DISCUSSION
CHAPTER 1
Synthesis of (+)-Cembrene-A

Patil, V.D. and coworkers isolated (132) a novel fourteen membered monocyclic diterpenoid hydrocarbon cembrene-A firstly as one of the constituent of "guggulu", a crude ayurvedic drug. It was also obtained by Herin and Tursh (133) from soft coral and by Vandrah et al. (134) from another soft coral (nepthea species). The structure of cembrene-A was elucidated on the basis of detailed spectrochemical studies (132), as (I) in which one isoprene unit is irregularly joined to three others.

\[
\begin{align*}
\text{I}
\end{align*}
\]

The Molecular ion peak \( (M^+ \text{ m/e} = 272) \) showed its molecular formula to be \( C_{20}H_{32} \). The base peak was adduced through retero Diels-Alder reaction and other peaks at m/e 93, 81, 67, 53 etc. are also consistent with the proposed structure. Catalytic hydrogenation of (I) gave octahydroderivative \( C_{20}H_{40} \) \( (M^+ \text{ m/e} = 280) \) indicating the presence of four olefinic linkages and a monocyclic skeleton.
UV spectrum exhibited no absorption maxima above 210 nm, indicating, thereby, the absence of conjugation. IR absorption spectrum (895, 1648, 1650 cm\(^{-1}\)) revealed the presence of a terminal double bond. Its PMR spectrum confirmed the proposed structure giving signals at $\delta$(CDCl\(_3\)): 1.57-1.58 (9H, s, vinylic methyls), 1.63 (3H, d, $J = 0.5$ Hz, vinylic methyl), 4.63 (2H, br s, terminal vinylic protons) and 5.03 (3H, superimposed triplets, vinylic protons).

The salient features of structure (I) are the presence of a fourteen-membered ring with an isopropenyl substituent and three trisubstituted trans vinylic bonds constituting a 1, 5, 9 triene system in the macrocyclic skeleton.

Literature does not record any attempt towards the synthesis of this hydrocarbon. The present approach to its synthesis utilizes the observation by Corey et al. (125-128) that medium and large sized rings containing 1,5 diene moiety can be easily prepared in good yields by the use of nickel tetracarbonyl catalyzed intramolecular cyclisation of bis terminal allylic bromides in polar solvents. This coupling reaction has been found to yield stereochemical mixture of trans-trans and cis-trans (2:1) irrespective of the homogeneity of the precursors when trisubstituted double bonds were involved (135). Therefore, the stereochemistry
of two double bonds in cembrene-A acyclic precursor was not an important consideration and thus, the nickel-carbonyl induced cyclisation of the appropriate allylic dibromide (XV) afforded the cyclic product after chromatographic separation with all double bonds having **trans** geometry. One of these double bonds was created through Claisen rearrangement of appropriately substituted vinyl ether prior to cyclisation.

For the synthesis of cembrene-A, the required bis terminal allylic bromide (XV) as the cardinal intermediate, was allowed to cyclise under above mentioned conditions to obtain the desired hydrocarbon (I). The acyclic dibromide was in turn procured, starting with 6,6-ethylenedioxy-2-methyl-2-heptene as shown below:

\[ \text{II} \rightarrow \text{III} \rightarrow \text{IV} \rightarrow \text{V} \rightarrow \text{VI} \]
6,6-Ethynedioxy-2-methyl-2-heptene (II), prepared as reported (136) was subjected to epoxidation (137) with m-chloroperbenzoic acid in methylene chloride at 10-15\degree C. The formation of epoxide (III) was confirmed through its PMR spectrum which exhibited signals at 

$$\delta_{\text{CDCl}_3} : 
\begin{align*}
1.1 & (9H, s, \text{ saturated methyls}), \\
1.2-1.4 & (4H, \text{ br s, saturated methylenes}), \\
2.51 & (1H, t, J = 7 \text{ Hz}, \text{ -OH } \text{ -C=C-}), \\
3.93 & (4H, s, \text{ -CH}_2\text{O-CH}_2\text{).}
\end{align*}$$

The epoxide (III) was smoothly cleaved with lithium diisopropylamide in refluxing anhydrous ether (120) to furnish 6,6-ethynedioxy-3-hydroxy-2-methyl-1-heptene (IV) in 50% yield. The formulation was established by its IR spectrum showing characteristic absorption bands at 3340 (–OH) and 895 cm\(^{-1}\) (–C = CH\(_2\)). The allylic alcohol (IV) was refluxed with excess of ethyl vinyl ether in the presence of mercuric acetate as catalyst (105) to afford the vinyl ether (V) in 80% yield. IR spectrum showed absence of absorption
in the hydroxyl region. The vinyl ether (V) was submitted to Claisen rearrangement under nitrogen atmosphere (106) to generate 8,8-ethylenedioxy-4-methyl-4(E)-nonen-1-al (VI) in 90% yield. The trisubstituted double bond was assigned trans configuration in view of earlier observations (119) and the presence of aldehydic function was revealed through its IR absorption bands at 2720 and 1710 cm⁻¹.

Modified Wittig reaction on the aldehyde (VI) with ethyl α-diethylphosphonopropionate in THF using NaH as base gave the conjugated ester (VII) after chromatography in 80% yield. IR absorption bands were observed at 1710 and 1645 cm⁻¹ (conjugated ester). Its PMR spectrum indicated it to be predominantly trans isomer. However, no attempt was made to separate cis and trans isomers because both isomers are expected to lead to same aldehyde (X) after reduction, vinyl ether formation and Claisen rearrangement.

\[ \delta_{CDCl_3} : \]
- 1.15-1.58 (8H, m, saturated methyls and methylene)
- 1.66 (3H, s, allylic methyl),
- 1.80 (3H, s, \( \gamma = C = CH_3 \) COOEt),
- 2.0-2.15 (6H, m, allylic methylenes),
- 3.90 (4H, s, \( \gamma = C = CH_2 \) OCH₂),
- 4.15 (2H, q, \( J = 7 \) Hz, - O - CH₂ -CH₃),
Reduction of ethyl 10, 10-ethylenedioxy-2,6-dimethyl-2(E),6(E)-undecadien-1-oate (VII) with LAH–absolute alcohol reagent in ether (138) furnished the allylic carbinol (VIII) in 80% yield. Its IR spectrum showed absorption band at 3350 cm⁻¹ (–OH) and PMR exhibited the signals at:

\[ \delta_{\text{CDCl}_3} : \]
- 1.22 (3H, s, saturated methyl),
- 1.37-1.7 (8H, d like, allylic methyl and saturated methylene),
- 2.05 (6H, m, allylic methylenes),
- 3.9 (6H, s, –CH₂ and –HC = C\text{COOEt})
- 4.8-5.15 (2H, m, vinylic protons).

