

Synthesis and Characterization of Isolongifoline and Acetyl longifoline

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Abstract: Isolongifoline was synthesised as a main component by Longifoline with the application of ion exchange catalyst–Indion 140. Actylation of longifoline with acetic anhydride in presence of cation ion exchange resin as catalyst yielded Isolongifoline and Acetyl longifoline. Isolongifoline and acetyl longifoline were achieved by washing with sodium bicarbonate and slow fractional distillation. The GC-FID, FT-IR and GC-MS analysis of sample lead to identification and purity of components in the reaction sample and purified sample. The reaction sample contains Isolongifoline (54.68%) followed by Acetyl longifoline (6.06%) and other terpene derivative, the purified sample of Isolongifoline contains high percentage of Isolongifoline (94.30 %) followed by Longifoline and other sesquiterpenes. The sample of Acetyl longifoline contains high percentage of Acetyl longifoline (33.91 %), Longifoline methyl ether (15.91%) followed by other sesquiterpene derivatives.

Key Words: Ion exchange Resin, Catalyst, Isolongifoline, Acetyl longifoline.

1. Introduction

Longifolene, C₁₅H₂₄ (decahydro-4, 8, 8-trimethyl-9-methylene-1-4-methanoazul ene), is present in the Indian turpentine oil obtained from Chirpine (*Pinus long folia*) to the extent of 5–7%. The economical utilization of this terpene hydrocarbon involves its transformation into isomeric product iso-longifolene and its derivatives, which have extensively used in perfumery industry due to their woody and floral odor. 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] The isomerization of longifoline to Isolongifolin in the presence of calys-montmorillonite, pillared clay and modified pillared clay was studies. The use of Al- and Zr-pillared clays at 180°C yielded reaction mixture with more than 70 % Isolongifoline.^[4] The isomerization of longifolene^[5] using montmorillonite clay K10 as catalyst at 120°C with 100% selectivity and more than 90% conversion. The synthesis of isolongifolene^[6] from acid catalyzed hydration of longifolene using acid treated silica gel. The synthesis of isolongifolene^[7] from camphene-1-carboxylic acid using multi-step process. The preparation of isolongifolene^[8] has been reported by hydration of longifolene using acetic acid and sulphuric acid in dioxane. The acid catalyzed rearrangement of longifolene^[9] to isolongifolene using bromoacetic acid. A new process preparing isolongifoline^[10] isomerizes directly from heavy turpentine oil in presence of catalyst Gon-4/ TiO₂

(A).The catalytic process for preparation of isolongifolene^[11] using nanocrystalline solid super acid. The Synthesis of Isolongifoline^[12] with solid super acid catalyst -TiO₂ modified with persulphate:-TiO₂/S₂O₈²⁻ a solid super acid was used to catalyse the isomerization of longifoline.Acetyl longifoline and hydroxymethyl longifoline. Acetyl Longifoline is prepared by Friedal-craft reaction and has woody-muskey ambergris reminiscent of acetyl cedrone. ^[13]Extensive work has been carried out in synthesis of Isolongifoline by using different medium and catalyst, limited work has been carried out for the synthesis of Acetyl longifoline. The object of the present study is the synthesis and characterization of Isolongifoline & Acetyl longifoline in presence of ion exchange catalyst which has several advantages over other method of synthesis of Isolongifoline and acetyl longifoline.

2. Experimental

2.1 Materials

Commercial Ion Exchange Resin- Indion-140 (Ion Exchange India), Longifoline (camphor and Allied products Bareilly), Acetic anhydride (Qualigen) were used. The details regarding the physical properties of resin used are given in Table 1.

Table 1 Characteristics of Ion Exchange Catalyst Indion 140

1	Appearance	Opague grey bed
2	Type	Strong acid cation exchange resin
3	Matrix Structure	Poly styrene divenyl benzene co-polymer
4	Functional group	Sulphonic acid
5	Ionic form	Hydrogen (H+)
6	Concentration of acid site	4.8 meq/ dry gram
7	Moisture content	Max. 1 %
8	Particle Size	0.42 – 1.2 mm
9	Max. operating condition	Max. 150 d.c

2.2 Method

In a 1 lit. Two-necked round-bottom flask, equipped with a thermometer pocket and and fractionating column. Oil bath is used for heating purpose and temperature is maintained by thermostat regulator. Raw material Longifoline (306 gm = 1.5 moles), Acetic Anhydride (204 gm = 2 mole) Indion 140 resin (15.3 gm = 3% of Total feed) are charged. Initially the pressure is adjusted to 150mmHg. The reaction mixture is magnetically stirred throughout the entire course of the reaction and the reaction temperature was slowly raised and maintained at 80 – 90⁰C.The acetic acid formed in the reaction is continuously fractionated out. The system pressure is gradually reduced from 150 mmHg to 25 mmHg, maintaining a steady reflux rate at a pot temperature of 80-90 ⁰C.Reaction is carried out up to 25 hrs. A reflux ratio of 20: 1 was used for fractionating the acetic acid formed in the reaction.

