SUMMARY

The present thesis entitled "The synthesis of New Compounds of potential value in perfumery from Bromo-longifolene" is divided into six chapters. A chapter wise description of the whole work is summarised below.

CHAPTER-I

This chapter deals with a brief and up-to-date review of past work done on Longifolene. The available data reveal that Longifolene has been synthesized by different workers. The Bromo-longifolene has been found to be good essential oil to synthesize new compounds of potential value in perfumery.

The first chapter deals with the isolation and occurrence of longifolene by different workers\textsuperscript{1-5}.

SIMMONSEN\textsuperscript{1} isolated longifolene first of all from Indian turpentine oil which is obtained from the oleo-resin of Pinus-roxburghii sarg.syn.P.Longifolia Roxb. It is present in the turpentine oil to the extent of 5-10% and is the main sesquiterpene constituent co-occurring with minor amounts of other sesquiterpenes, Longifolene, Longicyclene, caryophyllene, humulene, \( \beta \)-bisabolene\textsuperscript{2}. Pure, Longifolene, free from any traces of (\textendash )-caryophyllene\textsuperscript{3} has \([ \alpha ]_D^+ 54.06\) (CHCl\textsubscript{3}). (+)-Longifolene has since been found to be widely
distributed in the family of pineae. (-)-Longifolene has been isolated from the liverwort Scapania undulata (L) Dum and from fungus Helminthosporium sativum. (+)-Longifolene is one of the very few sesquiterpenoids being produced commercially in hundred ton quantities.

In this chapter the structure of Longifolene by past workers have also been discussed. Longifolene was readily recognized as a tricyclic sesquiterpene and its chemistry was extensively investigated by SIMMONSON and his co-workers during the period 1923-1934. These authors proposed a tentative structure (1) which, however, lacked any rigorous proof. However, in 1953, MOFFET and ROGGERS disclosed the complete structure determination of Longifolene hydrochloride by X-ray crystallographic analysis. Simultaneously, NAFFA and OURISSON published the results of their detailed chemical investigations which enabled them to extend structure (2) and (3) as the formulation for the parent hydrocarbon, (2) arising from (3) by a Wagner-Meerwein rearrangement during addition of hydrogen chloride.

![Diagram](attachment:diagram.png)

(1) (2) (3) (+) - Longifolene
Infrared\textsuperscript{10}, Raman\textsuperscript{10}, NMR\textsuperscript{11} and mass\textsuperscript{12} spectra of longifolene have been recorded and discussed. The crystal structure of longifolene hydrochloride (2) has been reinvestigated by 3-dimensional methods and new values for band lengths and bond angles deduced\textsuperscript{13}.

In this chapter synthesis of Longifolene have also been discussed. The first synthesis given by COREY, OHNO, VATAKENCHERRY, and MITRA\textsuperscript{14,15} shown in chart I. Full details of synthesis given in the chapter -I.

The next synthesis, due to MCMURRY and ISSER\textsuperscript{16} is outlined in chart-2 of the chapter-I and also full details of reactions have been given in this chapter.

The third longifolene synthesis, disclosed by VOLKAMANN, ANDREWS and JOHNSON\textsuperscript{17} and depicted in chart-3 of this chapter, had its genesis in a chance observation.

The latest synthesis (chart-4) utilizes an intra molecular photo addition-retro aldol reaction as the key-step in the construction of the tricarbocyclic frame-work. This synthesis given by WOODWARD, BRUTSCHY and H.BAER\textsuperscript{18}.

In this chapter structure, synthesis, mechanism of rearrangement of isolongifolene have also been described. Isolongifolene can...
now be prepared conveniently by the action of BF$_3$·Et$_2$O$^{19}$ or Amberlyst
-15$^{20}$ or acid-treated silica gel on longifolene.

The structure of isolongifolene has been elucidated$^{21,22}$ by a combination of spectroscopic methods and incisive chemical degrada­
dations.

