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UNIVERSITY OF MUMBAI



Syllabus for Semester III and IV
Program: M.Sc. (PSCHO)
Course: Organic Chemistry

Credit based semester and grading system with
effect from the academic year 2013-2014

UNIVERSITY OF MUMBAI

M.Sc. ORGANIC CHEMISTRY

Semester III and IV

Credit Based Semester and Grading System

To be implemented from the Academic year 2013-2014

SEMESTER III

Course Code	Unit	Topics	Credits	L/Week
PSCHO301	I	Organic reaction mechanisms	4	1
	II	Pericyclic reactions		1
	III	Stereochemistry-I		1
	IV	Photochemistry		1
PSCHO302	I	Name reactions with mechanism and applications	4	1
	II	Protection- deprotection, umpolung and electro-organic chemistry		1
	III	Enamines and ylides		1
	IV	Metals /Nonmetals in organic synthesis		1
PSCHO303	I	Heterocyclic Compounds-I	4	1
	II	Natural products – I		1
	III	Natural products – II		1
	IV	Advanced spectroscopic techniques-I		1
PSCHO304	I	Drug discovery, design & development	4	1
	II	Biomolecules – I		1
	III	Biomolecules – II		1
	IV	Biogenesis and biosynthesis of natural products		1
PSCHO3P1	Practicals		8	16

PSCHO3P2 PSCHO3P3 PSCHO3P4			
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SEMESTER IV

Course Code	Unit	Topics	Credits	L / Week
PSCHO401	I	Physical organic chemistry	4	1
	II	Supramolecular chemistry		1
	III	Stereochemistry – II		1
	IV	Asymmetric synthesis		1
PSCHO402	I	Radicals in organic synthesis	4	1
	II	Designing organic synthesis		1
	III	Newer methods in organic synthesis		1
	IV	Transition and rare earth metals in organic synthesis		1
PSCHO403	I	Heterocyclic compounds – II	4	1
	II	Natural products – III		1
	III	Natural products – IV		1
	IV	Advanced spectroscopic techniques - II		1
PSCHO404	I	Drug design, development and synthesis	4	1
	II	Biomolecules – III		1
	III	Biomolecules – IV		1
	IV	Green chemistry		1
PSCHO4P1 PSCHO4P2 PSCHO4P3 PSCHO4P4	Practicals		8	16

M. Sc. Organic Chemistry

Semester III

Course Code PSCHO301

Theoretical organic chemistry-I

Unit 1: Organic reaction mechanisms [15L]

1.1 Organic reactive intermediates, methods of generation, structure, stability and important reactions involving carbocations, nitrenes, carbenes, arynes and ketenes. [5L]

1.2 Neighbouring group participation: Mechanism and effects of anchimeric assistance, NGP by unshared/ lone pair electrons, π -electrons, aromatic rings, σ -bonds with special reference to bornyl and norbornyl systems (formation of non-classical carbocation) [3L]

1.3 Role of FMOs in organic reactivity: Reactions involving hard and soft electrophiles and nucleophiles, ambident nucleophiles, ambident electrophiles, the α effect. [2L]

1.4 Pericyclic reactions: Classification of pericyclic reactions; thermal and photochemical reactions. Three approaches: Conservation of orbital symmetry - Correlation diagram, Frontier molecular orbital approach [FMO] and Aromatic transition state approach [Huckel and Mobius]. [5L]

Unit 2: Pericyclic reactions [15L]

2.1 Cycloaddition reactions: $4n\pi$ and $(4n+2)\pi$ electron systems. Diels-Alder reactions, 1, 3-Dipolar cycloaddition and cheletropic reactions, ene reaction, retro-Diels-Alder reaction, regioselectivity, periselectivity, site selectivity and effect of substituents in Diels-Alder reactions. [7L]

2.2 Electrocyclic reactions: Conrotatory and disrotatory motions, $4n\pi$ and $(4n+2)\pi$ electron systems. [3L]

2.3 Sigmatropic rearrangements: H-shifts and C-shifts, supra and antarafacial migrations, retention and inversion of configurations. Cope (including oxy-Cope and aza-Cope) and Claisen rearrangements. Formation of Vitamin D from 7-dehydrocholesterol, synthesis of citral using pericyclic reaction. [5L]

Unit 3: Stereochemistry-I [15L]

3.1 Classification of point groups based on symmetry elements with examples (non-mathematical treatment). [2L]

3.2 Conformational analysis of medium rings: Eight and ten membered rings and their unusual properties, I-strain, transannular reactions. [2L]

