POLYMERS AND BIO-POLYMERS

I - M.Sc(Chemistry) / I - Semester

Choice Based Credit System(CBCS)

- By

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ORGANIC CHEMISTRY

I - M.Sc(Chemistry) / I - Semester

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NATURAL PRODUCTS

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I - M.Sc(Chemistry) / I - Semester

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QUANTITATIVE DATA, ANALYTICAL, ELECTRO CHEMICAL AND SEPARATION TECHNIQUES

I - M.Sc(Chemistry) / II - Semester

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I - M.Sc(Chemistry)

PAPER – V: Quantitative Data, Analytical, Electro Chemical and Separation Techniques

Unit 1: STATISTICAL TREATMENT OF DATA

Definition of error and uncertainity; Types of errors; Distribution of random errors; Precision and Accuracy; Standard deviation, Relative standard deviation; Confidential limit; Statistical treatment of data – F test, T test and Q test; Method of least squares; Significant figures, uncertainity evaluation, use of spread sheets in analytical chemistry and reporting data.

UNIT-2: SOLVENT EXTRACTION AND ION EXCHANGE

A. Solvent Extraction - General introduction -factors favouring solvent extraction. Quantitative treatment of solvent extraction - Extraction reagents. Applications:

(1). Determination of ferric ion as chloride.

(2). Determination of Molybdenum by thiocyanate method.

(3). Determination of silver by extraction as its ion association complex with 1,10-phenanthroline and pyrogallol red.

B. Ion exchange chromatography

General introduction. Action of ion exchange resins. Ion exchange chromatography. Ion exchange equilibria. Ion exchange capacity and its determination. Applications :

(1). Determination of the total cation concentration in water.

(2). Separation of the fluoride with the aid of cation exchanger.

(3). Separation of Cl^- and Br^- using anion exchanger

UNIT-3: CHROMATOGRAPHIC METHODS

Introduction, Definitions, Classifications in Chromatography.

A. Adsorption column chromatography: Types of columns, Experimental requirements, Development of column, Factors affecting column efficiency, Applications and experiments , Separation of (1) Methylene Blue and malachite green ; (2) Metal ions and ; (3) Chlorophylls and carotenoids.

B. Paper Chromatography : Theory, Principles and techniques. Development of chromatogram (Ascending and Descending), Two dimensional and Multi dimensional paper Chromatography, Measurement of R_f values, Applications and experiments , Separation of : (1) Amino acids (2) Cations and (3) Complexes.

C. Thin layer Chromatography : Preparation and development of plates. Advantages of TLC, Applications and Experiments – Separation of : (1) Ink Pigments (2) Dyes and (3) Amino acids. High Performance , Thin Layer Chromatography (HPTLC), Features and Applications.

D. Gas Chromatography: Principles and theory, Instrumentation – Columns and detectors, Types of chromatograms. Analysis of elution peaks, Applications in qualitative and quantitative analysis.

E. High Performance Liquid Chromatography: Introduction, characteristic features of HPLC, comparison of super critical fluid, fluid chromatography with HPLC and GLC; Principle of HPLC, Instrumentation; Components, Types of detectors. Applications HPLC on the separation of inorganic, Organic and Pharmaceutical compounds.

UNIT-4. ELECTROANALYTICAL TECHNIQUES

A. Polarography: Principle, Advantages of Dropping Mercury Electrode, diffusion current, migration current, half wave potential, ilkovic equation, reversible and irreversible polarographic processes**,** Quantitative polarographic analysis

B. Amperometric titrations: Principle – Determination of lead using oxalic acid titration curves, Determination of nickel using dimethylglyoxime

C. Cyclic Voltammetry: Principle, Randles-Sevcik equation (only statement and no derivation), Criteria for the cyclic volatmograms for reversible, irreversible, quasi-reversible waves, Identification of intermediates in organic reactions using cyclic voltammetry.