The synthesis of isolongifolene$^{23}$ along the lines depicted in chart 5 of this chapter. The deep-seated rearrangement of longi­
ofolene to isolongifolene with concomitant partial racemization of the product, was rationalized$^{24,25}$ in terms of series of 1,2 shifts, as outlined in chart-6. However, subsequently, BERSON et al$^{26}$ based on their extensive studies on methylnorbornyl cations, pointed out that the proposed endo, endomethyl shift (33 → 35; chart-6 of this chapter) should be energetically unfavourable and proposed a modi­fied pathway (chart-7 of this chapter), where in the much more prece­dented exo, exo (42 → 43) shift occurs. Still later, MCMURRY$^{27}$ suggested the intermediacy of longicyclene$^{28}$, in an effort to simplify (33 → 42; chart-8) the pathway, earlier suggested by BERSON and co-workers.

In a recent investigation$^{29,30}$ SUKHDEV and co-workers have clarified the mechanism of rearrangement which is given in chart-9 of this chapter.
In this chapter reactions of longifolene have also been discussed. Many reactions of longifolene have been investigated since elucidation of its structure, while others which were previously studied could be clarified only after this event. Much interesting chemistry has emerged from these studies by virtue of certain special features of the molecule with the kind of information now available, it is possible to clarify the reactions of longifolene essentially into four categories.

1. "Normal" addition, substitution reactions.
2. Reaction involving skeletal rearrangement.
3. Reactions leading to products from steric diversion.
4. Transannular reactions.

Which of these pathways predominates is governed by the nature of reagent and the reaction conditions. In general in the case of electrophilic additions, it is conceded that many reactions proceed through a cyclic activated complex, for example (48), which may be strongly bridged (49), weakly bridged (50) or may lead to a fully developed carbonium ion at the more substituted carbon atom (51). The importance of one or other of these ions may be expected to determine, in the present context, which of four pathways delineated above dominate product development. That in many reactions of longifolene products arising from more than one of these pathways have been encountered can be readily understood from the above considerations.
It appears worthwhile to discuss the reactions of longifolene in terms of the above four categories even though some reactions of longifolene are known to lead to products of more than one type. In such cases, the reaction has been discussed under only one head or both the heads, depending on whether one pathway is dominant or not. Besides, these four categories of reactions, some other pertinent transformations of longifolene and its derivatives are discussed under two additional heads:

(1) Conversion into other sesquiterpene skeletons, and
(ii) miscellaneous transformations. All the full description of the four types of reactions described in Chapter-1.

In this chapter iso-longifolene has also been described. Ultraviolet absorption of some longifolene derivatives have also been described.
Biosynthesis of longifolene have also been described in this chapter.

Use of longifolene in industries have also been described in this chapter. Several essential oils rich in oxygenated sesquiterpenoids find use in perfumery.

Now the basis of the present work have also been described in this chapter. The reaction with bromo-longifolene in more quick and the yield is also better than that in the case of longifolene alone. The electrophilic substitution in case of aromatic ring is well known to the organic chemists. However, recent development on the electrophilic substitution on Bromo-Longifolene based up on Friedel-Crafts reaction has opened new scope of work in preparing new synthetic compounds, because Bromo-longifolene is an aliphatic compound and it is available in abundance in India as a component of turpentine oil. After new compounds from Friedel Crafts reaction we have been prepared some other new compounds.

CHAPTER -2

In this chapter we have described the synthesis of acyl and aryl derivatives of Bromo-Longifolene by Friedel-Crafts reaction. In our investigations acetyl-bromo-longifolene and benzoyl-bromo-longifolene have been synthesized by the reaction of acetic
anhydride and phthalic anhydride on bromo-longifolene by using catalysts anhydrous aluminium chloride (AlCl₃) or Zinc chloride (ZnCl₂).

First, we have been described in this chapter the isolation of longifolene from turpentine oil. Turpentine oil is extracted from crude oleoresin by heating the resin in a Jacketed-still to steam temperature or the steam at low pressure is injected directly into the resin mass. The steam pressure is gradually increased as distillation proceeds. Turpentine oil which collects as the top layer of the distillate is drawn off, passed through lime water to remove any acidic impurities and further rectified and fractionated into reactions of light (Grade 1) and heavy (Grade II) grades. The oil is then made moisture free with anhydrous sodium sulphate. The success in the utilization of Indian terpentine oil has been mainly achieved by fractionation to recover its various constituents, particularly α-pinene for use in the synthesis of camphor. The fractionation of other constituents, viz., β-pinene and particularly car-3-ene and longifolene in high purity was paved the way for manufacture of many new products which were earlier produced only from pinenes.

