

M.Sc. Organic Chemistry

Scheme and Syllabus



School of Distance Education
Andhra University, Visakhapatnam, Andhra Pradesh

PREVIOUS

S.No.	Paper	Name of the Paper
1	Paper – I	General Chemistry
2	Paper – II	Inorganic Chemistry
3	Paper – III	Organic Chemistry
4	Paper – IV	Physical Chemistry

FINAL

S.No.	Paper	Name of the Paper
1	Paper – I	Organic Reaction Mechanism
2	Paper – II	Organic Spectroscopy
3	Paper – III	Organic Synthesis
4	Paper – IV	Natural Products and Biopolymers

PROGRAM OBJECTIVES:

PO1. To provide students in the scientific skills and chemical knowledge essential to develop and apply the knowledge in chemical sciences related to analysis of food and drug chemistry.

PO2. To provide knowledge, application, skills in water analysis

PO3. To equip students with effective scientific communication skills

PO4. To encourage the pursuit of lifelong education

PO5. To develop each student into a committed individual with ethical and social responsibility

PROGRAMME OUT COMES:

The Students Who Completes M.Sc Organic Chemistry Programms

1. Have strong foundations in the basic concepts of Organic Chemistry
2. Have good employment opportunities in pharmaceutical labs
3. Will get Jobs in various Chemical industries related to Pharma companies, polymer companies, pollution control boards etc.
4. Have excellent opportunities to pursue research
5. Can build their careers as Entrepreneurs by establishing “Start ups”.
6. Have an opportunity to pursue career teaching in chemistry at various levels.

PROGRAMME SPECIFIC OBJECTIVES:

The students who complete the M.Sc. Chemistry (Organic Chemistry Specialization) course shall:

1. Have strong foundation in the fundamentals and applications of chemical knowledge and understanding
2. Have the abilities to think critically, logically and analytically and solve problem in the area of chemical sciences, drug chemistry, medicinal chemistry and water pollution
3. Have the abilities to carry out chemical experiments, record and analyze the results and design advanced models
4. Have the abilities to use modern library and information retrieving tools to obtain information and assimilate to generate concepts and apply them in challenging situations

5. Have the abilities to effectively communicate their knowledge and skills to other chemists and non-chemists in oral or written formats
6. Secure suitable employment in the areas of chemical industries like pharmaceutical (R&D, QA & QC), polymers, , environmental and pollution control, nanotechnology and composite materials, teaching and research, etc.
7. Have the personal attributes and ethical sensibilities to enable them to function as effective scientists and citizens

M.SC. CHEMISTRY WITH SPECIALIZATION ORGANIC CHEMISTRY

First Year:

Paper-I General Chemistry

Paper-II Inorganic Chemistry

Paper-III Organic Chemistry

Paper-IV Physical Chemistry

Practicum:

Inorganic Chemistry Laboratory-1

Physical Chemistry Laboratory-1

Organic Chemistry Laboratory-1

SYLLABUS

Paper-I: GENERAL CHEMISTRY

Course Outcomes (COs)/Course Specific Outcomes (CSOs):

Upon completion of the course the students will be able to,

CO1: Learn and understand the selection rules and criteria for molecules to exhibit rotational and IR spectroscopy.

CO2: Understand the Classical and quantum mechanical theories of Raman spectroscopy and basic concepts of electronic spectroscopy.

CO3: Learn spectroscopic methods based on magnetic resonance principles.

CO4: Learn basics of group theory and its application in chemistry.

CO5: Understand the basic concepts of FORTRAN programming and its applications.

Learning Outcomes (LOs):

Upon completion of the course the student will be able

- To apply the spectroscopic methods for structure elucidation of molecules.
- To acquire knowledge of molecular symmetry and group theory and to solve chemical problems To write FORTRAN programs for simple chemical problems.

COURSE CONTENT:

Basic Quantum Chemistry:

Unit-I (15Lectures):

Wave equation – interpretation of wave function – properties of wave function – normalization and orthogonalisation – operators – linear and non-linear, commutators of operators. Postulates of quantum mechanics – setting up of operators observables – Hermitian operator – Eigenvalues of Hermitian operator.

Unit-II (15Lectures):

Wave mechanics of simple system with constant potential energy, particle in a box – factors influencing colour transition – dipole integral, Rigid rotator – simple harmonic oscillator. Hydrogen atom – solution of $R(r), Y(\theta, \phi)$ and orbitals. Equations probability density in orbitals – shapes of

Unit- III (10Lectures):

Perturbation theory—time independent perturbation—(Only first order perturbation to be dealt with)—application to ground state energy of helium atom—variation principle—applications—calculation of zero point energy of harmonic oscillator—Many electron atom—Hartree-Fock self-consistent field method (Qualitative treatment only).

Unit-IV (10 Lectures):

Valence bond approach—directed valence—hybridization covalent bond—calculation of ionic and covalent bond contributions in hydrogen molecule. (Fundamental concept only).

Molecular Spectroscopy:

Unit -V:

Basic concept of symmetry and group theory—symmetry elements—axioms of group theory—classification of molecules into point groups – representation of point groups – matrix representation – reducible and irreducible representations—reduction of reducible representation to an irreducible one—orthogonality theorem—character table and its anatomy (character table not to be derived)—use of character tables—application of group theoretical concepts to vibrational spectroscopy (infra-red and Raman).

Unit-VI (10 Lectures):

Rotational and Vibrational Spectra:

Rotation spectra of diatomic molecules— isotope effect—selection rules.

