cellulose. This is being attempted by chemical grafting of acrylonitrile and acrylamide on cellulose.

Attempts were made to effect grafting on cotton hanks with acrylonitrile under different experimental conditions, such as concentrations of initiator, nitric acid and monomer and period of grafting. A 40-80% increase in weight of cotton apparently due to the grafting, was obtained.

16. Chemical engineering studies:

Interfacial tension in two and three component systems:

Correlation and prediction of liquid-liquid interfacial tension in two phase binary or ternary systems is of considerable importance. Little data are available in this field.

Non-aqueous immiscible binary systems are being initially studied. Work on temperature effect on such systems is in progress.



A P P E N D I C E S

A.I Processes in production:

<u>Name of process</u>	<u>Firm exploiting the process and date of release:</u>
1. Anion exchange resins from melamine	M/s Tulsi Industries, Poona - non-exclusive (1963).
2. Antipriming compositions (sponsored)	Work completed in 1963. Produced by Indian Railways, Chittaranjan.
3. Can sealing composition	M/s Arya Chemical Works, Calcutta - Exclusive (1961).
4. Cation exchange resins from CNSL	M/s Tulsi Industries, Poona - exclusive (1961).
5. Dihydroisojasmone and peach aldehyde	M/s S.H. Kelkar & Co., Bombay - non-exclusive (1963).
6. Ethylene oxide condensates (sponsored)	Work completed in 1960. Produced by M/s Hico Products Ltd., Bombay.
7. Heat sealable coating compositions	Shri Chandmal Fakirchand Jain, Indore - non-exclusive (1964).
8. Hexyl resorcinol	M/s Unichem Laboratories, Bombay. exclusive (1961).
9. 4-Hydroxycoumarin and warfarin	M/s Unichem Laboratories, Bombay - exclusive (1961).
10. $\beta$ -Ionone	M/s S.H. Kelkar & Co., Bombay - Non-exclusive (1961).
11. Liquid rubber	M/s Chari & Co., Madras - non-exclusive (1961).
12. Nicotine sulphate	M/s Urvakunj Tobacco By-products, Dharmaj - non-exclusive (1961).
13. Rigid filters	M/s Ashim Filters, Allahabad - exclusive (1965).
14. Rubber base adhesives	M/s Chari & Co., Madras - non-exclusive (1961).
15. Silica gel (desiccant type) (sponsored)	Work completed in 1962. Produced by M/s Minco Products, Madras.
16. Sisal wax	M/s Aphali Pharmaceuticals Ltd., Ahmednagar - non-exclusive (1961).
17. Tetrab <sup>mo</sup> indigo (sponsored)	Work completed in 1961. M/s Shree Dyes, Poona have started experimental production.

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|---|--|
| 18. Thermistors   | M/s Semi-conductors, Ltd.,<br>Poona and M/s Tempo Industrial<br>Corp., Bombay - non-exclu-<br>sive (1960).                   |
| 19. Utilization of bye-products<br>of Hindustan Insecticides<br>Ltd., New Delhi (sponsored) | Work completed in 1963.<br>M/s Hindustan Insecticides<br>Ltd., Delhi are producing<br>chloral hydrate and ethyl<br>chloride. |
| 20. Water dispersible DDT   | M/s South India Research<br>Institute Pvt. Ltd., Vijaya-<br>wada - non-exclusive (1961).                                     |

II Processes Released and Awaiting Production:

- |  |  |
|--|--|
| 1. Acetanilide   | Released through project<br>engineering firm - exclusive<br>(1966). HOC Ltd., have<br>selected NCL process from the<br>world tenders invited. A<br>plant 2000 T/year will be set<br>up by HOC Ltd. |
| 2. Acriflavine<br>(sponsored)  | NCL work on the scheme<br>completed in 1966.   |
| 3. Ammophos (II)   | Released - non-exclusive<br>(1959) to one firm.  |
| 4. Bacterial diastase and<br>protease                                  | Released - exclusive (1959).<br>Plant set up and is being put<br>in commission with the help<br>of NCL scientists. Experi-<br>mental batches produced.   |
| 5. Berberine hydrochloride<br>(sponsored)                              | NCL work on the scheme<br>completed in 1965.   |
| 6. Chlorinated alkyl aryl<br>phenols as pesticides from<br>CNSL & BNSL | Released - non-exclusive<br>(1963) to one firm.  |
| 7. Coating composition for<br>textile bobbins                          | Released - exclusive (1960)  |
| 8. Covering material from<br>anacardic materials                       | Released - exclusive (1964)  |
| 9. Diethyl-m-aminophenol<br>(sponsored)                                | NCL work on the scheme<br>completed in 1966. Report sent.  |
| 10. Diethylstilbestrol   | Released - exclusive (1966).   |
| 11. Dioctyl and dibutyl<br>phthalate                                   | Released - non-exclusive ('66)<br>through project engineering<br>firm, who are offering a<br>turn-key plant for 10,000 T/year (Rs.6 crores)<br>to HOC Ltd., and private industry.                  |

12. Ethylacetoacetate  
Released - non-exclusive (1963) to two firms.
13. Hexachloroethane  
Released - non-exclusive (1965) to one firm.
14. Insoluble reaction products of polystyrene for use as cation exchange materials.  
Released - non-exclusive (1966) to one firm.
15. Mixed N.P. fertilizers  
Released - non-exclusive (1959) to one firm.
16. Opium alkaloids (sponsored)  
NCL work on the scheme completed in 1965. A new plant based on NCL process to be set up at Neemuch (4.7 T/year value Rs.1 crore).
17. Polyurethane printing rollers  
Released - non-exclusive (1964) to three firms. One firm to start production by March 1967.
18. Pressure sensitive adhesive tape.  
Released - exclusive (1961).
19. Reactive dyes (sponsored)  
NCL work on the scheme completed in 1966.
20. Rubberised cork sheets  
Released - non-exclusive (1966) to one firm.
21. Solvent and heat exchange liquids from CNSL  
Released - non-exclusive (1963) to one firm.
22. Styrene DVB-base cation exchange resin.  
Released non-exclusive (1963) to three firms. Two firms likely to start production in 1967.
23. Surface active agents from CNSL  
Released - non-exclusive (1963) to one firm.
24. Thiodiglycol (sponsored)  
NCL work on the scheme completed in 1961.
25. Vat dye (sponsored)  
NCL work on the scheme completed in 1966. Project report sent.
26. Vitamin C  
Released to M/s Hindustan Antibiotics Ltd., who will be setting up a plant for 125 T/year (Rs.94 lakhs) at Pimpri.

A. III Completed research projects, ready for exploitation and steps being taken to utilize them:

- |  |  |
|--|--|
| 1. Aniline                                       | A turn key plant 600 T/year is being offered to HOC and private party.   |
| 2. Chromatographic alumina                       | At present in production at FCP.   |
| 3. Chromatographic silica gel                    | - do -   |
| 4. Civetone                                      | Process offered to industry.   |
| 5. Costus root oil                               | Negotiation with Punjab Govt. and private parties in progress.   |
| 6. Dihydrocivetone                               | Process offered to industry.   |
| 7. Dihydrojasmone                                | - do -   |
| 8. Dihydroambrettolide and isoambrettolide       | - do -   |
| 9. Diethyl and dimethyl phthalate                | Complete know-how with engg. designs <del>with</del> for 750 T/year plant for each offered to a firm with whom negotiations are in progress. |
| 10. Dimethylaniline                              | A turn key plant (600 T/year) being offered to HOC and private parties.  |
| 11. Dithranol                                    | Negotiation for release in progress.   |
| 12. Exaltone and exaltolide                      | Process offered to industry.   |
| 13. Hard and soft ferrites                       | Negotiations for release in progress.  |
| 14. 4-Hydroxycarbostyryl                         | Process offered to industry.   |
| 15. dl-Menthol from citronellal                  | - do -   |
| 16. Monobethylaniline                            | Process offered as a turn-key plant (100 T/year) to industry.  |
| 17. Neo-lavandulol                               | Process offered to industry.   |
| 18. Phenoxy acetic acid                          | Negotiations for release in progress. At present in production at FCP unit.  |
| 19. Styrene DVB-base anion exchange resin        | Negotiations for release in progress.  |
| 20. Vapour phase chromatograph (proto-type unit) | - do -   |

A-IV New sponsored projects undertaken:

1. Aminotriazole Private party
2. Utilization of longifolene - do -
3. Utilization of  $\Delta^3$ -carene - do -
4. Utilization of terpene G - do -
5. Development of manufacturing process for rayon grade pulp from some species of wood - do -
6. Chlorinated copper phthalocynines - do -
7. Wood phenolics with special reference to their use in chemotaxonomy and their biosynthesis by tissue culture studies U.S. Department of Agriculture, USA. PL-480.
8. Calcium silicate Private party
9. Radio opaque dyes like urografin and biligrafin Private party

A-V Projects completed:

Studies in pine oil from Indian turpentine oil (sponsored) Private party

A-VI Process passed on to industry:

Rubberised cork sheet M/s Bharat Casements Pvt.Ltd. Baroda.  
Premium - Rs.8000/-  
Nature - non-exclusive

Preparation of insoluble reaction products of polystyrenes for use as cation exchange materials (Ind.Pat. 74356) M/s Tulsi Industries, Poona.  
Premium - nil.  
Recurring royalty - 5% on net sales  
Nature - non-exclusive

A-VII Services rendered to outside parties:

1. Supply of cultures:

This has been reported under Service Projects on page 54.