UNIT – 5 : ANALYTICAL SPECTROSCOPY

(a) Spectrophotometry, Beer -Lambert law, Method of analysis and applications - examples

(b) Spectrofluorimetry -Basics of the Method and Applications -Examples

(c) Flame photometry and Flame Emission Spectroscopy, Principles, Types of flames and types of burners. Types of instruments used, flame photometer and experimental technique, Interferences**:** chemical reactions in flames. Dissociation equilibria, ionization in flames, use of organic solvents. Applications, advantages & disadvantages, limitations. –Example of Water analysis

(d) Atomic Absorption Spectroscopy, Introduction, Principles, relation between flame emission and atomic absorption. Instrumentation, Interferences, background correction, Applications.

ORGANIC SPECTROSCOPY, DRUG DESIGN,CONFORMATIONAL ANALYSIS, & HETEROCYCLIC COMPOUNDS

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CONTENTS

I - M.Sc(Chemistry)

PAPER – VI ORGANIC SPECTROSCOPY, DRUG DESIGN,CONFORMATIONAL ANALYSIS, & HETEROCYCLIC COMPOUNDS

UNIT - 1: ^{13}C - NMR SPECTROSCOPY

^{13}CNMR – Spectroscopy – CW and PFT techniques. Types of CMR spectra–undecoupled proton decoupled. Off–resonance decoupled (SFORD): ^{13}C–chemical shifts, factors affecting the chemical shifts Homonuclear (^{13}C – ^{13}CJ), and heteronuclear (^{13}C–^{1}H, ^{13}C–^{2}HJ) couplings. Applications of ^{13}C–NMR Spectroscopy in confirmation of structure and stereochemistry of organic molecules and in determining the reaction mechanism and dynamic processes of organic reactions – examples. Multipulse techniques : HOMO and HETERO – 2D–J– resolved spectra. Explanation of the principle, application to structure elucidation of simple organic molecules.

UNIT - 2:APPLICATIONS OF MASS SPECTROMETRY AND OPTICAL ROTATORY DISPERSION

Mass Spectroscopy : Basic principles-instrumentation-magnetic sector instruments. Ion production electron impact ionization –chemical ionization. Mass spectra-Molecular ion –types of ions in mass spectra. Effect of isotopes on mass spectra. Mc Lafferty rearrangement. Ortho effect – Meta stable ions. Nitrogen rule. General fragmentation modes. Mass spectral fragmentation of some classes of organic compounds.

Optical Rotatory Despersion : Optical rotation. Circular birefringence, circular dichroism and cotton effect. Plain curves and anomalous curves and their applications. Axial halo keto rule and octant rule. Application to the study of configuration and conformations of organic molecules.

UNIT-3: DRUG DESIGN

Introduction to drug discovery. Drug discovery without lead – serendipity – Pencillins as example. Lead discovery – random and non–random screening of natural products – medical folklore, synthetic banks. Existing drugs from natural ligand or modular combinatorial synthesis. Computer aided designing (introductory treatment only). Drug metabolism studies – Phase I and Phase II metabolism. Clinical observations. Phase – I, Phase – II, Phase – III and Phase – IV trials (introductory treatment only).

Principle of drug design against agonist, antagonist drugs.

UNIT-4: CONFORMATIONALANALYSIS

Introduction to conformational isomerism and the concept of dynamic stereochemistry. Study of conformations in ethane and 1,2-disubstituted ethane derivatives like butane, dihalobutanes, halohydrin, ethylene glycol, butane-2,3-iol, amino alcohols and 1,1,2,2-tetrahaobutanes. Klyne-Prelog terminology for conformers and torsion angles. Conformations of unsaturated acyclic compounds (1-butene, propionaldehyde and butanone). Conformational diastereoisomers and conformational enantiomers. Factors affecting the conformational stability and conformational equilibrium-attractive and repulsive interactions. Use of physical and spectral methods in conformational analysis. Conformation effects on the stability and reactivity of acyclic diastereoisomers-steric and stereo electronic factors-examples. Conformation and reactivity: The Winstein-Holness equation and the Curtin-Hammett principle. Conformations of cyclohexanes, mono and di substituted cyclohexanes. Stereochemistry of decalins. Factors governing the reactivity of axial and equatorial substituents in cyclohexanes. Stereochemistry of addition to the carbonyl group of rigid cyclohexane ring.

