FACULTY OF SCIENCE

Department of Chemistry SATAVAHANA UNIVERSITY – KARIMNAGAR

M.Sc. ORGANIC CHEMISTRY

III SEMESTER SYLLABUS

(For the batch admitted during the academic year 2023-2024, Under Choice Based Credit System (CBCS))

Paper Code	Title	Workload Per Week		Marks			Crucdita	Duration
		Theory	Practical	Internal	External	Total	Credits	of the Exams.
MCHE (SPT) 301T	Spectral techniques	4		20	80	100	4	3 Hrs
MCHE (OC) 302T	Conformational analysis, asymmetric synthesis & Non benzenoid Aromatics	4		20	80	100	4	3 Hrs
MCHE (OC) 303T (E-I) (OR) MCHE (OC) 303T (E-II)	Modern organic synthesis (or) Heterocyclic Compounds	4		20	80	100	4	3 Hrs
MCHE (OC) 304T (E-I) (OR) MCHE (OC) 304T (E-II)	Natural Products	4		20	80	100	4	3 Hrs
MCHE (OC) 351P	Separation and identification of organic compounds		6		100	100	4	4 Hrs
MCHE (OC) 352P	synthesis of organic molecules and isolation of natural products		6		100	100	4	4 Hrs
TOTAL		16	12	80	520	600	24	

M.Sc. (Organic Chemistry) III Semester

Paper- I: MCHE (SPT) 301: Spectral techniques

SPT-09: 2DNMR techniques and combined applications of spectral techniques

SPT-10: NQR and Mossbauer Spectroscopy

SPT-11: ORD, Photo Electron and AUGER Electron Spectroscopy

SPT-12: X-ray Spectroscopy & X-ray Diffraction techniques

<u>SPT-09: 2DNMR and combined applications of spectral techniques:</u> (15Hrs)

a) 2D NMR: Introduction to Two Dimensional spectroscopic methods: Principle of 2-D NMR, Classification of 2D-experiments. Homonuclear and Heteronuclear 2D-J-resolved spectroscopy. Correlation spectroscopy (COSY) Homo COSY (¹H-¹H COSY), TOCSY (Total Correlation Spectroscopy), Hetero COSY (¹H,¹³C COSY,HMQC), long range ¹H, ¹³C COSY (HMBC), NOESY and 2D- INADEQUATE experiments.

b) Combined applications of spectral techniques: Introduction to the analytical approach towards the structure elucidation of simple Organic molecules by combined application of UV, IR, ¹H NMR ¹³C NMR and Mass spectra.

SPT-10: NQR and Mossbauer Spectroscopy:

(15 Hrs)

Nuclear Quadrupole Resonance: Quadrupole nuclei and quadrupole moments-prolate and oblate nuclear charge distributions-energies of quadrupolar transitions-electric field gradient, coupling constants and splitting

Mossbauer Spectroscopy: Principles, Experimental Considerations and Presentation of the Spectrum - Isomer Shifts – Quadrupole splitting and Magnetic hyperfine splitting - Selection Rules.

Iron Compounds: Low-spin and High-spin Fe(II) and Fe(III) Complexes - π -bonding Effects in Iron complexes - Study of High-spin Low-spin Cross-over c) Diamagnetic and Covalent Compounds - Structural aspects of Iron Carbonyls. Tin Compounds: Tin Halides and Organotin Compounds.

<u>SPT-11: ORD, Photo Electron and AUGER Electron Spectroscopy:</u> (15 Hrs)

Optical Rotatory Dispersion (ORD) spectroscopy:

Optical rotation, circular birefringence, circular dichroism and Cotton effect. Plain curves and Anomalous curves and their applications in determining configuration and in study of conformational changes. Empirical and semiempirical rules-The axial haloketone rule, the octant rule, Helicity rule, Lowe's rule. Application to the study of absolute configuration and conformations of organic molecules.

Photoelectron Spectroscopy:

Principle and Instrumentation, Types of Photoelectron Spectroscopy – UPS & XPS Binding Energies, Koopman's Theorem, Chemical Shifts.

Photoelectron Spectra of Simple Molecules: N_2 , O_2 , F_2 , CO, HF, NH_3 and H_2O - Vibrational Structure of PES Bands, Potential energy curves, Interpretation of Vibrational spectral data for ionized (M^+) species, Prediction of Nature of Molecular Orbitals. ESCA in qualitative analysis.