Infra-red spectra of diatomic molecules— isotope effect—selection rules— anharmonic oscillator – Normal modes of vibration— simultaneous vibration— rotation spectra— combination bands— overtones— Fermi resonance— concept of group frequencies— Raman effect (classical approach) – Applications of IR and Raman spectra.

Unit-VII (10 Lectures):

Electronic spectrum of a diatomic molecule— core structure— classification of bands— fine structure – band head and band shading – types of electronic transitions in molecules – applications of electronic spectra— charge transfer spectra.

Elements of Computer Programming:

Unit-VIII:

Basic components of computers— comparison of micro, mainframe and supercomputers— synopsis of software package in chemistry— Basic commands of MSDOS Format, copying operation, concept of directories, batch files, compilation of Fortran files, flowcharting M S Fortran : Integer and real variables and constants – Assignment and replacement statements – conditional statements (if-then-else, Goto)— repetition (Do statements with one inner loop) single dimensional arrays – Input, output statements – read and write with I, F and G formats – concept of function and Subroutine subprograms.

The following programs are to be practiced:

1. Rate constant of a first order reaction or Beer's law by least squares method (derivation not needed).
2. Roots of quadratic equation—application to hydrogen ion
3. Concentration of a strong acid.
4. Solving Vander-Waals equation or hydrogen ion concentration of a monoprotic weak acid (Gauss-Newton method).
5. Standard deviation and variance of univariate data
6. Basics of Database III—creating structures for a bibliographic data base and properties of chemical elements (Retrieval programs not needed.)

Books Prescribed:

1. Introductory Quantum Chemistry by A.K.Chandra (Tata McGraw Hill) 2nd Edition.
2. Quantum Chemistry and Spectroscopy (Problems and Solutions) by M.S.Pathania (Vishal Publications).
3. Atomic and Molecular Spectroscopy, Vols. 1,2,3 by Straw and Wangham.
4. Chemical Applications of Group Theory by F. A Cotton.
5. Introduction to Molecular Spectroscopy by C.N.Banwell.
6. MS Fortran (3.IV).
7. MS Disc operation system.
8. Database III—Allan Simpson.
9. Basics of Computers for Chemists—PC Jurs.

PAPER-II: INORGANIC CHEMISTRY

Course Objectives:

To make the students

CO1: Acquire the knowledge on applications of VSEPR, Valence Bond and Molecular orbital theories in explaining the structures of simple molecules and role of p and d orbitals in pi bonding.

CO2: Understand the concept of MO theory to square planar (PtCl_4^{2-}) and Octahedral complexes (CoF_6^{3-} , $\text{Co}(\text{NH}_3)_6^{3+}$). And Walsh diagram for H_2O molecule

CO3: Apply the knowledge and understanding of Understand the Orgel and Tanabe-Sugano diagrams for d^1 – d^9 octahedral and tetrahedral transition metal complexes of 3d series to newly prepared metal complexes

CO4: Develop interest in the areas of magnetic properties of transition and inner transition metal complexes – spin and orbital moments – quenching of orbital momentum by crystal fields in complexes.

CO5: To understand the concept of Term symbols and Electronic spectra and Magnetic properties of complexes

Learning Outcomes:

At the end of the course, the learners should be able to:

LO1: Explain idea of structure and bonding theories of inorganic compounds

LO2: Interpret Walsh diagram for other linear and bent molecules

LO3: Introduce electron counting rules for higher boranes

LO4: Analyse the preparation and structures of heteropoly acids

LO5: Understanding structure and bonding in coordination compounds

LO6: Explain selection rules, Tanabe-Sugano diagrams. Orgel diagrams

LO7: Experimentally identify the covalency in metal complexes.

LO8: To calculate the magnetic susceptibility of metal complexes

LO9: Understand and analyse structure-property correlation of coordination compounds

LO10: Design new coordination compounds based on a fundamental understanding of their electronic properties

COURSE CONTENT

Paper II - Inorganic Chemistry

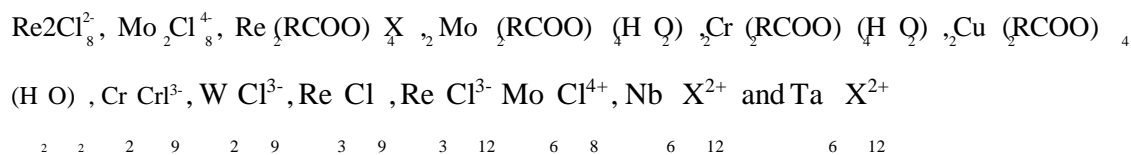
Unit-I

Term symbols - Russell - Saunders coupling, derivation of term symbols for various configurations.

Chemical Bonding : Application of VB, MO and VSEPR theories in explaining the structures of simple molecules - role of 'P' and 'd' orbitals in σ and π bonding.

Chemistry of main group elements : General trends in properties - boron hydrides. Carboranes, intercalation compounds, phosphorous - nitrogen, boron - nitrogen and sulphur cyclic compounds.

Chemistry of transition elements : Comparative study of the first, second and third transition series. Metal cluster compounds - favorable conditions for formation - Structure and bonding in the following halide and carboxylate metal - cluster compounds -



2 2 2 9 2 9 3 9 3 12 6 8 6 12 6 12

Unit - II

Chemistry of Inner Transition elements : Chemistry of Lanthanides - electronic configuration, Oxidation states, Lanthanide contraction and its consequences, magnetic and spectral properties - separation of lanthanides.

Chemistry of actinides - Synthesis of trans uranium elements electronic configuration, oxidation states, position in the periodic table, actinide contraction, comparison of magnetic and spectral properties with those of lanthanides.