2. Analytical services:

This has been reported under Service Projects on pages 54 to 56,

3. Technical aid involving experimental, instrumental, engineering and glass blowing services:

This has been reported under Service Projects on pages 56 to 58.

4. Demonstrations:

Vapour phase chromatograph (proto-type unit developed at NCL)	M/s Hyderabad Allwyn Metal Works, Hyderabad.
	M/s Scientific Instruments & Co., Bombay.

5. Training to outside persons:

Dr.P. Subba Rao, Saugar University, Saugar.	NMR spectroscopy
Dr.U.D. Gupta, Rajasthan University.	- do -
Dr.K. Raniah, Osmania University.	- do -
Dr.B.K. Sharma, Delhi University.	Radiation chemistry
Mr.M.L. Gupta, Saugar University, Saugar.	NMR, IR and VPC techniques.

6. Technical enquiries:

Govt. departments	...	59
Private parties	...	148
		-----
Total		207
		-----

A-VIII Seminars and lectures:

5 NCL scientists delivered lectures on different scientific subjects at NCL seminar.

10 NCL scientists delivered more than 15 lectures on different scientific subjects at various research institutes and universities in the country.

A-IX Publications and patents:

Publications:

1. Rao, R.V.G., Subba Rao, V.V. and Biswas, A.B.  
Thermal decomposition of neodymium oxalate and changes in surface areas of the products.  
J. Inorganic Nuclear Chemistry 28, 415 (1966).
2. Jain, S.C., Tavale, S.S. and Biswas, A.B.  
Abstract on the crystals of some  $\alpha$ -oxo acids.  
Volume of collected abstract of 7th International Congress and Symposium on Crystal Growth held at Moscow, USSR - No.8, 52, p.124 (1966).
3. Pant, L.M., Sakore, T.D. and Biswas, A.B.  
Abstract on the structure of nickel imidazole nitrate dihydrate. Volume of collected abstract of 7th International Congress and Symposium on Crystal Growth held at Moscow, USSR - No.9, 53, p.158 (1966).
4. Sabane, C.D., Sinha, A.P.B. and Biswas, A.B.  
On electrical properties of copper manganite.  
Ind. J. Pure & Appl. Physics 4, 187 (1966).
5. Chavan, A.M., Dhut, R.M., Lakbir Singh and Biswas, A.B.  
Thermogravimetric study of the reduction of co-precipitated nickel copper carbonates.  
Ind. J. Chem. 4, 211 (1966).
6. Ranade, A.C. and Subba Rao, V.V.  
Magnetic susceptibilities of some first row transition metal carboxylates.  
Ind. J. Chem. 4, 42 (1966).
7. Chandra (Mrs.), S.; Roy Chowdhary, P. and Biswas, A.B.  
Ultrasonic degradation of macromolecules in solution. A study of degradation kinetics by estimation of free radical scavenger DPPH and solution viscosity measurements.  
J. Appl. Polymer Sci. 10, 1089 (1966).
8. Joshi, A.V. and Sinha, K.P.  
Low temperature thermal conductivity of ferrimagnetic insulators.  
Proc. Phys. Soc. (London) 88, 685 (1966).
9. Ganguly, B.N., Upadhyaya, U.N. and Sinha, K.P.  
Indirect interaction involving impurity states in superconductors.  
Phys. Rev. 146, 317 (1966).
10. Shukla, G.C. and Sinha, K.P.  
Electron-phonon coupling in dielectrics.  
J. Phys. Chem. Solids 27, 1837 (1966).
11. Narendra Kumar and Sinha, K.P.  
Temperature dependent exchange narrowing of line width in EPR on interacting donors in Ge and Si.  
Z. Physik 197, 26 (1966).
12. Deokar, V.D. and Goswami, A.  
Effect of substrate temperature on Hall co-efficient of thin films.  
Ind. J. Pure Appl. Phy. 4, 288 (1966).



13. Badachhappc, S.B. and Goswami, A.  
Some electron diffraction studies on cuprous chloride films.  
Ind. J. Pure & Appl. Phys. 4, 168 (1966).
14. Rao, P.S., Nageswara Rao, N.B.S. and Reddy, M.P.  
Spectrophotometric determination of  $\alpha$ - and  $\beta$ -naphthols  
in a mixture.  
Ind. J. Chem. 9, 408 (1966).
15. Jain, S.C., Tavale, S.S. and Biswas, A.B.  
On the crystal structures of  $\alpha$ -oxoacids.  
Acta Cryst. 21, 445 (1966).
16. Hundekar, A.M., Srinivasan, K.S., Thankarajan, N. and  
Sen, D.N.  
Potable water from sea-water using briquetted silver  
barium zeolite.  
Ind. J. Appl. Chem. 28, 203 (1966).
17. Thankarajan, N. and Sen, D.N.  
Reactivity of chelated acetylacetone.  
Ind. J. Chem. 4, 94 (1966).
18. Ramaswamy, K.K. and Sen, D.N.  
Resorcin 2:4 dialdehyde and some of its chelate polymers.  
Ind. J. Chem. 4, 132 (1966).
19. Rao, M.V.R., Krishna Rao, G.S. and Sukh Dev.  
Studies in sesquiterpenes - XXIV - Synthesis of  
(-)-cadinene dihydrochloride.  
Tetrahedron 22, 1977 (1966).
20. Murthy, K.L., Nagasampagi, B.A., Rai, C. and Sukh Dev.  
Studies in sesquiterpenes - XXIII - Methyl cadalenes -  
Synthesis and characterization.  
Tetrahedron 22, 1949 (1966).
21. Patil, J.R. and Bose, J.L.  
Cyclic acetals and ketals of monosaccharides - Part I.  
J. Ind. Chem. Soc. 43, 161 (1966).
22. Kaul, B.L., Nair, P.M., Rama Rao, A.V. and Venkataraman, K.  
NMR spectra of azo-phenols and quinone hydrazones.  
Tetrahedron Letters No.32, 3897 (1966).
23. Bawdekar, A.S., Kelkar, G.R. and Bhattacharyya, S.C.  
Absolute configuration of parthanolide.  
Tetrahedron Letters No.11, 1225 (1966).
24. Umarani, D.C., Gore, K.G. and Chakravarti, K.K.  
Terpenoids XC - Khusimol, a new sesquiterpene alcohol.  
Tetrahedron Letters No.12, 1255 (1966).
25. Siscovic (Mrs.), E., Honwad, V.K. and Rao, A.S.  
Synthesis of 1-oxocoudeosomes.  
Tetrahedron Letters No.14, 1471 (1966).
26. Honwad, V.K. and Rao, A.S.  
Citral epoxide.  
Current Science 13, 333 (1966).
27. Rao, N.B.S.N., Rao, P.S. and Reddy, N.P.  
Radiolytic oxidation of naphthalene, aerated organic  
solution.  
Ind. J. Chem. 4, 244 (1966).

28. Pandya, K.P., Mascarenhas, A.F. and Sayagaver (Miss), B.M. Ubiquinone (coenzyme Q) of normal and crown gall tissue cultures of Parthenocissus.  
Ind. J. Biochem. 3, 127 (1966).
29. Mascarenhas, A.F., Rangachari, P.M. and Sayagaver, (Miss), B.M. Chemical examination of callus tissue of Papaver somniferum grown in vitro.  
Ind. J. Chem. 4, 191 (1966).
30. Kaplay, S.S. and Jagannathan, V. Purification of ox brain acetylcholinesterase.  
Ind. J. Biochem. 3, 54 (1966).
31. Sadana, J.C. Purification and characterization of nitrite reductase from Achromobacter fischeri.  
Biochimica Biophysica Acta 118, 426 (1966).
32. Sastri, S.R.S. and Pai, M.U. Correlation of latent heats of vaporisation.  
Ind. J. Techn. 4, 72 (1966).

Papers sent/read at symposia, seminar etc.:

1. Chakravarti, K.K. Chemical constituents of vetiver oil. Symposium on Recent Advances in the Development Production and Utilization of Medicinal and Aromatic Plants in India, Lucknow, April 1966.
2. Kelkar, G.R. Chemical Constituents of costus roots. Symposium on Recent Advances in the Development Production and Utilization of Medicinal and Aromatic Plants in India, Lucknow, April 1966.
3. Roy Chowdhury, P. Design and construction of an ultrasonic interferometer. Symposium on Electronic Instrumentation, Pilani, April 1966.
4. Seth, N.D. (i) Process for the manufacture of dioctyl and dibutyl phthalates, and (ii) process for the manufacture of acetanilide. Symposium on Opportunities for New Industries, Mysore, May 1966.
5. Narayanan, C.R. Conformation of ring A in terpenoids. Symposium on Chemistry of Wood, Hyderabad, June, 1966.
6. Kapur, S.L. Recent trends in plastic applications. All India Plastic Manufacturers Association Conference, Bombay, August 1966.

