

Synthesis and Characterization of Isolongifoline Ketone

Vipin Kumar^{1*}, A.K.Agarwal²

Department of Chemistry, Bareilly College Bareilly, M.J.P.Rohilkhand University
Bareilly (U.P.) 243005, India

*Corres. Author: vipinkrdil@rediffmail.com

Abstract : Isolongifoline ketone was synthesised as a main component by Isolongifoline (purity 87.01%) with the application of ion exchange catalyst - Tulsion T-421. Aerobic epoxidation of isolongifoline with hydrogen peroxide in acetic acid in presence of cation ion exchange resin as catalyst yielded isolongifoline epoxide. The rearrangement of isolongifoline epoxide to ketone was achieved by washing with sodium bicarbonate and slow fractional distillation. GC-FID, FT-IR and GC-MS analysis led to identification and purity of components in the reaction sample and purified sample. The sample is containing 15.80 % Ketone I (8-oxo-7-*H*-isolongifolane) and 77.17% Ketone 2 (8-oxo-7-*H*-isolongifolane) followed by other terpenes. GC-MS analysis lead one major peak isolongifoline ketone (8-oxo-7-*H*-isolongifolane) and two minor peak viz Isolongifoline alcohol and isolongifoline epoxide. The major peak constitute high percentage of Isolongifoline ketone (90.7%) followed by other ketone.

Key Words: Ion exchange Resin, Catalyst, Isolongifoline, Isolongifoline ketone, FTIR, GC-FID, GC-MS.

1. Introduction

Longifoline and its derivatives find a major role in fragrance industry. It is reported that the rearrangement of longifoline performed with BF₃.OEt₂ affords isolongifoline.^[1, 2, 3] Novel processes for producing isolongifoline ketone and its epimer which comprise treating isolongifoline with a per oxygen compound in an acidic medium to produce saturated ketone. This saturated ketone can also be epimerized as hereinafter disclosed to provide a more stable perfume ingredient.^[4] The OEA produced by the membrane was employed in as oxidant to convert the isolongifoline in to isolongifolinone with *cobaltous acetate as catalyst*. It was found that the conversion of isolongifolene increased with the oxygen concentration of the OEA and the reaction temperature. The maximum yield was obtained under the conditions of the oxygen concentration of 33.1% and the temp of 60 °C. Both the conversion and the yield increased with the flux of OEA.^[5] Cobalt- containing MCM-41 was used as a heterogeneous catalyst for the liquid phase aerobic oxidation of isolongifoline, one of the most available sesquiterpene. The oxidation of isolongifoline under mild solvent-free conditions results mainly (90% selectivity) in isolongifoline-9-one, a compound which occupies a vintage place in modern perfume industry.^[6]

The process is carried out by treating isolongifoline with a per- oxygen source such as hydrogen peroxide in the presence of acidic medium which is described as organic anhydride or acid. The reaction proceeds at a more satisfactory rate with the anhydride when a catalytic amount, desirably from about one to five percent of the weight of the anhydride. Preferred protonic acids for use herein are sulfuric acid and strong protonic acids such as methanesulphonic acid, p-toluenesulphonic acid, and the like. When carboxylic acids other than formic acid are used. The acid medium should contain a catalytic amount of strong protonic acid. The reaction is generally

carried out from 25 to 75°C. However it has been found that best results are obtained in many aspects of this invention by using temperature in the preferred range of from 30°C to 60°C.^[7, 8, 9] Oxidation of Isolongifoline by reaction with m-chloroperbenzoic acid yielded a mixture of a corresponding epoxide, ketone, and alcohol. Two other alcohols were obtained from the reduction of the epoxide and the ketone respectively.^[10]

Synthesis in fluoros phase-a convenient synthesis of Isolongifoline epoxide and its rearrangement to ketone: Aerobic epoxidation of isolongifoline 2 with Pivalaldehyde/oxygen in perfluoro-2-butyl tetrahydro furan in the presence of Mn (OAc)₃ · 2H₂O as catalyst Yielded Isolongifoline epoxide in good yield. The rearrangement of isolongifoline epoxide to ketone using trimethyl silane in CHCl₃ was achieved.^[11] A method for making isolongifolone involving reaction (-) isolongifoline with chromium hexacarbonyl and t-butyl hydroperoxide.^[12] Epoxidation of isolongifoline with per acids yields - epoxide. This epoxide is of little perfumery interest but rearrangement of the epoxide produces the saturated ketones – 8-oxo-7- -H-isolongifolane which has a desirable woody odour and has found use in perfumery. The Epimerization of this ketone to the 7 () H derivative is simple and this ketone is also of perfumery use as it possesses a sweet woody odour. The rearrangement of isolongifoline epoxide has been reported to yield two , -unsaturated alcohols, the rearrangement of the epoxide; under most reaction conditions these alcohols are formed in less than 50 % yield, the main product is 8-oxo-7- -H-isolongifolane.^[13,14,15] The Isolongifoline epoxide undergoes novel rearrangement on treatment with 1 % HCl in CHCl₃ or on being exposed to active adsorbent (Al₂O₃ or SiO₂ Gel). The latter reaction leads to tetracyclic derivatives. These reactions fully substantiate the stereochemistry assigned earlier to isolongifoline epoxide. The reaction of isolongifoline epoxide with 1 % HCl in CHCl₃ has been investigated. This led to the formation of 8-oxoisolongifolane besides an olifinic secondary alcohol. The secondary alcohol is now shown to possess the structure. Likewise, it was noticed that isolongifolene epoxide on exposure to active adsorbent (TLC) rapidly rearranged. It is now shown that treatment of isolongifolene epoxide with active Al₂O₃ (or SiO₂-gel) results its isomerization to another secondary alcohol.^[13] The stereochemistry of isolongifolene is a subject of academic discussion and it is still not known beyond all doubt if the epoxide is, in fact or . In the author's opinion the structure is more probable.^[16] Novel compounds of use in perfumery are obtained by performing a Prins reaction on isolongifoline. They include novel primary and secondary alcohols, their esters and corresponding aldehydes and ketones. The Prins reaction involves the reaction of an aldehyde with olefin, preferably in the presence as *Catalyst of a Lewis acid or mineral acid*.^[17]

Extensive work has been carried out in synthesis of Isolongifoline ketone by using different medium and catalyst. The object of the present study is the synthesis of Isolongifoline ketone in presence of ion exchange catalyst which has several advantages over other method of synthesis of Isolongifoline ketone.

2. Experimental

2.1 Materials

Commercial Ion Exchange Resin- Tulsion T-421 (Thermax), Isolongifoline (camphor and Allied products Bareilly), Hydrogen peroxide, Acetic acid (Qualigen) were used. The details regarding the physical properties of resin used are given in Table 1.