Mercuric acetate catalysed trans etherification of (VIII) with ethyl vinyl ether gave 10, 10-ethylenedioxy-2, 6-dimethyl-1-vinylxyo-2(E),6(E)-undecadiene (IX) in 85% yield after chromatographic purification. Its PMR spectrum gave the following signals at:

\[ \delta_{\text{CDCl}_3} : \]
- 1.2 (3H, s, saturated methyl),
- 1.5-1.7 (8H, d like, allylic methyls and saturated methylene),
2.05 (6H, br s, allylic methylenes),
3.9 (4H, s, \( \text{\text{CH}_2} \rightarrow \text{O} \),
4.0 (2H, s, -\( \text{C} = \text{CH}_2 \rightarrow \text{O} \)),
4.9 (2H, br s, -\( \text{O} - \text{C} = \text{CH}_2 \)),
5.1 (2H, t, \( J = 7 \text{ Hz} \), vinylic protons),
6.35 (1H, dd, \( J = 10, 17 \text{ Hz} \), -\( \text{O} - \text{CH} = \text{CH}_2 \)).

The vinyl ether (IX) on Claisen rearrangement under nitrogen atmosphere at 155-60° afforded pleasant smelling aldehyde (X) in quantitative yield. IR : 2710 and 1710 cm\(^{-1}\) (-CHO) and 895 cm\(^{-1}\) (-\( \text{C} = \text{CH}_2 \)). PMR spectrum exhibited signals at

\( \delta_{\text{CDCl}_3} \) : 1.23 (3H, s, saturated methyl),
1.4-1.7 (8H, br s, allylic methyls and \( \text{\text{CH}_2} \rightarrow \text{O} \)),
2.05 (5H, m, allylic methylenes and methyne),
2.4 (2H, m, -\( \text{CH}_2 \rightarrow \text{CHO} \)),
3.9 (4H, s, \( \text{\text{CH}_2} \rightarrow \text{O} \)),
4.8 (2H, s, \( \text{C} = \text{CH}_2 \)),
5.12 (1H, t, \( J = 7 \text{ Hz} \), vinyl proton),
9.7 (1H, -CHO).
10,10-Ethylenedioxy-3-isopropenyl-6-methyl-6(E)-undecadien-1-al (X) was submitted to modified Wittig reaction with ethyl α-diethylphosphonopropionate under usual conditions to furnish predominantly trans isomer of conjugated ester (XI), purified chromatographically, in 75% yield. However, isomers were not separated because both isomers would give the same cyclised product after nickel carbonyl induced cyclisation reaction. Its IR spectrum had absorption at 1710 cm⁻¹ (conjugated ester) and no absorption around 2710 cm⁻¹ (-CHO). Confirmation of trans stereochemistry was adduced from its PMR showing signals at

$$\delta_{\text{CDCl}_3}$$ :

1.2-1.5 (10 H, m, saturated methyls and methylenes),
1.66 (6H, br s, allylic methyls),
1.8 (3H, s, -CH = CH₃),
2.05 (7H, m, allylic methylene and methyne),
3.9 (4H, s, -CH₂ - CH₂ - CH₂ - CH₃),
4.15 (2H, q, J = 7 Hz, -CH₂ - CH₃),
4.8 (2H, s, -C = CH₂),
5.12 (1H, t, J = 7 Hz, vinyl proton).
Ethyl 12,12-ethylenedioxy-5-isopropenyl-2,8-dimethyl-2(E), 8(E)-tridecadien-1-oate (XI) was deketalized (139) with PTS in acetone-water mixture (10:1) at room temperature to obtain keto-ester (XII) in 90% yield after purification through chromatography. PMR spectrum confirmed its formulation indicating signals at

$$\delta_{\text{CDCl}_3} :$$

1.28 (3H, t, $J = 7$ Hz, -CH$_2$-CH$_3$),

1.63(6H, s, allylic methyls),

1.8 (3H, s, C-CH$_3$),

2.1(3H, s, -C-CH$_3$),

2.3(2H, t, $J = 7$ Hz, -CH$_2$-CH$_3$).

The keto-ester (XII) was subjected to modified Wittig reaction with ethyl $\alpha$-diethylphosphonoacetate through usual experimental procedure which produced an isomeric mixture of E, E, E and E, E, Z diester, diethyl 5-isopropenyl-2,8,12-trimethyl 2(E),8(E),12-tetradecatrien-1,14-dioate(XIII). No attempt was made at this stage also to separate the mixture of isomers of the diester because the stereochemical integrity around these olefinic linkages will end up into the same
sterioisomeric cyclisation product starting with mixture of isomers as mentioned earlier. Its PMR exhibited signals at

$\delta_{\text{CDCl}_3} : 1.16 \ (3\text{H}, \text{ t}, J = 7 \text{ Hz}, -\text{CH}_2\text{-CH}_3),

1.19 \ (3\text{H}, \text{ t}, J = 7 \text{ Hz}, -\text{CH}_2\text{-CH}_3),

1.66 \ (6\text{H}, \text{ br s}, \text{ allylic methyls}),

1.80 \ (3\text{H}, \text{ s}, H = \text{CH}_3)

2.1 \ (3\text{H}, \text{ s}, H = \text{COOEt})$ whereas in cis isomer this methyl gives singlet at 1.92),

2.15 \ (9\text{H}, \text{ m}, \text{ allylic methylenes and methyne}),

4.03 \ (2\text{H}, \text{ s}, J = 7 \text{ Hz}, -\text{CH}_2\text{-CH}_3),

4.07 \ (2\text{H}, \text{ s}, J = 7 \text{ Hz}, -\text{CH}_2\text{-CH}_3),

4.7 \text{ and } 4.74 \ (2\text{H}, H = \text{CH}_2),

5.07 \ (1\text{H}, \text{ t like}, \text{ vinyl proton}),

5.57 \ (1\text{H}, \text{ s}, H = \text{COOEt})

6.66 \ (1\text{H}, \text{ t like}, H = \text{CH}_3).

The reduction of conjugated diester (XIII) was accomplished safely with LAH-absolute alcohol reagent in dry ether to the corresponding diol (XIV) as a viscous liquid which was chromatographed over florisil to get
The allylic dibromide (XV) was cyclised under nitrogen atmosphere in the presence of nickel tetracarbonyl in dry DMF and the tlc analysis of the product indicated three spots ($R_f = .90, .80$ and .70 in n-hexane). The least polar component, expected to be the title hydrocarbon, was separated through preparative tlc as the major component and characterised by its Mass (M$^+$ m/e 272), IR and PMR spectrum which was comparable to that of the natural one.

