PART I : SECTION A

REVIEW OF PREVIOUS WORK ON FUNCTIONALISATION OF ANGULAR METHYL GROUPS AND SELENIUM DIOXIDE OXIDATION
This chapter describes the methods for the selective functionalisation of angular methyl groups in rigid systems like steroids and terpenoids.

Selective functionalisation is a process which makes use of the proximity of a functional group, such as a hydroxyl or an amino group, to a nonactivated carbon-hydrogen bond within the framework of a rigid molecule. There is a small group of photolytic reactions, however, which do serve to functionalise an unactivated saturated site. The application of intramolecular functionalisation of nonactivated carbons gave solution to specific synthetic problems.

The up-to-date methods for the functionalisation of angular methyl groups in rigid systems are mentioned below. Two reviews\(^1\) on the progress in attacking methods for nonactivated angular methyl groups with nitrite radical (Barton reaction), lead tetraacetate and hypohalites appeared in 1972. However, only the hypohalite method which has been utilised in the present work has been described in detail.

Principles of Functionalisation\(^1\)

The process of functionalisation proceeds through high energy intermediates capable of attacking unactivated C-H bonds. These
intermediates are free radicals or photoexcited groups in which the
attacking centres have some radical character. The desired selectivity
is achieved when the attacking species is in all cases generated within
the steroid or terpene molecule at a centre either sterically fixed in
close proximity to the angular methyl group or capable of attaining such
a position. All these processes involve intramolecular free radical
reactions. The positions from which attack at the angular methyl groups
in a steroid molecule has been realised are shown in the following
diagram:

These reactions have certain features in common (Scheme 1):

(a) The starting material contains a functional group with a weak
bond between two heteroatoms.
(b) This bond is cleaved homolytically by irradiation (Step A).
(c) The radical produced abstracts a hydrogen from a saturated carbon atom of the skeleton four atoms away, through a cyclic six-membered transition state (Step B).

(d) The other heteroatom radical, released from the skeleton, now bonds to the new carbon radical (Step C).

The formation of the hetero radical (Step A):

The radical \(-O^*\) is formed by homolysis of the \(-O-X\) bond either thermally or photolytically. In the reactions of alcohols with lead tetraacetate evidence suggests that the \(-O-X\) bond \([X = Pb(OAC)_3]\) has ionic character. In this case the exy radical is formed by a one electron transfer (thermally or photochemically induced) from oxygen to lead.

Scheme 1

when, \(X = NO\) (nitrite photolysis or Barton reaction),
\(X = Pb(OAC)_3\) (lead tetraacetate reaction),
\(X = Cl, Br, I\) (hypohalite).

The hydrogen transfer (Step B):

The efficiency of the abstraction of a hydrogen atom at one of the angular methyl groups in steroids is strongly dependent upon the
distance of the oxy radical from the hydrogen atoms of the angular methyl groups. The rate of hydrogen abstraction is maximum within the internuclear distance of 2.5 - 2.7 Å between the oxygen and the methyl carbon. The rate rapidly decreases with increasing distance and becomes very slow at distances over 3Å. In cases where the relation between oxygen and the methyl carbon is not rigidly fixed yields are still fairly high, provided the more stable conformation of the substrate shows the optimal C-O distance. This is the case for 20α-hydroxy steroids with respect to the C-18 methyl group.

Even in a rigid system the yield may be low due to other compelling reasons. One of them is intermolecular hydrogen abstraction process to regenerate the starting alcohol. The use of solvents like benzene which does not contain easily abstractable hydrogen atom can minimise the effect of intermolecular hydrogen abstraction process.

The sequence suggests that molecular conformation must allow a feasible cyclic six-membered transition state. The groups involved in the functionalisation process being cis, 1,3-diaxial are ideally situated to form such a transition state.
Reaction of the carbon radical (Step C):

The carbon radical formed in the hydrogen abstraction Step B will react with the radical \( X' \) formed in the homolysis of the \(-O-X\) bond. However, a cage reaction does not seem to be involved in this step. This has been established in the nitrite photolysis\(^2,3\) and probably applies to hypochalites as well. In the lead tetracetate reaction, the steps following the oxyradical formation leading to tetrahydrofuran derivatives are less clear.

**Hypochalite Reactions**

(a) **General aspects**:

Hypochalites are the best suitable reagents for functionalisation at the angular positions in steroids and terpenoids. However, the tendency for the homolytic decomposition is greatest for the hypsoiodites. Since hypsoiodites do not readily react with ketones or carbon-carbon double bonds under neutral conditions, they are generally more applicable than hypochlorites or hypobromites.

(b) **Preparation of the hypsoiodites**:

Alkyl hypsoiodites are easily prepared in situ from alkoide and iodine by exchange reactions of alcohols with reagents containing "positive" iodine. Hypsoiodites are formed from alcohols with mercuric oxide and iodine\(^4\), with t-butyl hypochlorite and iodine\(^4\), with t-butyl hypsoiodite (from potassium t-butoxide and iodine)\(^4\), with \(\mathrm{N}\)-bromosuccinimide and iodine\(^3\), with \(\mathrm{N}\)-iodosuccinimide\(^3\) and with acetyl hypsoiodite\(^5\).
The latter reagent is conveniently prepared from iodine and metal acetates such as silver acetate, mercuric acetate and very effectively from lead tetraacetate and iodine. The best solvents for the preparation of the hypoiodites are either saturated hydrocarbons, e.g., cyclohexane or halogenated hydrocarbons, e.g., carbon tetrachloride or methylene dichloride. It is not clear whether or not hypoiodites are formed in aromatic solvents such as benzene. However, cyclohexane is the most widely used solvent for hypoiodite reactions.