AUGER Electron Spectroscopy:

Principles, Instrumentation and Applications.

SPT-12: X-ray Spectroscopy & X-ray Diffraction techniques:

X-ray fluorescence (XRF) spectra: Absorption techniques, Absorption edge fine structure (AEFS spectra) and extended X-ray absorption fine structure (EXAFS) spectra Basic Theory, Applications, Instrumentation.

X-ray diffraction: Bragg condition. Miller indices. Experimental methods of X-ray diffraction. Laue method and Debye-Scherrer method. Primitive and nonprimitive unit cells. Index reflections. Identification of unit cells from systematic absences in diffraction pattern. Structure factor and its relation to intensity and electron density. Description of the procedure for an X-ray structure analysis. Typical examples, Advantages and Limitations of X-ray Diffraction.

Electron Diffraction by Gases: Principles - Radial Distribution Curves - Interpretation of Results for simple gas phase molecules-Advantages and Limitations.

Neutron Diffraction: Principles - Application in Hydrogen Bonding Studies - Combined use of X-ray and Neutron Diffraction Studies - Advantages and Limitations.

References:

1. Spectroscopic identification of organic compounds by R.M.Silverstein. G.C.Bassler and

T.E.Morrill.

- 2. NMR-A multinuclear introduction by William Kemp.
- 3. Principles of Instrumental analysis, Skoog, Holler and Nieman, Harcourt Asia PTE Ltd.
- 4. Principles of Instrumental Analysis, Skoog and Leary, Saunders College Publishing.
- 5. International series of Monographs, Vol. **53**: Photoelectron Spectroscopy, Edited by D. Beckerand D. Betteridge 1972.
- 6. Sructural methods in inorganic chemistry, E.A.V. Ebsworth.
- 7. Modern Spectroscopy, J. M. Hollas, John Wiley & sons.
- 8. Fundamentals of Molecular Spectroscopy, Banwell & McCash.
- 9. Introduction to Molecular Spectroscopy, G. M. Barrow, McGraw Hill.
- 10. Molecular Spectroscopy, J. D. Graybeal, McGraw Hill.
- 11. Basic principles of Spectroscopy, R. Chang, McGraw Hill.
- 12. Physical Methods in Chemistry, R. S. Drago, Saunders College.
- 13. NMR Spectroscopy: Basic principles, concepts and applications in chemistry, H. Gunther, John Wiley & sons.
- 14. Introduction to Magnetic Resonance, A. Carrington & A.D. Maclachalan, Harper & Row.
- 15. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry, R. V. Parish, Ellis Harwood.
- 16. NMR basic principles Atta-ur-Rahman.
- 17. Two dimensional NMR Spectroscopy-Applications for chemists and biochemists, edited by W. R. Croasmun & R. M. K. Carlson, VCH.
- 18. X-ray diffraction procedures for polycrysralline and amorphous materials, H. P. Klug & L. E. Alexander, John Wiley.
- 19. Physical Chemistry, Ira N. Levine, McGraw Hill.
- 20. Atkin's Physical Chemistry, P. Atkins & Julio de Paula, Oxford University Press.
- 21. Organic spectroscopy by William Kemp.
- 22. Spectroscopic methods in organic chemistry by D.H. Williams and I. Fleming.
- 23. Practical Pharmaceutical Chemistry by A. H. Beckett and J.B. Stenlake.

Paper-II: MCHE(OC) 302T: Conformational analysis, Asymmetric synthesis & Non benzenoid Aromatics

OC-13: Conformational analysis OC-14: Asymmetric synthesis-I OC-15: Asymmetric synthesis-II OC-16: Non benzenoid Aromatics

OC-13: Conformational analysis (Cyclic systems):

Study of conformations of cyclo hexanes mono and disubstituted cyclohexanes. factors governing reactivity of axial and equatorial substituted cyclohexane ring. Introduction to conformations of other monocyclic systems, cyclobutane, cyclopentane,cycloheptane. Stereochemistry of decalins, hydrindanes, perhydroanthracene. Conformational structures of piperidine, N-methyl piperidine.

Stereochemistry of addition to carbonyl group in rigid cyclohexanone system. conformational effects on the stability and reactivity of diastereomers in cyclic molecules. Steric and stereoelectronic factors.