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:1.5meter. Initial temperature: 140 ⁰C, Final Temperature: 230 ⁰C, Rate: 4 ⁰C @ minute, Detector- Flame Ionization Detector (FID), Temperature: 250 ⁰C, Inj. Port Temperature: 230⁰C, 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 & acetyl longifoline 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 Acetyl longifoline (132- 152 °C)

2.5 Characterization of Isolongifoline and Acetyl longifoline

Characterization was done by following methods.

2.4.1. 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

Purity of samples was analyzed by Gas Chromatograph Nucon 5700 with following chromatographic condition- Column: DB-Wax capillary, Length: 30 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.

2.4.3. GC-MS analysis

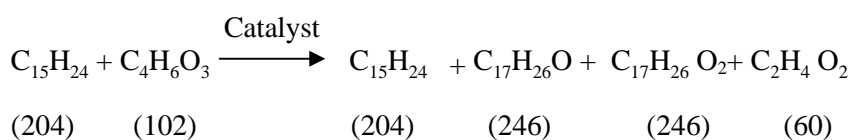
The GC-MS spectra were collected on Varian 1200 L single Quadrupole fitted with column (WCOT fused silica stationary phase 2VF-5cms length 30m) coupled with mass detector under following condition: Helium as carrier gas, injector temp- 230 °C, oven temp 50 °C – 270 °C at 10 °C/min. The MS operating parameters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

3. Results and Discussion

3.1. Synthesis of Isolongifoline and Acetyl longifoline

3.1.1. Reaction Scheme

Longifoline on reaction with Acetic Anhydride by using cationic Ion Exchange catalyst gives a mixture of Isolongifoline, Longifoline Acetate, Longifoline ether and acetic acid produced during the reaction. (Fig. 3.1)



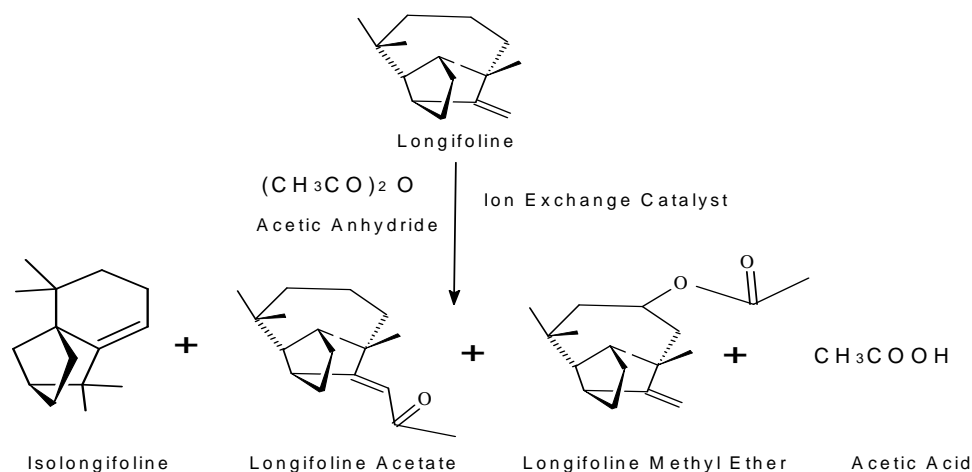


Figure 3.1 Synthesis of Isolongifoline and Longifoline derivatives

3.1.2 Proposed Reaction Mechanism

The reaction medium is not sufficiently polar, the $-\text{SO}_3\text{H}$ groups remain undissociated. In this case a simple homogeneous model may not fit the data adequately and a pseudo-heterogeneous approach is suggested. ^[14]

The reaction mechanism of isomerisation of Longifoline to Isolongifoline is shown in Figure 3.2 the idealised heterogeneous state is characterised by a direct interaction of the reactant with the polymer fixed acid. The degree of adsorption is limited by the fraction of accessible groups of the surface of the polymer. The exclusive interaction of the substrate with the surface requires a very hard, highly cross linked polymer and the absence of swelling. However in the real situation swelling cannot be completely excluded. Therefore the term quasi- or pseudo-heterogeneous catalysis is appropriate. In this case the catalytic agent is the sulphonic group itself, and from a molecular point of view the reaction occurs by concerted cyclinal mechanism with proton transfer. ^[15]