3.3 Stereochemistry of fused ring and bridged ring compounds: decalins, hydrindanes, steroids, and Bredt's rule. [4L]

3.4 Dynamic stereochemistry: Selection of substrate, Curtin-Hammett principle, Effect of conformation on reactivity of cyclohexane derivatives in the following reactions (including mechanism): electrophilic addition, nucleophilic substitution, elimination, molecular rearrangements, reduction of cyclohexanones and oxidation of cyclohexanols. [7L]

Unit 4: Photochemistry [15L]

4.1 Principles of photochemistry: quantum yield, electronic states and transitions, selection rules, modes of dissipation of energy (Jablonski diagram), electronic energy transfer: photosensitization and quenching process. [3L]

- 4.2 Photochemistry of carbonyl compounds: $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions, Norrish-I and Norrish-II cleavages, Paterno-Buchi reaction. Photoreduction, calculation of quantum yield, photochemistry of enones, photochemical rearrangements of α , β -unsaturated ketones and cyclohexadienones. Photo Fries rearrangement, Barton reaction. [8L]
- 4.3 Photochemistry of olefins: cis-trans isomerizations, dimerizations, hydrogen abstraction, addition and Di- π -methane rearrangement including aza-di- π -methane. [2L]
- 4.4 Photochemistry of arenes: 1, 2-, 1, 3- and 1, 4- additions. [1L]
- 4.5 Singlet oxygen and photooxygenation reactions. [1L]

Course Code-PSCHO302
Synthetic organic chemistry-I

Unit 1: Name reactions with mechanism and application [15L]

- 1.1 Mukaiyama esterification, Mitsunobu reaction, Baylis Hillman reaction, Suzuki coupling, Wacker process, Heck reaction, Sonogashira reaction. [7L]
- 1.2 Multicomponent reactions: Strecker synthesis, Hantzsch pyridine synthesis, Biginelli synthesis, Multicomponent reactions using alkyl isocyanides: Passerini and Ugi-4-component synthesis. [6L]
- 1.3 Domino/cascade reactions: Introduction with one example. [2L]

Unit 2: Protection-deprotection, umpolung and electro-organic chemistry [15L]

- 2.1 Protection and deprotection of the following functional groups: hydroxyl, carbonyl, amino and carboxyl with applications. [5L]
- 2.2 Concept of umpolung, generation of acyl anion equivalent using 1,3- dithianes, methyl thiomethyl sulfoxides, cyanide ions, cyanohydrin ethers, nitro compounds and vinylated ethers. [5L]
- 2.3 Electro-organic chemistry: Introduction, electrode potential, cell parameters, electrolyte, working electrode, choice of solvents, supporting electrolytes. Cathodic reductions of alkyl halides, aldehydes, ketones, nitro compounds, olefins, arenes; electro-dimerizations. Anodic oxidation: Kolbe type reactions, oxidation of alkylbenzenes. [5L]

Unit 3: Enamines and ylides [15L]

- 3.1 Methods of preparation of enamines: condensation of secondary amine and aldehyde or ketone, reaction between alkynes and secondary amines. Comparison of reactivity of enamines and enolates. Synthetic reactions of enamines including asymmetric reactions of chiral enamines derived from chiral secondary amines. [3L]
- 3.2 Phosphorus, sulfur and nitrogen ylides: Preparation, structure and comparison of reactivity. Reactions of phosphorus, sulfur and nitrogen ylides with carbonyl compounds, including mechanism and stereochemistry. Wittig reaction, Wittig-Horner reaction. [6L]
- 3.3 α C-H activation by nitro, sulfoxide, sulfone and phosphonate groups: generation of carbanions by strong bases (LDA/n-butyl lithium) and applications in C-C bond formation. Bamford-Stevens Reaction, Julia olefination and its modification, Bestmann-Ohira Reagent, Barton-Kellogg olefination, Steven's rearrangement. [6L]

Unit 4: Metals / Nonmetals in organic synthesis [15 L]

4.1 Mercury in organic synthesis: oxymercuration and demercuration of alkenes, mechanism and regiochemistry, solvomercuration, mercuration of aromatics and transformation of aryl-mercurials to aryl halides. [2L]

4.2 Organoboron compounds: applications of organo-boranes, generation of diboranes, hydroboration of alkenes and alkynes: mechanism, regiochemistry, stereochemistry, asymmetric hydroboration using chiral boron reagents and functional group reduction by diborane. [3L]