UNIT -5: HETE ROCYCLIC COMPOUNDS

Importance of heterocyclic compounds as drugs. Nomenclature of heterocyclic systems based on ring size, number and nature of hetero atoms. Synthesis and reactivity of Pyridine, Quinoline, Isoquinoline, Indole, Benzofuran, Benzothiophene, Pyrazole, Thiazole, Oxazole and Pyrimidine.

ORGANIC PHOTOCHEMISTRY,
PERICYCLIC REACTIONS & ORGANIC SYNTHESIS

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I - M.Sc(Organic)

PAPER – VII: ORGANIC PHOTOCHEMISTRY, PERICYCLIC REACTIONS & ORGANIC SYNTHESIS

UNIT - I: Organic Photochemistry

Organic Photochemistry: Molecular orbitals, carbonyl chromophore–triplet states, Jablonski diagram, inter–system crossing. Energy transfer. Energies properties and reaction of singlet and triplet states of and transitions.

Photochemical Reactions: Photoreduction, Paterno-Buchi reaction, Norrisch type I cleavage and Norrisch type II cleavage, Photo Fries rearrangement. Photochemistry of unsaturated systems – Olefins, cis-trans isomerisation and dimerasation. Photochemistry of 1,3-butadienes.

UNIT - II: Pericyclic Reactions

Characteristics-Types of pericyclic reactions-Electrocyclic, cycloaddition-cycloreversion and sigmatropic reactions-examples. 4n and 4n+2 electron type-stereospecificity. Therories involved in understanding pericyclic reactions-

(a) Frontier Molecular Orbital theory concept-Woodward-Hoffmann selection rules for electrocyclic, cycloaddition-cycloreversion and sigmatropic reactions based on FMO approach.

(b) Conservation of Molecular Orbital theory concept-Framing of Woodward-Hoffmann selection rules for electrocyclic, cycloaddition and cycloreversions based on conservation of Molecular Orbital approach.

(c) Aromatic Transition state theory-concept-Woodward-Hoffmann selection rules for electrocyclic reactions, cycloaddition-cycloreversions and sigmatropic reactions based on ATS aromatic transition state (Huckel-Mobius) approach.

UNIT-III: Synthetic Strategies and Protecting Groups

Introduction to organic synthesis. Disconnection approach – examples – Terminology – Definition of target molecule, functional group intercoversion (FGI), disconnection product, disconnection, synthons, reagents and retrosynthesis. Linear and convergent synthesis. Importance of order of events in organic synthesis – examples. Synthesis of Benzocaine, paracetamol, (+) – disparlure. Principles of Protection of alcohols, carboxylic acids, amines and carbonyl groups

UNIT IV: Reagents of Synthetic Importance (Oxidations and Reductions)

(a) Oxidations: (i) Alcohols to carbonyls : Cr(VI) oxidants, Swern oxidation, Silver Carbonate. (ii) Prevost and Woodward oxidation. (iii) Oxidations of allylic and benzylic C-H bonds: DDQ and SeO_2.

(b) Reductions: (i) Catalytic hydrogenation. (ii) Homogeneous hydrogenation–Use of Wilkinsons catalyst. (iii) Dissolving metal reductions including Birch reduction. (iv) Nucleophilic metal hydrides : $LiAlH_4$, $NaBH_4$. Electrophilic metal hydrides: BH_3, AlH_3. (v) Hydrogenolysis-use of tri-n-butyltin hydride.