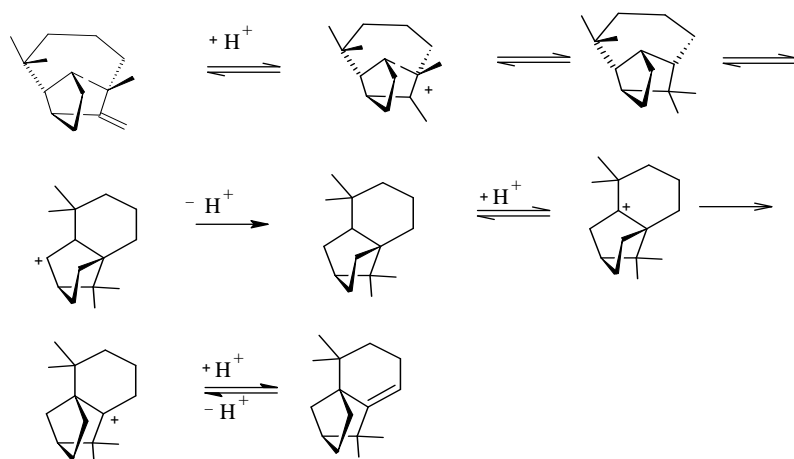


Figure 3.2 Acid Catalyzed Rearrangement of Lonifoline

Proposed reaction mechanism of acylation of Longifoline to Acetyl longifoline is shown in Figure 3.3, this is simply fridel craft acylation process.

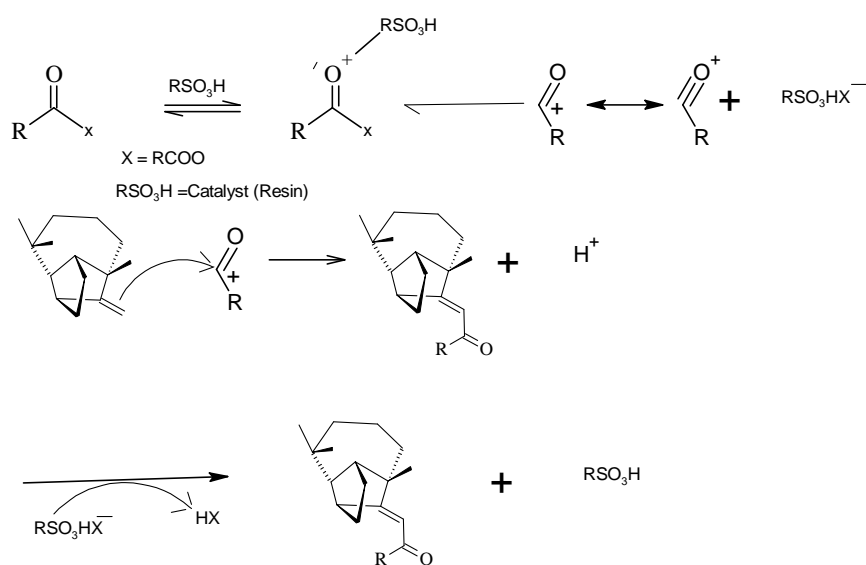


Figure 3.3 Reaction Mechanism of Acylation process in Longifoline

3.1.3 Analysis of Reaction sample

An aliquot of the reaction mixture was withdrawn and washed with Sod. Bicarbonate solution, make neutral and analyzed by Gas Chromatograph, yield of Isolongifoline and Acetyl longifoline is shown Table 3.1; the yield of Acetyl longifoline is very low because isomerization process goes simultaneously from Longifoline to isolongifoline.

Table 3.1: Catalytic conversion of longifoline over Catalyst Indion-140

Fraction	Feed Analysis Results	GLC profile (% age) in Reaction Time in Hrs				
		8 hrs	10 hrs	15 hrs	20 hrs	25 hrs
Longicyclene etc.		1.44	0.57	1.18	1.31	1.45
Isolongifoline		50.92	51.73	53.63	53.95	54.68
Longifoline		27.62	26.25	22.25	20.89	20.51
Low Boilers		9.05	9.32	9.43	9.34	9.32
Longifoline methyl ether		2.05	2.16	2.34	2.34	2.43
Unknown		4.09	5.05	5.08	5.65	5.86
Acetyl longifoline		4.53	4.55	5.65	6.05	6.06
High Boilers		0.33	0.37	0.44	0.47	0.66