4.3 Organosilicons: Important features of silicon governing the reactivity of C-Si compounds: preparation and important bond forming reactions of alkyl silanes, alkenyl silanes, aryl silanes and allyl silanes. β -silyl cations as intermediates. [3L]

4.4 Silyl enol ethers as enolate precursors, iodotrimethylsilane in organic synthesis. [2L]

4.5 Organotin compounds: preparation of alkenyl and allyl tin compounds and their applications in C-C bond formation. [3L]

4.6 Selenium in organic synthesis: Preparation of selenols/selenoxide, selenoxide elimination to create unsaturation, selenoxide and seleno acetals as α - C-H activating groups. [2L]

Course code - PSCHO303 Natural products and spectroscopy-I

Unit 1: Heterocyclic compounds-I [15L]

1.1 Heterocyclic compounds: Introduction, classification, common, systematic (Hantzsch-Widman) and replacement nomenclature of monocyclic (3-6 membered) and bicyclic (5-6 Membered) fused heterocycles (up to three hetero atoms). [5L]

1.2 Small ring heterocycles (3-4 membered): Introduction, nucleophilic ring opening reactions of oxiranes, aziridines, oxetanes and azetidines. [3L]

1.3 Reactivity and important methods of synthesis and general reactions of the following heterocycles: pyrazoles, imidazoles, oxazoles, isoxazoles, thiazoles, benzimidazoles, benzoxazoles, benzothiazoles. [7L]

Unit 2: Natural products-I [15L]

2.1 Carbohydrates: Introduction to naturally occurring sugars: Deoxysugars, aminosugars, branched sugars. Structure elucidation of lactose, D-glucosamine and mesoinositol (synthesis not expected). Structural features and applications of inositol, starch, cellulose, chitin and heparin. [5L]

2.2 Natural pigments: General structural features, occurrence, biological importance and applications of: carotenoids, anthocyanins, quinones, flavones, pterins and porphyrins (chlorophyll). Structure elucidation of β -carotene. Synthesis of ubiquinone from 3,4,5-trimethoxyacetophenone. [5L]

2.3 Insect pheromones: General structural features and importance. Synthesis of bombykol from acetylene, disparlure from 6-methylhept-1-ene, grandisol from 2-methyl-1,3-butadiene. [3L]

2.4 Alkaloids: Occurrence and physiological importance of morphine, coniine and papaverine. Structure elucidation of papaverine. [2L]

Unit 3: Natural products- II [15L]

3.1 Multi-step synthesis of natural products: Synthesis of the following natural products with special reference to reagents used, stereochemistry and functional group transformations:

- Woodward synthesis of Reserpine from benzoquinone
- Corey synthesis of Longifoline from resorcinol
- Gilbert-Stork synthesis of Griseofulvin from phloroglucinol
- E. Wenkert's synthesis of β -vetivone from acetone
- A.V.Ramarao synthesis of 4-demethoxydaunomycin from ethyl acetoacetate. [9L]

3.2 Prostaglandins: Classification, general structure and biological importance. Structure elucidation of PGE₁ and PGF_{1 α} (synthesis not expected). [3L]

3.3 Insect growth regulators: General idea, structures of JH₂ and JH₃. [1L]

3.4 Plant growth regulators: Structural features and applications of arylacetic acids, gibberelic acids and triacontanol. Synthesis of triacontanol (synthesis of stearyl magnesium bromide and 12-bromo-1-tetrahydropyranyloxydodecane expected). [2L]

Unit 4: Advanced spectroscopic techniques-I [15L]

4.1 IR spectroscopy: Application in structure elucidation. Principle and applications of FT-IR. [2L]

4.2 NMR spectroscopy: Application in structure elucidation. Relaxation phenomenon and relaxation time. First order, second order and higher order spectra. Methods of simplification of complex spectra. Double resonance, NOE, NOE difference spectroscopy and chemical shift reagents.

Spin system notations, AB, AX, AB₂-AX₂, AMX and A₂B₂-A₂X₂ spin systems with suitable examples. Coupling in aromatic and heteroaromatic systems, long range coupling. Spectra of diastereotopic systems. FT-NMR spectroscopy: Pulse sequences, pulse widths, spins and magnetization vectors. [7L]

4.3 ¹⁹F- NMR and ³¹P- NMR spectroscopy: Principles and applications. [2L]

4.4 Problems based on combined use of IR and PMR spectroscopic techniques. [4L]

Course code – PSCHO304 Medicinal and bioorganic chemistry

Unit 1: Drug discovery, design & development [15L]