Patents:

Filed:

106804  
Improvements related to the manufacture of carboxymethyl cellulose.  
Bendale, D.S., Mahajan, M.B. and Khadilkar, H.P.

Sealed:

95075

Utilization of groundnut shells for the manufacture of vanillin.

Vyas, G.M., Bendale, D.S., Mahajan, M.B., Bose, J.L., Modi, B.D., Sonawane, H.R. and Bigg, D.C.

Renewed:

55171

Treatment of cashewnut shell liquid for use in electrical insulating varnish. (upto 11.8.67).

Thakar, K.P. and Gupta, J.

57888

Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted aryl alkyl ketones. (upto 16.7.67).

Bose, J.L. and Shah, R.C.

60826

Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted deoxybenzoin and particularly of deoxyanisoin. (upto 18.6.67).

Bose, J.L. and Shah, R.C.

61585

A process for the manufacture of an ammonium phosphate-sulphate fertilizer. (upto 29.8.67).

Gupta, J., Sheshadri, K., Lobo, J. and Rao, M.N.

64959

A process for the preparation of dihydrojasnone. (upto 13.8.67).

Amin, J.H. and Bhattacharyya, S.C.

77224

Synthetic esters as speciality lubricants for low temperature performance and particularly for the lubrication of clocks and watches. (upto 18.6.67).

Patilak, K.D. and Subba Rao, B.C.

Italian pat. 675032 (Ind.Pat. 32822)

A process for the manufacture of high alpha cellulose dissolving grade pulps by alkaline pulping methods. (upto 17.6.67).

Vyas, G.M., Bendale, D.S. and Mahajan, M.B,

83364

Manufacture of hexachloroethane (upto 21.7.67).

Bhat, N.L., Goswami, M. and Pai, M.U.

A-X Library Holdings and New Additions:

Holding as on 1st April 1966		46,933
New additions from 1.4.66 to 30.9.66		
Books	352	
Bound volumes (journals)	629	
Thesis	6	
Microfilms	5	
Patents	38	
Translations	4	
Photo copies	2	
	-----	
	1036	1,036
		-----
	Total	47,969
		-----

A-XI Visits and Lectures of Foreign Scientists:

Prof. Friedrich Jung, Scientist, GDR.	Visit
Prof.V.M. Juchkevich, Prof.of Physics and Maths. and Chief of the Laboratory of Semi- conductors of the Academy of Science, USSR.	Visit
Dr.N. Blakebrough of Birmingham University of U.K.	"Some aspects of biochemical engineering".
Dr. Pionson of National Cash Register, USA.	Visit
Dr.G. Rajagopalan, Rockefeller University, New York.	"Some recent work on the amino- acids sequence determination of proteins (Pepsin)".
Mr.Maurice Goldsmith, Director, Science of Science Foundation, London and Editor, International Magazine - Scientific Films.	Visit
Prof.W. Kern, Director of the Institute of Organic Chemistry, University of Mainz, W.Germany.	Visit

General visits:

Large parties and many other small groups comprising of 450 visitors were taken round the laboratory and given brief introduction to the nature of NCL work.

A-XII Earnings:

Pilot plants	...	Rs.78,010.49
Misc. sales	...	Rs. 4,886.77
		-----
Total		Rs.82,897.26
		-----

A-XIII New appointments and Resignations:

list attached.

A-XIV Staff News:

Deputations and training:

Dr.A.B. Deshpande proceeded to Japan under Colombo Plan for 'Studies in Polymers' for one year (April 1966).

Shri V.S. Krishnamachar proceeded to Canada under Colombo Plan for 'Training in the field of microbiology with respect to maintenance of micro-organism. (May 1966).

Mr...D. Deshpande proceeded to France under Indo-French Co-operation agreement for training in 'Advance techniques in the field of applied research in chemical engineering' for a period of one year (June 1966).

Dr.Sukh Dev participated in the International Symposium on 'Natural Products' held at Stockholm, Sweden (June-July 1966).

Dr.B.D. Tilak attended 36th International Conference of Industrial Chemistry at Brussels (September 1966).

Symposia, seminar etc. attended:

More than 15 scientists attended summer schools, training courses, symposia, seminars etc., held in the country.

Degrees received:

1. Mr.V.K. Hinge	Ph.D.	Poona University
2. " A.S. Bawdekar	Ph.D.	- do -
3. " R.S. Joshi	Ph.D.	- do -
4. Miss H.M. Sayagaver	M.Sc.	Bombay University
5. Mr. A.H. Kapadi	Ph.D.	Poona University
6. " S.S. Koli	Ph.D.	- do -
7. " B.S. Krishnamurthi	Ph.D.	- do -
8. " B.G. Dhere	Ph.D.	- do -
9. " T.D. Sakore	Ph.D.	- do -
10. " K.C. Shrivastava	Ph.D.	- do -
11. " R.V. Pachhapurkar	Ph.D.	- do -
12. " R.G. Khurana	Ph.D.	- do -
13. " P.G. Sharma	Ph.D.	- do -
14. Mrs. S.V. Patwardhan	Ph.D.	Bombay University
15. Mr. S.S. Deshmane	Ph.D.	- do -
16. " S.C. Bisaria	Ph.D.	Agra University
17. " S.B. Mathur	Ph.D.	Poona University

Following are the staff members who are recognised guides, for different universities:

Dr. B.D. Tilak	Dr. K. Venkataraman
Dr. J. Gupta	Dr. A.B. Biswas
Dr. K.P. Sinha	Dr. H.B. Mathur
Dr. A. Goswami	Dr. (Miss) S.B. Kulkarni
Dr. L.M. Pant	Dr. A.P.B. Sinha
Dr. V.V. Dadape	Dr. D.N. Sen
Dr. P.R. Subbaraman	Dr. Sukh Dev
Dr. J.L. Bose	Dr. P.M. Nair
Dr. N.L. Dutta	Dr. C.R. Narayanan
Dr. K.K. Chakravarti	Dr. G.R. Kelkar
Dr. A.S. Rao	Dr. S.N. Kulkarni
Dr. V. Jagannathan	Dr. M.R.R. Rao

Dr.C. Sivaraman

Dr.J.C. Sadana

Dr.S.L. Kapur

Dr.N.D. Ghatge

Dr.L.K. Doraiswamy

Dr.M.U. Pai

A-XV

Following are the Indian universities for which NCL is the recognised centre for study and research:

Punjab	Agra	Poona
Karnatak	Bombay	Vikram
Banaras	Andhra	Madras
Shivaji		

A-XVI Aid under U.N. Special Fund, Colombo Plan, PL-480 etc.

1. Investigation of the effect of heat on tung oil and derivatives of tung oil and the characterization and identification of compounds resulting from heat treatments to extend the utilization of tung oil - sponsored by U.S.Dept. of Agriculture. Rs. 14,197/-
  2. Chemical and thermodynamic properties of refractory materials at high temperatures - sponsored by U.S.Dept. of Commerce. Rs.2,50,000/-
  3. Wood phenolics with special reference to their use in chemotaxonomy and their bio-synthesis by tissue culture studies - PL-480 Rs.2,09,678/-
- Total Rs.4,73,875/-

New Appointments  
(scientific and technical)

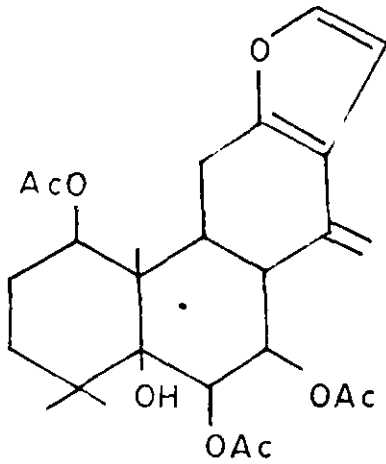
<u>S.No.</u>	<u>Name</u>	<u>Designation</u>	<u>Date of appointment</u>
1.	Mr. S.D. Yadav	J.S.A.	12. 4.66
2.	" M.R. Pawar	Fitter	28. 4.66
3.	" V.T. Gopalan	Apprentice	30. 4.66
4.	" A.N. Nadgir	S.L.A.	13. 5.66
5.	" A.B. Sahasrabudhe	S.L.A.	13. 5.66
6.	" S.R. Padalkar	S.L.A.	13. 5.66
7.	" M.D. Visal	S.L.A.	17. 5.66
8.	Dr.(Miss)R. Misra	S.S.A.	17. 5.66
9.	Mr. M.M. Patil	S.L.A.	17. 5.66
10.	" S.G. Joshi	Mechanic	30. 5.66
11.	" J.R. Patil	S.S.A.	1. 6.66
12.	" K.B. Kaushal	Sc.A1	30. 4.66
13.	" V.R. Kulkarni	S.L.A.	1. 6.66
14.	" S. Ghosh	S.S.A.	2. 6.66
15.	" B.M. Dubhash	J.S.A.	8. 6.66
16.	" R.N. Paul	S.S.A.	9. 6.66
17.	" P.A. Awasarkar	S.L.A.	14. 6.66
18.	" K.B. Wadekar	J.L.A.	14. 6.66
19.	" S. Guru	Garden Overseer	24. 6.66
20.	" H.J. Joglekar	Refrgn.Engineer	1. 7.66
21.	" A.S. Bhave	J.S.A.	11. 7.66
22.	" H.S. Soni	S.L.A.	11. 7.66
23.	" A.B. Landge	S.L.A.	15. 7.66
24.	Ms. S.A. Patwardhan	S.S.A.	8. 8.66
25.	Mr .V. Ramaswamy	S.S.A.	16. 8.66
26.	" R.S. Gopinath	S.S.A.	3. 9.66
27.	" S. Seshadri	Jr.Glass Blower	22. 8.66
28.	" Nirenjan Singh	Sc.B	2. 7.66
29.	" K.N.Sankaramurthy	J.T.A.	5. 9.66
30.	Dr. B.S. Rathore	Sc.B	17. 9.66
31.	Mr. D.G. Panse	S.L.A.	15. 9.66