Table 1 Characteristics of Ion Exchange Catalyst T-421 (Thermax)

Type	Strong acid cation exchange resin
Matrix Structure	Poly styrene divinyl benzene co-polymer
Functional group	Sulphonic acid
Ionic form	Hydrogen
Concentration of acid site	1.8 meq/ml (H ⁺)
Moisture content	Approx. 52 %
Particle Size	0.3-1.2mm
Max. operating condition	Max. 120 d.c.

2.2 Method

In a 1 lit. Three-necked round-bottom flask, equipped with a thermometer pocket and dropping funnel and mechanical stirrer. Water bath is used for heating purpose and temperature is maintained by thermostat regulator. Round-bottom flask is charged with 204 gm (1 mole) Iso-Longifoline, 180 gm (3 moles) Acetic Acid and 10 gm catalyst resin. Start the heating and temperature of reaction mixture is maintained at 30 – 35 °C, Dropping funnel is charged with 68 gm (1 mole) of 50 percent Hydrogen peroxide is added drop wise to solution with continuously stirring up to 1 hrs and temp is maintained below 50°C during addition of hydrogen peroxide by thermostat regulator. The reaction mixture is stirred throughout the entire course of the reaction and the reaction temperature was slowly raised and maintained at 55 – 60°C up to 5 hrs. Reaction mixture is transferred to beaker by decanting process and catalyst is remained in the reaction flask for further experimental run. Further three experiments were repeated by using the same remaining catalyst mass to check the catalytic performance, stability and recyclability with maximum use in 5 hrs reaction. The reaction mixture is withdrawn and washed with sodium bicarbonate solution and distilled to get pure Isolongifoline ketone.

2.3 Analysis of Reaction product (Reaction Monitoring)

Periodically, an aliquot of the reaction mixture was withdrawn and washed neutral and analyzed by Gas Chromatograph Nucon 5700 with following chromatographic condition-Column: FFPE-AT1000, Length: 1.5 meter. Initial temperature: 140 °C, Final Temperature: 230 °C, Rate: 4 °C @ minute, Detector- Flame Ionization Detector (FID), Temperature: 250 °C, Inj. Port Temperature: 230°C, Carrier Gas: Nitrogen, Rate- 30ml/min, Solvent: Acetone.

2.4 Washing and Distillation of Reaction product

The reaction mixture is transferred to separately funnel of 2 liters capacity and Organic layer is separated from aqueous layer. The organic mass is then successively washed with hot water (250 ml x 5), 10 % Sodium Carbonate Solution (50 ml x 2) and water (250 ml x 3) the organic layer is separated from the aqueous layer and dried over sodium sulphate. The reaction mixture of Isolongifoline Ketone is then made pitch free by pot-to-pot distillation under reduced pressure (3 mmHg), distillation is carried out with a 2: 1 reflux ratio. The reaction mixture is fractionated to get Isolongifone (117-130 °C/2 mm Hg), intercut (128 – 133 °C/2 mm Hg) and saturated Iso- longifoline ketone (132- 152 °C)

2.4 Characterization of the Isolongifoline Ketone

Characterization was done by following methods.

2.4.1. Fourier transforms infrared spectrophotometer (FTIR) Analysis

Fourier Transform Infrared (FTIR) spectra were collected on Thermo Nicolet Avatar 370 with a resolution of 4cm⁻¹ in the wavelength range of 400-4000cm⁻¹. A liquid sample was mixed with solvent Nujal mull.

2...4.2. GC-FID analysis of Isolongifoline Ketone

Sample of Isolongifoline ketone is analyzed by Gas Chromatograph Nucon 5700 with following chromatographic condition-Column: SE-30 capillary, Length: 30 mtr. Initial temperature: 140 °C, Final Temperature: 230 °C, Rate: 4 °C @ minute, Detector- Flame Ionization Detector (FID), Temperature: 250 °C, Inj. Port Temperature: 230°C, Carrier Gas: Nitrogen, Rate- 30ml/min, Solvent: Acetone.

2.4.3. GC-MS analysis:

The GC-MS spectra were collected on Varian 1200 L single Quadrupole fitted with column (WCOT fused silica stationary phase 2VF-5cms length 30m) coupled with mass detector under following condition: Helium as carrier gas, injector temp- 230 °C, oven temp 50 °C – 270 °C at 10 °C/min. The MS operating parameters were as follows : electron impact mode, 70 ev and ion source temperature 230 °C. Mass spectra were recorded over 10⁻⁸ -800 u range and scan range 1 – 3647, the identification of constituents was based on MS Library-NIST by comparing with the MS literature.

3. Results And Discussion

3.1. Synthesis of Isolongifoline Ketone

3.1.1. Reaction Scheme

Isolongifoline (ILF) on oxidation with Hydrogen peroxide in an acidic medium (Acetic Acid) in presence of ion exchange catalyst (strong protonic agent) gives Isolongifoline Ketone (Reaction 1, Figure 1)