Unit-III

Coordination compounds : Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries, Determination of crystal field splitting energy, calculation of crystal field stabilisation energies, Factors affecting crystal field splitting energies, spectrochemical series, Jahn - Teller effect, Ligand field theory.

Electronic spectra of transition metal complexes - Selection rules break down of selection rules, Orgel and Tanabe - Sugano diagrams, Spectra of octahedral and tetrahedral complexes.

Magnetic properties of free ions, spin and orbital moment and spin - orbit coupling - Quenching of orbital momentum by crystal fields in complexes.

Stability of complexes - Factors affecting stability, Chelate effect, Determination of stability constants of complexes, Spectro - photometric method and pH metric method.

Unit- IV

Inorganic reaction mechanisms: Inert and labile complexes - Explanation of lability on, the basis of CFSE.

Substitution reactions of metal complexes - D, Id, Ia and A mechanisms, Ligand replacement reactions of octahedral complexes - Acid hydrolysis, Anation and Base hydrolysis of cobalt (III) complexes, Ligand displacement reactions of square planar complexes of platinum (II) Trans effect, Mechanism of trans effect (theories), Electron transfer reactions of complexes, Inner and outer sphere mechanisms.

Text Books :

1. Advanced Inorganic Chemistry by F.A. Cotton and R. Wilkinson, John Wiley and Sons, 4th Edition New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, IV Edition, Harper International Edition, 1983.
3. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J.Sclbin, Affiliated East - West Press Pvt, Ltd, New Delhi.
4. Chemistry of Lanthanides by T.Moeller, Chapman and Hall. London, 1965.
5. Man - made Transuramium Elements by G.T. Seaborg.
6. Mechanism of Inorganic Reactions in solution by D.Benson, McGrawHill, London, 1968.

PAPER-III: ORGANIC CHEMISTRY

Course Objectives:

To make the students

CO1: Acquire the knowledge of aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

CO2: Understand aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

CO3: Apply the knowledge and understanding of aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products to new situations

CO4: Develop interest in the areas of aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

Learning Outcomes:

At the end of the course the learners should be able to:

LO1: Explain aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products.

LO2: Interpret aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

LO3: Compare aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

LO4:

Analyse aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

LO5: Solve aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

LO6: Identify aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

LO7: Apply aliphatic nucleophilic, aliphatic electrophilic, stereochemistry and conformational analysis, chemistry of heterocyclic compounds and chemistry of natural products

COURSE CONTENT:

Unit I : Structure and reactivity - localised and delocalised covalent bond concept of resonance and aromaticity - Huckel's rule aromaticity in benzenoid and non-benzenoid compounds, anti - aromaticity and homo-aromaticity. Nature of Organic reaction energy and kinetic considerations - types of Organic reactions - reagents - reactive intermediates, their formation and stabilisation - inductive and mesomeric effects.

Stereochemistry and stereoisomerism - conformational isomerism and analysis in acyclic and simple cyclic systems - substituted ethanes, cyclopentane, cyclohexane, cycloheptane, cyclooctane and decalins, Optical isomerism - optical activity molecular dissymmetry and chirality - elements of symmetry.

Fischer's projection - DL and R.S. Configurations relative and absolute configuration

- optical isomerism due to asymmetric carbon atoms optical isomerism in biphenyls, allenes and spirans optical isomerism of nitrogenous compounds, racemisation and resolution - geometrical isomerism and E.Z. configurations, properties of geometrical isomers.

Unit -II : Aromatic substitution reactions - electrophilic, nucleophilic and through benzyne - radical substitution of arenes - orientation of Nucleophilic substitution at a saturated carbon, S_NI, S_N2, S_Ni reaction - effect of structure nucleophile, leaving group solvent and C=O double bond. Additions involving electrophiles, nucleophiles and free radicals.

Elimination reactions-E₁, E₁cB, E₂ reactions - elimination versus substitution reactions.

Mechanism of some named reactions - aldol, Perkin, Benzoin Coannizaro wittig, Grignard, Reformatsky, wagner, Meerwein Hofmann, Claisen and Favorsky rearrangements

- Hydroboration - Oppenauer Oxidation, clemmensen reduction, wolf-Kischer reduction - Meerwein - Ponderf and Verley and Birch reductions. Mechanisms of name reactions - strok enamine reactions, Michael addition, Mannich reaction, Diels - Alder reaction, ene-reaction, Baeyer - Vileger reaction .

Unit - III : Chemistry of heterocyclic compounds, synthesis and reactivity of the following systems - pyridine, quinoline, isoquinoline, indole, benzofuran, benzothiofence - payzole, imidazole, oxazole, isoxazole, thiazole, isothiazole, pyridazone Pyrimidine and Pyrazine.

Spectra and structure-application of Organic Spectroscopy UV, IR-HMR and Mass spectral data.

Unit - IV : Chemistry of some typical natural products -A study of the following compounds involving their isolation, structure elucidation, Synthesis and biogenesis - Flavonoids

- quercetin, Cyanidin and genestein, Terpenoids, a-terpeneol, a-pinene, camphor, farnesol Alkaloids - atropine, nicotine, and quinine, purines - Caffeine.

Textbooks :

Configuration and ring structures of glucose and fructose, anomeric effects
1. Fifth Ed), by I.L. Finar, ELBS.

y (Fifth Edn.) by Morrison and Boyd. PHL, India.

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3. Organic Chemistry by Mukherjee, Singh and Kapoor, Vols. I and II, Wiley Eastern.