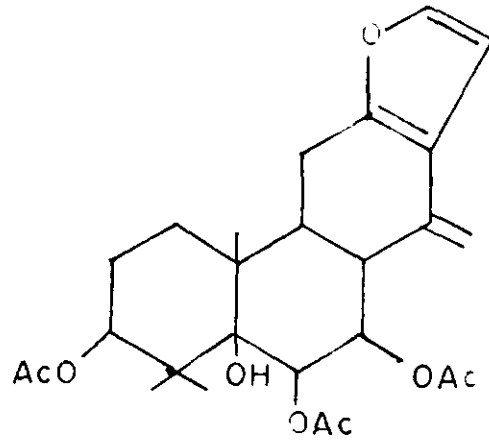
Resignations

<u>S.No.</u>	<u>Name</u>	<u>Designation</u>	<u>Date of resignation</u>
1.	Mr. M.V. Dhavlikar	Apprentice	1.4.66
2.	" C.D. Ware	Apprentice	16.4.66
3.	" K. Venkatappa	Gr.Apprentice	20.4.66
4.	" M.D. Tikekar	Jr.Glass blower	22.4.66
5.	" M.D. Kulkarni	<del>Apprentice</del>	10.5.66
6.	" S.R. Anand	Documentation Officer	3.5.66
7.	" K. Ganapathy	S.S.A.	<del>22</del> .5.66
8.	Dr.M.L. Maheshwari	S.S.A.	22.5.66
9.	Mr... Vaidyanathan	S.S.A.	25.5.66
10.	" Jatindar Kumar	S.S.A.	26.5.66
11.	" M.S. Joshi	S.L.A.	2.6.66
12.	" Y.D. Kulkarni	J.L.A.	16.6.66
13.	" V.V. Bhat	S.L.A.	30.6.66
14.	" Y.M. Chandhok	S.S.A.	2.7.66
15.	Dr. S.C. Bhattacharyya	Sc.E	18.7.66
16.	Mr. K.C.M. Raja	S.L.A.	1.8.66
17.	L.K. Badankal	Gr.Apprentice	1.8.66
18.	Dr. Ashok Kumar	S.S.A.	6.8.66
19.	Mr. K.S. Kulkarni	J.S.A.	10.8.66
20.	" R.G. Matathø	J.L.A.	16.8.66
21.	" V.V. Deekshitulu	S.L.A.	12.9.66

Chemical investigation of Putikaranja. (P.9)

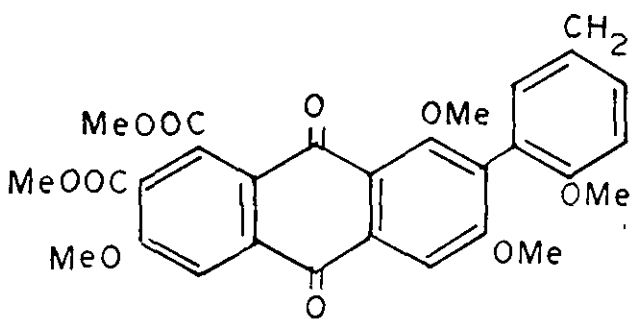


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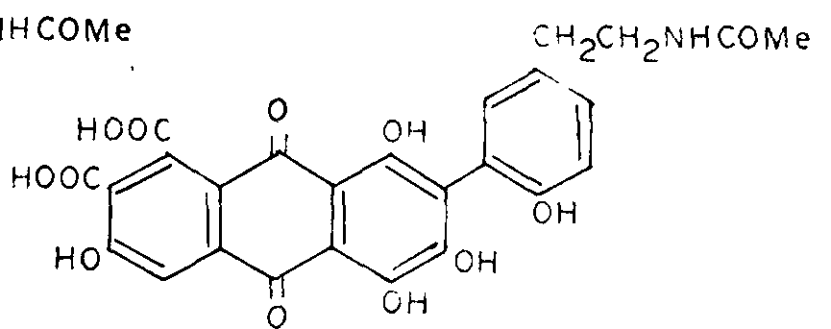


II

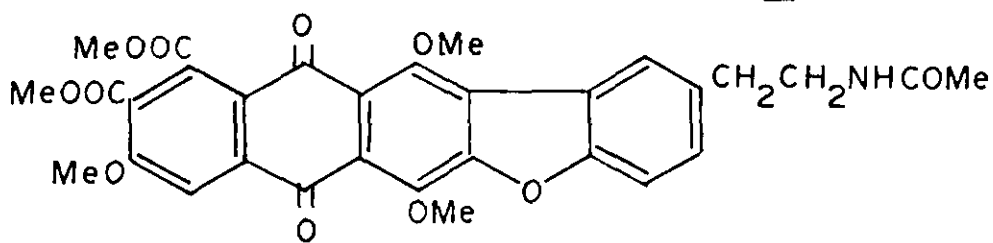
Lac dye. (P.12)



I

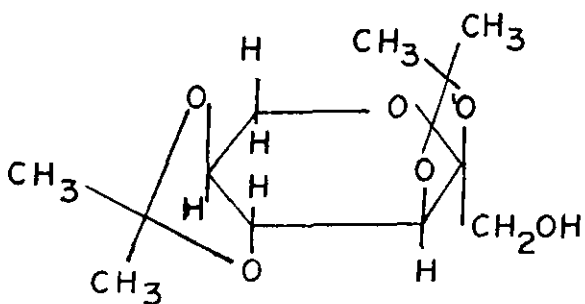


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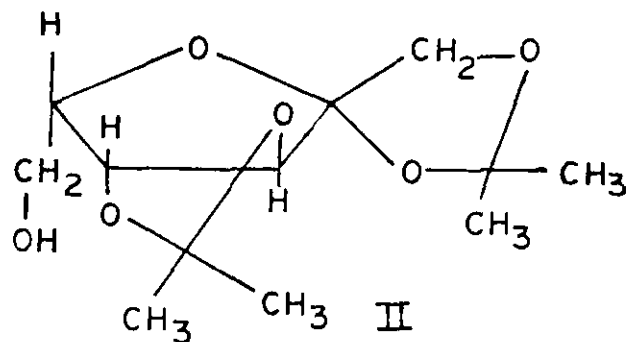


III

Cyclic acetals and ketals of monosaccharides. (P.48)