The longifolene obtained by the fractionation of Indian turpentine oil is purified by column chromatography. The purity has been determined by GLC. The structure of longifolene isolated
was established by relative retention time data in case of GLC further confirmed by its semimicro analysis and IR and NMR spectral data.

Thus longifolene isolated from Indian terpentine oil was brominated by heating with bromine liquid at higher temp. to get bromo-longifolene. Its structure was confirmed by semimicro analysis, IR, NMR spectral data.

The mechanism of acylation of bromo-longifolene have been described in this chapter. Synthesis of Acyl-Bromo-Longifolene and Aryl-Bromo-Longifolene from bromo-longifolene also described in this chapter which is summerized below.

Three conditions of the catalyst were tried in the Friedel Crafts reaction on Bromo-longifolene for Acyl-bromo-longifolene and Aryl-bromo-longifolene as given under.

1. By refluxing bromo-longifolene with acetic anhydride or phthalic anhydride in presence of anhydrous AlCl₃ or ZnCl₂.

2. By refluxing bromo-longifolene with acetic anhydride or phthalic anhydride in presence of orthophosphoric acid.

3. By dropwise addition of acetyl chloride or benzoyl chlo-
ride in the cold solution of bromo-longifolene and anhydrous $\text{AlCl}_3$.

The comparative efficiency of the three conditions of the catalysts were studied.

<table>
<thead>
<tr>
<th>Refluxing time in hrs.</th>
<th>Yield (in gm) in the presence of $\text{ZnCl}_2$ or Anhyd. $\text{AlCl}_3$</th>
<th>Yield (in gm) in the presence of $\text{H}_3\text{PO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>5</td>
</tr>
</tbody>
</table>

The yield of the products by third condition was also not good, it was only 6 g (12%) with the lesser amount of bromo isolongifolene.
The purity of the new products checked by TLC and new products purified by column chromatography. The structure of the compound confirmed by its semimicro analysis and infrared spectral data. All the experimental data given in detail in this chapter.

\[
\text{i) Acetic Anhydride} \\
\text{ii) Anhydrous AlCl}_3 \text{ or ZnCl}_2
\]

Bromo-longifolene (i) \hspace{1cm} \text{Acetyl-Bromo-Longifolene (II)}

\[
\text{i) phthalic Anhydride} \\
\text{ii) Anhydrous AlCl}_3 \text{ or ZnCl}_2
\]

Bromo-longifolene (i) \hspace{1cm} \text{Benzoyl-Bromo-Longifolene (III)}
CHAPTER - 3

In this chapter we have described the synthesis of new alcohols (hydroxy compounds) by the reduction of carbonyl groups of new acetyl-bromo-longifolene and benzoyl-bromo-longifolene.

First of all we have described the general phenomenon of reduction of carbonyls with metal hydrides i.e. reduction is regarded as both the addition of hydrogen to an unsaturated centre in an organic molecule and the replacement of another atom or group in that molecule by hydrogen. i.e. it includes both hydrogenation and hydrogenolysis.

Hydrogenation\textsuperscript{30,31} involving the nucleophilic reagents proceeds accordingly as given in scheme-1. The transference of a hydride ion, from the anion to the positively polarized and of a multiple bond such as a carbonyl group in aldehyde or ketone. Thus with LAH the hydride transference is quickly followed by formation of an aluminon hydride anion. The remaining three hydrogen atoms attached to the aluminium atom in this anion are in turn available for transference, but not so readily, since the electron with drawing inductive effect of the alkoxy group opposes the loss of the hydride ion. The hydride ion may be transferred intramolecularly to a fresh molecule of substrate to be reduced, or it may be transferred intramolecularly to some other
side site with in the same molecule. For example:

\[ \text{H}_3\text{Al} \quad \text{H}(-) \quad \text{O} \quad \text{C} \quad \text{R}_1 \quad \text{R}_2 \]

\[ \text{H}_3\text{Al} \quad \text{O} \quad \text{CHR}_1\text{R}_2 \]