4. Reaction Mechanism in Organic Chemistry by Mukherjee and Singh, Macmillan India.

5. A guide book to mechanism in Organic Chemistry by Peter Sykes, ELBS.

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Reference Books :

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Advanced Organic Chemistry by Jerry March (3rd Edn.) Wiley Eastern.

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Chemistry of Natural Products, K.W. Bentley (Ed.)

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Stereochemistry of carbon compounds by E. Eliet. McGraw Hill.

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Stereo Chemistry of Organic Compounds by D. Nasipuri,

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Chemistry of natural products by P.S. Kalsi Kalyani Publishers. 1983.

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PAPER-IV: PHYSICAL CHEMISTRY

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Course Outcomes (COs)/Course Specific Outcomes (CSOs)

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Upon completion of the course the students will be able to,

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CO1: Explain the basic concepts of Thermodynamics and its applications

CO2: Understand the concepts of thermodynamics of solutions.

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CO3: To understand the principle of micellisation.

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CO4: Understand the various kinetic theories, measurements of reaction rates.

CO5: Learn experimental techniques for measuring the kinetics of fast reactions and homogenous catalyzed reactions.

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Learning Outcomes (LOs):

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Upon completion of the course the student will be able to understand

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LO1: To apply the concepts of thermodynamics to various problems in chemistry.

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LO2: To predict various reaction mechanisms.

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LO3: To apply the concept of micellization to various chemical reactions.

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Paper IV - Physical Chemistry

COURSE CONTENT:

UNIT-I

States of Matter : Transport properties of gases - Thermal conductivity, viscosity

and diffusion, Theories of liquid structure - calculation of collision numbers.

Solids : X-ray diffraction studies - Fourier synthesis - crystal structure determination - lattice types and lattice dimensions - crystal defects - linear point and edge defects - Band theory solids - Theories of specific heats of solids - semiconductors and their properties.

Unit -II :

Physical Methods for the elucidation of molecular structure - magnetic properties of molecules - theories of magnetic susceptibility - Application of magnetic susceptibility measurements to coordination compounds - spin-spin interactions - Chemical shift and its origin - experimental methods - application of NMR studies in structural - elucidation - application to structure of ethanol, acetophenone, acetamide, dimethyl formamide and styrene

- electron spin resonance - principle and experimental technique - line shapes and line widths - g-value - hyperfine interactions - applications of ESR Studies to the structure of free radical, metal complexes and biological systems.

Unit III :

Thermodynamics : Free energy entropy and enthalpy - Chemical equilibrium - thermodynamic criteria of the chemical equilibrium - effect of temperature on equilibrium constant - Vant Hoff isochore - Maxwell relations - Gibbs-Duhem equation Duheme - Margules equation - classius - clapeyron equation - Nernst heat theorem and third law of thermodynamics - determination of absolute entropy electro kinetic potential - Membrane potential.

Unit IV :

Kinetics : Theories of reaction rates - collision and transition state theories - study of fast reactions using flow and relaxation methods - Kinetic isotope effects - reactions in solution - primary and secondary kinetic salt effects - Effect of dielectric constant - elementary ideas of linear free energy relations. Hammett and Taft equations - Chain reactions - consecutive parallel and opposing reactions involving uni molecular steps only - Catalysis - homogeneous and heterogeneous - acid - base and redox catalysis.

Unit V :

Photochemistry : Laws of photochemistry - photo physical processes fluorescence - delayed fluorescence and phosphorescence - Stern - volmer equation - Inter system crossing - internal conversion - photolysis - photosensitization and

photochemical equilibrium.

Unit VI:

Electrochemistry : Theories of strong electrolytes - Debye - Onsager equation - electrochemical cells - concentration cells with and without transference - effect of complexation on redox potential Determination of activity coefficients from E.M.F. data.

PRACTICAL I: INORGANIC CHEMISTRY

Course Objectives:

CO1: To develop an insight into the preparation of inorganic complexes

CO2: To understand the process of preparation of inorganic complexes

CO3: To acquire skills in the preparation of inorganic complexes

Learning Outcomes: At the end of the course, the learners should be able to:

LO1: Prepare various inorganic complexes

LO2: Develop skill in handling apparatus, measure the quantities and carry out the reaction and analyse the inorganic mixtures

LO3: Applies the skill in preparing new metal complexes and analysis of inorganic mixtures

LO4: Understand the regulations in handling and disposal of chemicals.

COURSE CONTENT

1. Synthesis of Inorganic Metal Complexes: Synthesis of 3d transition metal complexes of tetrahedral, square planar and octahedral geometries.

(i) Preparation of TetraammineCopper

(II) sulphate monohydrate (ii) Potassium tris-oxalatoferrate

(III) trihydrate (iii) Tris-thiourea copper(I) sulphate

2. Systematic Semi micro Qualitative Analysis of Inorganic six radical mixtures In systematic Semi micro qualitative inorganic analysis, inorganic mixture contains three cations and three anions. The analysis involves identification and confirmation of cations and anions containing one less familiar cation (Tungsten, Molybdenum, Zirconium, Thorium, Titanium, Uranium, Cerium, Vanadium, Lithium, Berkelium Etc... and one interfering anion Anions: CO_3^{2-} , S^{2-} , SO_3^{2-} , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, PO_4^{3-} , CrO_4^{2-} , AsO_4^{3-} , F^- , BO_3^{3-} Cations : Ammonium (NH_4^+), 1st group: Hg, Ag, Pb, Tl, W ; 2nd group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo; 3rd group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be 4th group: Zn, Mn, Co, Ni 5th group: Ca, Ba, Sr 6th group: Mg, K, Li Note: A minimum of 4 inorganic mixtures must be analysed in this Semester

PRACTICAL II: PHYSICAL CHEMISTRY

Course Objectives:

CO1: To maintain laboratory ethics, safety and cleanliness

CO2: To Preparation and standardization of solutions

CO3: To have hands-on experience/practical knowledge in performing Physical chemistry experiments

CO4: To develop skills on handling instruments like conductometry and perform different types of acid-base titrations

CO5: To plot accurate graphs of the desired scale for the calculations of Langmuir and Freundlich isotherms

CO6: To Prepare the solution of the desired concentration and the desired volume in Cuprammonium cation.