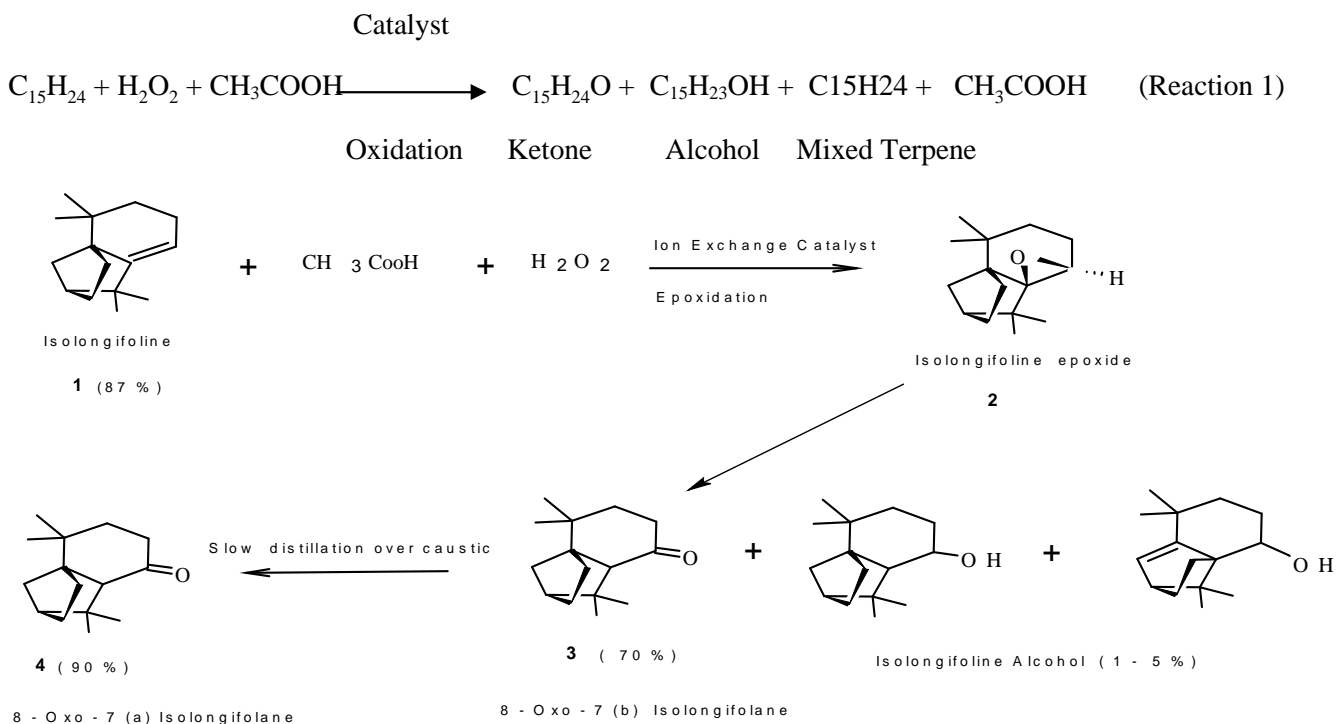


Figure 1: Synthesis of Isolongifoline Ketone

3.1.2 Proposed Reaction Mechanism

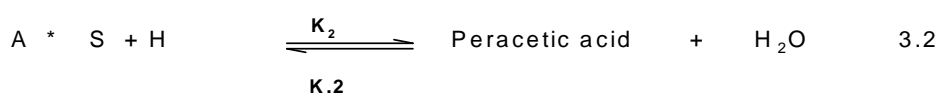
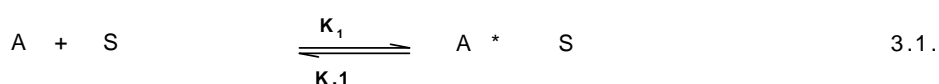
The principle difference between catalysis by homogeneous catalysts and by resins is that with resins catalysis overlaps with diffusion, adsorption and desorption processes. These effects depends on the nature of the matrix, reactant system and solvent (if any) used in the reaction. In order for the reaction to occur, the reactants must get to the active sites and the products must be removed. The different steps that may have an influence on the reaction rates are therefore analogous to those of any heterogeneously catalyzed reaction^[18] are as follows. Mass transfer of the reactants from the bulk fluid to the external surface of the resin particles. Diffusion of reactants from the pore mouth through the resin pores to the immediate vicinity of the counter ions. The catalyzed chemical reaction itself (referred to as the surface reaction) Diffusion of products from the interior of the resin to the external surface. Mass transfer of products from the external resin bead to the bulk fluid. The different rate controlling steps can be further complicated by the matrix structure of the specific resin as well its behavior in the particular reaction mixture of interest. The rate of a resin-catalyzed reaction will be function acidity as well as the accessibility of the sites. The acidity is a function of the type and the number of acid groups on the polymer matrix, degree of crosses linking as well the reaction medium. Accessibility is a function of degree of cross linking, particle size, porosity, reaction medium, diffusivity of reactants and products.^[19]

Temperature gradients might exist within the particle, which may also influence the rate of the overall reaction. In the same manner, a temperature gradient can exist across the external film. Temperature gradients exist in the particle catalyst T-421H and Indion 225 indicate the different reaction temperature condition. No conversion observed at temp 40⁰ c in catalyst T-421H, however reaction observed in Indion 225 at temp 40⁰ c.

In heterogeneous catalysis, adsorption of reactants, chemical reaction and desorption of the products are steps that occur in series and all are grouped together under the term surface reaction.^[20] Resin catalysis use either a pseudo-homogeneous or a pseudo-heterogeneous approach in liquid phase surface reaction. The pseudo-homogeneous model is based on the theory that the counter ions (H⁺) are mobile and solvated and thus in a condition which is, in principle, not different from that in a corresponding homogeneous solution. The reaction mechanism in homogeneous catalysis by dissolved electrolyte and heterogeneous catalysis is then essentially the same and the only difference between homogeneous and heterogeneous catalysis is the internal and external diffusion processes. The idealized homogeneous case requires complete swelling of the matrix. In the presence of polar compounds, solvation of polymer-bound- SO₃H takes place. This means that the - SO₃H groups are totally dissociated. The H⁺ ions can move freely in the liquid within the pores and act as the active centers while the - SO₃⁻ ions remains fixed on the polymer surface. The reaction mechanism is assumed to be the same as one observed with the electrolyte but confined to the liquid within the catalyst mass. This approach is particularly applicable in cases where the reactant or the reaction solvent is strongly polar^[21]

The negatively charged polymer, although not directly involved in the catalytic activation of substrate, now forms a special microenvironment for the catalytically active centers.^[22] The actual concentration of the different components of the reaction mixture in the resin phase may not be the same as the bulk solution- even in the absence of any mass transfer effects. There may be preferential distribution of some of the components depending on their compatibility with resin phase microenvironment due to the preferential association of specific molecules with the negatively charged matrix.

The mechanism route of oxidation reaction catalyzed by cross-linked polystyrene-divenylbenzene sulphonic acid (Figure 2) shows that first mechanism step involves protonation of carbonyl oxygen on carboxylic group. Second step is the nucleophilic attack of the hydrogen peroxide to yield a tetrahedral intermediate. Third step a proton is lost at one oxygen atom and gained at another to form another intermediate, which further loses a molecule of water that gives peracetic acid. In final step, Peracetic acid act as oxidizing agent and react with Isolongifoline to form isolongifoline epoxide and acetic acid. Hence, rapid reactant adsorption/desorption equilibrium with surface reaction as the rate-limiting step (3.2) is likely the initial reaction mechanistic paths under our reaction, which are shown as below.



Where H represents Hydrogen peroxide, A represents Acetic acid. S is a vacant acid site on the solid catalyst surface. The catalytic reaction of the peracetic acid formation is characterized by adsorption of only acetic acid and peracetic acid on the active catalyst site, and irreversible surface reaction is the overall rate-determining step. In conventional preparation of isolongifoline epoxide, reaction takes place via formation of peracetic acid by reaction of acetic acid and hydrogen peroxide, heterogeneous acidic catalyst (Resin). This reaction of peracetic acid formation is reversible, which proceed to an equilibrium between reactants and Peracetic acid, The concentration of isolongifoline epoxide varied with the concentration of Isolongifoline to Hydrogen peroxide used and the molar ratio of Acetic acid to Hydrogen peroxide and loading of catalyst in different ratio. The epoxidation is a heterogeneous catalytic process characterized by the presence of a solid phase (catalyst), an aqueous phase (acetic acid, hydrogen peroxide, and water) and an isolongifoline.