3.2. Characterization of Isolongifoline and Acetyl Isolongifoline

3.2.1 FT-IR Analysis of Isolongifoline

Figure 3.4 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}

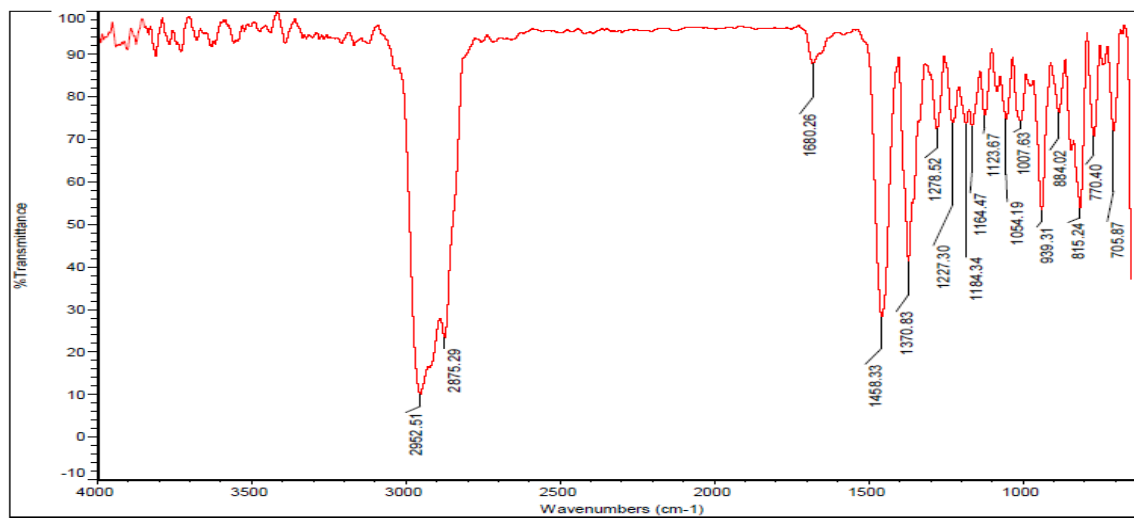


Figure 3.4 FT-IR spectra of Iso-Longifoline

3.2.2 FT-IR Analysis of Acetyl Longifoline

Figure 3.5 shows the FT-IR spectra of Acetyl Longifoline. Acetyl Longifoline is the main product of acetylation of Longifoline. The purified mixture of Acetyl longifoline is subjected to infrared (IR) spectroscopy and shows a carbonyl absorption at 1692 cm^{-1} , gem-dimethyl absorption at 1375 cm^{-1} , and an absorption attributable to a methylene group at 1457 cm^{-1} adjacent to a carbonyl group.

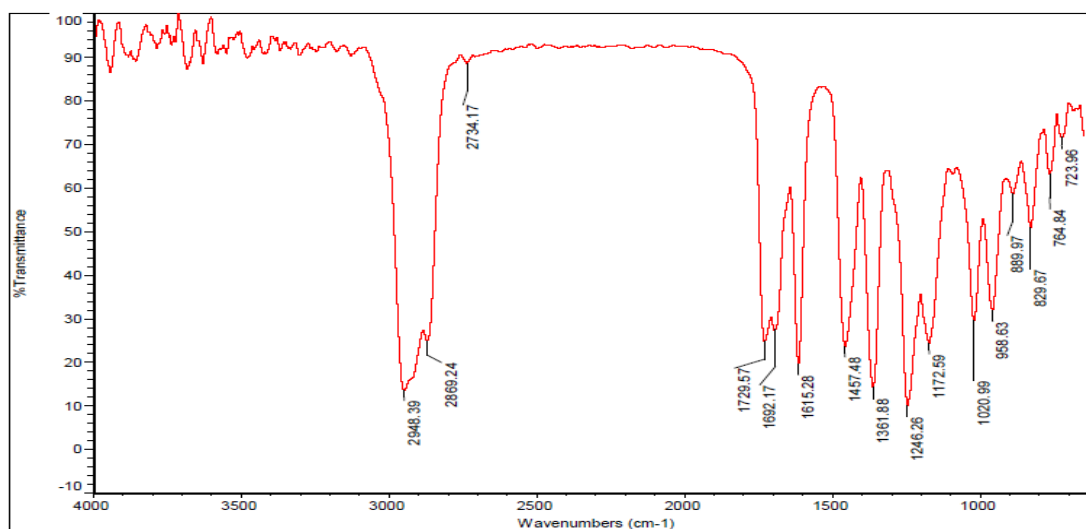


Figure 3.5 FT-IR spectra of Acetyl-Longifoline

3.2.3. GC-FID analysis of Isolongifoline

GC-FID chromatogram of the Isolongifoline sample is shown in figure 3.6. The main component of sample are isolongifoline (2H-2,4a-Methanonaphthalene, 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-, (2S)-) and longifoline. The results of GC-FID analysis indicate that sample is containing 94.30 % Isolongifoline and 0.89 % Longifoline and other terpens.