(c) Decomposition of hypoiodites:

Hypoiodites may be decomposed thermally (e.g., boiling cyclohexane or carbon tetrachloride) although there are no clear indications that the process involves a chain reaction similar to the one postulated for aliphatic hypochlorite decompositions. The thermal hypoiodite decomposition can be induced by excited iodine molecules in cyclohexane in presence of light with a wavelength of 500-550 nm. Usually tungsten lamps and mercury arc lamps are used.

(d) Special features and stereochemical influences:

Mercuric oxide-iodine procedure seems to be the simplest. It has only been applied to very few cases and only others (1) have been obtained.

A considerable extension of the synthetic utility of the hypoiodite reaction is achieved if the steroid hypoiodite (2) is generated
from the alcohol and acetyl hypoiodite and then decomposed in a nonpolar solvent. In this case ionic hydrogen iodide elimination in the 1,5-iodohydrin intermediate (3) is slow, thereby allowing (3) to be converted into an iodo hypoiodite (4).

Decomposition of (4) gives rise to an iodo ether (5). It has been shown\(^7\) that the ratio of the rates of the reactions (3) \(\rightarrow\) (1) and (3) \(\rightarrow\) (4), which determine the products \(\bigcup\) (1) or (5) \(\bigcup\), depends mainly on two factors:

1. The efficiency with which hypoiodites are formed and/or homolytically decomposed;

2. the conformation of the \(-\text{CH}_2\text{I}\) grouping\(^8\) in the intermediates (3) and (4).

The rotation of an axial \(-\text{CH}_2\text{I}\) group in a polycyclic saturated system is severely hindered by axial substituents on the same face; therefore
preferred orientations for both an 18-(6) and 19-CH₂I (7) in steroids can be written. In 6\(\beta\)-hydroxy-12-iodo steroids (7) the orientation of the reacting centres -O-CH₂-I resembles the arrangement in the transition state of an SN2 displacement reaction and consequently the activation energy for the transition (3) \(\rightarrow\) (1) is low.

If the oxygen atom in (7) is placed at positions 2\(\beta\), 4\(\beta\) or 11\(\beta\) the linear relationship of -O-CH₂-I cannot be reached\(^8\). Therefore if faster (i) is favourable the reaction should proceed with a second hydrogen abstraction from (3) to (5). The same arguments apply to 11\(\beta\) and 20-oxo derivatives with respect to an 18-CH₂-I group. Here again products of type (5) are expected.

In steroids of the 5\(\beta\)-H series, however, the situation with respect to C-19 substitution (8) changes. Displacement is now favoured from 11\(\beta\) whereas abstraction is favoured from 6\(\beta\). Accordingly, 11\(\beta\), 19-ethers and 6\(\beta\), 19-hemiacetals or lactones are the main products\(^9,10\).
With $11\beta$-hydroxy steroids $11\beta$, 19-ether formation competes with hemi-acetal formation. This is a consequence of steric hindrance of the $11\beta$-oxygen by the C-18 and C-19 iodomethyl groups which reduces the rate of hypoiodite formation $\xrightarrow{(3)} \rightarrow (4)$ even though the conformation of the iodomethyl is similar to that shown in (7).

The formation of the iodo compound (9) as side product is frequently observed during lead tetraacetate, silver acetate and iodine oxidation of 20-hydroxy steroids (10). Both the 17\(\alpha\) and 17\(\beta\) epimers are obtained.

The formation of the iodo compound may be explained by the following mechanism.
Applications of hypoiodite reaction:

The hypoiodite reaction has been used for the functionalisation of the angular methyl groups in steroids particularly for the synthesis of 19-norsteroids and other important compounds of higher synthetic value. It is also proved to be helpful in determining the correct structure and stereochemistry of the compounds. In most cases cyclohexane as solvent and lead tetraacetate and iodine as the iodinating agent are used. Best results are obtained when the molar ratios of substrate: iodine: lead tetraacetate are kept around 1:1.25:5.

2β, 19-ethers are obtained from saturated 2β-hydroxy steroids. 2β, 19-lactones are simultaneously produced either directly or by oxidation of the hemiacetal formed\(^\text{14}\). 4β-hydroxy steroids also yield 4β, 19-lactones as major product\(^\text{15}\). Extensive work has been done in converting 6β-hydroxy steroids to 6β, 19-oxide steroids\(^\text{4,11,16-21}\). Reactions were carried out on substrates carrying a substituent at C-5 also.

Moriarty and Kapadia\(^\text{22}\) reported that the compound (11) having an olefinic linkage between C\(_5\) and C\(_6\) on treatment with lead tetraacetate and iodine underwent oxidative fragmentation with loss of hydroxymethyl group at C\(_{10}\), to produce the compound (12). However, treatment of 3β-acetoxy-5, 6β-oxide-5β-cholestan-19-ol (13) with lead tetraacetate iodine led to the formation of 3β-acetoxy-5, 6β:11β, 19-dioxo-5β-cholestan (14)\(^\text{23}\).
Evidently, the hydrogen atom to be abstracted was the one attached to C₁₁ and not to C₂, C₄ or C₈, since the internuclear distance between the oxo radical and the C₁₁ 6-carbon atom was minimum. Hypoiodite reactions were also studied with C-nor-D-hemosteroids²⁴-²⁶.

So far, various types of functionalisation in the field of steroids have been discussed. The application of the above methods in terpene chemistry during the last few decades is discussed below.
Under suitable reaction conditions, simultaneous functionalisation of the angular methyl groups at C$_{10}$ and C$_{13}$ in 11$\beta$-hydroxy-lanostan-3$\beta$-yl-acetate$^{27}$(15) could be performed with lead tetracetate iodine reaction. Functionalisation of the C$_8$ methyl group in the rosane skeleton$^{28}$ was reported by Nakano et al. in 1971. Kitadani reported that isopimarane-8$\beta$-ol (16)$^{29}$ underwent similar oxidation to afford the oxide (17) and iodo oxide (18).
Extension of these functionalisation studies to hopan-7β-ol (19) and hopan-15β-ol (20) and their 21α-β epimers were made by Corbett et al. In each case the major product was an oxide as shown.