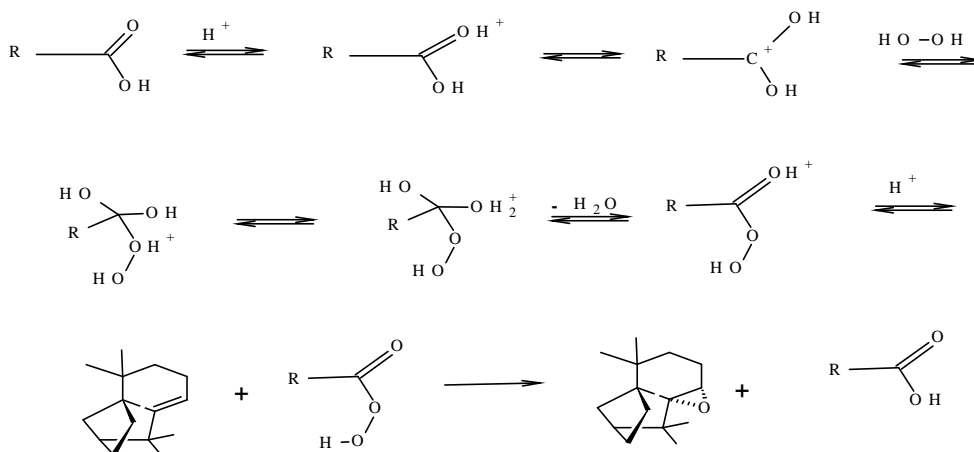


Figure 2: Mechanistic Route of acid catalyzed Epoxidation Reaction

Isolongifoline epoxide undergoes novel rearrangement on treatment with sodium bicarbonate solution. This leads to the formation of a ketone **3** (approx. 70%) readily identified as 8-oxo-7-H-isolongifolane (**3**) and the olefin secondary alcohol (1-5%) by way of a Wagner-Meerwein rearrangement. Ketone **3** on slow distillation over caustic to form ketone **4** (Approx 90%) readily identified as 8-oxo-7-H-isolongifolane (Figure 3)

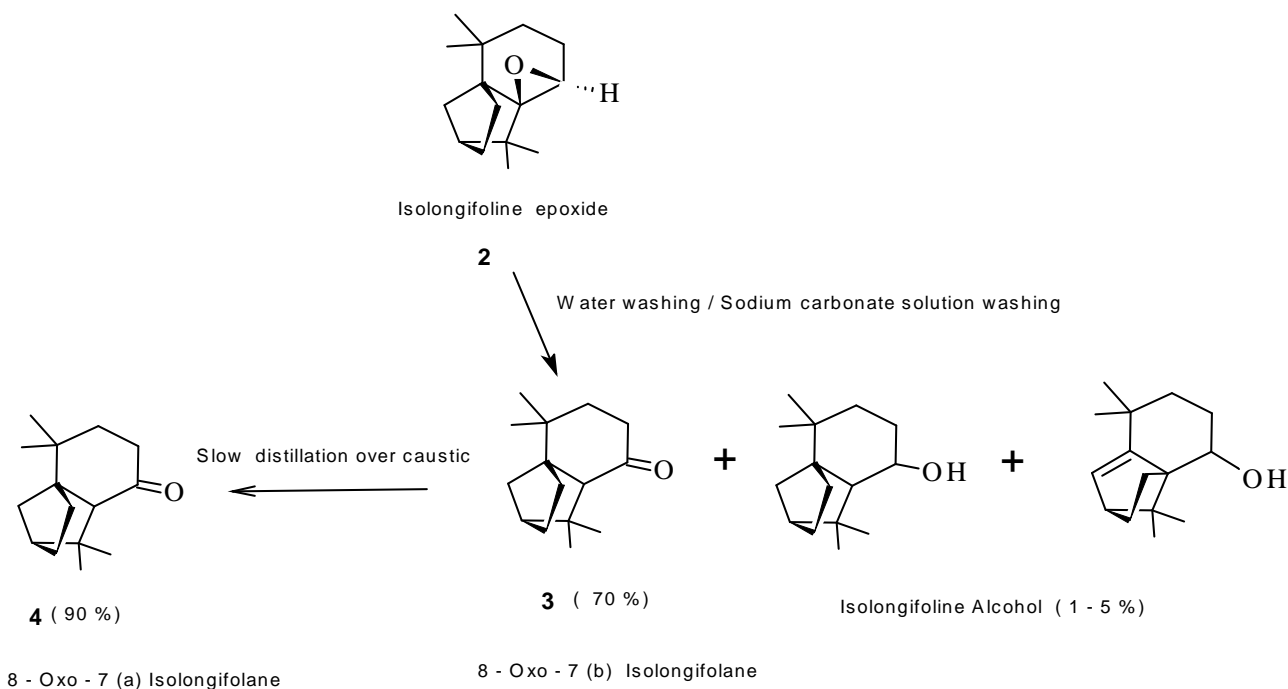


Figure 3: Rearrangement of Isolongifoline Epoxide

Epoxidation of isolongifoline with per acids yields the -epoxide. This epoxide on rearrangement produces the saturated ketones - 8-oxo-7-H-Isolongifolane. The Epimerization of this ketone to the 7 () H derivative is simple and this ketone is also of perfumery use as it possesses a sweet woody odour. The rearrangement of isolongifoline epoxide has been reported to yield two , -unsaturated alcohols, the rearrangement of the epoxide ; under most reaction conditions these alcohols are formed in less than 5% yield, the main product is 8-oxo-7- -H-isolongifolane. In our experiments reaction mixture is washed with hot water and sodium carbonate to obtain saturated ketone **3** (Epimer I), In Epimerization process washed isolongifoline ketone distilled over caustic to get more stable ketone **4** (Epimer II).

3.1.3 Analysis of Reaction sample

An aliquot of the reaction mixture was withdrawn and washed neutral and analyzed by Gas Chromatograph, yield and selectivity of ketone is shown in Table 2 and Figure 4. Selectivity of ketone is good and catalyst shows good re-cyclability as catalyst.