**Scheme - 1**

Reduction of aldehydes or ketones with sodium borohydride differ from lithium aluminium hydride reductions, in requiring the presence of electrophilic catalyst such as a portic solvent or a lithium or magnesium cation in order for reactions\(^{32,33}\). The observations\(^{34,35}\) suggest that reduction occurs by transfer of a hydride ion to the carbonyl oxygen atom. As in the case of LAH reduction all four of the hydrogen atoms of sodium borohydride...
may be utilized in the reduction of ketone molecules. Consequently borohydride reduction have been suggested to proceed in the series of steps, illustrated in Scheme-2.

\[
\begin{align*}
(\text{CH}_3)_2 \cdot \text{CH} - \text{O} - \text{H} & \quad \text{1st Step} \quad \rightarrow (\text{CH}_3)_2 \cdot \text{CH} \cdot \text{OH} + \text{H}_3\text{B}^{-} \cdot \text{O} - \text{CH(}\text{CH}_3\text{)}_2 \\
\text{H}_3\text{B}^{-} \cdot \text{H} & \quad \text{2nd Step} \quad \rightarrow \text{H}_2\text{B}^{-} \cdot <\text{O}^{-} - \text{CH(}\text{CH}_3\text{)}_2 > \quad \text{2} \\
\text{H}_3\text{B}^{-} \cdot <\text{O}^{-} - \text{CH(}\text{CH}_3\text{)}_2 > & \quad \text{3rd Step} \quad \rightarrow \text{H}_2\text{B}^{-} \cdot <\text{O}^{-} - \text{CH(}\text{CH}_3\text{)}_2 > \quad \text{2} \\
\text{H}_2\text{B}^{-} \cdot <\text{O}^{-} - \text{CH(}\text{CH}_3\text{)}_2 > & \quad \text{4th Step} \quad \rightarrow (\text{CH}_3)_2\text{CO} \\
\text{G}^{-} & \quad \text{IVth Step} \\
\text{B}^{-} & \quad (\text{CH}_3)_2\text{CO} \\
\end{align*}
\]

\text{Scheme - 2}

It is customary in hydride reduction to employ a slight excess of the reducing reagent in the event that some of metal hydride is unintentionally destroyed by reduction with hydroxyl containing materials present in the reaction medium. The isolation of organic products from sodium borohydride reductions is usually
accomplished by diluting the reaction mixture with water or dilute aqueous base and then extracting the organic product from the aqueous solution containing boric acid salts. It should be noted that acidification of the reaction solutions containing excess sodium boro-hydride can generate diborane which may cause further reduction of groups in the initial reaction product. The reaction of the alkoxy boron intermediates with water presumably occurs as in the Scheme-3.

\[
B(-)(OR)_4 \leftrightarrow RO(-) + B(OR)_3 \xrightleftharpoons{H_2O} \\
ROH + HO \rightarrow B(-)(OR)_3 \\
HO \rightarrow B(-)(OR)_3 \xrightleftharpoons{H_2O} ROH + (RO)_2B \rightarrow O(-) \\
\]

Now the synthesis of new alcohols has been accomplished by the reduction of Acetyl-bromo-longifolene and Benzoyl-bromo-longifolene. In order to get good yield, the reduction of ketonic group of Acetyl-bromo-longifolene has been accomplished by sodium borohydride in the presence of methanol as a portic solvent. New compounds purified by column chromatography.
The purity of alcohol was checked by TLC. The adsorbent was silica-gel-G and the spraying reagent 5% vanillin in con. \( H_2SO_4 \). After spraying, the plate was heated in an oven temperature maintained at 100°C for 5 minutes. The physical constants of the alcohol were determined and the results obtained are as follows:

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point B.P.</td>
<td>124°C</td>
</tr>
<tr>
<td>Refractive Index ( n_D )</td>
<td>1.4880</td>
</tr>
<tr>
<td>Specific Gravity ( d_{30} )</td>
<td>0.9451</td>
</tr>
<tr>
<td>Optical Rotation ([ \alpha ]_D )</td>
<td>+68.30°</td>
</tr>
</tbody>
</table>

The structure of compound confirmed by IR and semimicro analysis.