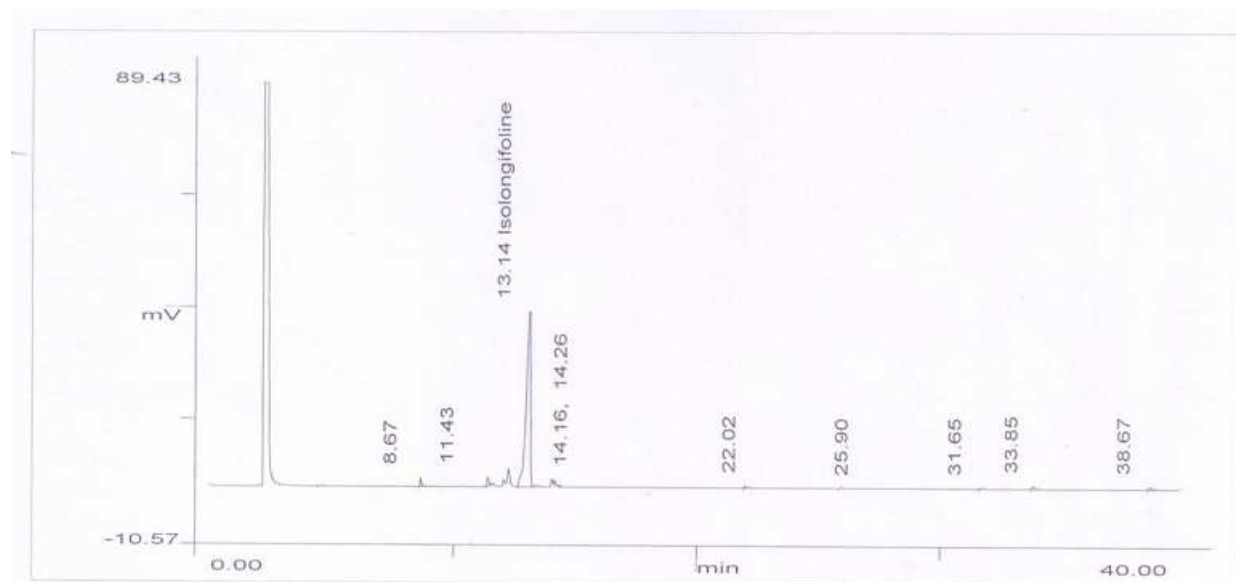


Figure 3.6 GC-FID chromatogram of Isolongifoline

3.2.4. GC-FID analysis of Acetyl longifoline

GC-FID chromatogram of the acetyl longifoline sample is shown in figure 3.7. The main component of sample are longifoline methyl ether and acetyl longifoline (Ethanone, 1-(1,2,3,4,7,7a-hexahydro-1,4,4,5-tetramethyl-1,3a-ethano-3aH-inden-6-yl)-) The results of GC-FID analysis indicate that sample is containing 15.91 % longifoline methyl ether and 33.91% acetyl longifoline and other derivatives of acetylation.

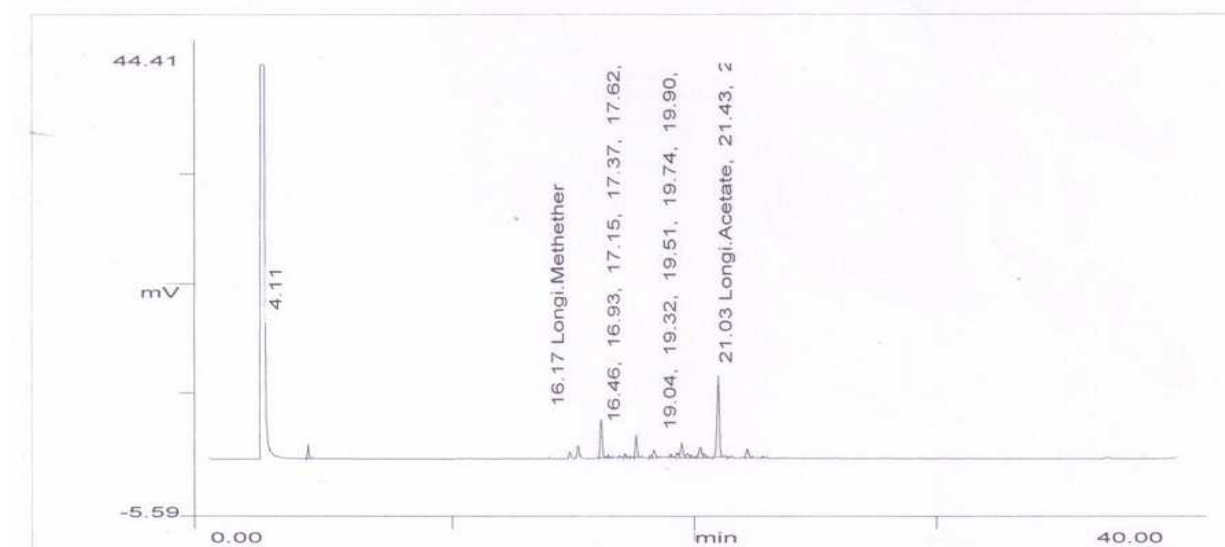


Figure 3.7 GC-FID chromatogram of Acetyl longifoline

3.2.5. GC-MS analysis of Isolongifoline

The chemical constituents of the sample were analysed by GC-MS. GC-MS analysis lead to identification of 2 major components namely longifoline (RT- 15.23), Isolongifoline (RT- 15.63) the total ion chromatogram (TIC) of the isolongifoline sample is shown in figure 3.8. The percentage composition of individual component was computed from GC-MS data based on MF and RMF, The structure and mass spectra of Isolongifoline (RT- 15.63), longifoline (RT- 15.23) are shown in figure 3.9 and 3.10 respectively.