3β-friedelanol (21) on photochemical oxidation with lead tetracetate in presence of iodine followed by Jones' oxidation of the product furnished the γ-lactone of 3β-hydroxy-friedelal-24-oic acid (22).
Selenium dioxide is a reagent most often used for the oxidation of methylene groups $\alpha$ to a carbonyl to give $\alpha$-dicarbonyl compounds.

$$R-C-CH_2-R' \xrightleftharpoons{SeO_2} R-C=C-R'$$

Other unsaturated groups - double and triple bonds and aromatic rings - also activate the methylene group. Substrates most easily oxidised contain two aryl groups on the methylene group. The mechanism probably involves a selenate ester of the enol$^3$$^2$. 

$$\begin{align*}
C_6H_5-C-CH_2-C_6H_5 & \xrightarrow{SeO_2} C_6H_5-C=CH-C_6H_5 \quad H_2O, CH_3COOH \\
C_6H_5-C=CH-C_6H_5 & \xrightarrow{H_2O, CH_3COOH} C_6H_5-C=C-C_6H_5 \quad -H_2O, -Se
\end{align*}$$
Selenium dioxide is often used to generate a second double bond in the compound of the type (23) or of the type (24) thus affording the corresponding heterocyclic dienes.

Although most of the synthetically useful applications of selenium dioxide oxidation of organic compounds lead to the introduction of carbonyl groups or other unsaturation and therefore, do not ordinarily introduce new asymmetric centres, the oxidation of olefins to allylic alcohols may involve the creation of a new asymmetric centre. The allylic oxidation of a series of alkylated cyclohexenes by selenium dioxide in wet dioxane has been found to proceed stereoselectively (Scheme 2).
### Scheme 2

**Reagent:** $\text{SeO}_2$

**Medium:** Aq. dioxane

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Products</th>
</tr>
</thead>
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<td><img src="" alt="Product 1" /></td>
</tr>
<tr>
<td><img src="" alt="Substrate 2" /></td>
<td><img src="" alt="Product 4" /></td>
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<td><img src="" alt="Product 7" /></td>
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</tr>
<tr>
<td><img src="" alt="Substrate 6" /></td>
<td><img src="" alt="Product 16" /></td>
</tr>
</tbody>
</table>

**Yields:**
- 12%
- 41%
- 8%
- 48%
- 20%
- 22%
- 39%
- 12%
- 7%
- 20%
- 4.3%
- 5.2%
- 35%
- 3%
- 4.5%
- 0.6%
- 3.4%
Buchi and Vœst\textsuperscript{36} established that selenium dioxide selectively attacked trimethylated olefins and the order of preference for attack by SeO\textsubscript{2} was found to be CH > CH\textsubscript{2} > CH\textsubscript{3}. In spite of considerable amount of studies\textsuperscript{27,44} the mechanism of allylic oxidation of olefins by selenium dioxide has been the subject of controversy over the last few years.

Schaefer \textit{et al.\textsuperscript{44}} suggested the mechanism as shown (Scheme 3) below.

\textbf{Scheme 3}

\begin{center}
\includegraphics[width=0.7\textwidth]{Scheme3.png}
\end{center}

The observation of rearrangement products\textsuperscript{45} in a system such as (25) agreed with the formation of an allylic cation at C-6 which then underwent
Vagner–Meerwein rearrangement followed by proton loss to generate the aromatic system (26) and (27).

Another example \(^{46}\) involved the oxidation of (28) in ethanol to give (29) – (32).

Trachtenberg et al. \(^{47a}\), however, proposed a different mechanism as shown in Scheme 4.
Although the oxidant as shown (Scheme 4) was protonated selenium dioxide, it might instead well be some hydrated (or solvated) form of this, in which case the first two steps of the mechanism \(^{47b}\) would be altered as shown below.

\[
\text{CH}_3 - \text{CH}_3 \quad \text{SeO}_2, \text{H}_2\text{O} \xrightarrow{\text{dioxan reflux}} \quad \text{CH}_3
\]

\[
\text{HO-} - \text{Se-} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{H}
\]

\[
\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{CH}_3
\]

\[
\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{CH}_3
\]

35\% + other products 3\%
The first step did not imply a concerted $\mathcal{S}_2 + \mathcal{S}_2$ cycloaddition but rather a typical Markovnikov type electrophilic addition with attack occurring through oxygen to generate positive character at the tertiary carbon, followed by cyclization. In agreement with the electrophilic attack were the observations that dienes were more reactive than olefins. Olefin reactivity increased with alkyl substitution, and electron feeding groups slightly accelerated the rate of oxidation.

Though Viberg and Nielsen\textsuperscript{43} favoured initial formation of an allyl seleninic acid (33) which then underwent solvolysis to products (Path a, Scheme 5), Schaefer\textsuperscript{44} and Trachtenberg\textsuperscript{47} argued against the involvement of allyl seleninic acids (33). However Sharpless \textit{et al.}\textsuperscript{48}, while studying the mechanism of oxidation of olefins by selenium dioxide, evidenced for the intermediacy of allyl seleninic acids (33) (Scheme 5).

They proposed a $\mathcal{S}_2,2,3$ sigmatropic rearrangement (Path b) of the allyl seleninic acid (33) to a selenium (II) ester (34) which occurred as a likely alternative to the solvolytic pathway (a). Carbonyl products formed in selenium dioxide oxidations might in part arise directly from the selenium (II) ester (Path e).
Recently Lawrie et al. \(^{49}\) reported a mechanism of ring aromatisation with molecular rearrangement in the conversion of 11-exelano stan-3\(\beta\)-yl-acetate (35) to the C-mer-D-homosteroid (36) (Scheme 6).