IR spectrum showed bands for different groups. A band at 3300 cm\(^{-1}\) for hydroxy group, a band at 1660 cm\(^{-1}\) for trisubstituted double bond and bands at 1378 and 1365 cm\(^{-1}\) for gem-dimethyl group and 540 cm\(^{-1}\) for bromine and a band at 1460 cm\(^{-1}\) for \( CH_3 \) group.

Similarly, the reduction of Benzoyl-Bromo-Longifolene has been done to get the hydroxy compound. This new compound was checked by TLC for its purity. New compound was purified by column chromatography. For checking of its purity by TLC adsorbent was silica-gel-G and the spraying reagent, 5% vanillin in con \( H_2SO_4 \).
After spraying, the plate was heated in an oven temperature main­tained at 100°C for 5 minutes. The physical constants of the new alcohol were determined and the results obtained as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (B.P.)</td>
<td>112°C</td>
</tr>
<tr>
<td>Refractive Index ($n_D^{30}$)</td>
<td>1.3440</td>
</tr>
<tr>
<td>Specific Gravity ($d_30^{30}$)</td>
<td>0.8451</td>
</tr>
<tr>
<td>Optical Rotation ($[\alpha]_D^{25}$)</td>
<td>(+) 65.30°</td>
</tr>
</tbody>
</table>

We get more yield of alcohol from Benzoyl-Bromo-Longifolene than alcohol from acetyl-bromo-longifolene. The structure of compound was confirmed by semimicro analysis and infra-red spectra.

IR spectrum showed bands for different groups. A band at 3000 cm$^{-1}$ for hydroxy group and a band at 1378 and 1360 cm$^{-1}$ for gem-dimethyl group. A band at 1380 cm$^{-1}$ for -C - CH$_3$ group and a band at 1455 cm$^{-1}$ for -CH$_3$ group and bromine showed a band at 500 cm$^{-1}$.

The refractive index of liquid compounds was determined on Toshniwal-make Jasco automatic polarimeter model-DIP-180. TLC carried out on silica-gel-G and the spot were located by spraying with 5% vanillin in con.H$_2$SO$_4$. Gas chromatography data on the retention times of the compounds synthesized, was prepared on
Perkin-Elmer-Chromatograph model 3920. The purity of products was carried out over silica gel impregnated with 10% (w/w) silver nitrate. The boiling point of the compounds were determined in an electrically heated block (Toshniwal-make) and are uncorrected. The IR was recorded on Perkin-Elmer-137 infrared or 337 grating instrument and the values are expressed in cm⁻¹. All the experimental work conditions and details data have been described in this chapter.

(i) Sodium Borohydride
(ii) Methanol

Acetyl-Bromo-Longifolene

Acetyl hydroxy-bromo-longifolene

III

Benzoyl-bromo-longifolene

Benzoyl-hydroxy-bromo-longifolene

V
In this chapter we have described the synthesis of New esters from Acetyl-hydroxy-bromo-longifolene and Benzoyl-hydroxy-bromo-longifolene.

Firstly we have described about the general organic esters and their preparation. Organic esters are widely distributed in nature and are found both as plant and animal products. Many of the esters of the type RCOOR have pleasant odours and contribute to the characteristic fragrance of fruits, flowers and various essential oils. For the production of commercial perfumes and flavours numerous organic esters are made synthetically and are used either alone or blended with natural products. However, the sharpness of odour of the ester is gradually decreased as the acids and alcohols used in their formation increase the molecular weight but the characteristic odour of the ester is completely modified.

The most common laboratory method for the preparation of esters utilizes the condensation between a carboxylic acid and an alcohol catalyzed by acids such as HCl, H$_2$SO$_4$, BF$_3$ or P-toluene sulphonic acid.

The esterification reaction is in equilibrium reaction
and it can be displaced towards the product side by removal of water or by the use of an excess of one of the reactants.

Several of the more common condensation methods for the preparation of esters involve either the condensation of alcohols or alkyl halides with carboxylic acids or their derivatives as shown below:

\[
\begin{align*}
&\text{RCOOH} \\
&(\text{RCO})_2\text{O} \\
&\text{RCOCl} + \text{R'}\text{OH} \rightarrow \text{RCOOR'} \\
&\text{RCOOH} \\
&(\text{and lactones})
\end{align*}
\]

Primary alcohols give better yields of esters than secondary alcohols and tertiary alcohols, while phenols react only to a very small extent\(^{39}\).