1.1 Introduction, Important terms used in medicinal chemistry: receptor, therapeutic index, bioavailability, drug assay and drug potency. General idea of factors affecting bioactivity: Resonance, inductive effect, bioisosterism, spatial considerations. Basic pharmacokinetics: drug absorption, distribution, metabolism (biotransformation) and elimination. Physical and chemical parameters like solubility, lipophilicity, ionization, pH, redox potential, H-bonding, partition coefficient and isomerism in drug distribution and drug-receptor binding. [7L]

1.2 Procedures in drug design: Drug discovery without a lead: Penicillin, Librium. Lead discovery: random screening, non-random (or targeted) screening. Lead modification: Identification of the pharmacophore, Functional group modification, Structure-activity relationship, Structure modification to increase potency and therapeutic index: Homologation, chain branching, ring-chain transformation, bioisosterism, combinatorial synthesis (basic idea). [8L]

Unit 2: Biomolecules-I [15L]

2.1 Amino acids, peptides and proteins: Chemical and enzymatic hydrolysis of proteins to peptides, amino acid sequencing. Secondary structure of proteins, forces responsible for holding of secondary structures, α - helix, β -sheets, super secondary structure. Tertiary structure of protein: folding and domain structure. Quaternary structure. [4L]

2.2 Nucleic acids: Structure and function of physiologically important nucleotides (c-AMP, ADP, ATP) and nucleic acids (DNA and RNA), replication, genetic code, protein biosynthesis, mutation. [6L]

2.3 Chemical synthesis of oligonucleotides: Phosphodiester, Phosphotriester, Phosphoramidite and H- phosphonate methods including solid phase approach. [5L]

Unit 3: Biomolecules-II [15L]

3.1 Chemistry of enzymes: Introduction, nomenclature, classes and general types of reactions catalyzed by enzymes. Properties of enzymes: i) Enzyme efficiency/catalytic power ii) Enzyme specificity; Fischer's 'lock and key' and Koshland 'induced fit' hypothesis. Concept and identification of active site. [6L]

3.2 Factors affecting enzyme kinetics: Substrate concentration, enzyme concentration, temperature, pH, product concentration etc. Reversible and irreversible inhibition. [4L]

3.3 Mechanism of enzyme action: transition-state theory, orientation and steric effect, acid-base catalysis, covalent catalysis, strain or distortion. Mechanism of chymotrypsin catalyzed hydrolysis of a peptide bond. [5L]

Unit 4: Biogenesis and biosynthesis of natural products [15L]

4.1 Biogenesis: Precursors, primary and secondary metabolites. Acetate hypothesis. Mevalonate and Shikimic acid pathways. [7L]

4.2 General principles involved in the biosynthesis of amino acids, alkaloids, steroids and terpenoids. [3L]

4.3 Biosynthesis of selected natural products: L-tryptophan, cholesterol, ephedrine, citronellol. [5L]

Semester III: Practicals

Course Code: PSCHO3P1

Separation of a solid ternary mixture using micro-scale technique

1. Separation of solid components of a ternary mixture (water insoluble/soluble including carbohydrates) based upon differences in the physical and the chemical properties of the components.
2. Purification of the three components, measurement of their mass and determination of their physical constants.
3. Calculation of percentage yields of the individual components. (Identification of the components is not expected).

Course Code:PSCHO3P2

Estimation of drugs

1. Estimation of penicillin by iodometric titrations.
2. Estimation of streptomycin using uv-visible spectrophotometer.
3. Estimation of paracetamol by hydrolysis.
4. Estimation of aspirin in the given tablet using uv-visible spectrophotometer.
5. Estimation of diazepam by non-aqueous titrations.
6. Estimation of vitamin C by iodometric titrations.

Course Code: PSCHO3P3

Organic preparations (1.0 g scale)

1. Benzilic acid rearrangement: Benzilic acid from benzil
2. Sandmeyer reaction: p-Nitroiodobenzene from p-nitroaniline
3. Heterocyclic compound: 7-Hydroxy-4-methylcoumarin from resorcinol
4. Acetylation: Mannitol hexaacetate from mannitol
5. Claisen-Schmidt reaction: Dibenzalacetone from benzaldehyde
6. Oxidation: Fluorenone from fluorene
7. Acetylation: Acetylferrocene from ferrocene

Learning points:

1. Students are expected to know (i) the planning of synthesis, effect of reaction parameters including stoichiometry, and safety aspects including MSDS (ii) the possible mechanism, expected spectral data (IR and NMR) of the starting material and final product.
2. Students are expected to purify the product by recrystallization, measure its mass, check the purity by TLC, determine physical constant and calculate percentage yield.