The initially formed \(\Delta^{11}\)-exyl selenium ester (37) rearranged to the 11-oxo-ester (38) in which the selenium (II) ester group was equatorial and antiparallel to the 13,14-bond.

Displacement of the ester group by the electrons of this bond with loss of a proton from C-12, C-17 or C-18 led to an intermediate (39) having the C-mer-D-homo skeleton. Successive allylic oxidations then led to the cation (40) from which by methyl migration and loss of a proton, the fully aromatic ketone (36) was formed.
Scheme 6

(35) $\xrightarrow{\text{SeO}_2 \cdot \text{H}^+} (37)$

(38) $\xrightarrow{-\text{HO} \cdot \text{Se} \cdot \text{O}^+ \cdot \text{H}^+} (39)$

(40) $\rightarrow (36)$
PART I: SECTION B

PRESENT WORK (THEORETICAL)
The present work describes the method for the functionalisation of the C-25 methyl group of 3β-acetoxy-friedoolean-7β-ol (41)\(^{50,52}\) (Scheme 7), prepared from putranjivadiol (42), a naturally occurring pentacyclic triterpene whose structure and stereochemistry were settled earlier in this laboratory\(^{50,51}\).

The axial 7β-hydroxyl group in (41) suffers from severe 1,3-diaxial interactions by three angular methyl groups at C-24, C-25 and C-26. If the internuclear distance of the oxy radical from the carbon atom of the angular methyl group is within 1 Å, then it would be expected that hypohalite oxidation\(^{1b}\) might effect functionalisation of any or all of the methyl groups.

Indeed here is an ideal case (45) for the functionalisation of any of the three methyl groups i.e., C-24, C-25 and C-26 by the attack of the oxy radical at C-7. However, it is observed from (45) that the
Scheme 7

(42) \[ \text{LAH} \rightarrow (42a) \]

(41) \[ \text{Pb(OAc)}_4 - I_2, \text{CaCO}_3, \text{h}_2 \rightarrow (43) \]

(44) \[ \alpha, R = \text{OAc}, R' = \text{Na} \\
\beta, R = \text{OAc}, R' = \text{CH}_3 \]
methyl group at C-25 is most sterically hindered and hence it would get steric assistance preferentially for functionalisation. As mentioned earlier the process of functionalisation would involve intramolecular free radical reactions.

Irradiation of a mixture of (41), lead tetraacetate, iodine and calcium carbonate in cyclohexane for 3 h with a 500 W tungsten lamp furnished a gummy mixture which could be resolved by Sengupta et al. into three components (43), (44a) and (44b) on chromatography over silica gel.

The least polar fraction (3%) was identified as epifriedelanyl acetate (43), presumably formed by hydrogen radical exchange with cyclohexane (Scheme 8).
A small part of the alcohol (41) was converted to the iodo-derivative (46) before the oxygen radical could be formed. Now the iodo compound (46) could give the radical (47) by a simple process of photochemical dissociation. Ultimately this radical (47) could abstract a proton from cyclohexane to furnish epi-friedelanyl acetate (43).
In the present work from the reaction mixture it has been possible to isolate yet another compound (48) devoid of acetoxy group in the 3-position. Compound (48) resisted catalytic hydrogenation indicating the hindered nature of the double bond.

The structure of the compound (48) was established on the basis of physical evidences e.g., IR, PMR and mass spectral fragmentations as discussed below.

**Structure of the Compound (48)**

**Infrared Spectrum (Fig.1) of the Oxide Compound (48):**

Infrared spectrum of the compound (48) showed no band in the region 1730 and 1252 cm\(^{-1}\) characteristic for acetoxy group, but showed a band at 850 cm\(^{-1}\) which suggested the presence of an ether linkage. It also showed bands at 1360 cm\(^{-1}\) and 1380 cm\(^{-1}\) (gem-dimethyl group).
PMR Spectrum (Fig. 2) of the Compound (48):

**Table 1**

<table>
<thead>
<tr>
<th>Chemical shift (δ)</th>
<th>Splitting pattern</th>
<th>No. of protons</th>
<th>Coupling constant (J) in Hz</th>
<th>Probable assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.25</td>
<td>Doublet</td>
<td>1</td>
<td>5 Hz</td>
<td>Proton at C-7</td>
</tr>
<tr>
<td>3.75, 3.69</td>
<td>Two doublets</td>
<td>2</td>
<td>3.4 Hz (in each case)</td>
<td>Methylene protons of the -O-CH₂- group at C-25</td>
</tr>
<tr>
<td>0.92, 0.96, 0.97, 0.99, 1.03, 1.05, 1.12</td>
<td>Singlet 3 (each)</td>
<td></td>
<td></td>
<td>Seven tertiary methyl groups</td>
</tr>
</tbody>
</table>

As expected, the signal for one tertiary methyl group was absent in (48). Obviously functionalisation of an angular methyl group had taken place to form an ether linkage. Absence of any olefinic proton in the PMR spectrum of compound (48) suggested the tetrasubstituted nature of the double bond. Moreover, the spectrum showed the absence of -O-CH₂CH₃ signal thus suggesting that the compound (48) did not bear any acetoxy group. Due to the rigidity of the cyclic ether skeleton the two methylene protons at C-25 could not lie in the same plane. There was a distinct bond angle between these two protons and consequently they were magnetically non-equivalent; hence they split each other presenting a pair of doublets. The other signals (Table 1) were in complete agreement with the structure (48).
Mass Spectrometric Fragmentation (Fig. 3) studies of the Compound (48) (Chart 1):

The application of mass spectrometry and the study of important fragmentation patterns in the elucidation of the structure of pentacyclic triterpenes have been found to be very useful. The nature of the carbon skeleton of (48) as well as the location of the tetrasubstituted double bond was settled by the general appearance of the mass spectral fragments. The mass spectra (Fig. 3, Chart 1) of compound (48) showed a peak at m/e 205 corresponding to the ion (49), thus demonstrating that the C-26 methyl group had not been affected. A peak at m/e 300 corresponded to the ion (50) which established that functionalisation had taken place at C-25. The base peak appeared at m/e 218 which corresponded to the ion (51). Other prominent peaks were at m/e 424 (M⁺), 409 (M⁺ - CH₃), 393 (M⁺ - CH₂OH), 203, 190, 189 and 241.