Learning Outcomes:

At the end of the course, the learners should be able to:

LO1: To be able to develop/practical skills to solve problems in chemistry.

LO2: To extend the principle of Conductometric titration to other kind of reactions.

LO3: To learn to use the concept of phase diagram for different systems

LO4: To apply adsorption isotherms for other reactions.

COURSE CONTENT:

1. Conductometry a) Conductometric titration of strong acid (HCl) vs strong base (NaOH) b) Conductometric titration of weak acid (CH₃COOH) vs strong base (NaOH) c) Conductometric titration of mixture of acids (HCl + CH₃COOH) vs strong base (NaOH)

2. Determination of Cell constant of conductivity cell

3. Determination of Dissociation constant of weak acid by conductometric Method

4. Determination of Critical solution temperature of phenol-Water system

5. Determination of effect of electrolyte (NaCl) on the miscibility temperature of Phenol- Water system

6. Determination of composition of Cuprammonium cation using partition coefficient method

7. To verify Langmuir and Freundlich isotherm for absorption of acetic acid onto activated

PRACTICAL III: ORGANIC CHEMISTRY

Course Objectives:

CO1: To develop an insight into the preparation of organic compounds in various reactions

CO2: To understand the process of preparation of organic through various reactions

CO3: To acquire skills in the preparation of organic compounds, their separation, purification and identification

Learning Outcomes:

At the end of the course, the learners should be able to:

LO1: Prepare various organic compounds using various reactions

LO2: Develop skill in handling apparatus, measure the quantities and carryout the reaction, separate the products, purify them and analyse the products formed

LO3: Applies the skill in preparing novel organic moieties

COUSE CONTENT:

Synthesis of Organic compounds Synthesis, purification and characterization of about ten organic compounds involving one or two stages. List of some suggested compounds

1. β -Naphthyl methyl ether from β -Naphthol
2. m-dinitrobenzene from Nitrobenzene
3. Azo dye from primary amine
4. Aromatic acid from ester
5. Benzanilide from aniline
6. p-nitroaniline from Acetanilide
7. p-Bromo acetanilide from aniline
8. Phthalimide from phthalic acid
9. 1,2,3-Tribromo benzene from aniline

PAPER I - ORGANIC REACTION MECHANISMS, PERICYCLIC REACTIONS AND PHOTOCHEMISTRY

Course Objectives:

CO 1: Acquire the knowledge of reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

CO 2: Understand reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

CO 3: Apply the knowledge and understanding of new situations reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

CO 4: Develop interest in the areas of reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

Learning Outcomes:

At the end of the course, the learners should be able to:

LO 1: Explain reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 2: Interpret reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 3: Compare reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 4: Analyse reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 5: Solve reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 6: Identify reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

LO 7: apply reactions and mechanisms of Substitution, Elimination, Addition, Pericyclic and Organic Photochemistry

COURSE CONTENT

PAPER-1: ORGANIC REACTION MECHANISMS

UNIT-1:

1. Aliphatic Nucleophilic Substitution Mechanisms Nucleophilic substitution: Substitution reactions of ambident nucleophiles, neighbouring group participation of O, S, N, halogens, aryl groups, alkyl and cycloalkyl groups in nucleophilic substitution reactions. Sigma, Pi bond participation in acyclic and bicyclic systems (Non-classical carbocations) Substitution at allylic, trigonal and Vinylic carbons, hydrolysis of esters, Meyer's aldehydes, ketones, and carboxylic acids, alkylation with trialkyl boranes.

2. Aliphatic Electrophilic substitutions: SE' SE and SE' mechanisms hydrogen exchange, migration of double bonds, halogenation of aldehydes, ketones, acids, acylhalides sulphoxides and sulphones, aliphatic diazonium coupling, nitrosation at Carbon and nitrogen, diazo transfer reaction carbene and nitrene insertion, formation of sulphur yield, metallation with organometallic compounds and with metals. Decarboxylation of aliphatic acids. Haloform reaction and Haller-Baner reactions.

3. Aromatic nucleophilic substitution: A general introduction to different mechanisms of aromatic substitution SN Ar, AN and eryne Von richter rearrangement, sommlet, Hauser rearrangement Smiles rearrangement.

4. Radical substitution Mechanism: Reaction at Sp^3 carbon: Reactivity in aliphatic substrates reactivity at bridged position, reactivity at SP^2 carbon. Reactivity in aromatic substrates, neighbouring group assistance in free radical reactions, effect of reactivity in the attacking radical effect of solvent on

reactivity halogenation at an alkyl carbon and allylic carbon. hydroxylation at aromatic carbon by means of Fenton's reagent. oxidation of aldehydes to carboxylic acids, formation of cyclic ethers with $Pb(OAc)_4$ Reed reaction, sandmeyer reaction, kolla reaction and Hunsdiecker reaction.