OC-14: Asymmetric synthesis-I:

Introduction & terminology: Topicity in molecules groups and faces. Selectivity in synthesis: enantioselectivity and diastereoselectivity. Introduction to diasteroselective synthesis and double stereo differentiating reactions –diastereomeric excess (de) and enantiomeric excess (ee)

Strategies for stereo control in diastereoselective synthesis (preliminary conceptual treatment): small templates, molecular walls, ring forming reactions, pericyclic reactions, co-ordination metal centers, use of Π-donor complexes, chiral auxiliaries, achiral auxiliaries, intra annular and extra annular stereo control.

Nucleophilic additions to cyclic, acyclic carbonyl compounds: Cram's rule, Felkin-Anh model. Addition to chelated carbonyl compounds: Prelog's rule. Addition of –H and –R to cyclic ketones (formation of axial and equatorial alcohols)

Aldol reactions: (A) achiral enolates with achiral and chiral aldehydes. (B)chiral enolates with achiral aldehydes and chiral aldehydes.

OC-15: Asymmetric synthesis-II:

Stereoselective transformation of C=C (double) bond: Diastereoselective synthesis involving catalytic hydrogenation, Hydroboration, Simmons-Smith reaction, Prevost reaction. *Enantioselective synthesis with chiral non racemic reagents:* Hydroborations with chiral boranes, Reductions with chiral complex hydrides and chiral organometallic compounds.

Enantioselective synthesis with chiral non racemic catalysts: Catalysis by chiral transition metal complexes with reference to sharpless enantioselective epoxidations and enantioselective hydrogenations.

OC-16: Non benzenoid Aromatics:

Concept of aromaticity, Robinson's sextet theory, ring current concept, to distinguish aromatic, non aromatic & antiaromaticmolecules. Huckels rule applications & limitations of the Huckel's rule.

various nonbenzenoid aromatic molecules: synthesis& aromatic properties of cyclopropenium cation derivatives, cyclopentadienyl anion systems,

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cycloheptatrienylcation(tropilium cation), cyclooctatetraenyl dianion, fulvenes, metallocenes, annulenes, hetero annulenes, azulenes, fullerenes(C_{60}), sydnones, antiaromatic compounds, alternate and non alternate hydrocarbons.

- 1. Stereochemistry of carbon compounds by Ernest L Eliel
- 2. Stereochemistry of organic compounds-principles & applications by D Nasipuri.
- 3. Stereochemistry, conformation & mechanism by PS Kalsi
- 4. Asymmetric synthesis by Nogradi
- 5. Asymmetric organic reactions, J.D.Morrison & H.S.Mosche

Paper III: MCHE (OC) 303T: Modern Organic Synthesis

OC-17- Synthetic Reagents OC-18- New Synthetic Reactions **OC-19-** Synthetic strategies-I **OC-20-** Synthetic strategies-II

OC-17 Synthetic Reagents:

i) Oxidations: a) Alcohol to carbonyls; Cr^{VI} oxidants (Jones reagent, PCC. PDC) IBX, DMP, TPAP, Swern oxidation b) alkenes to diols: Prevost and Woodward oxidation c) Oxidative cleavage of 1,2-diols: Periodic acid and Lead tetraacetate d) Oxidation of allylic and benzylic C-H bonds: DDO and SeO₂.

ii) Reductions: a) Catalytic hydrogenation: Heterogeneous catalytic reduction and Homogenous (Wilkinsons's catalytic hydrogenation). b) Non-metallic reductions: Diimide reduction c) Dissolving metal reductions: Birch reduction. d) Nucleophilic metal hydrides: LiAlH₄, NaBH₄, and their modifications. e) Electrophilic metal hydrides: BH₃, AlH₃ and DIBAL. f) Use of tri-n-butyl tin hydride.

OC-18: New synthetic reactions:

1. Metal mediated C-C and C-X coupling reactions: Suziki coupling, Heck reaction, Stille coupling, Sonogishira cross coupling, Buchwald-Hartwig coupling Reaction and Negishi-Kumada.

2. C=C Formation Reactions: Shapiro reaction, Bamford-Stevens reaction, McMurrey reaction, Julia-Lythgoe olefination and Peterson's stereoselective olefination.