Table 2: Conversion & Selectivity of ILF Ketone over Catalyst Thermax T-421 H in different reaction cycle

Reaction cycle	Purity of ILF (%)	Selectivity of ketone (%)
1	87.01	90.05
2		89.44
3		84.55
4		81.45

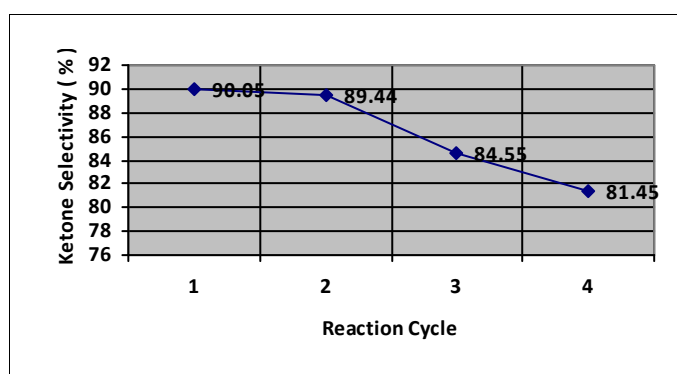


Figure 4: Selectivity of ILF Ketone over Thermax T-421H in different Reaction cycle

3.3. Characterization of Isolongifoline and Isolongifoline Ketone

3.3.1 Fourier transform infrared spectrophotometer (FT-IR) Analysis

Figure 5 shows the FT-IR spectra of Iso-Longifoline. The isolongifolene is subjected to infrared (IR) spectroscopy and shows a gem-dimethyl absorption at 1370 cm^{-1} , and an absorption attributable to a methylene group at 1458 cm^{-1} .

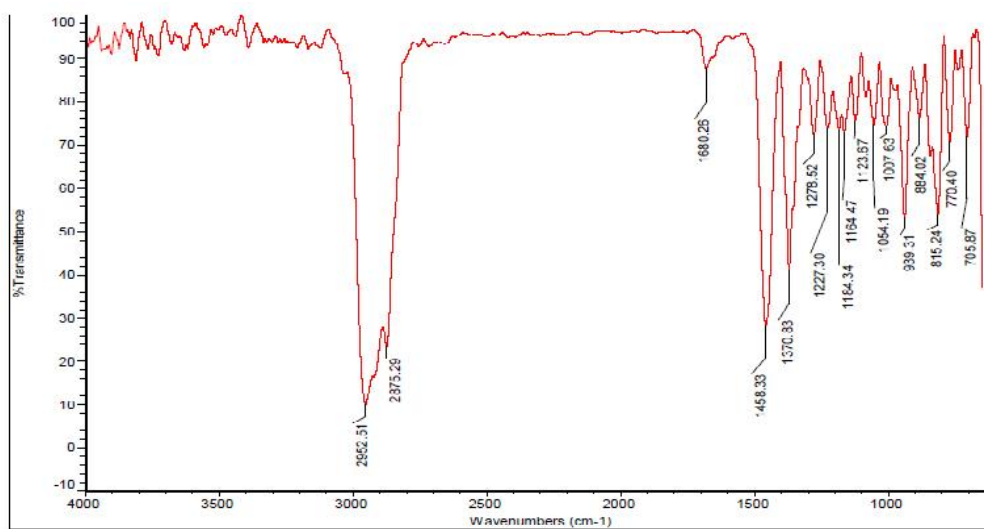


Figure 5: FT-IR spectra of Iso-Longifoline Ketone

Figure 6 shows the FT-IR spectra of Isolongifoline Ketone. Isolongifoline Ketone is the product of oxidation of Isolongifoline. The purified saturated isolongifolene ketone is subjected to infrared (IR) spectroscopy and shows a carbonyl absorption at 1695 cm^{-1} , gem-dimethyl absorption at 1375 cm^{-1} , and an absorption attributable to a methylene group at 1462 cm^{-1} adjacent to a carbonyl group.

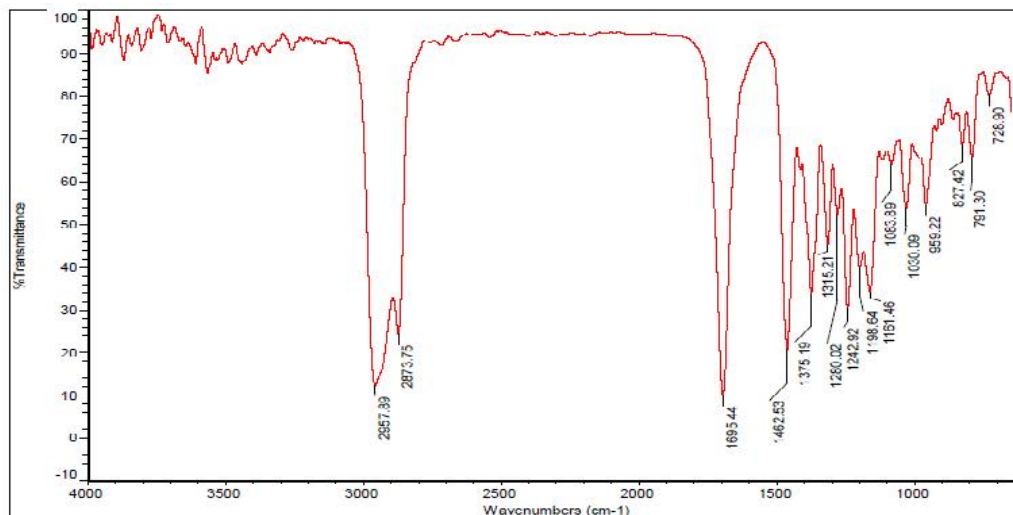


Figure 6: FT-IR spectra of Iso-Longifoline ketone

3.3.2. GC-FID analysis of Isolongifoline Ketone

GC-FID is very useful tool to analyze the sample of known constituents. GC-FID chromatogram of the Ketone sample is shown in figure 7. The main component of sample are Ketone 1 (8-oxo-7-H-isolongifolane) and Ketone 2 (8-oxo-7-H-isolongifolane). The results of GC-FID analysis indicate the purity of ketone containing 15.80% Ketone 1 and 77.17% Ketone 2. Peak of both ketone is very close at RT 16.14 (ketone 1) and RT 17.19 (ketone 2), it indicates the incomplete conversion of ketone 1 to ketone 2 during distillation.