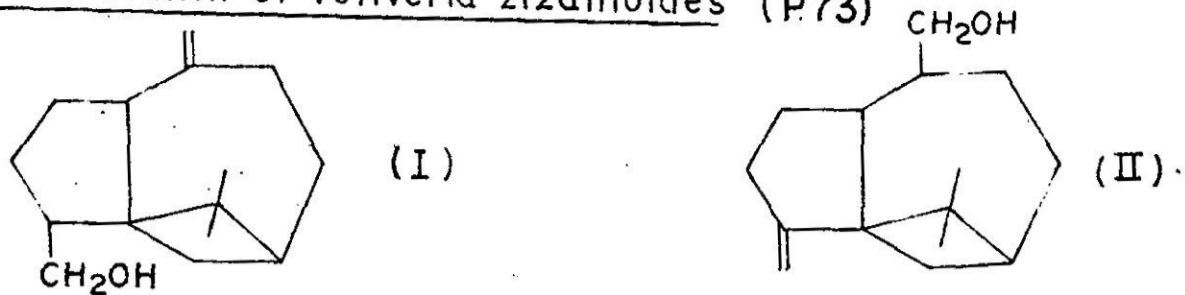


I

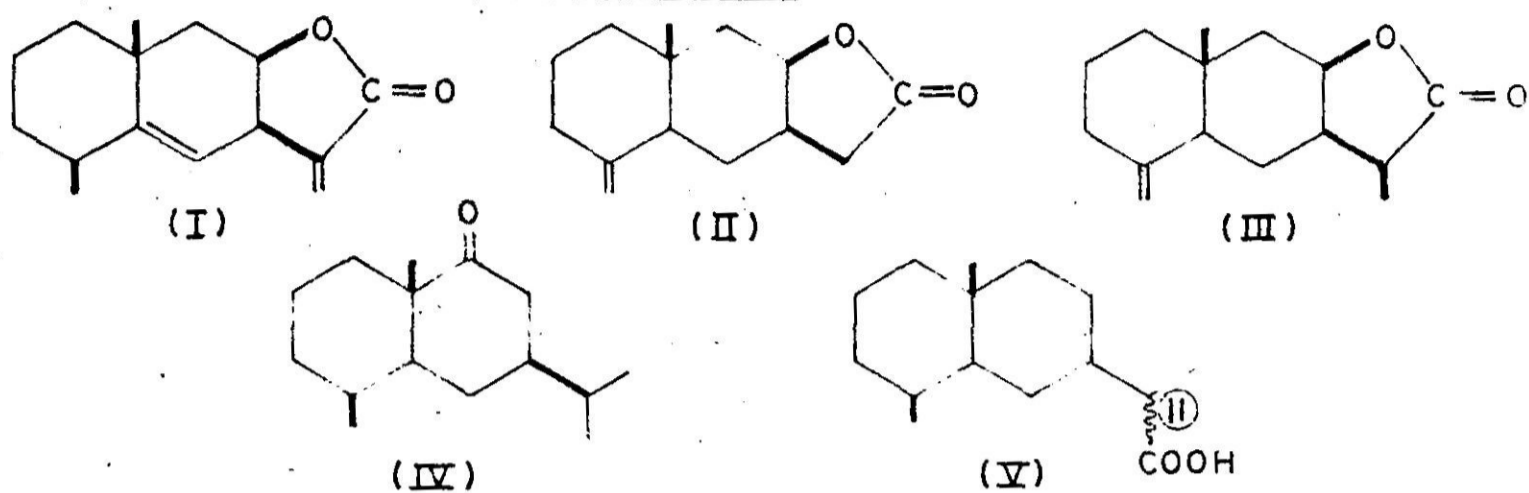


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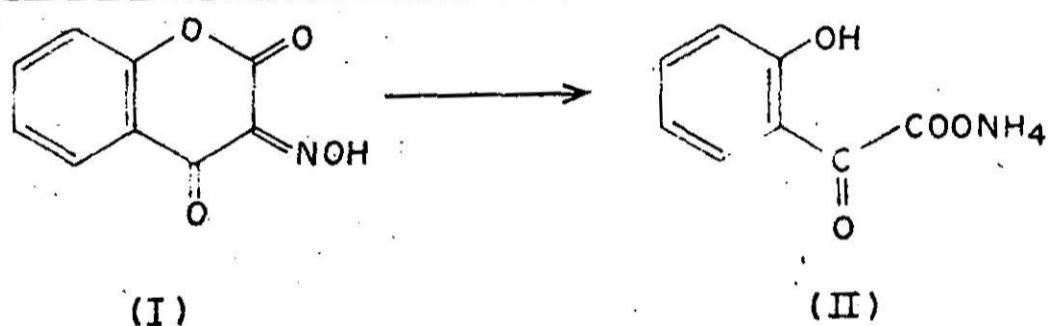
Chemical examination of vetiveria zizanioides (P.73)



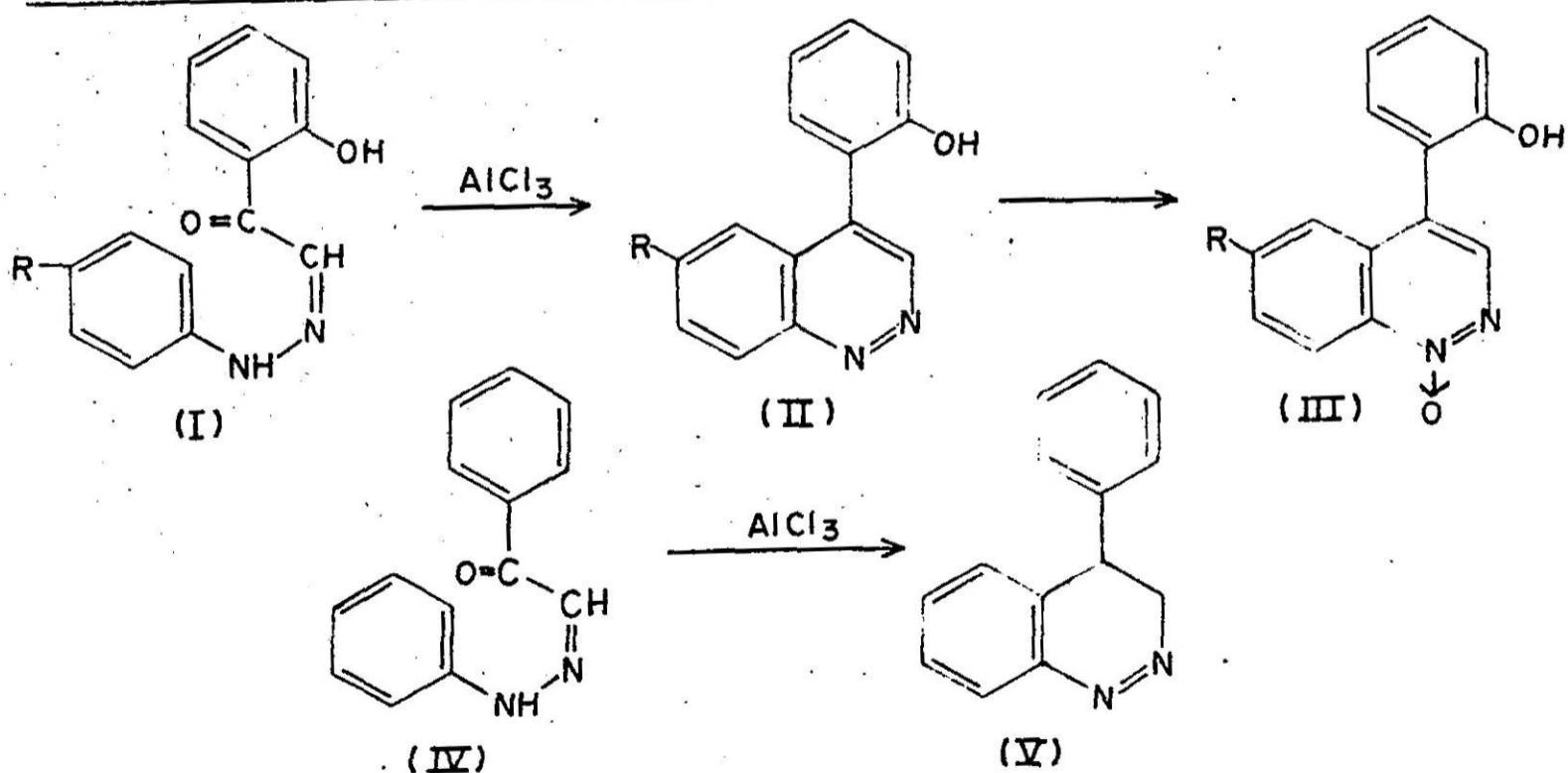
Chemical examination of Inula racemosa (P.74)



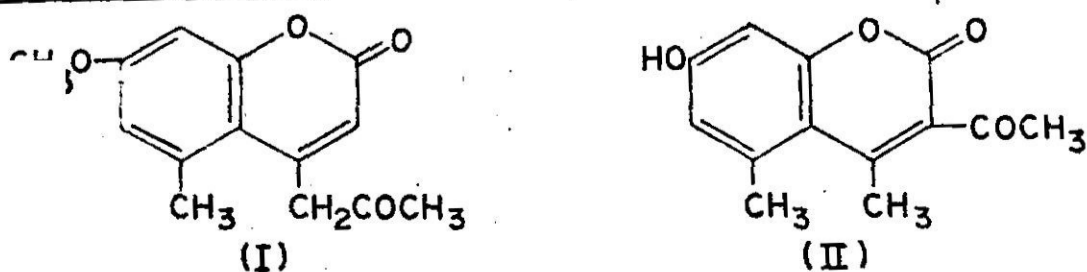
Meerwin arylation of 4-hydroxycoumarins : (P.76)



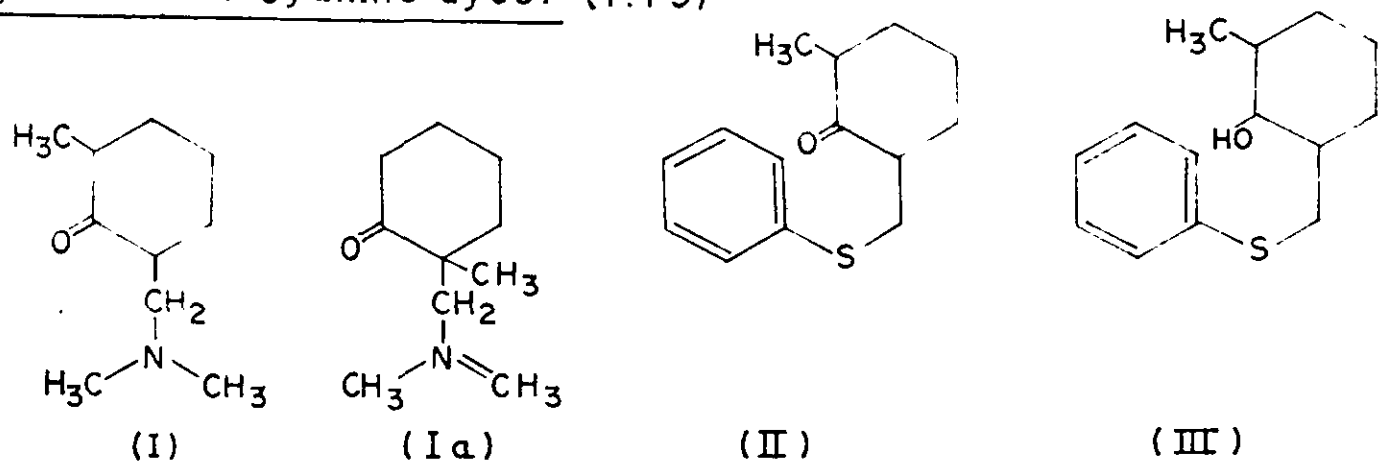
Synthetic studies on 4-arylcinnolines : (P.76)