IR: $\nu_{\text{max}}$ : 3055, 2950-2850, 1650, 1440, 1370, 895 and 840 cm$^{-1}$.

and PMR exhibited the following signals at

$\delta_{\text{CDCl}_3}$ : 1.26 (2H, br ss, saturated methylene),
1.48, 1.56, 1.58, 1.66 (3H each, s each, allylic methyls),
2.07 (13H, m, allylic methylenes and methyne),
4.66 (2H, br s, $-C = \text{CH}_2$),
5.03 (3H, m, vinyl protons).
CHAPTER II
Synthesis of \( \beta \)-Springene

\( \beta \)-Springene an acyclic diterpenoid has been isolated by Burber and coworkers (141) from the dorsal cutaneous secretion of the antelope *Antidorcas marsupialis*, commonly known as springbok, as a major volatile component. On the basis of spectral studies (141), it has been shown to be 7, 11, 15-trimethyl-3-methylenehexadeca-1,6(E),10(E),14-tetraene (XVI).

\[
\begin{align*}
\text{XVI}
\end{align*}
\]

Mass spectrum of the hydrocarbon (XVI) below m/e 133 closely resembles that of \( \beta \)-farnesene (XVII) therefore, \( \beta \)-springene was assumed to be an acyclic hydrocarbon. The comparison of its C\(^{13}\) NMR with that of two model compounds \( \beta \)-farnesene and squalene (XVIII) confirmed the proposed structure (XVI).

\[
\begin{align*}
\text{XVII} \\
\text{XVIII}
\end{align*}
\]
The excellent agreement of $^{13}$ C NMR shifts of $C_1$ to $C_6$ and $C_{20}$ in $\beta$-farnesene and $C_7$ to $C_{19}$ shifts in squalene with the shifts of these carbon atoms in (XVI), unequivocally confirmed the structure (XVI) for $\beta$-springene as well as the trans configuration of $C_6$ and $C_{10}$ double bonds. Vig et al. (142) have also established its structure through its synthesis. However, during the present synthetic work, the title compound was synthesized utilizing important reactions such as Claisen rearrangement, Wittig reaction and Grignard reaction. The outline of the scheme leading to its synthesis is depicted below:

THPO

CH$_2$OH

$\rightarrow$

THPO

CHO

XX

THPO

O

XXI

$\rightarrow$

THPO

O

XXII

$\rightarrow$

THPO

CHO

XXIII

THPO

O

XXIV
42

CH$_2$OH

XXV

THP O

XXVI

XXVII

XXVIII

XXIX

XXX
4-Tetrapyranyloxy-butan-1-ol (XIX) prepared according to the reported procedure (143), was oxidised with pyridinium chlorochromate and small amount of anhydrous sodium acetate (144) in dry dichloromethane to get corresponding aldehyde (XX) in 60% yield. It was characterised by its IR absorption bands at 2710 and 1710 cm\(^{-1}\). This aldehyde (XX) on Grignard reaction with isopropenylmagnesium bromide in THF at 0-5° furnished 3-hydroxy-2-methyl-6-tetrahydro-pyran-3-yloxy-1-hexene (XXI), purified through distillation followed by chromatography in 50% yield. Its IR absorption bands at 3400 (-OH) and 895 cm\(^{-1}\) (\(-\mathrm{C} = \mathrm{CH}_2\)) confirmed its formulation. The allylic alcohol (XXI) was submitted to mercuric acetate catalysed trans etherification with ethyl vinyl ether to produce vinyl ether (XXII) in 70% yield. Its IR spectrum showed no absorption in alcoholic region. Claisen rearrangement on heating this vinyl ether (XXII) for 30 min in a sealed tube under nitrogen atmosphere at 145-50° provided sweet smelling aldehyde (XXIII) with
trans stereochemistry of double bond (119). IR : 2710 and 1710 cm⁻¹.

4-Methyl-8-tetrahydropyranlyoxy-4(E)-octen-l-al (XXIII) was again subjected to Grignard reaction with isopropenyl-magnesium bromide to obtain the allylic alcohol (XXIV) which was transformed into its vinyl ether (XXV) under a aforementioned conditions. This vinyl ether on Claisen migration at 160-65° afforded 4, 8-dimethyl-12-tetrahydropyranlyoxy-4(E),8(E)-dodecadien-l-al (XXVI) in quantitative yield. Its IR spectrum showed characteristic absorption bands at 2710 and 1710 cm⁻¹. PMR exhibited the signals at 

$\delta_{\text{CDCl}_3} : 1.3$ to $1.7$ (14H, m, saturated methylenes and allylic methyls),
2.0 (8H, br s, allylic methylenes),
2.35 (2H, m, $-\text{CH}_2\text{-CHO}$),
3.33 to 3.7 (4H, m, $-\text{CH}_2\text{-O-CH-O-CH}_2$),
4.5 (1H, s, $-\text{O-CH-O-}$),
5.15 (2H, t, $J = 7$ Hz, vinyl protons),
9.8 (1H, $-\text{CHO}$).

Wittig reaction (66) on the aldehyde (XXVI) with isopropylenetriphenylphosphorane in DMSO in the presence of NaH as a base furnished 5, 9, 13-trimethyl-1-tetrahydro-pyranlyoxy-4(E),8(E), 12-tetradecatriene (XXVII) in 70 %
yield after chromatographic purification. Absence of IR absorption bands in corbonyl region confirmed its formation. Its PMR spectrum exhibited the following signals at 

$$\delta_{CDCl_3} : 1.3-1.7 \text{ (2OH, m, saturated methylene and allylic methyls)},$$

$$2.0 \text{ (1OH, br s, allylic methylenes)},$$

$$3.3-3.7 \text{ (4H, m, -CH_2-O-CH-O-CH_2-)},$$

$$4.5 \text{ (1H, s, -O-CH-O-)},$$

$$5.15 \text{ (3H, br t, vinyl protons).}$$

The protective pyranyl moiety in (XXVII) was removed (145) by stirring it with methanol/PTS to get corresponding alcohol (XXVIII), separated by chromatography over alumina in 90% yield. Its IR spectrum showed a prominent absorption band at 3400 cm$^{-1}$ (–OH) and absence of bands characteristic of pyranyl group (910, 880, 820 cm$^{-1}$). PMR spectrum gave signals at 

$$\delta_{CDCl_3} : 1.5-1.75 \text{ (14H, d like, allylic methyls and saturated methylene)},$$

$$2.07 \text{ (1OH, br s, allylic methylenes)},$$

$$3.62 \text{ (2H, t, J = 7Hz, -CH_2OH)},$$

$$5.13 \text{ (3H, br t, vinyl protons).}$$
Pyridinium chlorochromate oxidation of alcohol (XXVIII) in methylenechloride provided the aldehyde (XXIX) in 50% yield. IR: 2710 and 1710 cm\(^{-1}\). Its PMR spectrum exhibited the following signals at

\[ \delta_{\text{CDCl}_3}: \]
- 1.66 (12H, \( \delta \) like, allylic methyls),
- 2.07 (10H, br \( s \), allylic methylenes),
- 2.35 (2H, \( m \), \(-\text{CH}_2\text{-CHO}\)),
- 5.15 (3H, br \( t \), vinyl protons),
- 9.8 (1H, \(-\text{CHO}\)).