UNIT-II:

5. Addition Elimination Mechanisms: (a) Addition to carbon multiple bonds- Addition reactions involving electrophiles, nucleophiles and free radicals, cyclic mechanisms, orientation and stereochemistry, Hydrogenation of double and triple bonds, hydroboration, Birch reduction. Michael reaction, addition of oxygen and N_2O_4 ; (b) Addition to carbon-heteroatom multiple bonds: Mannich reaction AH reductions of Carbonyl compounds acids, esters, nitriles, addition of Grignard reagents, Reformatsky reaction, Tollen's reaction, witting reaction, Prins reaction; (c) Elimination reactions: Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations-saytzeff and Hofmann elimination propolitic elimination.

6. Rearrangements: Classification and general mechanistic treatment of nucleophilic, free radical and electrophilic rearrangements, Wagner-Meerwein related reactions, Tiffman Demzanox rearrangement, α -ketone arrangement, Neber, Hofmann, Bayer-villiger, Stevens witting rearrangements.

UNIT-III:

Molecular orbital symmetry, frontier orbitals of ethylene, 1,3-Butadiene, 1, 3, 5-Hexatriene, allyl system, classification of pericyclic reactions FMO approach, Woodward - Hoffman correlation diagram method and perturbation of molecular (PMO) approach for the explanation of pericyclic reactions under thermal and photochemical conditions.

Electrocyclic Reactions: Conrotatory and disrotatory motions ($4n$) and ($4n+2$), allyl systems and secondary effects.

Cycloadditions: Antarafacial and suprafacial additions, notation of cycloadditions, ($4n$) and ($4n+2$) systems with a reater emphasis on ($2+2$) and ($4+4$)-cycloadditions, ($2+2$)-additions of ketones secondary effects of substitutes on the rates of cycloadditions and chelotropic reactions.

Sigmatropic Rearrangements: suprafacial and antarafacial shifts of H. Sigmatropic shifts involving carbon moieties, retention and inversion of configurations, (3.3) and (5.5) Sigmatropic rearrangements detailed treatment of Claiser and Cope rearrangements fluxional tautomerism, α Za-Cope rearrangements introducesters and Barton reaction.

UNIT-IV: ORGANIC PHOTOCHEMISTRY:

Photochemical energy plank Condon Principle, Jablonski diagram singlet and triplet states, dissipation of photochemical energy, photosensitization, quenching, quantum efficiency and quantum yield, experimental methods of photochemistry.

Photochemistry of carbonyl compounds n-II, II - II* transitions Norrish type I and Norrish type II cleavages, paterno- Buchi reaction. Photoreaction photochemistry of enone - Hydrogen abstraction, rearrangement of α : β - unsaturated ketones and cyclohexadienes, Photochemistry of p-Benzoquinones, photochemistry of unsaturated systems-Olefins, cis Trans-Isomerisation and dimerisation hydrogen abstractions and, addition acetylenes dimerisation, dienes - photochemistry of 1,3-butadiens ($2+2$) additions leading to cage structures photochemistry of cyclohexadienes.

Photochemistry of aromatic compounds - excited state of benzene its 1, 2 - 1,31- 4 additions, photo Fries rearrangements, photofires reactions of anilides, photosubstitution reactions of benezene derivatives.

Photochemistry of pyridinium yields, pyrolysis of nitriles esters and batton reaction.

TEXT BOOKS:

1. Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, McGraw Hill and Kogakush
2. Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
3. Pericyclic reactions by S.N. Mukherji, Macmillan.

REFERENCE BOOKS:

1. Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S.Richardson.
2. The modern structural theory in Organic Chemistry by LN. Ferguson, Prentice Hall.
3. Physical Organic Chemistry by Jack Hine, Mc Graw Hill

PAPER II- ORGANIC SPECTROSCOPY

Course Objectives:

CO 1: Acquire the knowledge of UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

CO 2: Understand UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

CO 3: Apply the knowledge and understanding of new situations UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

CO 4: Develop interest in the areas of UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

Learning Outcomes:

At the end of the course, the learners should be able to:

LO 1: Explain UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 2: Interpret UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 3: Compare UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 4: Analyse UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 5: Solve UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 6: Identify UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

LO 7: Apply UV, Infrared, NMR and Mass Spectroscopic techniques and structural elucidation of organic compounds using the data obtained

COURSE CONTENT:

PAPER-II: ORGANIC SPECTROSCOPY

UNIT-1: 100 periods

Infrared spectroscopy, ultraviolet spectroscopy, Optical rotatory dispersion and circular dichroism. 25 periods

Infrared spectroscopy: Units of frequency wave length and wave number, molecular vibrations, factors influencing vibrational frequencies, the IR spectrometer, sampling techniques, characteristic frequencies of organic molecules and interpretation of spectra.

Ultraviolet spectroscopy: Introduction, the absorption laws, measurement of the spectrum, chromophores, standard works of reference, definitions, applications of UV spectroscopy to Conjugated dienes, trienes, unsaturated carbonyl compounds and aromatic compounds.

Optical rotatory dispersion and circular dichroism: Phenomena of ORD and CD. Classification of ORD and CD Curves: Cotton effect curves and their application to Stereochemical problems; the Octant rule and its application to alicyclic ketones.

UNIT-II: 35 Periods

Nuclear Magnetic Resonance Spectroscopy (Proton and Carbon-13 NMR) and Electron spin Resonance spectroscopy (ESR).