The synthesis of Acetyl-Ester of Bromo-longifolene have been accomplished by the reaction of acetyl chloride with Acetyl-hydroxy-bromo-longifolene in presence of pyridine to react with liberated acid. The yield of the product was 43 gms. The purity of the material was checked by TLC. The physical constants of the oil thus prepared were determined and given below:
The oil was examined by GLC and the percentage of the product have been calculated. The GLC was operated under certain conditions which are already given in this chapter. The results of the GLC examination have been described in the Table-I of this chapter. The new product purified by column chromatography, procedure of which have been discussed in this chapter.

Structure of the new compound confirmed by its semimicro analysis and infrared spectra.

The synthesis of ester from benzoyl-bromo-longifolene have been accomplished by the reaction of benzoyl-hydroxy-bromo-longifolene with benzoyl chloride in the presence of pyridine. The purity of the new product was checked on TLC. The physical constants of the oil were determined and given below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point</td>
<td>B.P.</td>
<td>140°C</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>n&lt;sup&gt;30&lt;/sup&gt;&lt;sub&gt;D&lt;/sub&gt;</td>
<td>1.4823</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>d&lt;sup&gt;30&lt;/sup&gt;&lt;sub&gt;30&lt;/sub&gt;</td>
<td>0.9989</td>
</tr>
<tr>
<td>Optical Rotation</td>
<td>[α]&lt;sup&gt;25&lt;/sup&gt;&lt;sub&gt;D&lt;/sub&gt;</td>
<td>(+) 19.7°</td>
</tr>
</tbody>
</table>
The product was examined by GLC and the percentage of the compound have been calculated. GLC was operated under certain conditions given in this chapter and also the results of GLC have been described in Table-III of this chapter.

The new product was purified by column chromatography adsorbent taken was 10% silver nitrate impregnated silica gel.

The structure of the compound have been established by its semi-micro analysis and IR spectral data.
CHAPTER - 5

In this chapter we have described the synthesis of Ethers by addition of alcohols on Bromo-longifolene. Alcohols and phenols add to olefins in reactions which are catalyzed, the mechanism is electrophillic, with $H^+$ as attacking species. The resulting carbonium ion combines with a molecule at alcohol. A brief outline of this mechanism is given below:

\[ \text{-C} = \text{C}^- + \text{H}^+ \rightarrow \text{-C} = \text{C}^\oplus + \text{ROH} \]

\[ \text{-C} = \text{C}^- \rightarrow \text{-C} = \text{C}^- + \text{OR} \]

The addition, therefore, follows Markownikoff's rule. Primary alcohols give better results than secondary but tertiary alcohols are inactive.

Alcohols, ethers, amines, and alkyl-halides add to double bond as follows:

\[ \text{-C} = \text{C}^- + \text{RCH}_2\text{OH} \rightarrow \text{-C} = \text{C}^- \]

These reactions are most successful when the olefines
contains electron withdrawing groups such as halogen or carbonyl groups.

The synthesis of 9-alkoxy-2,6,6 trimethyltricyclo [5,4,0, 0²,8] undecane have been accomplished by the reaction of primary alcohols on Bromo-Longifolene in the presence of H₂SO₄ or in the presence of boron trifluoride at 100°C. The refluxing of the reagents have been carried out over a water bath for 10 hrs.

Methoxy-ether of bromo-longifolene have been synthesized by the reaction of Bromo-longifolene with methanol in the presence of Con H₂SO₄ or BF₃-etherate. The comparative efficiency of BF₃-etherate and con.H₂SO₄ have been studied. The results of this comparative study have been given in Table-I of this chapter.

The product was examined by TLC in presence of some traces of side products and reactants was noted. For the separation of pure product the mixture was subjected to column chromatography. The purity of the compound was established by GLC. The physical constants were determined and they are listed as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point</td>
<td>B.P. 10</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>d³₀</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>n_D³₀</td>
</tr>
<tr>
<td>Optical Rotation</td>
<td>[α]_D²⁵</td>
</tr>
</tbody>
</table>
The structure of the new product was confirmed by its semimicro analysis and infrared spectral data.