Grignard reaction of vinylmagnesium bromide on the aldehyde (XXIX) in THF at 5-10° furnished 7,11,15-trimethyl-1,6(H),10(H),14-Hexadecatetraen-3-ol (XXX) which was chromatographed over alumina to get pure alcohol (XXX) in 85% yield. Its IR spectrum exhibited the characteristic bands at 3450 (\(-\text{OH}\)) and 898 cm\(^{-1}\) (\(-\text{MC = CH}_2\)). The PMR spectrum showed signals at

\[ \delta_{\text{CDCl}_3}: \]
- 1.25-1.4 (2H, br \( t \), saturated methylene),
- 1.5-1.8 (12H, \( \delta \) like, allylic methyls),
- 2.1 (10H, \( m \), allylic methylenes),
- 5.0-5.3 (5H, \( m \), \(-\text{CH} = \text{CH}_2\) and vinyl protons),
- 5.8-6.1 (1H, \( m \), \(-\text{CH} = \text{CH}_2\)).
Oxidation of the alcohol (XXX) with pyridinium chlorochromate in methylenechloride produced the enone 7, 11, 15-trimethyl-1,6(E),10(E),14-hexadecatetraen-3-one (XXXI) in 55% yield. It was purified through filtration over a short pad of alumina eluting with ether : dichloromethane (4:1) because the chromatography results in its cyclisation as reported (142). A prominent IR absorption band at 1675 cm\(^{-1}\) (conjugated ketone) was observed. Its PMR spectrum gave signals at

\[ \delta_{\text{CDCl}_3} \]

- 1.5-1.8 (12H, br d, allylic methyls),
- 2.1 (1OH, br s, allylic methylenes),
- 2.35-2.5 (2H, br s, -CH\(_2\) - CH = CH\(_2\)),
- 5.15 (3H, br t, vinyl protons),
- 5.8 and 6.3 (1H and 2H, m each, -CH = CH\(_2\)).

The enone (XXXI) was finally submitted to Wittig reaction with methylenetriphenylphosphorane in DMSO under usual conditions to furnish \(\beta\)-springene in 40% yield which was purified through chromatography over florisil. Confirmation of the structure of this synthetic product was adduced from its IR and PMR spectra which is indicated below:

IR : 3075, 2950-2850, 1640, 1620, 1450, 1370,
    1270, 1150, 1030, 980, 915, 890 and 820 cm\(^{-1}\).
The PMR spectrum exhibited signals at

$\delta_{\text{CDCl}_3}$: 1.66 (12H, br d, allylic methyls),
2.07 (12H, br s, allylic methylenes),
5.0-5.4 (7H, m, vinyl protons),
5.9 (1H, dd, $J = 10, 17$ Hz, $-\text{CH} = \text{CH}_2$).
(i) Synthesis of (+) 13-Hydroxy-6,10,14-trimethylpentadeca-5(E), 9(E),14-trien-2-one

A recent report by Ravi B.N. and coworkers (146) has described the isolation of an acyclic bisnorditerpenic alcohol as one of the constituent from brown alga C. monilioformis and proposed the structure (XXXII) for it exclusively on the basis of detailed spectroscopic evidences.

The presence of hydroxyl and carbonyl groups was revealed by its IR spectrum (3300 and 1715 cm$^{-1}$). PMR spectrum indicated the presence of two vinylic protons ($\delta 5.06, 2H, t, J = 7\text{ Hz}$), a vinyl methylene (4.92 and 4.82, 1H each, br s), a secondary alcohol (4.02, 1H, t, $J = 7\text{Hz}$), a methyl ketone (2.12, 3H, s) and three vinylic methyls (1.72, 3H, s and 1.60, 6H, s).

Its mass spectrum showed molecular ion peak $M^+ m/e = 278$, therefore, the molecular formula C$_{18}$H$_{30}$O$_2$. Other prominent peaks at m/e 43 and 125 due to cleavage of C$_2$-C$_3$ and C$_7$-C$_8$ carbon chain are consistent with the
proposed structure. The peak at m/e 71 (\(^{1}CH(OH)C(Me)=CH_2\))
confirmed the position of hydroxy group.

The trans stereochemistry of C9 and C5 olefinic bonds was established by its C\(^{13}\) NMR resonance frequencies at 6 16.0 (q, 2c) due to C6-CH\(_3\) and C10-CH\(_3\) and the configuration R was confirmed by Horan's method. Literature does not seem to record any synthetic evidence for the structure (XXXII). The present studies describe a facile synthesis of this compound through an unambiguous route employing. Claisen rearrangement as an important step for the fixation of trans double bond. The sequence of reactions utilized follows as:

\[
\begin{align*}
\text{XXXIII} & \\
\text{XXXIV} & \\
\text{XXXV} & 
\end{align*}
\]
The starting material 10, 10-ethylenedioxy-2,6-dimethyl-2,6(E)-undecadiene (XXXIII) used for the projected synthesis was prepared as reported in literature (147).

The compound (XXXIII) was subjected to selective epoxidation with one equivalent mole of m-chloroperbenzoic
acid in dichloromethane at low temperature to obtain epoxide (XXXIV) which was purified by chromatography over silica gel in 70% yield. PMR signals at δ 1.1-1.25 (9H, br s, saturated methyls) and 2.57 (1H, t, J = 7 Hz, -CH = CH2) confirmed the formulation. The epoxide ring in (XXXIV) was cleaved with lithium diisopropylamide under nitrogen atmosphere to furnish 10,10-ethylenedioxy-3-hydroxy-2,6-dimethyl-1,6(E)-undecadiene (XXXV) in 50% yield after purification through distillation followed by chromatography. Its IR spectrum showed characteristic bands at 3400 (-OH) and 895 cm⁻¹ (-CH = CH₂). The PMR spectrum exhibited signals at

δ CDCl₃ : 1.20 (3H, s, saturated methyl),  
1.5-1.8 (10H, m, allylic methyls and saturated methylenes),  
2.07 (4H, m, allylic methylenes),  
3.93 (5H, brs, -CH(OH)-CH₂ and -CH = CH₂),  
4.85 and 4.9 (2H, s each, -CH = CH₂),  
5.15 (1H, t like, vinyl proton).