Course Code: PSCHO3P4

Techniques of purification and green methods of synthesis

Set I: Techniques of purification:

1. Steam distillation
2. Vacuum distillation
3. Column chromatography

Set II: Green methods of synthesis (microwave induced)

1. Synthesis of Schiff's base from aniline and p-anisaldehyde in the presence of lime juice
2. Synthesis of coumarin by Knoevenagel reaction using salicylaldehyde, and ethyl acetate in presence of a base.

3. Synthesis of dihydropyrimidones- Biginelli reaction: acid-catalyzed three component reaction between vanillin, ethyl acetoacetate and thiourea.
4. Synthesis of acetanilide from aniline.

Learning points:

Set I: Techniques of purification

1. Students are expected to perform a purification technique using a known mass or volume of the given substance.
2. Check the purity of the purified compound by TLC, measure its mass and physical constant.

Set II: Green methods of synthesis (Microwave induced)

Students are expected to purify the product by recrystallization, measure its mass, determine physical constant and calculate percentage yield.

Semester IV

Course Code PSCHO 401

Theoretical organic chemistry-II

Unit 1: Physical organic chemistry [15L]

1.1 Structural effects and reactivity: Linear free energy relationship (LFER) in determination of organic reaction mechanism, The Hammett equation, substituent constants, theories of substituent effects, interpretation of σ -values, reaction constants ρ , Yukawa-Tsuno equation. [7L]

1.2 Uses of Hammett equation, deviations from Hammett equation. Dual parameter correlations, Inductive substituent constants. The Taft model, σ_I and σ_R scales, steric parameters E_s and β . Solvent effects, Okamoto-Brown equation, Swain-Scott equation, Edward and Ritchie correlations, Grunwald-Winstein equation, Dimroth's E_T parameter. [8L]

Unit 2: Supramolecular chemistry [15L]

2.1 Principles of molecular associations and organizations as exemplified in biological macromolecules like nucleic acids, proteins and enzymes. [3L]

2.2 Synthetic molecular receptors: receptors with molecular cleft, molecular tweezers, receptors with multiple hydrogen sites. [3L]

2.3 Structures and properties of crown ethers, cryptands, cyclophanes, calixarenes, rotaxanes and cyclodextrins. Synthesis of crown ethers, cryptands and calixarenes [6L]

2.4 Molecular recognition and catalysis, molecular self assembly. [3L]

Unit 3: Stereochemistry- II [15L]

3.1 Racemisation and resolution: Mechanism of racemisation, methods of resolution: chemical, kinetic and equilibrium asymmetric transformation and through inclusion compounds. [3L]

3.2 Determination of enantiomer and diastereomer composition: Isotope dilution method, enzymatic method, chromatographic methods. Methods based on NMR spectroscopy: use of chiral derivatising agents (CDA), chiral solvating agents (CSA) and Lanthanide shift reagents (LSR). [3L]

3.3 Correlative methods for configurational assignment: chemical, optical rotation, quasi-racemate and NMR spectroscopy. [4L]

3.4 Molecular dissymmetry and chiroptical properties: Linearly and circularly polarized light. Circular birefringence and circular dichroism. ORD and CD curves. Cotton effect and its applications. The octant rule and the axial α -haloketone rule with applications. [5L]

Unit 4: Asymmetric synthesis [15L]

4.1 Principles of asymmetric synthesis: Introduction, the chiral pool in Nature, methods of asymmetric induction – substrate, reagent and catalyst controlled reactions. [3L]

4.2 Synthesis of α -amino acids (Corey's diastereoselective hydrogenation of cyclic hydrazones), synthesis of L-DOPA [Knowles's Monsanto process]. [1L]

4.3 Asymmetric reactions with mechanism: Aldol and related reactions including Cram's rule, Sharpless enantioselective epoxidation, hydroxylation, aminohydroxylation, Diels-Alder reaction, reduction of prochiral carbonyl compounds and olefins. [8L]

4.4 Use of chiral auxiliaries in diastereoselective reductions, asymmetric amplification. Use of chiral BINOLs, BINAPs and chiral oxazolines and oxazolidines in asymmetric transformations. [3L]

Course Code PSCHO402 Synthetic organic chemistry-II

Unit 1: Radicals in organic synthesis [15 L]

1.1 General aspects: Electrophilic and nucleophilic radicals and their reactivity with π -rich/deficient olefins. [1L]

1.2 Inter- and intramolecular aliphatic C-C bond formation using tin hydride, carbon hydride, thio donor (Barton's reaction). [2L]