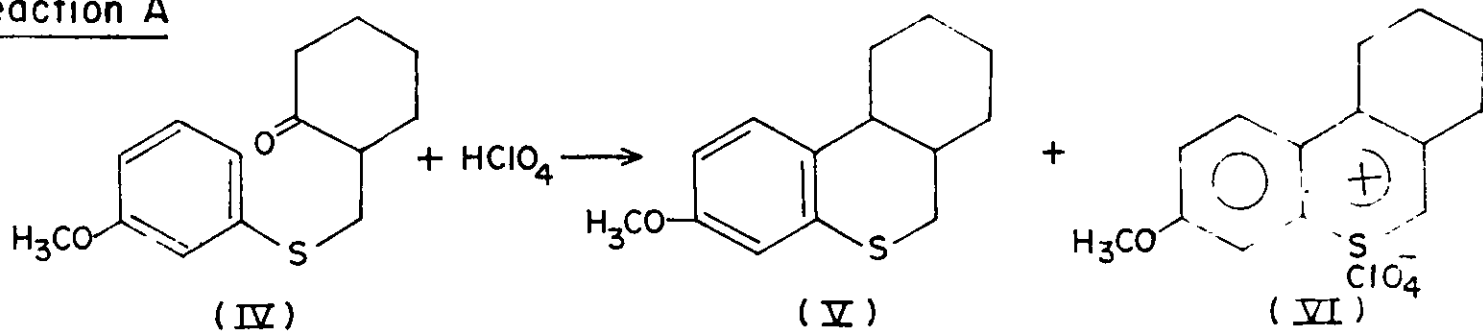
4-Acetomethylcoumarins (P.76)



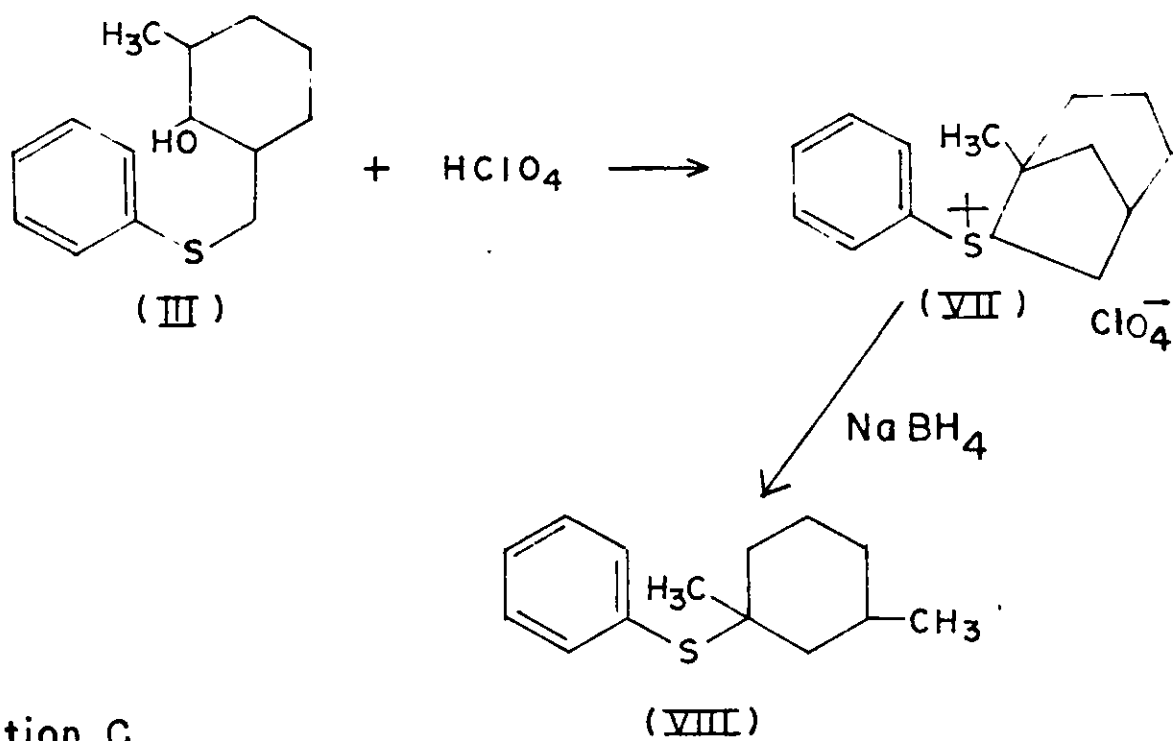
Synthesis of Cyanine dyes. (P.79)



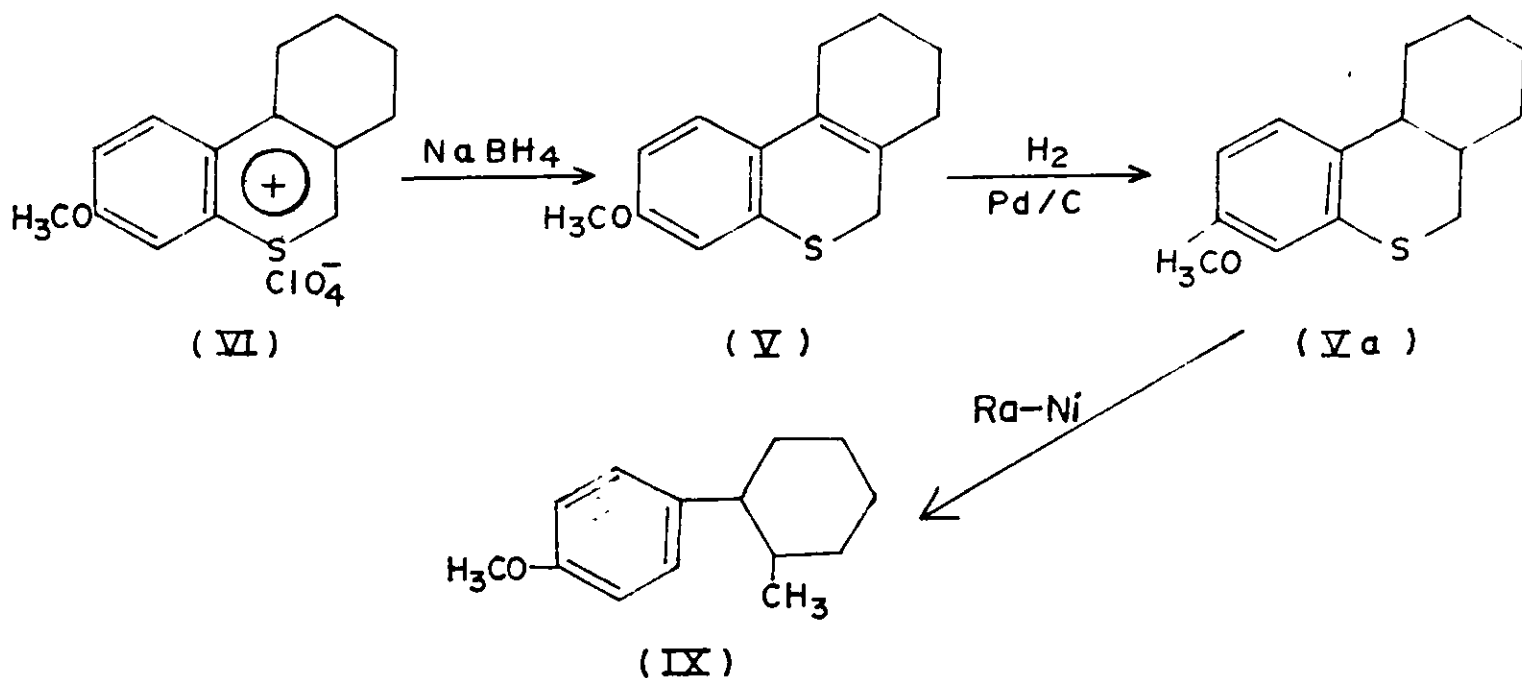
Reaction A



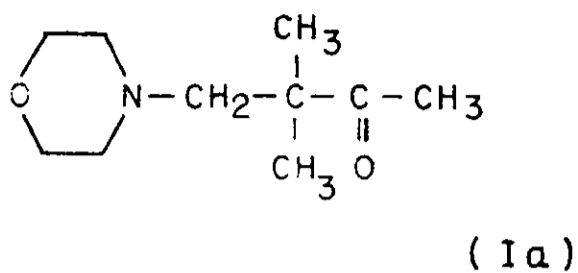
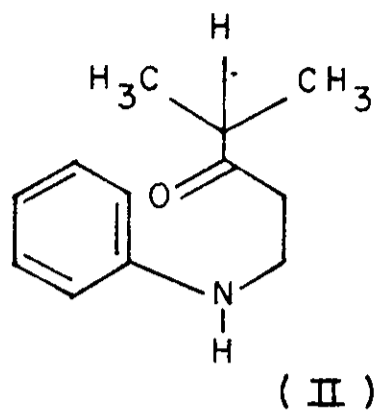
Reaction B