3. Multicomponent Reactions: Ugi, Biginelli, Hantzsch and Mannich reactions.

4. Other important synthetic reactions: Baylis-Hilman reaction, Stork-enamine reaction and Michael reactions.

OC-19: Synthetic strategies-I:

Introduction & Terminology: Target, synthem, synthetic equivalent, functional group interconversion (FGI), functional group addition, functional group elimination. Criteria for selection of target. Linear and convergent synthesis, Retrosynthetic analysis and synthesis involving chemoselectivity, regioselectivity, reversal of polarity and cyclization. Introduction to one group c-c and c-x disconnections, Disconnections of carbonyl compounds, alcohols, ether and sulphides.

OC-20: Synthetic strategies-II:

Introduction to two group c-c and c-x disconnections, two group c-x disconnections: 1,1difunctioalised, 1.2 -difunctionalised and 1.3 -difunctionalised compounds.

Two group c-c disconnections: Diels-Alder reaction, 1,3–difunctionalised compounds, 1,5difunctionalised compounds, Michael addition and Robinson annulation. Control in carbonyl condensations, explanation with examples oxanamide and mevalonic acids.

Strategic bond: Definition, choosing guidelines for disconnection-disconnection of c-x bonds, disconnect to greatest simplification using symmetry in disconnection, disconnection corresponding to known reliable reaction, high yielding steps and recognizable starting materials. Application of the stragies to the synthesis of (+) Disparlure, retronecene and Longifolene.

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- 1. Modern methods of organic synthesis by w Carruthers
- 2. Organic synthesis by Michael B Smith
- 3. Organic synthesis by O House
- 4. Reagents for organic synthesis by Fieser, vol 1-11(1984)
- 5. Organic synthesis by C Willis and M Willis
- 6. Reagents in organic synthesis by B.P Mundy and others
- 7. Name reactions by Jie Jack Li
- 8. Organic chemistry Claydon and others 2005
- 9. Disconnection approach by Steward Warren

Paper-4: MCHE (OC) 304T: General Organic Chemistry

OC-21 Heterocyclic compounds **OC-22 Reaction Mechanisms –II OC-23** Natural products and Protection of functional groups **OC-24** Chemistry of Steroids

OC-21: Heterocyclic compounds

Synthesis, reactivity, aromatic character and importance of the following heterocycles: Pyrazole, Imidazole, Oxazole, Thiazole, Isoxazole, Isothiazole, Pyridazine, Pyrimidine. Pyrazine, benzimidazole, benzoxazole and benzthiazole.

OC-22: Reaction Mechanisms –II

Study of the following special mechanistic aspects in organic chemistry Principles of microscopic reversibility with reference to esterification – ester hydrolysis(with H_2SO_4) & hydration of alkenes – dehydration of alcohols (with H_2SO_4) – Super acids – Long living carbocations – Simultaneous and stereo specific 1,2 shifts – Cascade of ring expansions – Acylation of amines and acyl esters – Oxidative coupling through carbanions – Conversion of aryl iminoesters to diarylamides, Chapmann rearrangement-Cyclodehydration of aldehydes and ketones - Von Ritcher rearrangement - Hoffman Loffler, Freytag reaction - Robinson's annulations -Knoevenagel condensation, The Darzens condensation.

OC-23: Natural products and Protection of functional groups:

- a) Natural Products: Classification and examples of natural products- Flavonoids, Flavones, flavanols, Flavanones, Catchins, Anthocyanins, steroids, quinonoids, Ouinones-General techniques of isolation and purification of natural products -Color reactions, spot tests and other basic identification techniques in natural products -Basic separation techniques used in various types of natural products.
- b) Protection of functional groups: Principles of (1) protection of alcohols Ether formation: methyl, benzyl, allyl, methoxy ethoxy methyl (MEM), THP, silyl, and TBDMS ethers; Ester formation– methyl, benzoyl, tosyl, and p-nitro benzoyl ester (2) protection of diols - acetal, ketal and carbamate formation (3) protection of carboxylic acids – Ester formation: methyl, benzyl, t-butyl, p-nitrobenzyl, pbromophenacyl, and silvl esters (4) protection of amines - Amide and Carbamate formation formyl, acetylation, benzoyl, benzyloxy carbonyl (CBZ), with tert butyloxycarbonyl (BOC), tert-butyl azido formyl, phthaloyl, di-tert-butyl pyrocarbonyl, Fluorenylmethyloxycarbonyl (FMOC), and triphenyl methyl groups (5) protection of – acetal, ketal, 1,3-dioxolane, 1,3-dioxane, carbonyl groups 1,3-dithiolane, 1,3oxathiolane and 1,3-dithiane formation.