(i) Methanol

(ii) BF₃-etherate or Con.H₂SO₄

Bromo-Longifolene

Methoxy-ester

Ethoxy-ether of Bromo-longifolene have been synthesized by the reaction of Bromo-longifolene with ethanol in presence of con. H₂SO₄ or in presence of BF₃-etherate.

The product was examined by TLC. The product obtained showed the presence of side products and unreacted Bromo-longifolene on TLC. Therefore, it was subjected to column chromatography. The purity of the compound was established by GLC. The physical constants were determined and were as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tr>
<td>Specific Gravity</td>
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</tr>
<tr>
<td>Refractive Index</td>
<td>1.3530</td>
</tr>
<tr>
<td>Optical Rotation</td>
<td>(+) 0.80°</td>
</tr>
</tbody>
</table>
The structure of the ethoxy-ether was confirmed by its semimicro analysis and infrared spectral data.

\[
\begin{align*}
\text{(i) Ethanol} & \quad \text{(ii) BF}_3\text{-etherate or} \quad \text{con.} \text{H}_2\text{SO}_4 \\
\text{Bromo-longifolene} & \quad \text{Ethoxy-ether}
\end{align*}
\]

n-proxy-ether of Bromo-longifolene have been synthesized by the reaction of Bromo-longifolene with n-propanol in the presence of con.\text{H}_2\text{SO}_4 or BF$_3$-etherate.

The product was examined by TLC and the impurities present in the product were removed and the compound was isolated in pure form by column chromatography. The purity of the compound was established by GLC. The physical constants were determined and the results are as follows:

- **Boiling Point** \( B.P. \) \( 10^\circ C \) \( 135^\circ C \)
- **Specific Gravity** \( d_{30} \) \( 1.0323 \)
- **Refractive Index** \( n_D^{30} \) \( 1.5450 \)
- **Optical Rotation** \( [\alpha]_D^{25} \) \( (+) 1.30^\circ \)

The structure of the new product was confirmed by its
In this chapter we have described all the results and their discussion of all experiments.

According to our plan the longifolene which was isolated from turpentine oil was subjected to bromination to get Bromo-longifolene. Bromo-longifolene was subjected to acylation and arylation by using Friedel-Crafts reaction. The compound thus formed were converted into hydroxy-groups (alcohols) and these alcohols were converted into esters. Bromo-longifolene also subjected to form different type of ethers. The reaction with bromo-longifolene is more quick and the yield is also better than that in the case of longifolene alone.
The compound thus formed were checked by TLC and purified by column chromatography and preparative TLC. Thus structure of the compounds were determined by their semimicro analysis and Infrared spectral data. The structures are the same as expected according to the reactions. This is confirmed by the same previous studies. Its references 31,43-48 etc. in the chapter-I.

The molecular formula of the new products i.e. for acyl and aryl derivatives of bromo-longifolene, alcohols (hydroxy compound groups); esters and ethers were established and confirmed by their semimicro analysis which are given in Tables in chapter-6.

We know that acetyl-bromo-longifolene (65a), acetyl longifolene (65); w-hydroxy-methyl-longifolene (60) and isolongifolene ketone (198) (these structures have been described in Chapter 1st) have already reached wide acceptance and are being manufactured by different companies. With our findings above it will add more and more in the field of synthetic perfumes.

As such it is fully established that the natural products of turpentine in which bromo-longifolene is one of the constituent can be used as synthetic perfume by applying Friedel - Crafts reaction and can be used as food flavour value, these results given in screening of the compounds.
The IR spectrum clearly showed band at 1358 cm\(^{-1}\) for acetyl group, at 1360 cm\(^{-1}\) for benzoyl group, bands at 3300 and 3000 cm\(^{-1}\) for hydroxy groups, bands at 1710 and 1230 cm\(^{-1}\) for ester group of Acetyl-ester, band at 1705 cm\(^{-1}\) and 1250 cm\(^{-1}\) for ester group of Benzoyl-ester, bands at 1130 cm\(^{-1}\) for methoxy group, 1105 cm\(^{-1}\) for ethoxy group, 1130 cm\(^{-1}\) for n-propoxy group as mentioned in chapter-6.