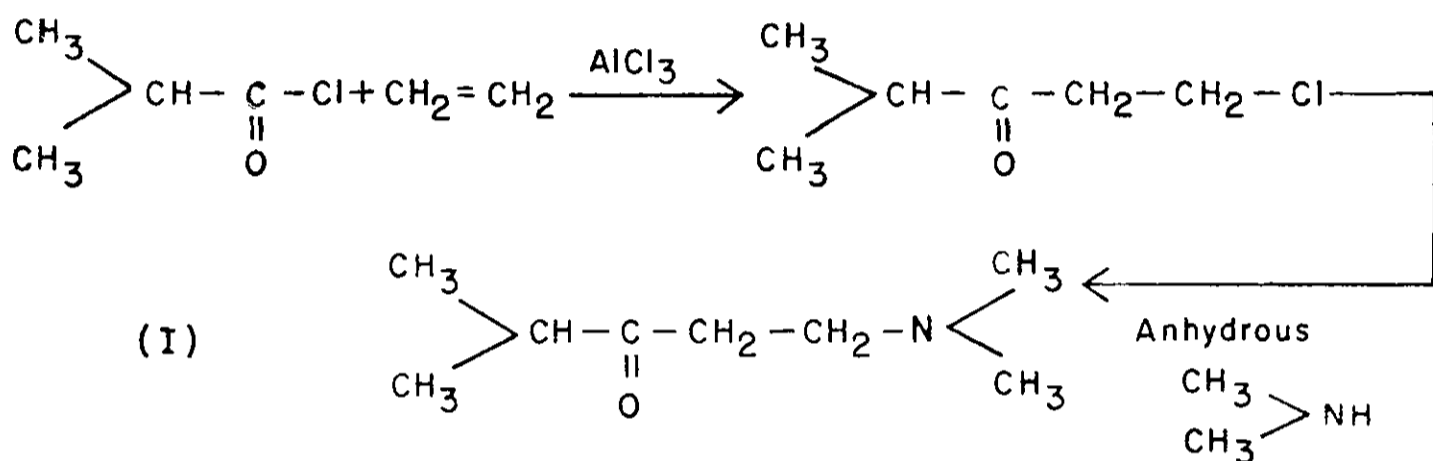
Reaction C



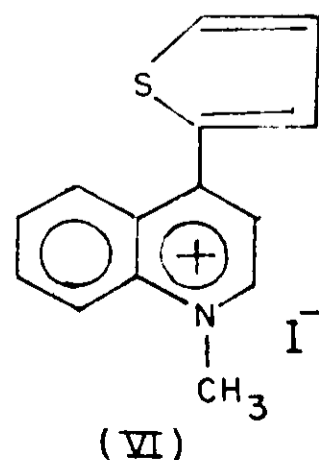
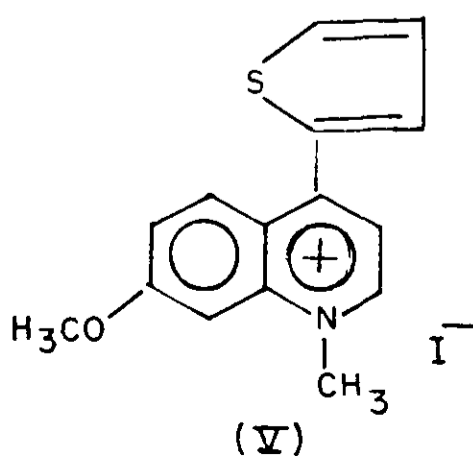
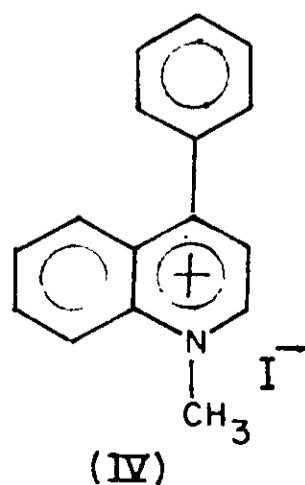
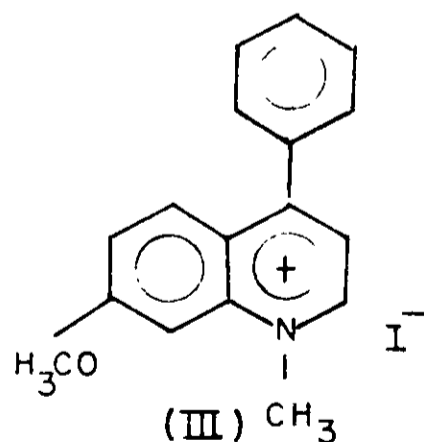
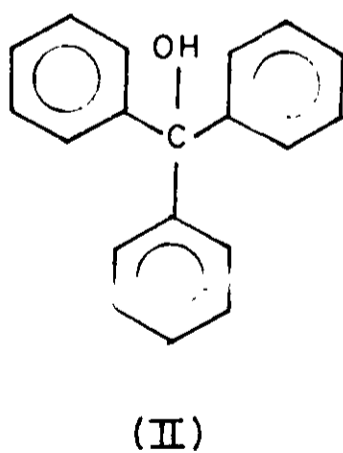
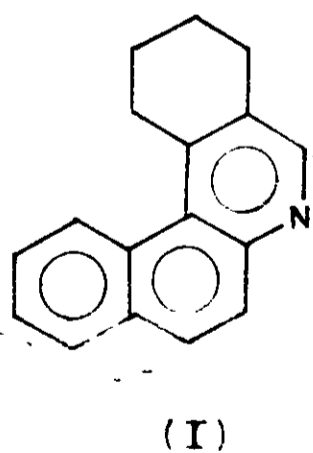
Hydride transfer studies in dyes and N-heterocyclics (P.79)



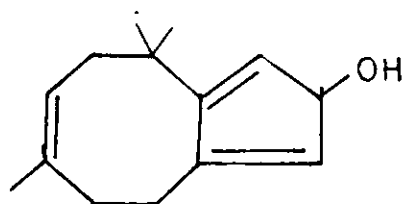
Reaction A



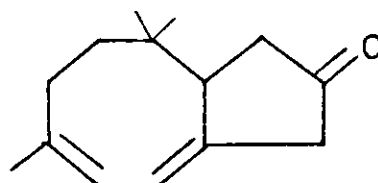
Biologically active heterocyclic compounds. (P.80)



Base catalysed reaction of lithioethylene diamine. (P 81)

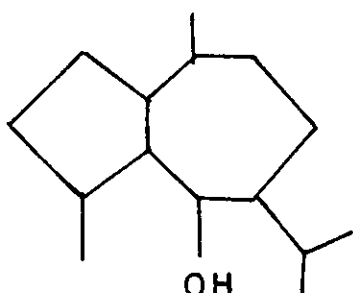


(I)

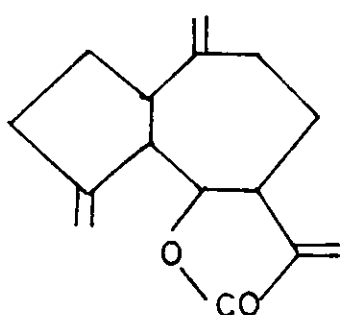


(II)

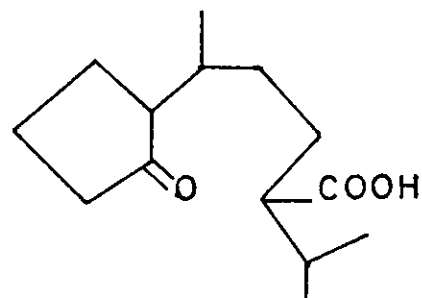
Studies on chemical transformations of dehydrocostus lactone. (P 82)



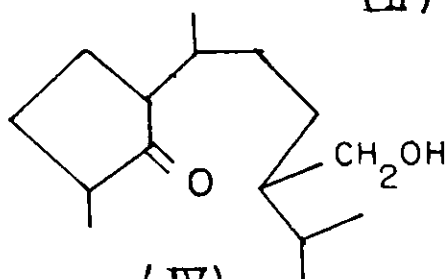
(I)



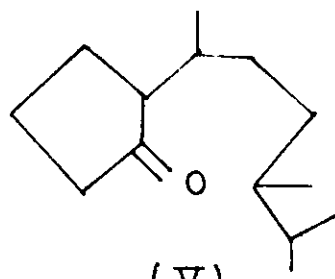
(II)



(III)

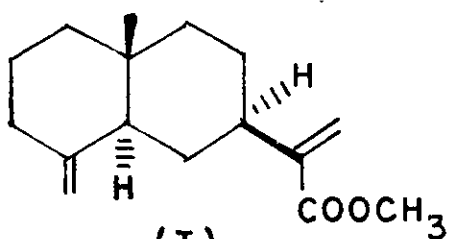


(IV)