(c) Organometallic Reagents: Preparationa and application of the following in organic synthesis: (a) Grignard reagnts, Organo Lithium and Organo copper reagents.

UNIT -V: Asymmetric Synthesis

Introduction and terminology : Topocity in molecules Homotopic, stereoheterotopic (enantiotopic and diastereotopic) groups and faces – symmetry, substitution and addition criteria. Prochirality nomenclature : Pro–R Pro–S, Re and Si. Methodology or asymmetric synthesis-1.

1. Substrate controlled asymmetric synthesis : Nucleophilic addition to chiral carbonyl compounds. 1,2–asymmetric induction, Cram's rule and Felkin–Anh model.
2. Chiral auxiliary controlled asymmetric synthesis : Use of chiral auxiliaries in Diels–Alder.
3. Chiral reagent controlled asymmetric synthesis : Asymmetric reduction using BINAL–H. Asymmetric hydroboration using IPC_2 BHand $IPCBH_2$.
4. Chiral catalyst controlled asymmetric synthesis : Sharpless and Jacobsen epoxidations.
5. Asymmetric aldol reaction, Diastereoselective aldol reaction and its explatnation by Zimmerman–Traxel model.

ADVANCED NATURAL PRODUCTS

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Unit-III

Unit-IV

I - M.Sc(Chemistry)

PAPER – VIII ADVANCED NATURAL PRODUCTS

UNIT- I: CARBOHYDRATES AND PROTEINS

Carbohydrates: Occurrence, importance and synthesis of monosaccharides containing functional groups such as amino, halo and sulphur. Structure elucidation and synthesis of sucrose. Conformational structures of D(+)ribose, 2-deoxy D-ribose, sucrose, lactose, maltose and cellobiose. Structural features of starch, cellulose and chitin (structure elucidation not expected).

Proteins: Acid and enzymatic hydrolysis of proteins. Determination of amino acid sequence in polypeptides by end group analysis. Chemical synthesis of di and tri peptides.

UNIT-II:TERPENOIDS

Classification – isoprene and special isoprene rules. Occurrence, isolation, structure elucidation, stereochemistry and total synthesis of (i) santonin (ii) abeitic acid and (iii) β–carotene. Biosynthesis of mono and diterpenoids.

UNIT- III: ALKOLOIDS

Definition, medicinal importance occurrence and classification of alkaloids. General methods used for structural determination of alkaloids. Isolation, structural elucidation, stereochemistry and total synthesis of (i) Quinine (ii) Morphine (iii) Reserpine. Biosynthesis of morphine.

UNIT-IV: STERIODS, HARMONES AND PROSTAGLANDINS

Occurrence, isolation, structure determination, stereo chemistry and total synthesis of (i) cholesterol (ii) androsterone (iii) testosterone (iv) estrone and (v) progesterone. Biosynthesis of cholesterol.

Occurrence, classification and physiological activity of prostaglandins. Structure determination and synthesis of PGE_1 and PGE_2.

UNIT-V: NUCLEIC ACIDS AND ENZYMES

Nucleic Acids: Primary, secondary and tertiary structure of DNA, Types of RNA - mRNA, tRNA and rRNA. Replication, transcription and translation. Genetic code. Protein biosynthesis.

Enzymes: Definition, Classification based on mode of action. Mechanism of enzyme catalysis. Lock and Key model and Induced–Fit model. Factors affecting enzyme catalysis. Enzyme inhibition–reversible and irreversible inhibition. Enzymes in organic synthesis. Immobilized enzymes.

Recommended Books

1. Comprehensive Organic Chemistry by D.R. Barton and W.D. Ollis.
2. Standard methods in plant analysis by Reach and Tracey
3. Natural production by Kalsi.
4. Text book of Organic Chemistry Vol II by I. L. Finar.
5. An introduction to the chemistry of terpenoids and Steroids by William templetion.
6. Systematic identification of flavonoid compounds by Mabry & Markhan.