The allylic alcohol (XXXV) subjected to mercuric acetate catalysed trans etherification with ethyl vinyl ether
afforded vinyl ether (XXXVI), which was separated from the unreacted alcohol by chromatography in 70% yield. Absence of IR absorption band in hydroxyl region indicated its formation with the support of PMR signals at $\delta$ 4.93 (4H, s, terminal methylenic protons) and 6.15 (1H, dd, $J = 10, 17$ Hz, -O-CH = CH$_2$). The vinyl ether (XXXVI) on Claisen rearrangement generated the aldehyde 12,12-ethylenedioxy-4,8-dimethyl-4(E),8(E)-tridecadien-1-al (XXXVII) in quantitative yield. The trans geometry of double bond was assigned according to earlier observations (119). IR absorption band at 2710 and 1710 cm$^{-1}$ (-CHO) were observed. Its PMR spectrum gave the following signals at $\delta$ CDCl$_3$

1.22 (3H, s, saturated methyl),

1.63 (6H, s, allylic methyls),

2.05 (8H, m, allylic methylenes),

2.36 (2H, m, -CH$_2$-CHO),

3.93 (4H, s, -CH$_2$-CHO),

5.15 (2H, t like, vinyl protons),

9.9 (1H, -CHO).

The aldehyde (XXXVI) was subjected to Grignard reaction with isopropenylmagnesium bromide in THF at 0-5° to get allylic alcohol (XXXVIII) in 50% yield after
chromatographic purification. Its IR spectrum showed absorption band at 3400 cm\(^{-1}\) (\(-\text{OH}\)) and PMR spectrum indicated the signals at 

\[ \delta_{\text{CDCl}_3} : \]

- 1.22 (3H, s, saturated methyl),
- 1.5-1.7 (13H, m, saturated methylenes and allylic methyls),
- 2.03 (8H, br s, allylic methylenes),
- 3.93 (4H, s, \(\overset{\text{CH}_2}{\text{C}}\overset{\text{O}}{\text{O}}\)),
- 4.74 and 4.8 (2H, s each, \(-\text{HC} = \text{CH}_2\)),
- 5.1 (2H, \(\delta\), \(\delta = 7\text{Hz},\) vinyl protons).

The allylic alcohol (XXXVIII) was deketalized in acetone/water mixture in the presence of small amount of PTS to get the title compound (XXXII) which was purified through chromatography over alumina eluting with pet.ether:ether (1:2) (TLC single spot). Its spectroscopic data (IR and PMR) was consistent with that reported for naturally isolated one. The IR spectrum showed following bands at \(\nu_{\text{max}} : 3450, 3080, 2940, 2840, 1710, 1650, 1460, 1390, 1180, 900\) and 780 cm\(^{-1}\).

Its PMR spectrum exhibited the signals at
$\delta_{\text{CDCl}_3}$: 1.4 (2H, t, saturated methylene),
1.66 (9H, br s, allylic methyls),
2.07 (11H, allylic methylenes and $-\hat{C}^-\text{CH}_3$),
2.33 (2H, t, $J = 7\text{Hz}, -\hat{C}^-\text{CH}_2^-\hat{C}^-\text{CH}_3$),
3.96 (1H, t, $J = 7\text{Hz}, -\hat{C}(\text{OH})^-\hat{C}^-\text{CH}_2$),
4.76 and 4.86 (1H, s each, $-\hat{C} = \text{CH}_2$),
5.1 (2H, t like, vinyl protons).
Synthesis of 6,10,14-Trimethyl pentadeca-5(E),9(E)-dien-2,13-dione

A $C_{18}$-terpenic diketone has been isolated by R. Kazlauskas et al. (148) from brown alga C. moniliformis as a homogenous oil. The formulation (XXXIX) was assigned to this terpenoid on the basis of spectral studies.

\[ \text{XXXIX} \]

High resolution mass spectrum indicated the elemental composition of (XXXIX) as $C_{18}H_{30}O_2$ ($M^+ m/e 278.2245$) while its low resolution mass spectral analysis fully supported the assigned structure showing major fragments at $m/e 260 \ (M^+ - H_2O)$, 192, 125, 97, 71 $[(CH_3)_2-CH-C \equiv O^+]$ and 43 $[(CH_3 - C \equiv O^+), \text{base peak}]$.

The IR spectrum revealed the presence of saturated carbonyl groups (1715 cm$^{-1}$) and PMR spectrum signals at $\delta 2.08 \ (3H, s)$, 1.02 $\ (6H, t, J = 7 \text{ Hz})$ and 2.44 $\ (1H, \text{ heptet, } J = 7 \text{ Hz})$ confirmed the position of keto groups. Other PMR signals were also consistent with the proposed skeleton (XXXIX).
Earlier no attempt has been made for the synthesis of this diketone. Present studies include an unambiguous synthesis of this naturally occurring terpenoid starting with aldehyde (XXXVII), prepared as reported earlier. The scheme follows as:

Grignard reaction on aldehyde (XXXVII) with isopropylmagnesium iodide in THF furnished 2,2-ethylene-dioxy-13-hydroxy-6,10,14-trimethyl-5(E),9(E)-pentadecadiene (XL) in 75% yield after chromatographic purification. IR absorption band at 3400 cm\(^{-1}\) (\(-\text{OH}\)) and PMR spectrum confirmed the formulation showing signals at
Oxidation of the alcohol (XL) with pyridinium chlorochromate and sodium acetate in dichloromethane afforded the ketone (XLI) in 52% yield. Its IR spectrum showed absorption band at 1710 cm⁻¹ (keto group). The PMR spectrum gave the following signals at

$$\delta_{CDCl_3} \quad : \quad 0.93 \ (6H, d, J = 7Hz, -CH_3CH_3),$$

$$1.22 \ (3H, s, -C-CH_3),$$

$$1.5-1.8 \ (10H, m, saturated methylenes and allylic methyls),$$

$$2.07 \ (8H, m, allylic methylenes),$$

$$3.33 \ (1H, m, -CH(OH)-CH(CH_3)_2),$$

$$3.93 \ (4H, s, -CH_2-CH_2),$$

$$5.15 \ (2H, t like, vinyl protons).$$
Finally, the deketalization of (XLI) under usual conditions gave the title compound (XXXIX) in 80% yield. It was purified by chromatography over neutral alumina (TLC single spot) and characterised through its IR and PMR spectra.