The measurement of spectra; the chemical shift; the intensity of NMR signals and integration: factors affecting the chemical shifts; spin-spin coupling to ^{13}C ; IH-IH first order coupling: some simple II-IH splitting patterns; the magnitude of

III-IH coupling constants; improving the NMR spectrum, the many pulse experiment, new techniques in FT NMR spectroscopy, the separation of chemical shift and coupling on to different axes (2D-NMR: cosy), spin decoupling, the nuclear overhauser effect; associating the signals from directly bonded

^{13}C and IH

ESR: Derivative curves: values and hypertive splitting

UNIT-III:

20 Periods

Mass spectroscopy: Basic Principles: instrumentation; the mass spectrometer, isotope abundances, the moleculaton, metastable ions, fragmentation processes; fragmentation associated with functional groups; rearrangement and mass spectra of some Chemical classes.

UNIT-IV: 20 Periods

Structural elucidation of Organic compounds by a combined application of the spectral methods of Units I-III.

TEXTBOOKS:

1. Spectroscopic Methods in Organic Chemistry. Fourth Edition D.M. Williams and I. Fleeming, Tata - McGraw Hill, New Delhi, 1990. For all spectral methods except ORD and CD and ESR.
2. Organic Spectroscopy, Second Edition, W.Kemp, ELBS Macmillan, 1987 For ORD and CD and ESR.

BOOKS FOR REFERENCE;

1. Book 2 mentioned above.

2. Applications of absorption spectroscopy of Organic Compounds J.R Dyer, Prentice Hall of India, New Delhi, 1984.

3. Spectrometric Identification of Organic Compounds, Fourth Edition, R.M. Silverstein; GC. Vassler and T.C.Merrill, John Wiley, Singapore, 1981.

For ORD and CD "Applications of Optical Rotation and Circular Dichroism," GC. Barret, in "Elucidation of Organic structures by Physical and Chemical Methods" Part 1 (Eds.) K.W. Bentley and G.W.Kirby John Wiley, 1972, Chapter VIII (only those aspects mentioned in the syllabus).

PAPER III – ORGANIC SYNTHESIS

Course Objectives:

To make the students

CO 1: Acquire the knowledge of formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

CO 2: Understand formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

CO 3: Apply the knowledge and understanding of formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis to new situations

CO 4: Develop interest in the areas of formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

Learning Outcomes:

At the end of the course, the learners should be able to:

LO 1: Explain formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 2: Interpret formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 3: Compare formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 4: Analyse formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 5: Solve formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 6: Identify formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

LO 7: apply formation of C-C and C=C bonds, organic polymers, unactivated C-H bonds, Asymmetric Synthesis

COURSE CONTENT :

PAPER-III: ORGANIC SYNTHESIS

UNIT-1:

1. Formation of Carbon-Carbon single bonds: Alkylations via enolate-the enamine and related reactions- umploung (dipole inversion) - the aldol reaction-applications of organopalladium, organonickel and organocopper reagents applications of thiocarbonions-selenocarbonions and sulphur yields, synthetic applications of carbines and carbenoids.

UNIT-II:

2. Formation of carbon-carbon double bonds: Elimination reactions Pyrolytic, syneliminations-sulphoxide- sulphonate rearrangement-the witting reaction-alkenes form arylsulphonyl-hydrazones-claisen rearrangement of allyl vinyl ethers.

3. Methods of polymerisation (a) Addition polymerisation (b) Condensation polymerisation and (c) Radical polymerisations (two examples of each method).

4. Reactions of unactivated carbon-hydrogen bonds: The Hoffmann Lieffier-Freytag reaction-the Barton reaction-photolysis of organic hypothalites.

UNIT-III:

5. Synthetic applications of organobornaes and organosillanes.

Organoboranes: Preparation of Organoboranes viz hydroboration with BH₃-THF, dicylonexyl borane, disiamyl borane, theryl borane, 9-BBN and disopincomphyl borne, functional group transformations of Organobranes- Oxidation, protonolysis and rearrangements. Formation, of carbon of carbon-bonds viz Organoboranes carbonylation, the cyanobrate process and reaction of alkenyl boranes and trialkaliknyl borates.

Organolilanes: Synthetic applications of trimethylsilyl chloride dimethyl-t-butylsilyl chloride, trimethylsilylcyanide, trimethylsilyl chyanide,

trimethylsilyl iodide and trimethylsilyl triflate, synthetic applications of silyl carbanion and B-silyl carbonium ions.

6. Phase transfer catalysis-Principle and applications.

UNIT-IV:

7. Oxidation: Oxidations of hydrocarbons, alkenes, alcohols aldehydes and ketones oxidative coupling reactions. Use of $Pb(OAc)_4$, NBS, CrO_3 , SeO_2 , MnO_2 , DCC-alkoxyphosphonium ylides, $KMnO_4$, OsO_4 , peracids and $TI(III)$ Nitrate.

8. Reaction: Catalytic hydrogenation (homogeneous and heterogeneous), reduction by dissolving metals, reduction by hydride transfer reagents, reduction with hydrazine and dimide, selectivity in reduction of nitroso and nitro compounds, reductive cleavage.

9. Design of Organic Synthesis: Retrosynthesis the disconnection approach-basic principles convergent and linear Synthesis.

Note: The course consists of 95 lectures of 50 minutes duration.

TEXT BOOKS:

1. Some Modern Methods of Organic Synthesis W.Carruthers, Third Edition, Cambridge University Press, Cambridge, 1988.

2. Organic Synthesis: The disconnection approach, S.Warrent John Wiley & sons, New York, 1984.

BOOKS FOR REFERENCE:

1. Modern Synthetic Reactions, Herbert O. House, Second Edition, W.A. Benjamin Inc. Menlo Park, California, 1972.

2. Organic Synthesis viz Boranes, Herbert C. Brown Gray, W. Kramer Alan B. Levy and M. Mark Midland John Wiley & Sons, New York, 1975.