1.3 Cleavage of C-X, C-Sn, C-Co and C-S bonds in the generation of radicals. [3L]

1.4 Trapping by electron transfer reactions using manganese triacetate. [1L]

1.5 Radical-radical processes: oxidative couplings, single electron oxidation of carbanions to generate radicals, dehydrodimerization and reductive couplings. [3L]

1.6 C-C bond formation in aromatics: Introduction, electrophilic and nucleophilic radical reactions on aromatics, radical reactions on heteroaromatics: alkylations and acylations. [3L]

1.7 Hunsdiecker halodecarboxylation, autooxidation [2L]

Unit 2: Designing organic synthesis [15L]

2.1 Methodology in organic synthesis: convergent and divergent synthesis, functional group interconversions, general methods of synthesis of 4-7 membered rings, disconnection approach and retrosynthetic analysis, idea of synthons and synthetic equivalents. Retrosynthesis of acyclic saturated and unsaturated systems, monocyclic, bicyclic and aromatic compounds. [11L]

2.2 Synthesis of some complex molecules: synthetic routes based on retrosynthetic analysis for following molecules: prostaglandin A₂, atropine and camphor. [4L]

Unit 3: Newer methods in organic synthesis [15L]

3.1 Basic principles and applications of the following in organic synthesis: Crown ethers, cryptands, micelles, cyclodextrins, clay and zeolites and phase transfer catalysts. [9L]

3.2 Introduction to polymer supported reagents and organocatalysts. [3L]

3.3 Principles and applications of ultrasound and microwaves in organic synthesis. [3L]

Unit 4: Transition and rare earth metals in organic synthesis [15 L]

4.1 Introduction, basic concepts, 18 electron rule, bonding in transition metal complexes, oxidative addition, reductive elimination, migratory insertion. [3L]

4.2 Palladium in organic synthesis: π -bonding of Pd with olefins, applications in C-C bond formation, carbonylation, alkene isomerisation, cross coupling of organometallics and halides. Catalysis of cycloaddition reactions and heteroatom coupling to produce bonds between aryl/vinyl groups and N, S or P atoms. [3L]

4.3 Olefin metathesis using Grubb's catalyst. [1L]

4.4 Applications of nickel, cobalt, iron, rhodium and chromium carbonyls in organic synthesis. [4L]

4.5 Applications of samarium iodide including reduction of organic halides, aldehydes and ketones, α -functionalised carbonyl compounds and nitro compounds. [1L]

4.6 Applications of Cerium (IV) in synthesis of heterocyclic quinoxaline derivatives and its role as a deprotecting agent. [1L]

4.7 Sc(OTf)₃ and Yb(OTf)₃ as water tolerant Lewis acid catalysts in aldol condensation, Michael reaction, Diels-Alder reaction, Friedel-Crafts reaction, oxidation reactions. [2L]

Course code: PSCHO403 Natural products and spectroscopy-II

Unit 1: Heterocyclic compounds-II [15L]

Reactivity, important methods of synthesis and general reactions of the following heterocycles: pyridines, pyridine-N-oxide, pyridazines, pyrimidines, pyrazines, s-triazines, quinolines, isoquinolines, indoles, purines, oxazines, coumarins. [15L]

Unit 2: Natural products-III [15L]

2.1 Steroids: General structure, classification. Occurrence, biological role, important structural and stereochemical features of the following: corticosteroids, steroidal hormones, steroidal alkaloids, sterols and bile acids. [5L]

2.2 Synthesis of 16-DPA from cholesterol and plant sapogenin. [2L]

2.3 Synthesis of the following from 16-DPA: androsterone, testosterone, oestrone, oestriol, oestradiol and progesterone. [5L]

2.4 Synthesis of cinerolone, jasmolone, allethrolone, exaltone and muscone. [3L]

Unit 3: Natural products-IV [15L]

3.1 Vitamins: Classification, sources and biological importance of vitamin B₁, B₂, B₆, folic acid, B₁₂, C, D₁, E (α -tocopherol), K₁, K₂, H (β - biotin). Synthesis of the following:

Vitamin B₁ including synthesis of pyrimidine and thiazole moieties

Vitamin B₂ from 3, 4-dimethylaniline and D(-)-ribose

Vitamin B₆ from: 1) ethoxyacetylacetone and cyanoacetamide

2) ethyl ester of N-formyl-DL-alanine(Harris synthesis)

Vitamin E (α -tocopherol) from trimethylquinol and phytol bromide

Vitamin K₁ from 2-methyl-1, 4-naphthaquinone and phytol. [7L]