Thus the fact that only the C-25 methyl group had been functionalised was definitely established from mass spectra.
CHART 1

m/e 300 (12.95%)

m/e 408 (6.37%)

C$_{30}$H$_{48}$O (70.25%)

m/e 203 (4.14%)

m/e 218 (100%)

m/e 205 (39.88%)

m/e 189
The above physical data could only be explained if the compound (48) had the structure:

\[
\text{Formation of the compound (48) (Scheme 9):}
\]

The acetoxy group in (44a) being $\beta$-axial was in an ideal situation for elimination of a molecule of acetic acid with the formation of a double bond (52). As soon as, the double bond was formed in the acidic environment it was immediately protonated with the concomitant shift of $C_5 - \text{Me}$ to the $C_4$-position with the generation of a tertiary carbo-cation (53). Now this carbo-cation (53) could be stabilized by the elimination of a proton either from C-6 or from C-10. However, it was stabilized by the elimination of a proton from C-10 to give the thermodynamically more stable product (48)$^{58,59}$. 
Oxidation of the Compound (48) with Selenium dioxide:

To establish the position of the double bond, compound (48) was subjected to oxidation with selenium dioxide in acetic acid medium with the expectation of getting a heterocyclic diene (54). Interestingly enough, instead of the diene (54), a naphthalenic hydrocarbon (55) was obtained where A/B rings were fully aromatised with the migration of a methyl group. The mechanism of aromatisation with methyl migration had its analogy as stated earlier.
The structure of the compound (55) was established on the basis of physical evidences e.g., UV, IR, PMR and Mass spectral fragmentations as discussed below.

**UV Spectrum (Fig. 4) of the Compound (55):**

In cyclohexane the compound (55) showed absorption maxima at 229 nm (log $\varepsilon$, 4.79); 239 nm (log $\varepsilon$, 4.97); 288 nm (log $\varepsilon$, 4.67); 315 nm (log $\varepsilon$, 4.18); 322 nm (log $\varepsilon$, 4.01) and 330 nm (log $\varepsilon$, 4.23) which suggested the presence of a substituted naphthalene system.
FIG. 4. UV SPECTRUM OF NAPHTHALENIC HYDROCARBON.
Infrared Spectrum (Fig. 5) of the Compound (55):

Infrared spectrum of the compound (55) showed bands at 1600 cm\(^{-1}\), 1580 cm\(^{-1}\), 1510 cm\(^{-1}\) and 1460 cm\(^{-1}\) diagnostic of aromatic structure and caused by C=C skeletal in-plane vibrations. The second band appeared only as a shoulder of the first. The bands at 1360 cm\(^{-1}\) and 1385 cm\(^{-1}\) were due to the gem-dimethyl group.

PMB Spectrum (Fig. 6) of the Compound (55):

Table 2

<table>
<thead>
<tr>
<th>Chemical shift ((\delta))</th>
<th>Splitting pattern</th>
<th>No. of protons</th>
<th>Coupling constant ((J)) in Hz</th>
<th>Probable assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.37 (\uparrow) 7.40 (\uparrow)</td>
<td>Pair of doublets</td>
<td>2</td>
<td>9 (in each case)</td>
<td>Aromatic protons (H_a) and (H_b)</td>
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<tr>
<td>7.80 (\uparrow) 7.83 (\uparrow)</td>
<td>Pair of doublets</td>
<td>2</td>
<td>9 (in each case)</td>
<td>Aromatic protons (H_c) and (H_d)</td>
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<tr>
<td>3.12</td>
<td>ill-defined multiplet</td>
<td>2</td>
<td></td>
<td>Benzylic protons on C-11</td>
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<tr>
<td>2.58 (\uparrow) 2.46 (\uparrow)</td>
<td>Singlet</td>
<td>3 (each)</td>
<td></td>
<td>Two aromatic methyl groups in ring-A</td>
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<tr>
<td>0.94, 0.97, 1.00, 1.16, 1.26</td>
<td>Singlet</td>
<td>3 (each)</td>
<td></td>
<td>Five tertiary methyl groups</td>
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</tbody>
</table>
As expected, the four aromatic protons ($H_a$, $H_b$, $H_c$ and $H_d$) located on ring-A and ring-B were deshielded due to the ring current effect and ultimately resonated in the downfield region $7.37 \delta$ to $7.83 \delta$. The two methyl groups attached to ring-A experienced slightly reduced local diamagnetic shielding because of the weak electron release from alkyl group to the aromatic ring-A. These two methyl groups were also strongly deshielded because of the ring current effect and hence the resonance signals appeared in the downfield region ($2.58 \delta$ and $2.46 \delta$). Owing to the electron-donating effect of the two methyl groups the electron density at the carbon atoms to which the protons ($H_a$ and $H_b$) were attached was increased and the ultimate result was that these protons were diamagnetically shielded. So the positions of absorption of these aromatic protons ($H_a$ and $H_b$) were slightly in the higher field compared to the positions of the signals for the protons ($H_c$ and $H_d$). The protons ($H_a$ and $H_b$) being magnetically non-equivalent split each other presenting a pair of doublets with the coupling constant $9$ HZ (in each case) responsible for ortho coupling. Similar situation arose for the protons ($H_c$ and $H_d$) and an ortho coupling was observed with the value of $9$ HZ (in each case).
Mass Spectra (Fig. 7) of the Compound (55) (Chart 2):