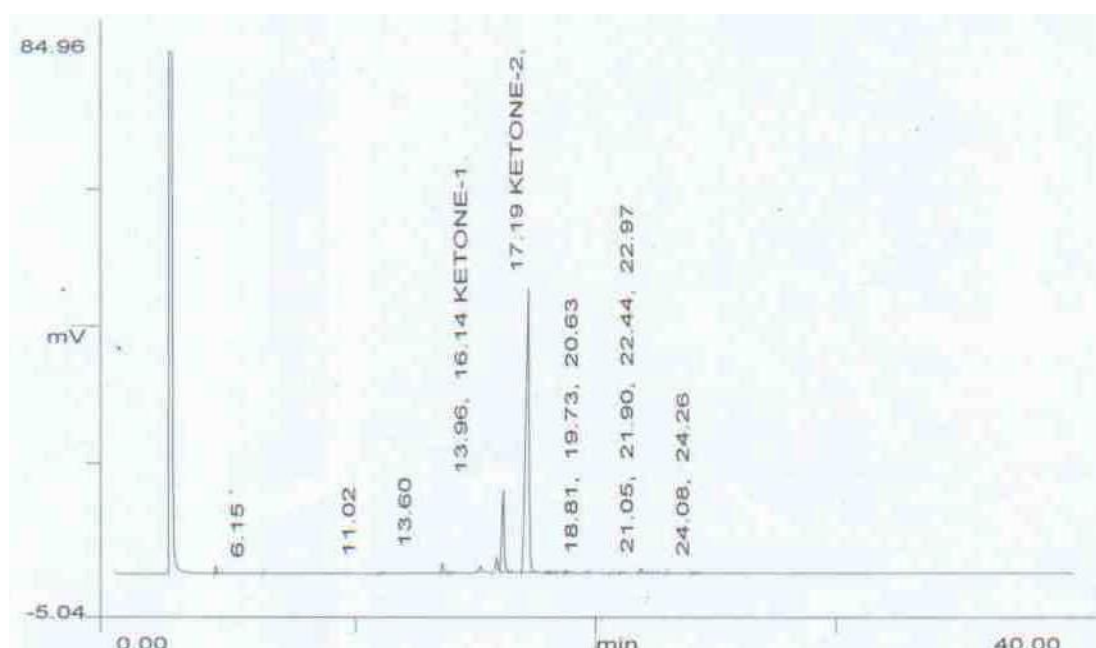


Figure 7: GC-FID chromatogram of Isolongifoline Ketone

3.3.3. GC-MS analysis of Isolongifoline Ketone

The GC-MS is very useful tool for analysis, the chemical constituents of the sample were analysed by GC-MS. GC-MS analysis lead to identification of one major component namely Isolongifoline ketone (RT- 19.05), and other minor component Isolongifoline alcohol (RT- 17.55) and isolongifoline epoxide (RT-17.91). The total ion chromatogram (TIC) of the Ketone sample is shown in figure 8. Sometime identification is limited when a single chromatographic peak contains several compounds so that the recorded mass spectra are difficult to interpret however the presence of minor constituents confirmed based on MS Library search NIST by comparing with the MS literature data. The main component of sample is the Isolongifoline ketone, the percentage composition of individual components of major peak (Isolongifoline Ketone peak) was computed from GC-MS data based on MF and RMF and shown in Table 3. The major peak contains high percentage of Isolongifoline ketone constituting 90.70% followed by other oxygenated sesquiterpenes ketone constituting of 5.52% major peak composition. Figure 9 – 11 shows the structure and mass spectra of Isolongifoline ketone, Isolongifoline alcohol and Isolongifoline epoxide.

Table 3: Main chemical constituents of the Major peak (Ketone peak)

Compound	Prob%	MF	RMF
Isolongifoline Ketone	90.70	913	913
2R,6s-2,6,8,8-Tetramethyltricyclo [5.2.2.0(4,6)] undecan-3-one	1.85	739	739
2H-2,4a-Ethanonaphthalen-8(5H)-one, hexahydro-2,5,5-trimethyl-	1.38	731	753
Neoclovene oxide	1.00	722	722
4a,7-Methano-4aH-naphth [1,8a-b]oxirene, octahydro-4,4,8,8-tetramethyl-	0.78	716	716
9-Cedranone	0.66	712	712
Cyclopenta[c]pentalen-3(3aH)-one, octahydro-1,2,3a,6-tetramethyl-	0.66	712	712
1,4-Methanoazulen-7(1H)-one, octahydro-1,5,5,8a-tetramethyl-	0.50	705	705
1,4-Methanoazulen-9-one, decahydro-1,5,5,8a-tetramethyl-, [1R-(1,3a,4,8a)]-	0.47	703	703
2H-2a,7-Methanoazuleno[5,6-b]oxirene, octahydro-3,6,6,7a-tetramethyl-	0.39	699	699