3.2 Antibiotics: Classification on the basis of activity. Structure elucidation of penicillin-G and cephalosporin-C. Synthesis of penicillin-G and phenoxymethylpenicillin from D-penicillamine

and t-butyl phthalimide malonaldehyde (synthesis of D-penicillamine and t-butyl phthalimide malonaldehyde expected). [6L]

3.3 Naturally occurring insecticides: Sources, structure and biological properties of pyrethrums (pyrethrin I), rotenoids (rotenone), azadirachtin. Synthesis of pyrethrin I. [2L]

Unit 4: Advanced spectroscopic techniques [15L]

4.1 ^{13}C -NMR spectroscopy: Introduction, ^{13}C - chemical shifts, calculation of ^{13}C - chemical shifts, proton coupled ^{13}C - spectra, proton decoupled ^{13}C - spectra. Off- resonance decoupling, DEPT technique, heteronuclear coupling of carbon to ^{19}F and ^{31}P . [4L]

4.2 Two-dimensional NMR spectroscopy: Introduction, COSY and HETCOR techniques, (including interpretation of COSY and HETCOR spectra). NOESY and ROESY techniques. [4L]

4.3 Problems based on combined use of spectroscopic techniques/ advanced techniques. [3L]

4.4 ESR and Fluorescence spectroscopy: Principles and applications. [3L]

4.5 Applications of NMR in medicine. [1L]

Course code: PSCHO404
Medicinal, bioorganic and green chemistry

Unit 1: Drug design, development and synthesis: [15L]

1.1 Introduction to Quantitative Structure Activity Relationship studies. QSAR parameters - Steric effects: The Taft and other equations; Methods used to correlate regression parameters with biological activity: Hansch analysis - A linear multiple regression analysis.[5L]

1.2 Introduction to modern methods of drug design and synthesis - computer-aided molecular graphics based drug design, drug design via enzyme inhibition (reversible and irreversible), biotechnology and drug design. [3L]

1.3 Concept of prodrugs and soft drugs: a) Prodrugs: Prodrug design, types of prodrugs, functional groups in prodrugs, advantages of prodrug use. b) Soft drugs: Concept and properties [3L]

1.4 Synthesis and application of the following drugs: Fluoxetine, oxyphenbutazone, cetirizine, esomeprazole, fluconazole, zidovudine, methotrexate, diclofenac, labetalol, fenofibrate. [4L]

Unit 2: Biomolecules - III [15L]

2.1 Chemistry of coenzymes. Structure, mechanism of action and bio-modeling studies of the following coenzymes: nicotinamide adenine dinucleotide, flavin adenine dinucleotide, thiamine pyrophosphate, pyridoxal phosphate, Vitamin B₁₂, biotin, lipoic acid, Coenzyme A. [12L]

2.2 Oxygen activation in biological systems with reference to cytochromes. [3L]

Unit 3: Biomolecules – IV [15L]

3.1 Role of main enzymes involved in the synthesis and breakdown of glycogen. [2L]

3.2 Enzyme catalyzed organic reactions: Hydrolysis, hydroxylation, oxidation and reduction. [6L]

3.3 Enzymes in organic synthesis. Fermentation: Production of drugs/ drug intermediates by fermentation. Production of chiral hydroxy acids, vitamins, amino acids, β -lactam antibiotics. Synthesis of chemicals via microbial transformation, synthesis of L-ephedrine. Chemical

processes with isolated enzymes in free form (hydrocyanation of m-phenoxybenzaldehyde) / immobilized form (production of 6-aminopenicillanic acid). [7L]

Unit 4: Green chemistry [15L]

4.1 Introduction, basic principles of green chemistry. Designing a green synthesis: Green starting materials, green reagents, green solvents and reaction conditions, green catalysts. [1L]

4.2 Use of the following in green synthesis with suitable examples:

- a) Green reagents: dimethylcarbonate, polymer supported reagents.
- b) Green catalysts: Acid catalysts, oxidation catalysts, basic catalysts, phase transfer catalysts [Aliquat 336, benzyltrimethyl ammonium chloride (TMBA), Tetra-n-butyl ammonium chloride, crown ethers], biocatalysts.
- c) Green solvents: water, ionic liquids, deep eutectic solvents, supercritical carbon dioxide.
- d) Solid state reactions: solid phase synthesis, solid supported synthesis.
- e) Microwave assisted synthesis: reactions in water, reactions in organic solvents, solvent free reactions.
- f) Ultrasound assisted reactions. [10L]