OC-24: Chemistry of steroids

Structure, stereochemistry and synthesis of the following stereoidal molecules: Cholesterol, androsterone, testosterone, oestrone, oestradiaol, oestriol, pregnancy harmones (progesterone) - chemistry of adrenocortico steroids (corticosterone and cortisone).

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- 1. Heterocyclic Chemistry, T.Gilchrist
- 2. An introduction to the Chemistry of heterocyclic compounds, R.M.Acheson
- 3. Heterocyclic Chemistry, J.A.Joule & K.Mills
- 4. Principles of Modern Heterocyclie Chemistry, A.Paquette
- 5. Heterocyclic Chemistry, J,A.Joule & Smith
- 6. Handbook of Heterocyclic Chemistry, A.R.Katritzky
- 7. Organic chemistry Claydon and others 2005
- 8. Advanced Organic Chemistry by Jerry March
- 9. Mechanism and Structure in Organic Chemistry S.Mukerjee
- 10. Guide Book to mechanism in Organic Chemistry,6th Edition,Peter Sykes
- 11. Text book of organic chemistry, Vol 2, I.L.Finar.
- 12. Natural products, P.S.Kalsi.
- 13. Biochemistry, Eliot and Eliot
- 14. Lehninger principles of Bio chemistry, D.L. Nelson & M.M.Cox.

Paper III: MCHE (OC) 303(CB1)T: (ELECTIVE-1): Heterocyclic Compounds

OC(CB1)-I: Nonaromatic heterocyclic Compounds OC(CB1)-II: Five membered heterocycles with more than two hetero atoms OC(CB1)-III: Larger ring and other heterocyclic Compounds OC(CB1)-IV: Fused heterocyclic Compounds

OC(CB1)-I: Nonaromatic heterocyclic Compounds

Different types of strains, interactions and conformational aspects of nonaromatic heterocycles. Synthesis, reactivity and importance of the following ring systems. Aziridines, Aziridines, Oxiranes, Thiiranes, Diazirenes, Diaziridines, Oxaziridines, Azetidines, Oxetanes and Thietanes

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(15 Hrs)

OC(CB1)--II: Five membered heterocycles with more than two hetero atoms (15 Hrs)

Synthesis, Properties, aromatic character and importance of Triazoles (1,2,3-Triazoles and 1,2,4-Triazoles), Oxadiazoles(1,2,3-Oxadiazoles,1,2,4-Oxadiazoles, 1,3,4-Oxadiazoles and 1,2,5-Oxadiazoles), Thiadiazoles(1,2,3- Thiadiazoles, 1,2,4-Thiadiazoles, 1,2,5-Thiadiazoles, and 1,3,4- Thiadiazoles) and 1,2,3,4-Tetrazoles

OC(CB1)--III: Larger ring and other heterocyclic Compounds (15 Hrs)

Synthesis, Properties and importance of Azepines, Oxepins, Thiepins, Diazepines, Oxepans, Spirans, Azocines and Azonines. Synthesis of selenophenes, Tellerophenes and phospholes

OC(CB1)--IV:Fused heterocyclic Compounds

Synthesis, Properties and importance of Chromone, Indolizine, Phenanthridine, Quinolizines, Quinoxalines, Benzodiazoles, Benzotriazoles, Imidazopyridines, Benzooxepines, Benzodiazepines,

- 1. Heterocyclic Chemistry, T.Gilchrist
- 2. An introduction to the Chemistry of heterocyclic compounds, R.M.Acheson
- 3. Heterocyclic Chemistry, J.A.Joule & K.Mills
- 4. Principles of Modern Heterocyclie Chemistry, A.Paquette
- 5. Heterocyclic Chemistry, J,A.Joule & Smith
- 6. Handbook of Heterocyclic Chemistry, A.R.Katritzky

Paper IV: MCHE (OC) 304(CB2)T: (ELECTIVE-2) NATURAL PRODUCTS

OC(CB2)--I: Chemistry of flavanoids **OC(CB2)-II:** Antibiotics OC(CB2)--III: Fats, oils and fatty acid derivatives OC(CB2)--IV: Prostaglandins, porphyrins and carotenoids

OC(CB2)-I: Chemistry of flavanoids

Classification of flavonoids-General methods of synthesis of anthocyanins, flavones and flavonols-Chemistry of the following flavonoids:Anthocyanins (pelargonidin and cyaniding); Flavones (chrysin); flavanols (quercitin, Isoflavone, diadzein). Biological importance of flavonoids.