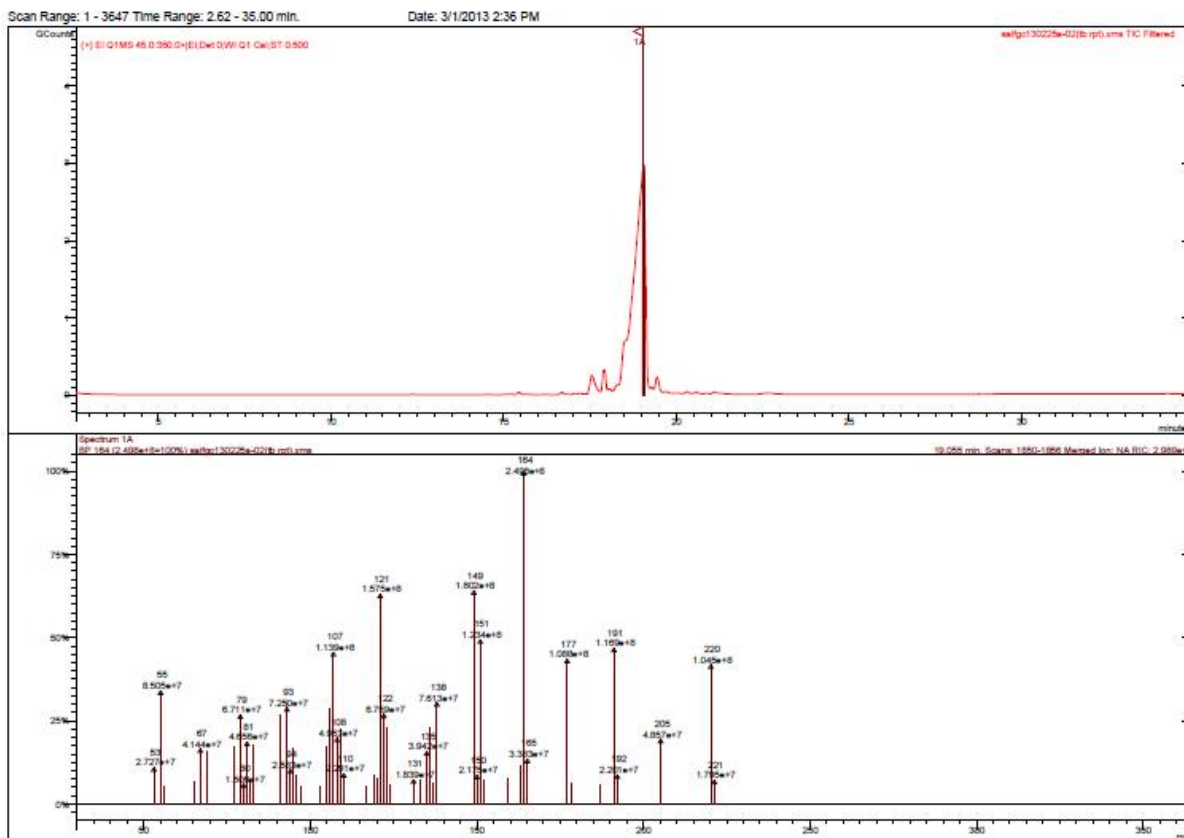


Figure 8: GC-MS Total ion chromatogram (TIC) of the Ketone sample showing three major chemical constituents

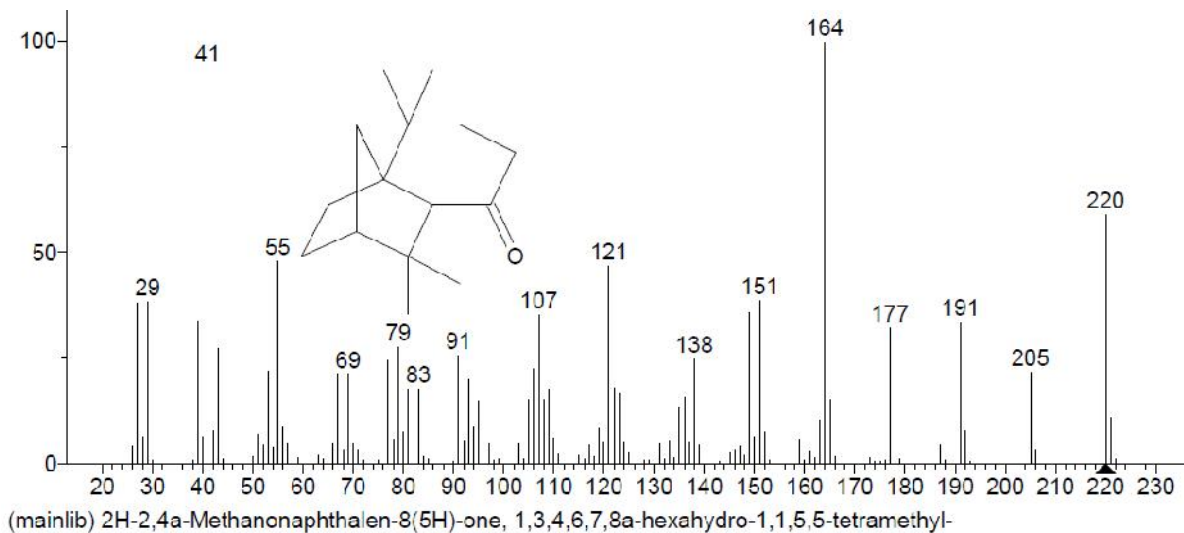


Figure 9: Structure and mass spectra of Isolongifoline Ketone

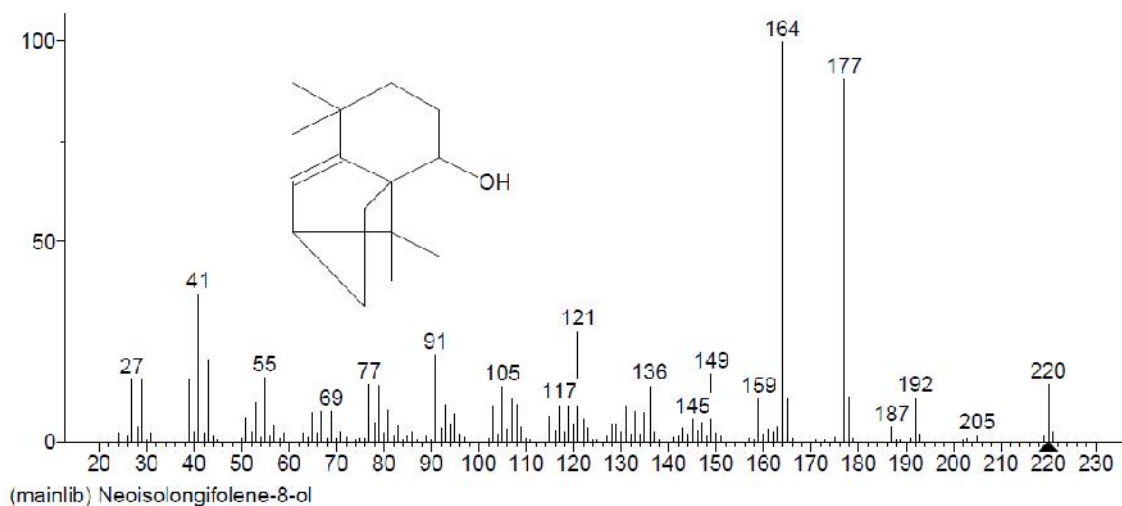


Figure 10: Structure and mass spectra of Neisolongifoline alcohol

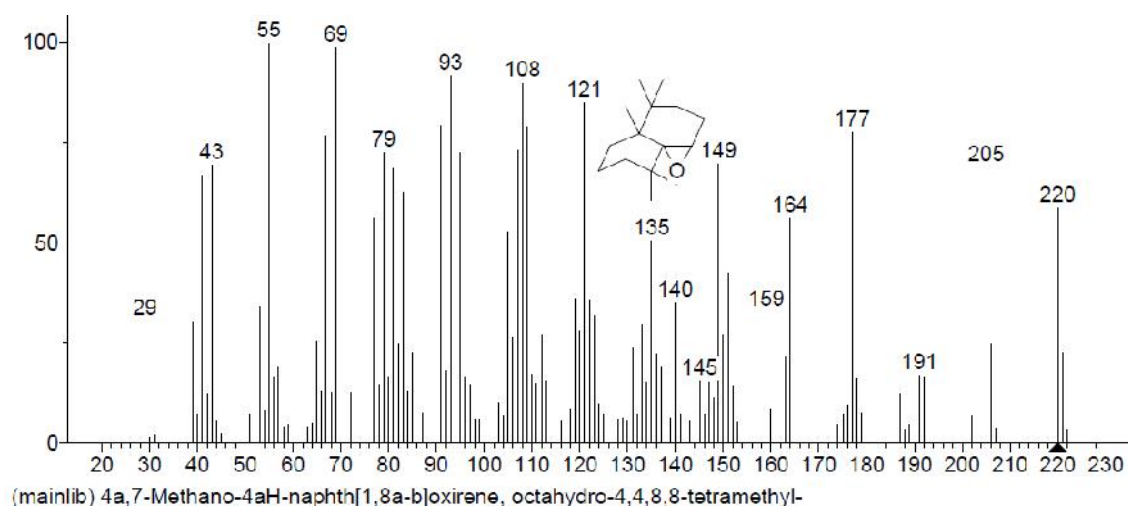


Figure 11: Structure and mass spectra of Isolongifoline epoxide

Conclusion:

In this work Isolongifoline ketone have been synthesised by using cation ion exchange resin as catalyst. The conclusion that have been drawn that Ion exchange resin can be used as catalyst in epoxidation reaction and shows good yield of isolongifoline ketone in reaction. Under the action of catalytic system described in this paper the process of Isolongifoline oxidation on the one hand and the epoxidation on the other hand is induced by different intermediate species. Isolongifoline epoxide undergoes novel rearrangement on treatment with sodium bicarbonate solution which lead the formation a ketone 8-oxo-7-H-isolongifolane (approx.70%) and the olefinic secondary alcohol (1- 5%) by way of a wagner-Meerwein rearrangement. The Ketone 8-oxo-7-H-isolongifolane on slow distillation over caustic to form 8-oxo-7-H-isolongifolane. The characterization of sample was carried out by FTIR, GC-FID, GC-MS analysis, The results of GC-FID analysis indicate the purity of ketone containing 15.80 % Ketone I (8-oxo-7-H-isolongifolane) and 77.17% Ketone 2 (8-oxo-7-H-isolongifolane). The IR spectra of purified saturated isolongifolene ketone shows a carbonyl absorption at 1695 cm^{-1} , gem-dimethyl absorption at 1375 cm^{-1} , and an absorption attributable to a methylene group adjacent to a carbonyl group at 1462 cm^{-1} . GC-MS is very useful tool for analysis of sesquiterpene derivatives and it is much easier to identify the peaks of chromatogram without standard. GC-MS analysis lead to identification of 3 major component namely Isolongifoline ketone, Isolongifoline alcohol, and isolongifoline epoxide. The main component of sample is the Isolongifoline ketone. The major peak contains high percentage of Isolongifoline

ketone constituting 90.70% followed by other oxygenated sesquiterpenes ketone constituting of 5.52% major peak composition.

Acknowledgement:

The Authors are thankful to Dr. R.B.Singh, Head of the department of chemistry and Dr. R.P.Singh, Principal, Bareilly College Bareilly for providing facility to carry out research work. The Authors also thank STIC, Cochin University, Cochin for FTIR and GC-MS analysis.

References

1. U.R.Nayak, S.Dev (1960). Tetrahedron 8,42-48
2. R.E Beyler, G.Ourisson, J. (1965). Org.Chem. 30, 2838-2839
3. R.Ranganathan, U.R.Nayak, T.S.Santhankrishnan, Dev Sukh (1970). Tetrahedron 26, 621-630.
4. Johan B, Hall, Oakhurst, N.J. (1973). International flavors & Fragrances Inc., New York, N.Y. US Patent 3,718,698, 19, 11.
5. Fawen Wu, Zhinhong Xu, Zhixing wang, Yiqiang Shi, Zhibing Zhang (2010).Chemical Eng. Journal, 158, 426-430.
6. Patricia A Robles-Dutenhefner, Kelly A. da Silva rocha. Edesia M.B. Sousa and Elena V. Gusevskaya, (2009).Cobalt-catalyzed oxidation of terpene:Co-MCM-41as efficient shape Selective heterogeneous catalyst for aerobic oxidation of isolongifoline under solvent free conditions: Journal of catalysis, 265, 72-791.
7. Jason et al (1962).260/568 BX patent 3,042,722 7.
8. Mitchell et al(1956). 260/586BX Patent 2,770,637 11.
9. Thigpen et all (1970). 260/586 BX Patent 3,522,278 7.
10. Journal of agricultural and food chemistry (1994). ISSN 0021-8561, coden:jafcau, 42 (1) 138-142.
11. K.S. Ravikumar, Jean-Pierre Begue, Daniele Bonnet- Delpont, Michele Qurevitch (2000) (Laboratories Biocis Associeau CNRSN CENTRE D'Etvdes Pharmaceutiques 92296, Chalenary Malabry France Journal of Fluorine Chemistry 102 51 –53 (Eng.) Elsevier Science S.A. Chemical Abstract: 133, 17647d, 133(2), 666.
12. Zhang: Aiiun (silver spring MD), Caroll; John (Beltsville MD), Wang; Shifa (Nanjing, CN) Klun; Jerome A, protomac, MD (2008).Patent 7378557.
13. Santhanakrishnan T.S.; Sobti, R.Nayak, U.R.and Dev Sukh, Tetrahydron, (1970). 26, 657.
14. Eshinasi, F.H.Shaffer, G.W. and Warteles, A.P. (1970).Tetrahedron Lett. 3523.
15. Lala, L.K and Hall, J.B.J. (1970).org. Chem., 35.
16. Banthorpe, D.V.Curtis, A.J. and Fordham, W.D. (1972).Tetrahedron Lett, 3865.
17. Hifzur Rahman Ansari, Rayleigh; Nerville Unwin, surbiton; Horst Richard Wagner, woodford Green, all of England (1978).US Patent 4,100,110.
18. Fogler, Scott.H. (1999). Elements of chemical Reaction Engineering, 3rd Ed. Prentice Hall, New Jercey, 592.
19. Chakrabarti, A. and Sharma, M.M. (1993).Cationic exchange resins as catalysis, Reactive Polymers, 20 (1-2) 1-45.
20. Gates, Bruce, C. (1992). Catalytic chemistry John Wiley & Sons, Inc., 187.
21. Khan, S.H., Rahman, K. (1996). Inversion of sucrose solution by ion exchange: evaluation of Reaction rate and diffusivity "The chemical Engineering Journal, 61, 7-12.
22. Tejero, J.Chunhil, J.F., Iborra, M., Fite, C. and Parra, D. (1996). Scope and limitations of Mechanistic inferences from kinetic studies on acidic macro porous. The MTBE Liquid Synthesis case "Applied catalysis A: General, 134, 21-36.