The molecular ion peak was at m/e 388. The base peak appeared at m/e 209 which corresponded to the ion C$_{16}$H$_{17}^+$ (56). The appearance of prominent peaks at m/e 205 corresponding to the ion (49), m/e 235 corresponding to the ion (57), m/e 221 corresponding to the ion (58) and m/e 183 corresponding to the ion (59) suggested that the compound (55) had a naphthalene skeleton.
Formation of the Compound (55) (Scheme 10):

The B-ring of compound (48) was first aromatised to produce (60) presumably by free-radical mechanism (Scheme 10). The C-1 position of A-ring (60) being benzylic was highly active and was attacked by selenium dioxide through a free radical mechanism to yield the selenium (II) ester (61). When this ester group left a carbo-cation (62) was generated at C-1 and elimination of a proton took place from C-2 to produce the intermediate (63). Further oxidation then led to the intermediate (64) which then led to the cation (65). Methyl migration from C-4 to C-3 and loss of a proton from C-3 led to the naphthalenic hydrocarbon (55).

Scheme 10
PART I : SECTION C

PRESENT WORK (EXPERIMENTAL)
Isolation of Putranjivadiene (42) from the Bark of Putranjiva roxburghii:

Dried and powdered bark of *Putranjiva roxburghii* (1 kg) was extracted with benzene for 20 h in a soxhlet apparatus. The benzene extract, after removal of solvent, was digested with ether and filtered, thus separating the ether soluble and ether insoluble parts. The ether soluble part was then separated into acidic and neutral fractions. The isolation scheme is shown in Chart 3.

**Chart 3**

Dried and powdered bark of *P. roxburghii*  
Extracted with hot benzene  
Benzene extract  
Benzene removed and residue digested with ether  
Ether soluble part  
5% cold alkali  
Neutral ether soluble part (A)  
Alkali soluble fraction (acidic) (B)  
Ether insoluble part, dissolved in boiling chloroform and filtered through a bed of alumina  
Filtrate  
Solvent removed Residue (C)
The ether insoluble fraction and the ether soluble fraction were treated separately as described below.

Treatment of the Ether Soluble Fraction:

The ether soluble portion was washed with ice-cold 5% aqueous potassium hydroxide solution (5×100 ml) and then with ice-cold water until the aqueous layer was neutral and finally dried over anhydrous sodium sulphate. Removal of solvent yielded a partially crystalline Fraction A (13.7 g), which was examined as outlined below.

Treatment of Fraction A (Chart 2):

The ether soluble material (Fraction A, 13.7 g) was chromatographed over a column of silica gel (500 g). The column was eluted with different solvent mixtures as shown in Table 3.

Table 3
Each fraction collected was 50 ml in volume

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 4</td>
<td>Pet ether</td>
<td>Waxy material</td>
</tr>
<tr>
<td>5 - 8</td>
<td>Pet ether : Benzene (4:1)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>9 - 12</td>
<td>Pet ether : Benzene (3:2)</td>
<td>Trace oil</td>
</tr>
<tr>
<td>13 - 16</td>
<td>Pet ether : Benzene (2:3)</td>
<td>Solid, m.p. 248-252°</td>
</tr>
<tr>
<td>17 - 28</td>
<td>Pet ether : Benzene (1:4)</td>
<td>Solid, m.p. 270-276°</td>
</tr>
<tr>
<td>29 - 32</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
<tr>
<td>33 - 40</td>
<td>Benzene : Ether (3:2)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>41 - 44</td>
<td>Benzene : Ether (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>45 - 48</td>
<td>Benzene : Ether (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>49 - 52</td>
<td>Ether</td>
<td>Yellow gum</td>
</tr>
</tbody>
</table>
Examination of the Solid, m.p. 248-252° (Fractions 13-16): Friedelin

The solid (0.06 g), m.p. 248-252°, from fractions 13-16 of the above chromatogram (Table 3) was crystallised from a mixture of chloroform and acetone, when a pure solid, m.p. 257-260° identical (m.m.p. and Co-TLC) with an authentic sample of friedelin was obtained.

Rechromatography of the Solid, m.p. 270-276°:

The solid (1.2 g), m.p. 270-276° from fractions 17-28 of the above chromatogram (Table 3) was rechromatographed over a column of silica gel (200 g) as outlined in Table 4.

Table 4

Each fraction collected was 25 ml in volume

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 4</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>5 - 8</td>
<td>Pet ether : Benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>9 - 12</td>
<td>Pet ether : Benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>13 - 16</td>
<td>Pet ether : Benzene (2:3)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>17 - 28</td>
<td>Pet ether : Benzene (1:4)</td>
<td>Solid, m.p. 278-281°</td>
</tr>
<tr>
<td>29 - 32</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
<tr>
<td>33 - 36</td>
<td>Benzene : Ether (4:1)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>37 - 40</td>
<td>Benzene : Ether (3:2)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>41 - 44</td>
<td>Benzene : Ether (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>45 - 48</td>
<td>Benzene : Ether (1:4)</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Examination of the Solid, m.p. 278–281°: Putranjivadione (42)

The crystalline solid (0.8 g), m.p. 278–281° from fractions 17–28 of the above chromatogram (Table 4) on crystallisation from a mixture of chloroform and acetone yielded putranjivadione (42), m.p. 284–289°, identical (m.m.p. and Co-TLC) with an authentic sample.