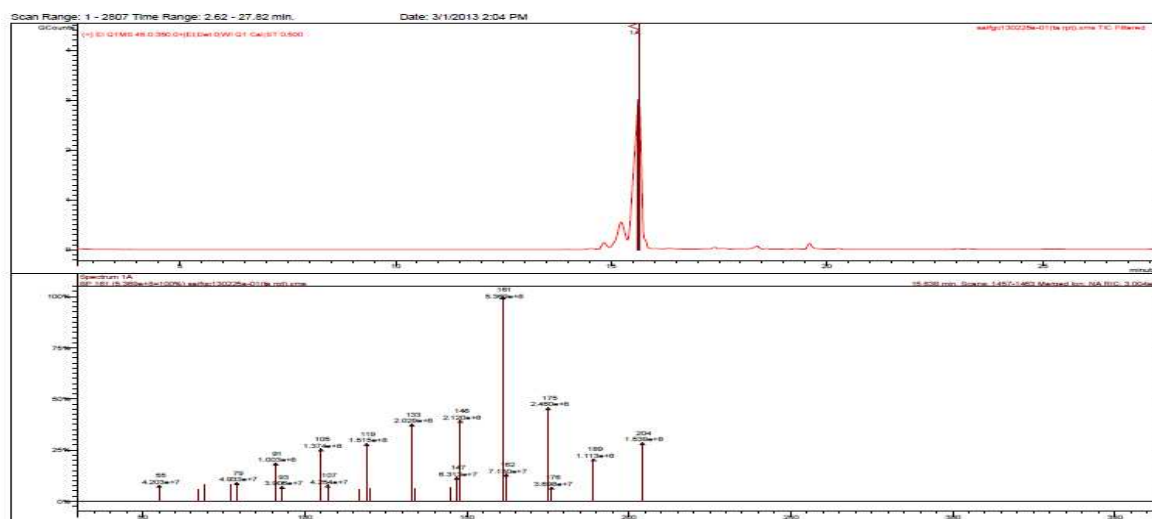


Figure 3.8 GC-MS Total ion chromatogram (TIC) of the Isolongifoline sample showing three major chemical constituents