OC(CB2)--II: Antibiotics

Classification of antibiotics - Isolation, structure determination, stereo chemistry and mode of action of the following antibiotics: Terramycin, Penicillin-G, Cephalosporin-C, Streptomycin, Chloramphenicol.

OC(CB2)-: Fats, oils and fatty acid derivatives

Definition, Classification and analytical characteristics of fats-methods of determining the glycerides, composition of fats, structural determination and synthesis of fatty acids methods of determining fatty acid composition of fats-Structure determination and synthesis of glycerides-bio-synthesis of fatty acids-unusual fatty acids.

OC(CB2)-IV:Prostaglandins,porphyrins and carotenoids

Prostaglandins-occurrence, nomenclature, classification and physiological activity. Structure determination and synthesis of PGE_2 and $PGF_{2\alpha}$ – Porphyrins: Structure and synthesis of Haemoglobin and chlorophyll – Introduction, structure determination and synthesis of α carotene, β -carotene, γ -carotene, Lycopene.

References:

- 1. Text book of organic chemistry, Vol 2, I.L.Finar.
- 2. Natural products, P.S.Kalsi.
- 3. Biochemistry, Eliot and Eliot
- 4. Lehninger principles of Bio chemistry, D.L.Nelson & M.M.Cox.

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PRACTICALS:

Paper V: MCHE (OC) 351P: Separation and identification of organic compounds:

Separations of two component mixtures by systematic chemical methods and their identification by chemical reactions-separation by using solvent ether, 5% aqueous sodium bicarbonate, 5% sodium hydroxide and dil. hydrochloric acid solutions, checking the purity of the two components by TLC, identification of the compounds by a systematic study of the physical characteristics (mp/bp), extra elements (nitrogen, halogens and sulfur), solubility, functional groups, preparation of crystalline derivatives and identification by referring to literature. A minimum of 10 mixtures should be separated and analyzed by these procedures.

References:

- 1. Text book of practical organic chemistry, Vogel
- 2. Text book of practical organic chemistry, Mann and Saunders.

MODEL QUESTION PAPER

1) Separate the given mixture, Identify the unknown organic compounds by qualitative analysis and prepare two derivatives of it.

SCHEME OF EVALUATION				
Assessment	Marks: 100			
Separation of Mixture	20			
Identification of active compound	30			
Identification of neutral compound	30			
Record samples & viva-voce	20			

Paper VI: MCHE (OC) 352P: synthesis of organic molecules and isolation of natural products:

Organic preparations:

2- phenyl indole (fisher indole synthesis), 7-hydroxy -3-methylflavone (Baker-venkatraman reaction), 2,5-di hydroxy acetophenone (fries reaction) benzilic acid from benzoin (benzillic acid rearrangement), benzpinacol (photochemical reaction), 7-hydroxy coumarin (pechman synthesis), benzanilide (Beckmann rearrangement), vanillyl alcohol from vanillin (NaBH₄ reduction), 4-chloro toluene from 4-toluedine (sandmayer reaction), 2,4-nitro phenols (nitration and separation by steam distillation).

Isolation of the following natural products:

Caffeine from tea leaves (solvents extraction), Piperine from pepper (soxhlet extraction),

Eucalyptus oil from leaves (steam distillation), Lycopene from tomatoes

References:

- 1. Text book of practical organic chemistry, Vogel
- 2. Text book of practical organic chemistry, Mann and Saunders.

MODEL QUESTION PAPER

Synthesize the given organic compound, recry0stallise and calculate the yield of product.
Isolate the Lycopene from tomatoes

SCHEME OF EVALUATION				
Assessment	Marks: 100			
Preparation	50			
Isolation	30			
Record samples & viva-voce	20			