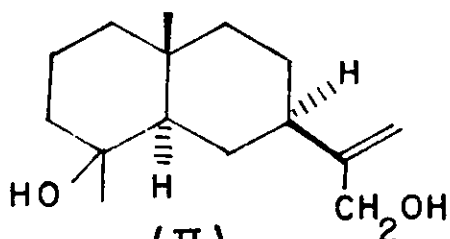


(V)

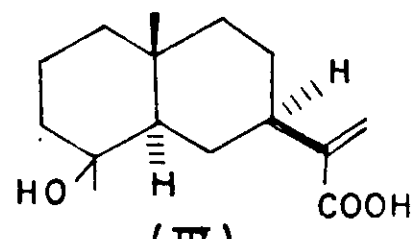
Acidic constituents of costus root oil. (P 83)



(I)

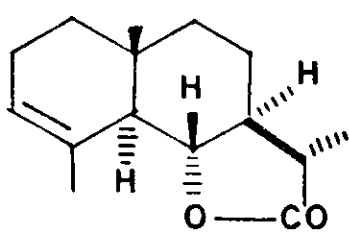


(II)

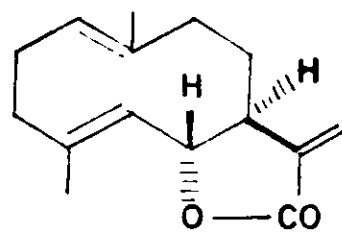


(III)

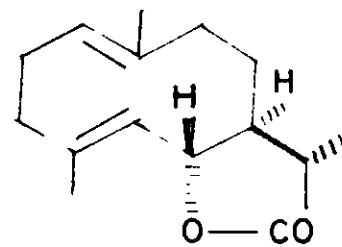
Conversion of costunolide into eudesmane type compounds. (P 83)



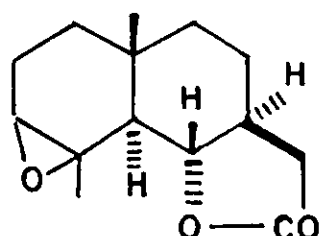
(I)



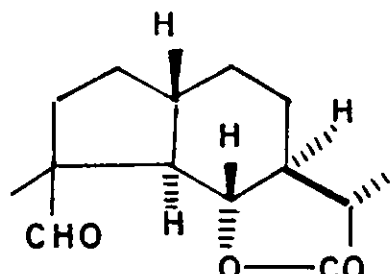
(II)



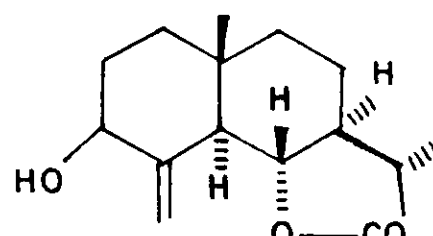
(III)



(IV)

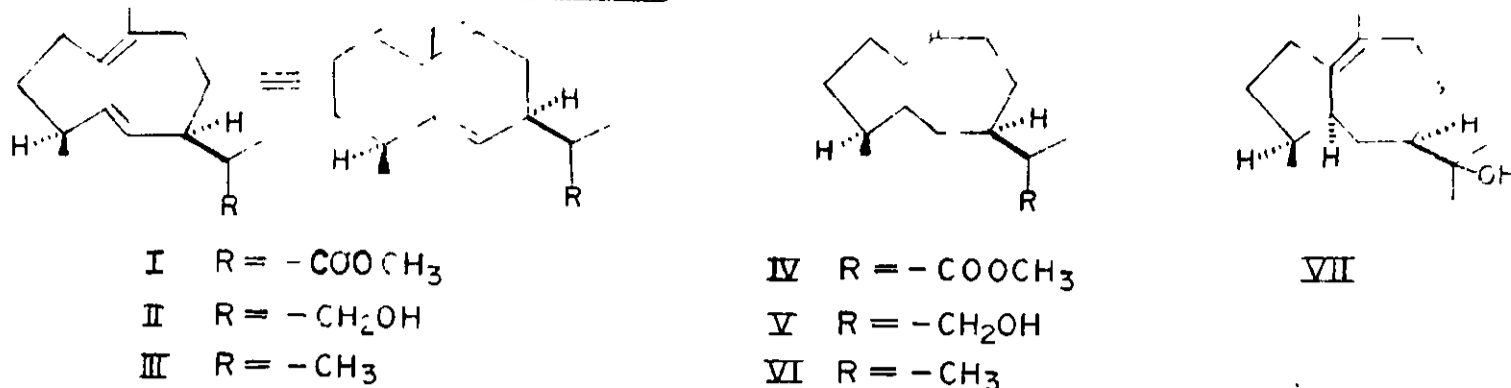


(V)

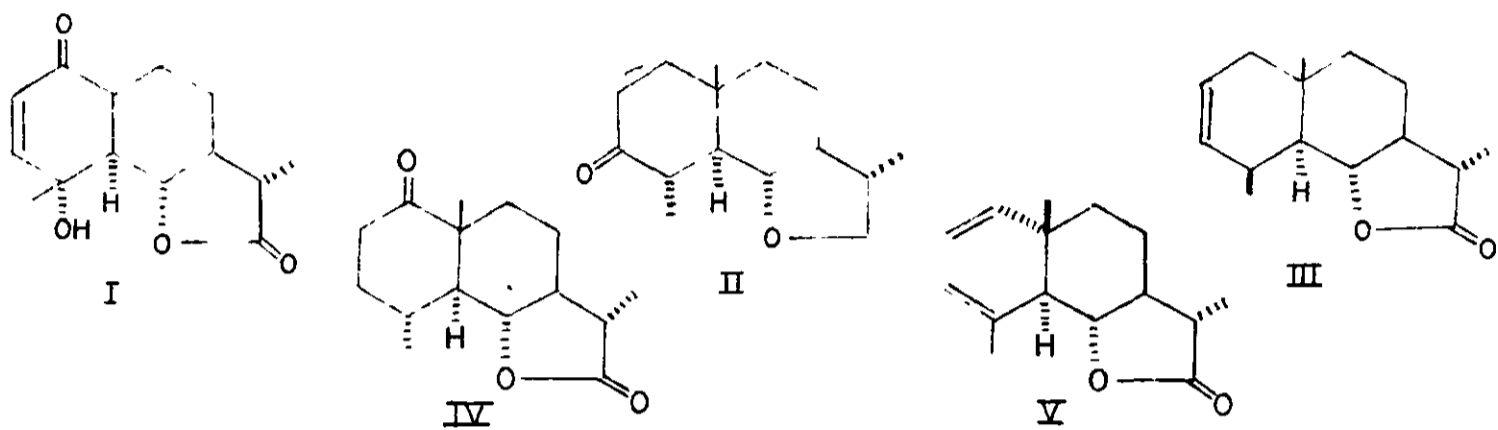


(VI)

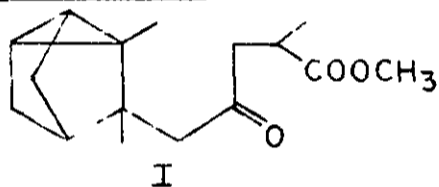
Transformation products of costunolide (P.84)



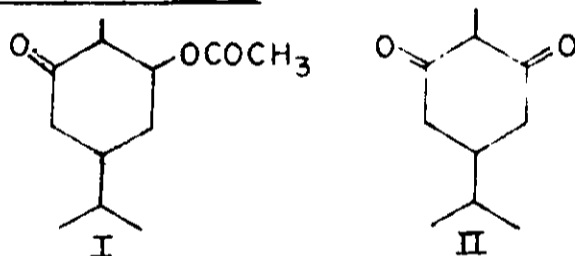
Synthesis of compounds related to selinane & elemene : (P 84)



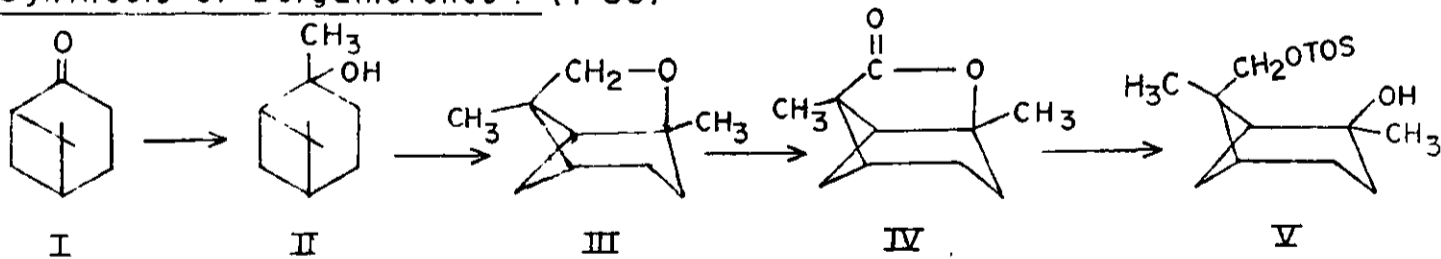
Synthetic approach in santalene-longifolene series.(P.85)



Transformation products in carvone series : (P.85)



Synthesis of Bergamotenes . (P 86)



Transformation product of endesmol and elemol : (P86)