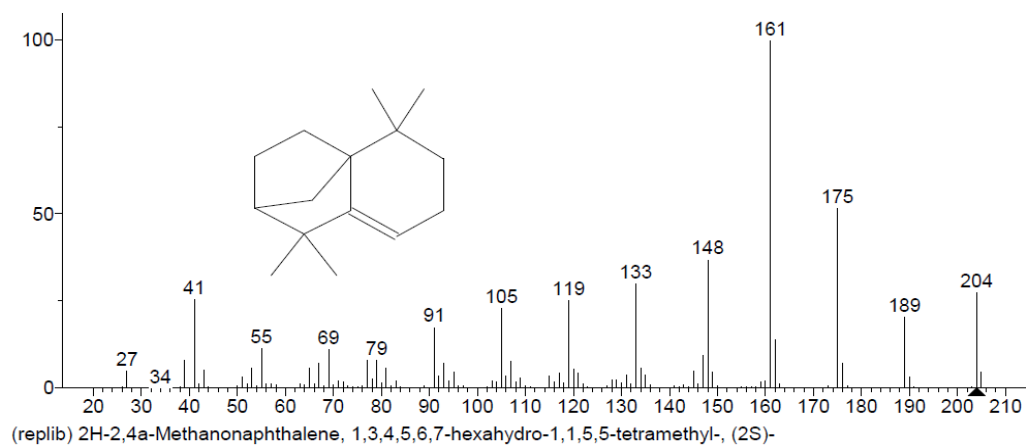


Figure 3.9 Structure and mass spectra of Isolongifoline

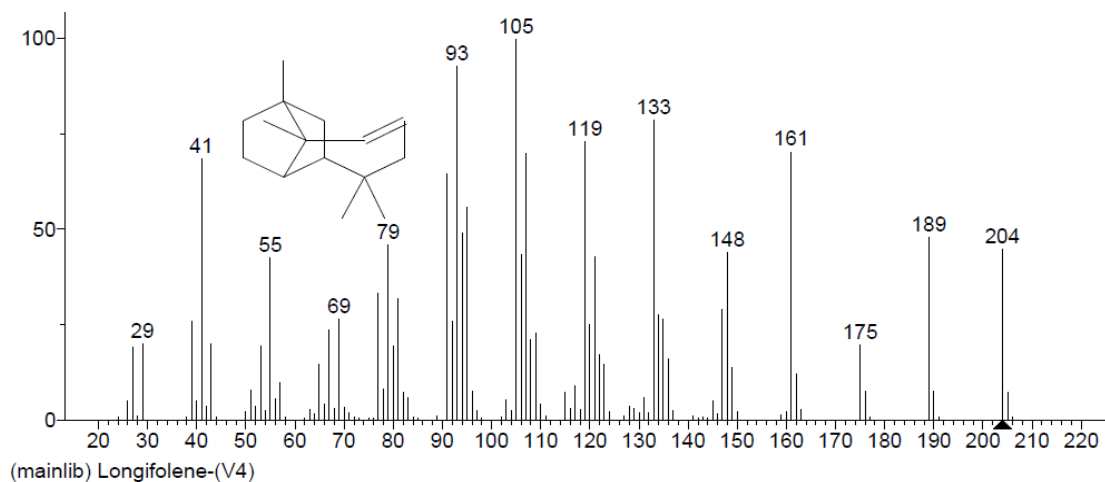


Figure 3.10.Structure and mass spectra of Longifoline

3.2.6. GC-MS analysis of Acetyl Longifoline

The chemical constituents of the sample were analysed by GC-MS. The GC-MS analysis led to identification of 2 major components namely Isolongifoline methyl ether (RT- 19.40), Acetyl Isolongifoline (RT- 20.48). The total ion chromatogram (TIC) of the sample is shown in figure 3.11. The structure and mass spectra of acetyl Isolongifoline and longifoline methyl ether are shown in figure 3.12 and 3.13 respectively.

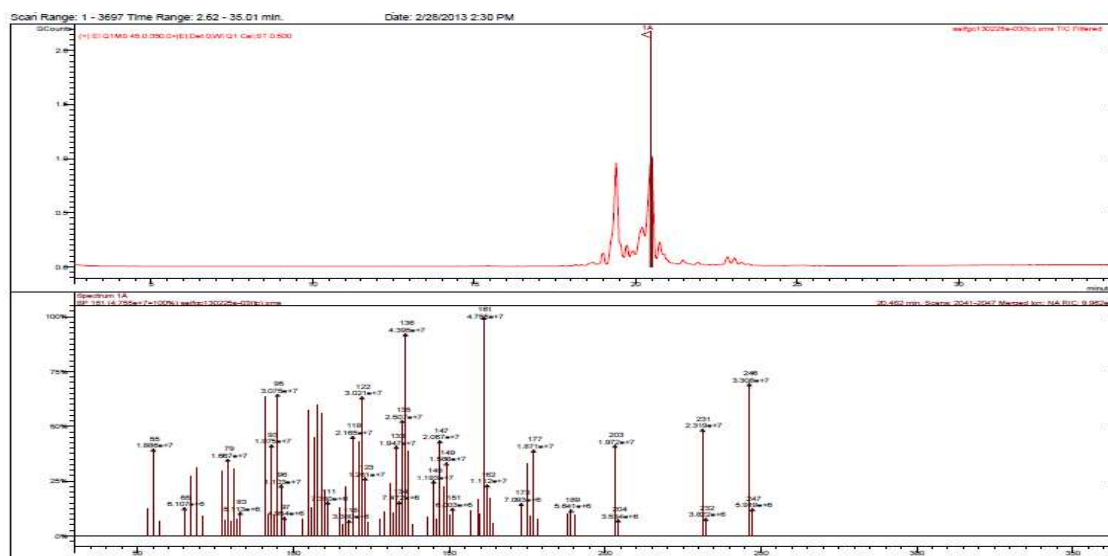


Figure 3.11GC-MS Total ion chromatogram (TIC) of the Acetyl Longifoline sample showing three major chemical constituents