Treatment of Fraction B (Chart 3):

A solution of the other insoluble fraction (2 g) in a minimum volume of chloroform was placed over a column of activated alumina (200 g). The column was then eluted with different solvent mixtures as shown in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 4</td>
<td>Pet ether</td>
<td>Waxy material</td>
</tr>
<tr>
<td>5 – 8</td>
<td>Pet ether : Bensene (4:1)</td>
<td>Yellow gum</td>
</tr>
<tr>
<td>9 – 12</td>
<td>Pet ether : Bensene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>13 – 18</td>
<td>Pet ether : Bensene (3:2)</td>
<td>Solid, m.p. 246–252°</td>
</tr>
<tr>
<td>19 – 26</td>
<td>Pet ether : Bensene (1:4)</td>
<td>Solid, m.p. 270–276°</td>
</tr>
<tr>
<td>27 – 31</td>
<td>Bensene</td>
<td>Nil</td>
</tr>
<tr>
<td>32 – 36</td>
<td>Bensene : Ethyl acetate (4:1)</td>
<td>Solid, m.p. 300–308°</td>
</tr>
<tr>
<td>37 – 40</td>
<td>Bensene : Ethyl acetate (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>41 – 44</td>
<td>Bensene : Ethyl acetate (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>45 – 48</td>
<td>Ethyl acetate</td>
<td>Yellow oil</td>
</tr>
</tbody>
</table>
Fractions 19–26 of the above chromatogram (Table 3) were combined to give a solid (0.4 g), which on repeated crystallisations from a mixture of chloroform and acetone yielded a further crop of putranjivadione (42), m.p. 284–289°.

Lithium Aluminium Hydride Reduction of Putranjivadione (42):
Putranjivadial (42a)

Putranjivadione (42, 0.5 g) was added to a suspension of lithium aluminium hydride (0.6 g) in tetrahydrofuran (80 ml) and the mixture after refluxing for 6 h was allowed to stand overnight. It was cautiously treated with cold water and the organic materials were extracted with chloroform. The chloroform layer was washed with water, dried over anhydrous sodium sulphate and evaporated, when a crude solid (0.5 g), m.p. 248–262° was obtained. This was dissolved in a minimum amount of benzene and placed over a column of silica gel (100 g). The column was then eluted with different solvent mixtures as shown in Table 6.

Table 6
Each fraction collected was 25 ml in volume

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–4</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>5–12</td>
<td>Pet ether : Benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>13–20</td>
<td>Pet ether : Benzene (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>21–24</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
<tr>
<td>25–28</td>
<td>Benzene : Chloroform (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>29–40</td>
<td>Benzene : Chloroform (3:2)</td>
<td>Solid, m.p. 261–264°</td>
</tr>
<tr>
<td>41–50</td>
<td>Benzene : Chloroform (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Examination of the Solid, m.p. 261-264° (Fractions 29-40) : Putranjivadiol (42a)

The combined solid (0.42 g), m.p. 261-264° from fractions 29-40 of the above chromatogram (Table 6) on crystallisation from a mixture of chloroform and methanol yielded a solid, m.p. 270-274°, identical (m.m.p. and Co-TLC) with an authentic sample of putranjivadiol (42a).

Acetylation of Putranjivadiol (42a) : Putranjivadiol monoacetate (41)

A solution of putranjivadiol (42a, 2.5 g) in pyridine (25 ml) and freshly distilled acetic anhydride (25 ml) was warmed on the water bath for 3 h and then allowed to stand overnight at room temperature. The reaction mixture was then poured into ice-cold water, whereby a solid separated which was filtered, washed with water and dried. The crude acetate thus obtained was taken in a small amount of benzene and placed over a column of silica gel (200 g). The column was then eluted with different solvent mixtures as shown in Table 7.

Table 7
Each fraction collected was 25 ml in volume

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 8</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>9 - 28</td>
<td>Pet ether : Benzene (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>29 - 36</td>
<td>Pet ether : Benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>37 - 50</td>
<td>Benzene</td>
<td>Solid, m.p. 238-240°</td>
</tr>
<tr>
<td>51 - 56</td>
<td>Benzene : Chloroform (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Examination of the Solid, m.p. 238-240° (Fractions 37-50) :

Putranjivadiol monoaecetate (41)

The combined solid (2.3 g) from fractions 37-50 of the above chromatogram (Table 7) on crystallisation from a mixture of chloroform and acetone yielded pure putranjivadiol monoaecetate (41), m.p. 240-245°.

Preparation of Lead tetraacetate :

Red lead (75 g) was added in small portions to a well stirred solution of pure glacial acetic acid (300 ml) and acetic anhydride (50 ml) and the mixture was kept at 65°. Each portion of red lead was added only after the red colour produced by the previous portion disappeared. Towards the end of the reaction the temperature of the mixture was raised to 80°. On cooling white crystals of lead tetraacetate appeared in the reaction mixture. These were filtered and crystallised from hot glacial acetic acid to yield lead tetraacetate (20 g).

Lead tetraacetate - Iodine Oxidation of Putranjivadiol monoaecetate (41) :

A suspension of lead tetraacetate (5 g, freed from acetic acid in high vacuum) and dry calcium carbonate (1.66 g) in 200 ml cyclohexane was warmed to 80°. Then iodine (1.20 g) and putranjivadiol monoaecetate (41, 1.29 g) were added and the mixture was heated under reflux with stirring under irradiation using a 500 V tungsten lamp. On cooling, the deep pink reaction mixture was filtered through celite. The filtrate was washed with 50 ml of 10% sodium thiosulphate solution, then with water and dried over
anhydrous Na₂SO₄ and evaporated. An oily brown residue (1.80 g) thus obtained was chromatographed over a column of silica gel (200 g). The column was eluted with different solvent mixtures as shown in Table 8.