4.3 Comparison of traditional processes versus green processes in the syntheses of ibuprofen, adipic acid, 4-aminodiphenylamine, p-bromotoluene and benzimidazole. [4L]

Semester IV: Practicals

Course Code: PSCHO4P1

Paper I: Separation of solid-liquid/ liquid-liquid ternary mixture using micro-scale technique

1. Separation of components of ternary mixtures (solid-liquid or liquid-liquid) based upon differences in the physical and the chemical properties of the components.
2. Purification of the three components, measurement of their mass and determination of their physical constants.
3. Calculation of percentage yield of the individual components.
(Identification of the components is not expected).
(Minimum 6 experiments)

Course Code: PSCHO4P2

Paper II: Identification of any unknown organic compound with preparation, purification and physical constant of derivative. (Minimum 8 organic compounds)

Course Code: PSCHO4P3

Isolation / Estimation of natural products

1. Extraction of clove oil from cloves.

2. Extraction of nicotine dipicrate from tobacco.
3. Estimation of proteins by Biuret method using spectrophotometer.
4. Estimation of glucose by Folin Wu method.
5. Estimation of citral using hydroxylamine hydrochloride.
6. Estimation of saponification value of oil.

Course Code: PSCHO4P4

**Interpretation of spectral data of organic compounds
(UV, IR, PMR, CMR and Mass spectra).**

A student will be given UV, IR, PMR, CMR, and Mass spectra of a compound from which preliminary information should be reported within first half an hour of the examination without referring to any book/reference material. The complete structure of the compound may then be elucidated by referring to any standard text-book/reference material etc
(Minimum 8 spectral analysis)

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References for Course Code PSCHO 303 and 403: Paper III

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8. An introduction to medicinal chemistry-Graham L. Patrick, OUP Oxford, 2009.
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11. Strategies for organic drug synthesis and design - D. Lednicer Wiley
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Course Codes: PSCHO3P1 TO PSCHO4P4

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7. Macro-scale and Micro-scale Organic Experiments, K. L. Williamson, D. C. Heath.
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11. Laboratory Manual of Organic Chemistry, Fifth edition, R K Bansal, New Age Publishers.
12. Organic structures from spectra, L. D. Field, S. Sternhell, John R. Kalman, Wiley, 4th ed., 2011.

1. The candidate is expected to submit a journal certified by the Head of the Department /institution at the time of the practical examination.
2. A candidate will not be allowed to appear for the practical examination unless he/she produces a certified journal or a certificate from the Head of the institution/department stating that the journal is lost and the candidate has performed the required number of experiments satisfactorily. The list of the experiments performed by the candidate should be attached with such certificate.
3. Use of non-programmable calculator is allowed both at the theory and the practical examination.

Scheme of examination for M.Sc. Organic Chemistry Semester III and IV.

Internal Theory examination (40 Marks)

1. One seminar based on curriculum / publication of a research paper/ presentation of a research paper in seminar or conference (to be assessed by teacher of the institution teaching PG learners).
 - a) Selection of the topic, introduction, write up, references. **15 marks**

- | | |
|--------------------------------------------------------------------------------------------------------------------------------|-----------------|
| b) Presentation. | 15 marks |
| 2. Active participation in routine class instructional deliveries. | 05 Marks |
| 3. Overall conduct as a responsible learner, communication and leadership qualities in organizing related academic activities. | 05 Marks |

There will not be any internal examination for practical.

External Theory Examination (60 Marks)

Paper	Time allotted in hours	Maximum marks
Paper- I	2.5	60
Paper-II	2.5	60
Paper-III	2.5	60
Paper-IV	2.5	60

It is recommended that a total of five questions be set, based on the syllabus with due weightage to the number of lectures allotted per topic. The candidates are expected to answer all five questions. Question 5 will be based on all four units and the remaining questions will be based on the units as indicated below

	Semester- III	Semester-IV
Q.1	Unit-I	Unit-I
Q.2	Unit-II	Unit-II
Q.3	Unit-III	Unit-III
Q.4	Unit-IV	Unit-IV
Q.5	From all four units	From all four units

Semester End Practical Examination (50 Marks)

Laboratory Work	40 Marks
Journal	05 Marks
Viva	05 Marks

The practical examination will be held for two days as described below. The candidates will be examined practically and orally on each day.

Papers	Day	Experiments	Time duration in hours	Maximum marks
Paper I	Day -1 M	1	3.5	50
Paper I	Day-1 E	1	3.5	50
Paper I	Day-II M	1	3.5	50
Paper I	Day-II E	1	3.5	50