PAPER IV – NATURAL PRODUCTS AND BIOPOLYMERS

Course Objectives:

CO 1: Acquire the knowledge of isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

CO 2: Understand isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments and Biopolymers.

CO 3: Apply the knowledge and understanding of new situations isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

CO 4: Develop interest in the areas of isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

Learning Outcomes:

At the end of the course, the learners should be able to:

LO 1: Explain isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 2: Interpret isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 3: Compare isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 4: Analyse isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 5: Solve isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 6: Identify isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

LO 7: Apply isolation, structural elucidation, stereochemistry, synthesis and biological properties of selected antibiotics, terpenes, alkaloids, flavonoids and natural pigments

COURSE CONTENT

PAPER IV: NATURAL PRODUCTS AND BIOPOLYMERS

Study of isolation, structure, stereochemistry, synthesis, biogenesis and biological properties of the following classes of natural products from plant, animal, and microbial sources and biopolymers.

UNIT-1: ACETOGENINS AND SHIKIMATES:

A. Microbial metabolites: Pencillin G cephalosporin-C and streptomycin.

B. Prostaglandin 15 RPGA., podophyllotoxin, etoposide and retene.

UNIT-II: TERPENES AND STEROIDS:

Forskolin, taxol, azadirachtin, cholesterol, progesterone and 6-amyrin.

UNIT-III: ALKALOIDS

Morphine, reserpine, strychnine, vincristine, colchicine and camptothecin.

UNIT-IV: BIOPOLYMERS:

A. Peptides: α -Aminoacids, their general properties and synthesis. Synthesis of peptides by Merrifield solid phase synthesis. Chemistry of oxytocin and dolastatin-10.

B. Nucleic acids: Basic concepts of the structures of RNA and DNA and their hydrolysis products nucleotides, nucleosides and heterocyclic bases.

Note: The scope of the topics of this unit, i.e., Unit IV is limited to the material contained in the books by Finar and Heathcock mentioned below.

REFERENCE MATERIAL:

1. Organic Chemistry, Volume 2, Stereochemistry and chemistry of natural products, I.L. Finar, 5th Edition, ELBS, 1975 (overall and for Unit IA, cholesterol, progesterone, morphine and Unit IV)

2. Chemical Aspects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996.

3. Chemistry of Natural Products: A Unified Approach, N.R. Krishnaswamy, University Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999.

(Overall and for certain aspects of rotenone, azadirachtin, p-amyrin, morphine, reserpine, strychnine, and colchicine).

4. Introduction to Organic Chemistry, A. Streitweiser, CH. Heathcock and E.M. Kosover, IV Edition, Macmillan, 1992. (For Merrifield synthesis of peptides, and also for other aspects of Unit IV).

5. Primary literature, For Unit IB. forskolin, taxol, azadirachtin, Unit III (minus morphine) and dolastatin- 10, Details and copy of the relevant material are available with the Department of Organic Chemistry, FD &W, Andhra University, Visakhapatnam.

Details of primary literature:

Prostaglandin 15R PGA, Introduction: "Biochemistry" D.E. Metzler, AP, 1977, pp. 705-707.

Nomenclature

Structure:TL, 1969, 5185.

Podophyllotoxin and etoposide: 1. Chem. Revs. 55, 957, 1955; 2. Phytochemistry, 54, 115-120, 2000.

Rotenone: Rodd, 2nd Ed. IVE, p. 257-58, 1977.

Forskolin TL, 1977,19,1669; UC, 1977,15B, 880 (structure) Tetrahedron, 48, 963, 1992 (synthesis).

Taxol JACS, 1971, 93, 2325 (structure), Tetrahedron, 1996, 45, 14081-102, 14103-146, 14147-176 (synthesis).

Azadirachtin: JCS Perkin 1,1972, 2445; JACS, 1975, 97,1975; JCS Chem Comn. 1985, 968; ibid, 1986, 46; Compendium of Indian Medicinal plants, Vol. 4,1985-89, R.R Rastogi and B.N. Mehrotra, CDRI & Publications & Information Directorate, New Deth', pp. 87-35.

Reserpine: Alkaloids, Manske, Vol. VIII, 1965, pp.287-335.

Strychnine: Alkaloids, Manske, Vol. VIII, 1965, pp. 592-672.

Vincristine:JACS, 1964, 86, 1441, Alkaloids, Manske, Vol. VIII, 1965, pp. 269-285.

Colchicine: Alkaloids, Manske, Vol. XXIII, 1984, pp. 1-62; Vol. XI, 1968, pp. 407-58, Vol. 1! 1952; pp. 261-330.

Camptothecin: JACS, 1966, 88, 3888, Alkaloids,

Manske Vol. XXI, 1983, pp. 101-39.

Dolastatin-10: JACS, 1987. 109, 6883 (structure), *ibid*, 1989, 111, 5463; JCS Perkin I, 1996, 859 (synthesis).

M.Sc. Organic Chemistry Final Year Praticum:

Practical-I:

Multi stage organic synthesis

Multistage Organic synthesis involving three or four stages Paracetamol, 6-Methyluracil, Methyl orange, p-Aminobenzoic acid, Acridone and 2-Iodobenzoic acid

Practical-II:

Chromatography and Viva-Voce

1. Thin layer chromatography: Determination of purity of a given sample and identification of unknown organic compounds by comparing the R_f values of known standards.
2. Separation by column chromatography
3. Viva-Voice