**Table 8**

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 4</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>5 - 8</td>
<td>Pet ether : Benzene (9:1)</td>
<td>Solid A, m.p. 269-273°</td>
</tr>
<tr>
<td>9 - 14</td>
<td>Pet ether : Benzene (4:1)</td>
<td>Solid B, m.p. 175-180°</td>
</tr>
<tr>
<td>15 - 25</td>
<td>Pet ether : Benzene (3:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>26 - 34</td>
<td>Pet ether : Benzene (3:2)</td>
<td>Solid C, m.p. 200-205°</td>
</tr>
<tr>
<td>35 - 40</td>
<td>Pet ether : Benzene (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>41 - 48</td>
<td>Pet ether : Benzene (2:3)</td>
<td>Solid D, m.p. 115-120°</td>
</tr>
<tr>
<td>49 - 55</td>
<td>Pet ether : Benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>56 - 60</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
</tbody>
</table>

**Examination of Solid A : Epi-friedelanol acetate (43)**

Solid A (0.027 g), m.p. 269-273° from fractions 5-8 of the above chromatogram (Table 8) upon repeated crystallisations from light petroleum ether (40-60°) gave pure crystalline flakes, m.p. 274-276°, $\left[\alpha\right]_D^\circ +11.3°$, identical (m.m.p. and Co-TLC) with an authentic specimen of epi-friedelanol acetate (43).
Examination of Solid B: 7,25-Oxido-D/E-friedoolean-5(10)-ene (48)

Solid B (0.3 g), m.p. 175-180° from the fractions 9-14 of the above chromatogram (Table 8) upon repeated crystallisations from chloroform-acetone mixture gave pure crystalline flakes of (48), m.p. 185-190°, [α]D -3.6°.

Homogeneity:

On thin layer chromatograms, using the following solvent systems (Table 9) 7,25-Oxido-D/E-friedoolean-5(10)-ene (48) produced a single iodine staining spot indicating its homogeneity.

Table 9

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent systems</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bensene : Chloroform (9:1)</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>Bensene : Chloroform (4:1)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Correct elemental analysis could not be obtained for the compound (48). IR, PMR and Mass spectral studies have been discussed in theoretical section.

Examination of Solid C: 3β-Acetoxy-7β,25-oxido-friedooleanane (44a)

The gummy crystalline solid C (0.4 g), m.p. 200-205° obtained from fractions 26-34 of the above chromatogram (Table 8) on crystallisation from
petroleum ether afforded needle-like crystals of 3\(\beta\)-acetoxy-7\(\beta\),25-oxide-friedooleanane (44a), m.p. 215-218\(^\circ\), \(\overline{[\alpha]}_D^29 +44.7\), identical with an authentic specimen (m.m.p. and Co-TLC) of (44a).

**Examination of Solid D : 3\(\beta\)-Acetoxy-7\(\beta\),25-oxide-24-iodo-friedooleanane (44b)**

Solid D (0.25 g), m.p. 115-120\(^\circ\) from the fractions 41-48 (Table 8) was crystallised from petroleum ether when pure crystals of the iodo-derivative (44b), m.p. 123-125\(^\circ\), \(\overline{[\alpha]}_D^29 +50\) were obtained. Compound (44b) was found to be identical with an authentic specimen (m.m.p. and Co-TLC).

**Selenium Dioxide Oxidation of 7,25-Oxido-ItE-friedoolean-5(10)-ene (48) : Naphthalenic hydrocarbon (23)**

A solution of (48, 0.1 g) in glacial acetic acid (15 ml) was heated on a steam bath for 1 h with selenium dioxide (0.1 g). The reaction mixture was filtered hot through Whatman filter paper (No. 42). The filtrate was diluted with water and taken up in ether. The ether layer was washed with water, dried over anhydrous sodium sulphate and evaporated, when a crude solid (0.1 g) was obtained. This was dissolved in a minimum amount of benzene and placed over a column of silica gel (100 g). The column was then eluted with different solvent mixtures as shown in Table 10.
Table 10

Each fraction collected was 5 ml in volume

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 3</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>4 - 10</td>
<td>Pet ether</td>
<td>Solid A, m.p. 260-265°</td>
</tr>
<tr>
<td>11 - 20</td>
<td>Pet ether : Benzene (9:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>21 - 30</td>
<td>Pet ether : Benzene (4:1)</td>
<td>Solid B, m.p. 175-180°</td>
</tr>
<tr>
<td>31 - 35</td>
<td>Pet ether : Benzene (3:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>36 - 40</td>
<td>Pet ether : Benzene (3:2)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Examination of Solid A: Naphthalene Hydrocarbon (55)

Solid A (0.04 g), m.p. 260-265° from the fractions 4-10 of the above chromatogram (Table 10) was crystallised from a mixture of ethylacetate and acetone, when needle like crystals of (55) appeared, m.p. 270-273°, $\left[\alpha\right]_D +36.3°$.

Found: C, 89.49; H, 10.45 (M+ 388).

Calculated for C$_{29}$H$_{40}$: C, 89.62; H, 10.38%

Homogeneity:

On thin layer chromatograms, using the following solvent systems (Table 11) the compound (55) produced a single iodine staining spot indicating its homogeneity.
UV, IR, PMR and Mass spectral studies have been discussed in theoretical section.

**Examination of Solid B : 7,25-Oxido-DiE-friedoleslan-5(10)-ene (48)**

Solid B (0.06 g), m.p. 175-180° from the fractions 21-30 of the above chromatogram (Table 10) on crystallisation from a mixture of cloroform and acetone furnished 7,25-oxido-DiE-friedoleslan-5(10)-ene (48), m.p. 185-190° (the melting point was undepressed with the starting material).
PART I : SECTION D

REFERENCES
REFERENCES