Its IR spectrum indicated absorption band at

\[ \nu_{\text{max.}} : \quad 2960, 2920, 2850, 1710, 1450, 1360, 1175, 895, 795, 770 \text{ cm}^{-1}. \]

The PMR spectrum exhibited the signals at

\[ \delta_{\text{CDCl}_3} : \quad 1.07 (6H, d, J = 7 \text{ Hz}, -C-CH(\text{CH}_3)), \]

\[ 1.66 (6H, s, \text{allylic methyls}), \]

\[ 2.07 (11H, \text{br s, allylic methylene and } -C-\text{CH}_3), \]

\[ 2.2-2.6 (5H, \text{br s, CH}_3-C-\text{CH}_2 \text{ and } -\text{CH}_2-C-\text{CH}_2), \]

\[ 5.03 (2H, t \text{ like, vinyl protons}). \]
(iii) Synthesis of (+) 13,14-Epoxy-6,10,14-trimethylpentadeca-5(E), 9(E)-dien-2-one

Kazlauskas R. and coworkers have reported the isolation of the farnesylacetone epoxide, a colourless oil from C. moniloformis (148). Detailed spectroscopic studies have shown it to have the structure (XLII).

The molecular ion peak $M^+ m/e = 278.2244$ indicated its molecular formula to be $C_{18}H_{30}O_2$. The presence of methyl ketone was established by its IR spectrum (1710 cm$^{-1}$), PMR signal at $\delta 2.00 (3H, s)$ and $C^{13}$ NMR ($\delta 208.0, s$). Trisubstituted epoxide grouping was inferred from its PMR signals at $\delta 1.18$ and $1.22 (s$ each, $-HC\to C\to CH_3$) and $2.5 (1H, s, J = 7$ Hz, $-HC\to O\to C<$).

No attempt has been made to synthesize this compound earlier. However, the present studies embody an unambiguous route to synthesize the title compound making use of well known Wittig reaction. The sequence of reactions employed is depicted below:
Wittig reaction on aldehyde (XXXVII), with isopropylene triphenylphosphorane in DMSO using NaH as base provided 2,2-ethylenedioxy-6,10,14-trimethyl-5(E),9(E)-13-pentadecatriene (XLIII) which was purified through column chromatography in 50% yield. Its PMR spectrum confirmed the formulation showing signals at

$$\delta_{\text{CDCl}_3}: 1.22 \text{ (3H, s, saturated methyl)},$$

$$1.66 \text{ (12H, m, allylic methyls)},$$

$$2.03 \text{ (10H, m, allylic methylenes)},$$
3.93 (4H, s, \( \succ C \begin{array}{c} 0 - \text{CH}_2 \end{array} \)),

5.15 (3H, \( \dagger \) like, vinyl protons).

The compound (XLIII) was submitted to selective epoxidation with one mole equivalent of m-chloroperbenzoic acid in methylene chloride at 0-5° to get epoxide (XLIV) which was purified through chromatography over silica gel. Its FMR spectrum showed the following signals at \( \delta_{\text{CDC1}} \):

1.20 (9H, br s, saturated methyls),
1.5-1.7 (10H, m, allylic methyls and saturated methylenes),
2.03 (8H, m, allylic methylenes),
2.5 (1H, \( \dagger \) like, \( - \text{CH} - \text{C} \)),
3.93 (4H, s, \( \succ C \begin{array}{c} 0 - \text{CH}_2 \end{array} \)),
5.15 (2H, \( \dagger \) like, vinyl protons).

The epoxide 13, 14-epoxy-2,2-ethylenedioxy-6, 10, 14-trimethyl-5(E), 9(E)-pentadecadiene (XLIV) was deketalized under usual conditions to afford the title compound (XLII) which was purified through chromatography over silica gel to get pure (TLC single spot) 13, 14-epoxy-6, 10-dimethyl-5(E), 9(E)-pentadecadien-2-one (XLII). The identity of
the synthetic sample (XLII) was confirmed through comparison of its IR and PMR spectra with that reported in literature.

Its IR spectrum showed absorption bands at

\[ \nu_{\text{max.}} : 2960, 2920, 2850, 1710, 1650, 1450, 1370, 1170, 1120, 890 \text{ and } 830 \text{ cm}^{-1}. \]

The PMR spectrum gave the following signals at \( \delta_{\text{CDCl}} \):

- \( 1.22 (6H, \delta, \text{saturated methyls}) \),
- \( 1.66 (6H, \delta, \text{allylic methyls}) \),
- \( 2.03 (8H, \delta, \text{allylic methylenes}) \),
- \( 2.12 (3H, \delta, -CH_3) \),
- \( 2.33 (2H, \delta, J = 7 \text{ Hz}, -CH_2-C-CH_3) \),
- \( 2.5 (1H, \delta \text{ like }, -HC-C<) \),
- \( 5.12 (2H, \delta \text{ like}, \text{vinyl protons}) \).
CHAPTER IV
An acyclic norsesquiterpenic ketone, having a molecular formula $C_{14}H_{24}O$ has been isolated (149) by Higgs and Faulkner from the Caribbean sponge *Plakortis halichondrioides* as a minor metabolite. The ketone, related in structure to Plakortin, a lipid soluble antibiotic from same source, was assigned structure (XLV) exclusively on the basis of spectral studies (149).

The presence of $\alpha$, $\beta$-unsaturated carbonyl function was inferred through its IR absorption band at 1690 cm$^{-1}$ and UV spectrum absorption at $\lambda_{\text{max}}$ 237 nm ($\varepsilon$, 18900 in methanol). The PMR spectrum exhibited signals at $\delta$ 1.07 (3H, t, $J = 7$Hz) and 2.44 (2H, q, $J = 7$Hz) indicating the presence of an ethyl ketone moiety. The signals at $\delta$ 6.0 (1H, $s$) and 2.1 (3H, $s$) are due to proton at C$_4$ and methyl at C$_5$ which indicate trans geometry of C$_4$-C$_5$ double bond. The other signals at $\delta$ 0.85 (3H, t, $J = 7$Hz),
0.95 (3H, t, J = 7 Hz), 5.07 (1H, dd, J = 15, 9 Hz), and 5.39 (1H, dt, J = 15, 6.6 Hz) are also consistent with the proposed structure (XLV).

Literature does not seem to record any synthesis of the title compound. However, the confirmation of this structure has been sought through an unambiguous synthesis. It employs Claisen rearrangement to fix the trans geometry of the disubstituted olefinic bond and the technique of acid catalysed rearrangement of tertiary vinylic alcohol in acetic acid to primary allylic acetates (122,123) for the fixation of the trisubstituted double bond at the desired position with a required trans-stereochemistry. The sequence of reactions utilized in this synthesis is shown below:
2-Pentyl-1-ol (XLVI) was prepared by alkylation of dilithio derivative of propargyl alcohol with ethyl bromide in the presence of Li/Liq.NH$_3$ (150) using Fe(NO$_3$)$_3$ as catalyst and THF as co-solvent. Its IR spectrum showed bands at 3500 and 2350, 2230 cm$^{-1}$ characteristic of hydroxyl function and acetylenic bond respectively. The alcohol (XLVI) was partially hydrogenated in the presence of Lindlar's catalyst (151) in dry hexane containing few drops of quinoline to furnish 2(Z)-penten-1-ol (XLVII). IR spectrum of (XLVII) indicated bands at 3400, (-OH), 1650 and 720 cm$^{-1}$ (cis double bond) and no absorption in acetylenic region. PMR further supported the formulation giving signal at $\delta$ 5.3 (2H, m) for olefinic protons.