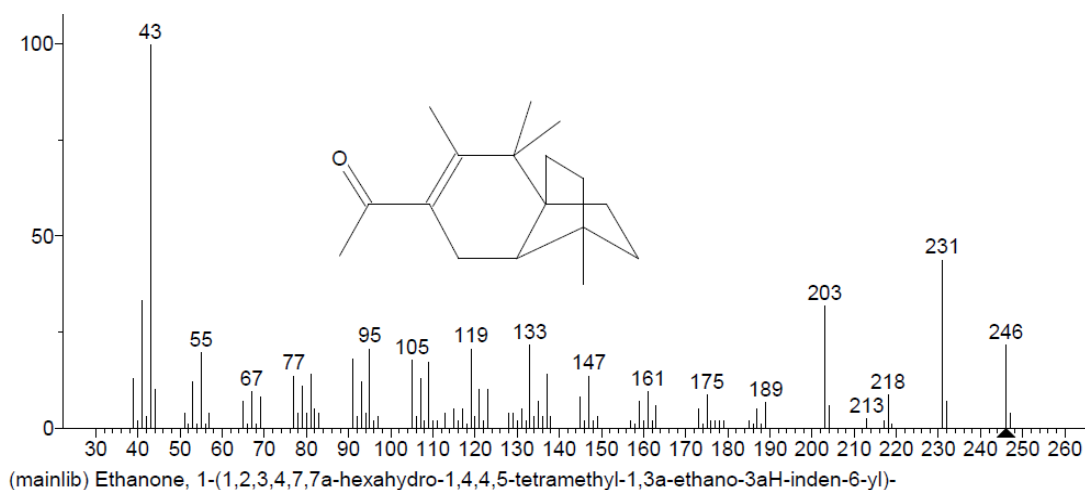


Figure 3.12 Structure and mass spectra of Acetyl Longifoline

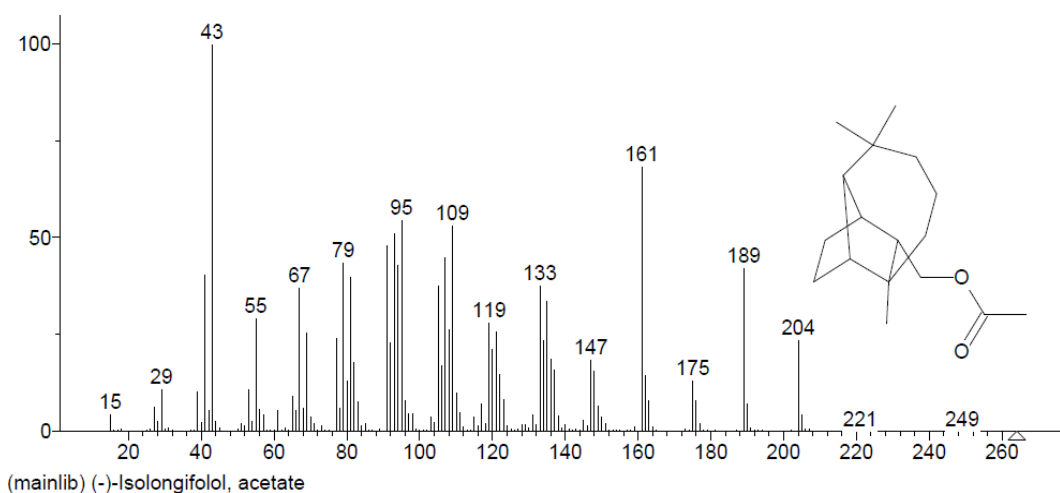


Figure 3.13 Structure and mass spectra of Isolongifoline methyl ether

Conclusion:

In this work Isolongifoline and Acetyl longifoline have been synthesised by using cation ion exchange resin as catalyst. The conclusion that has been drawn is that ion exchange resin can be used as a catalyst in isomerisation and acetylation reactions and shows a good yield of isolongifoline in reaction, while the acetylation reaction is poor due to the formation of acetic acid in the reaction cycle, which causes the rearrangement of longifoline to isolongifoline and inhibits the formation of acetyl longifoline. The process of isomerisation is fast as compared to the acetylation process, which leads to the formation of Isolongifoline (54.68%), Acetyl longifoline (6.06%), and Longifoline methyl ether (2.43%) by way of isomerization and acetylation processes. The characterization of purified samples of Isolongifoline and acetyl longifoline was carried out by FTIR, GC-FID, and GC-MS analysis. The FTIR spectra of purified isolongifoline shows a gem-dimethyl absorption at 1370 cm^{-1} , and an absorption attributable to a methylene group at 1458 cm^{-1} . The FTIR spectra of Acetyl longifoline shows a carbonyl absorption at 1692 cm^{-1} , gem-dimethyl absorption at 1375 cm^{-1} , and an absorption attributable to a methylene group adjacent to a carbonyl group at 1457 cm^{-1} . GC-MS analysis of Isolongifoline sample led to the identification of 2 major components, namely Isolongifoline and longifoline in the Isolongifoline sample. The GC-MS analysis of Acetyl longifoline sample led to 2 major components, namely longifoline methyl ether and acetyl longifoline. The GC-FID results of Isolongifoline sample indicate that the sample is containing 94.30% Isolongifoline and 0.89% Longifoline and other terpenes. The GC-FID results of acetyl longifoline sample indicate that the sample is containing 33.91% acetyl longifoline and 15.91% longifoline methyl ether and other derivatives of

acetylation. The GC-MS is very useful tool for analysis of sesquiterpene derivatives and it is much easier to identify the peaks of chromatogram without standard. The GC-MS analysis of Isolongifoline sample lead the identification of two major components namely isolongifoline and longifoline. The GC-MS results of acetyl longifoline sample lead the identification of two major components namely acetyl longifoline and longifoline methyl ether (isolongifolol acetate)

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