Oxidation of this alcohol with pyridinium chlorochromate and sodium acetate in methylenechloride afforded the aldehyde (XLVIII) with trans double bond (144). The characteristic IR absorption bands at 2710 and 1690 cm$^{-1}$ (conjugated aldehyde) were observed. The aldehyde (XLVIII) was subjected to Grignard reaction with ethyl magnesium bromide
in THF to obtain secondary alcohol 3-hydroxy-4(E)-heptene (XLIX) in 80 % yield. It was characterised by IR absorption band at 3400 cm\(^{-1}\) (-OH). The PMR spectrum confirmed the structure exhibiting signals at

\[\delta_{\text{CDCl}_3} : \]
- 0.85 and 1.0 (3H each, t each, \(J = 7\text{Hz}, \) saturated methyls),
- 1.5 (2H, m, saturated methylene),
- 2.05 (2H, q, \(J = 7\text{Hz}, \) allylic methylene),
- 4.1 (1H, q, \(J = 7\text{Hz}, -\text{CH(OH)}-\text{C}_2\text{H}_5\)),
- 5.1-5.4 (2H, m, vinyl protons).

The allylic alcohol (XLIX) on trans etherification with ethyl vinyl ether using mercuric acetate as catalyst provided the vinyl ether (L) in 70 % yield after purification by chromatography. Its IR spectrum showed absence of hydroxyl function. This vinyl ether was subjected to Claisen rearrangement under nitrogen atmosphere at 145-50\(^\circ\) to generate the sharp smelling aldehyde (LI) quantitatively with trans double bond (119). The formulation was confirmed through its IR absorption bands at 2710 and 1710 cm\(^{-1}\)(-CHO). The Grignard reaction on 3-ethyl-4(E)-hepten-1-al (LI) with methylmagnesium iodide in dry ether furnished the alcohol (LII) which after distillation was oxidised with
pyridinium chlorochromate in dichloromethane to the methyl ketone (LIII). Grignard reaction of vinylmagnesium bromide, on the methyl ketone (LIII) in THF produced 5-ethyl-3-methyl-1,6(E)-nonadien-3-ol (LIV) in 70 % yield. Its IR spectrum was transparent in carbonyl region, but showed new absorption bands at 3400 (-OH) and 910 cm$^{-1}$ (terminal methylene). The tertiary vinylic alcohol (LIV) was transformed into primary allylic acetate (LV) by treatment with acetic anhydride-glacial acetic acid in the presence of p-toluene sulphonic acid (122). Its PMR revealed the trans geometry of trisubstituted double bond showing signals at

$$\delta_{CDCl_3}$$ : 0.85-1.1 (6H, m, saturated methyls),
1.7 (3H, s, allylic methyl),
2.05 (5H, br s, allylic methylenes and methyne),
2.1 (3H, s, -O-CH$\text{CH}_3$),
4.55 (2H, d, $J = 7$ Hz, -CH$_2$-O-)
5.1-5.4 (3H, m, vinyl protons).

The acetate (LV) was saponified through refluxing with potassium hydroxide in aqueous methanol to procure the allylic alcohol (LVI) which was purified by chromatography in 80 % yield. IR : 3400 cm$^{-1}$. Its PMR gave signals at
$\delta_{\text{CDCl}_3} : 0.85-1.0$ (6H, m, saturated methyls),
1.65 (3H, s, allylic methyl),
2.05 (5H, m, allylic methylenes and methyne),
4.1 (2H, d, $J = 7$Hz, $\text{-CH}_2$-OH),
5.1-5.4 (3H, m, vinyl protons).

The allylic carbinol (LVII) was oxidised with pyridinium chloromate to get the aldehyde (LVII). IR : 2750 and 1680 cm$^{-1}$. The PMR spectrum showed the following signals at

$\delta_{\text{CDCl}_3} : 0.85-1.0$ (6H, m, saturated methyls),
2.15 (3H, s, allylic methyl),
5.1-5.4 (2H, m, $-\text{CH} = \text{CH}-$),
5.8 (1H, d, $J = 7$Hz, $\text{C(CH}_2\text{)} = \text{CH}$-CHO),
10.0 (1H, s, -CHO).

5-Ethyl-3-methyl-2(E),6(E)-nonadien-1-al (LVII) was submitted to the Grignard reaction with ethylmagnesium bromide in THF to afford the alcohol (LVIII) which was purified by chromatography. Its PMR spectrum exhibited the signals at

$\delta_{\text{CDCl}_3} : 0.85-1.1$ (9H, m, saturated methyls),
1.65 (3H, s, allylic methyl),
2.05 (5H, m, allylic methylenes and methyne ),
4.1 (1H, m, -CH(OH)-C₂H₅),
5.1-5.4 (3H, m, vinyl protons).

The allylic alcohol (LVIII) was finally subjected to oxidation with pyridinium chlorochromate in dichloromethane and the resulting ketone was purified by chromatography over neutral alumina to get the pure (TLC single spot) title compound (XLII). It was characterised through comparison of its spectral data (IR and PMR) with that reported in literature for the natural one.

IR absorption bands were observed at
\[ \nu_{\text{max.}} : \quad 2960, 2940, 2850, 1690, 1630, 1460, 1390, \]
\[ 1275, 1135, 1050, 980, 890 \text{ and } 800 \text{ cm}^{-1}. \]

PMR spectrum gave the following signals at
\[ \delta_{\text{CDCl₃}} : \quad 0.85-1.1 (9H, s, saturated methyls), \]
\[ 2.1 (3H, s, allylic methyl), \]
\[ 2.44 (2H, m, -C - CH₂-CH₃), \]
\[ 5.1-5.4 (2H, m, -CH = CH- ), \]
\[ 6.0 (1H, s, - C = CH - C - ). \]
Synthesis of 2,6,10-Trimethyldodeca-2(E),6(E),10(E)-trien-1,12-diacetate

Bohlmann and coworkers (152) have isolated the diacetate derivative of farnesol from *Trancetam odisissunum* and proposed the structure (LIX) exclusively on the basis of spectroscopic evidences.

![Structure LIX](image)

The prominent bands at 1740 and 1230 cm\(^{-1}\) in its IR spectrum suggested the presence of acetoxy groups. The mass spectrum showed the parent ion peak at m/e 262, 193, indicating, thereby, the molecular formula \(\text{C}_{19}\text{H}_{26}\text{O}_{2}\). The base peak at m/e 43 (Me- C\(\equiv\) O\(^+\)) and other major fragments at 202 (M\(^+\)-ACOH) and 186 (202-Me) fully support the proposed structure (LIX).

The PMR spectrum exhibited signals at \(\delta 4.52 (2\text{H, br d}), 4.44 (2\text{H, s})\) and 2.03 (3\text{H, s}), 2.05 (3\text{H, s}) revealed the presence of two acetoxy functions at C\(_1\) and C\(_{12}\) positions while signals at \(\delta 5.11, 5.35\) and 5.45 (1\text{H each, t each}) and at 1.68, 1.57, 1.62 (3\text{H each, s each}) indicated the
presence of three trisubstituted olefinic double bonds with methyl substituents. $^{13}$C NMR shifts showed the trans geometry of trisubstituted double bonds.

Literature does not seem to record any synthetic evidence for the terpenoid (LIX). This part of present dissertation describes its synthesis which incorporates Claisen rearrangement and modified Wittig reaction as the key steps for the generation of double bonds of desired trans stereochemistry at specific positions. The starting material was prepared by protecting hydroxyl group of the geraniol as tetrahydropyranyl ether (145). The sequence of reactions is depicted as:

\[
\begin{align*}
\text{THPO} & \quad \text{LX} \\
\text{THPO} & \quad \text{LXI} \\
\text{THPO} & \quad \text{LXII}
\end{align*}
\]
2,6-Dimethyl-8-tetrahydropyranloxy-2,6(E)-octadiene (LX) on selective epoxidation with one equivalent mole of m-chloroperbenzoic acid in the presence of anhydrous sodium acetate in dichloromethane furnished the epoxide (LXI) which was separated through chromatography over silica gel in 70% yield. PMR spectrum showed the signals at $\delta$ 1.2 (6H, br s) and 2.5 (1H, t, $J = 7$Hz). This oxirane ring in (LXI) was cleaved with lithium diisopropylamide to get allylic alcohol (LXII). It was purified through distillation followed by chromatography and transformed into its vinyl ether (LXIII) with excess of ethyl vinyl ether, using mercuric acetate as catalyst, in 70% yield after chromatography. The vinyl ether (LXIII) on Claisen rearrangement under nitrogen atmosphere at 160-165° gave sweet smelling aldehyde 4,8-dimethyl-10-tetrahydropyranloxy-4(E),8(E)-decadien-1-al (LXIV) in quantitative yield. Its IR spectrum indicated characteristic bands at 2710 and 1710 cm$^{-1}$ (-CHO). The PMR spectrum exhibited the signals at $\delta_{\text{CDCl}_3}$:

- 1.5-1.72 (12H, m, allylic methyls and saturated methylenes),
- 2.03 (6H, m, allylic methylenes),
- 2.35 (2H, m, -CH$_2$-CHO).
The aldehyde (LXIV) was subjected to modified Wittig reaction with ethyl $\alpha$-diethylphosphonopropionate in THF using NaH as base to produce conjugated ester (LXV) as a mixture of cis and trans isomers. The predominant trans isomer was separated through chromatography. IR: 1710 and 1270 cm$^{-1}$ (conjugated ester). The PMR spectrum confirmed the trans stereochemistry of the double bond giving signals at

$\delta$ (CDCl$_3$): 1.3 (3H, t, $J$ = 7 Hz, $-O-CH_2-CH_3$)
1.66-1.8 (15H, m, allylic methyls and saturated methylenes),
2.07 (8H, br s, allylic methylenes),
3.3-3.9 (4H, m, $-CH_2-O-CH-O-CH_2-CH_2$),
4.15 (2H, $q$, $J$ = 7 Hz, $-CO-CH_2-CH_3$),
4.5 (1H, $q$, $-O-CH-O$),
5.15 (2H, $t$ like, vinyl proton),
6.66 (1H, $t$, $J$ = 7 Hz, $\ce{^1H}C=\ce{^3CH}$),
7.6 (1H, $s$, $-CHO$).
The reduction of ester group was accomplished with LAH-absolute alcohol reagent in ether to get 2,6,10-trimethyl-12-tetrahydropyranyloxy-2(E),6(E),10(E)-dodecatrien-1-ol (LXVI) which was purified through chromatography. Its IR spectrum showed absorption band at 3400 (-OH). The PMR spectrum exhibited the signals at

$$\delta_{\text{CDCl}_3} : 1.4-1.7 \ (15H, \text{ m, allylic methyls and saturated methylenes}),$$

$$2.05 \ (8H, \text{ m, allylic methylenes}),$$

$$3.3-3.7(4H, \text{ m, } -\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-),$$

$$3.9 \ (2H, \text{ s, } -\text{CH}_2\text{OH}),$$

$$4.5 \ (1H, \text{ s, } -\text{O}-\text{CH}_2\text{O}),$$

$$5.10 \ (1H, \text{ t, } J = 7\text{Hz, vinyl proton}),$$

$$5.33 \ (2H, \text{ t, } J = 7\text{Hz vinyl protons}).$$

The tetrahydropyranyloxy group in (LXVI) was removed in methanol/PTS to get the diol (LXVII) in 90% yield after chromatography over silica gel. Broad IR absorption band at 3400-3250 cm$^{-1}$ (diol) was observed. Its PMR showed the following signals at

$$\delta_{\text{CDCl}_3} : 1.6 \ (9H, \text{ br s, allylic methyls}),$$

$$2.05 \ (8H, \text{ br s, allylic methylenes}),$$
2,6,10-Trimethyl-2(E),6(E),10(E)-dodecatrien-1,12-diol (LXVII) was finally converted into its diacetate derivative (LIX) with acetic anhydride and glacial acetic acid in the presence of PTS and purified through chromatography over neutral alumina using pet. ether : ether (8:2) as eluent. The identity of the synthetic sample was made through comparison of its IR and PMR spectra with that reported in literature for natural occurring one.

The IR spectrum showed the following absorption bands:

\[ \nu_{\text{max.}} \quad : \quad 2960, 2850, 1740, 1460, 1390, 1260, 1060, \text{and} \ 1035 \ \text{cm}^{-1}. \]

Its PMR exhibited the signals at

\[ \delta_{\text{CDCl}_3} \quad : \quad 1.6 \ (9H, \ br \ s, \ allylic \ methyls), \]
\[ 2.0-2.05 \ (14H, \ m, \ allylic \ methylenes \ and \ C-CH_3 \ protons), \]
\[ 4.15 \ (4H, \ d \ like, \ -CH_2-OAC \ protons), \]
\[ 5.1 \ (1H, \ t, \ J = 7Hz, \ vinyl \ proton), \]
\[ 5.35 \ (2H, \ t, \ J = 7Hz, \ vinyl \ protons). \]