SUMMARY

The work embodied in the present thesis has been divided into three parts:

A. The first part (Part I) consists of the action of N-bromo succinimide (NBS) on some triterpenoids in dimethyl sulphoxide.

B. The second part (Part II) deals with autoxidation of friedelin.

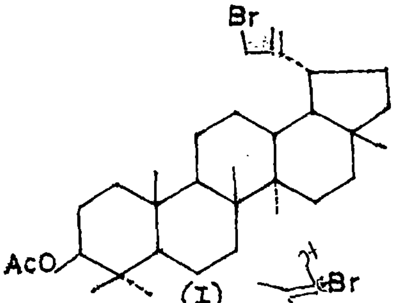
C. The third part (Part III) comprises of the investigations carried out on the benzene extract of the root of Gyno Cardia Odorata R. Br. (Flacourtiaceae).

PART I

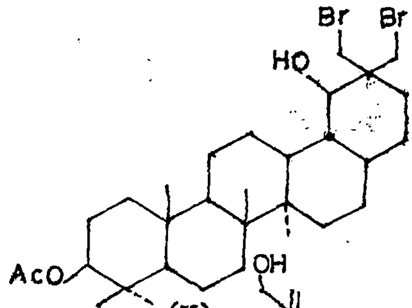
Chapter I deals with a short review of the action of NBS on some triterpenoids and steroids. Special emphasis has been given on bromination and dehydrobromination, oxidation of allylic methylene to carbonyl group and allylic hydroxylation.

Chapter II, Section A describes the isolation discussion and characterisation of the products formed as result of the reaction of NBS with lupenyl acetate. Compounds (I), (II), (III) and (IV) have been isolated and characterised from elemental analysis, IR, mass, ^{1}H NMR and ^{13}C NMR spectra.

(II)



(I)



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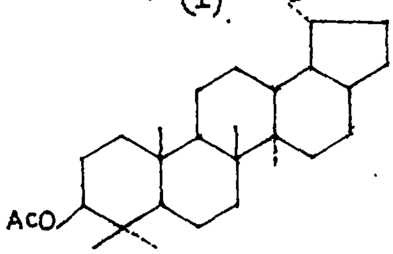

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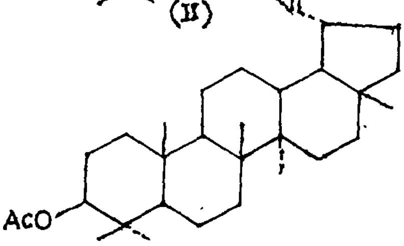
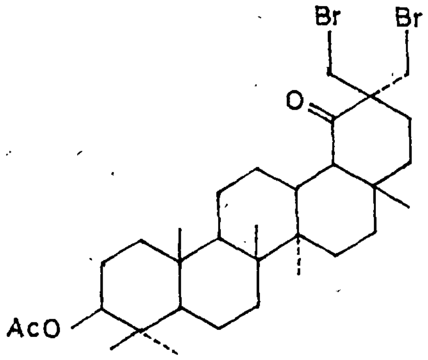


(IV)

Elemental analysis and mass spectrum value M^+(648, 644) of Compound (II) established the molecular formula to be $C_{33}H_{52}O_3Br_2$ m.p. 258-60°. The compound (II) responded Beilstein test but showed negative TNM test. In the IR spectrum, the compound showed peaks at 3330, 1732, 1250 and 1280-1270 cm^{-1}. ^1H NMR spectrum of the compound showed peaks in the region δ0.84-1.06, 3.56, 3.72, 3.81, 3.87, 4.01, 4.45 ppm. From these data it is evident that the compound (II) contained a hydroxy group and two bromine atoms in the molecule in addition to acetate group. ^{13}C NMR of the compound showed a doublet at 73.05 in addition to the doublet at 80.92 which was due to C-3 carbon bearing the acetoxy group. The additional doublet at 73.05 ppm. is most probably due to carbon containing newly introduced hydroxyl group. APT spectrum of ^{13}C values at 14.40, 15.95, 16.16, 16.51, 18.29, 21.32 and 27.91 ppm showed the presence of 7-CH_3, at 18.15, 21.14, 23.61, 25.00, 26.36, 28.29, 34.12, 36.54, 37.68, 38.07, 38.29, 49.02 showed 12 $>CH_2$ and at 37.78, 45.54, 49.12, 55.18, 73.05 ppm showed 6-$\overset{|}{\underset{|}{C}}H$ in molecule.

The formation of dibromohydroxy compound (II) has been proposed to take place following rearrangement of lupane system to oleanane system. It has been suggested in mechanism that 30-bromo-lup-20(29)-en-3β acetate (I) is formed by allylic bromination which in presence of polar solvent DMSO has been attacked by the bromonium ion generated from NBS on the π bond at C-20-29 leading to the formation of carbonium ion which probably compels carbon skeleton transformation from lupane to oleanane system. During this transformation a new carbonium ion is generated at C-19 which is stabilised by abstraction of hydroxyl ion to produce the compound (II). The mechanism of formation of (II) has been shown schematically.

Appearance of double doublet at 4.01 ppm in ^1H NMR spectrum was the most confusing feature of this compound (II), because it was expected to give a singlet if the hydroxy group is situated at C-19 position. So the most likely position of the location of this hydroxy group could be C-21 which would then explain the appearance of this doublet of a doublet at 4.01 ppm. The formation of this C-21 hydroxy compound would involve 1, 3 migration of a proton from C-21 to C-19 position giving rise to the formation of carbonium ion at C-21. During this transformation a new carbonium ion is formed at C-19. From the mechanistic point of view it is expected that C-19 hydroxy group is expected to be formed. In order to make an unambiguous decision on the structure of the compound (II), two derivatives viz. keto (V) and acetate (VI) have been prepared. The structure of dibromohydroxy compound (II) was confirmed from the ^{1}H NMR of keto derivative (V).

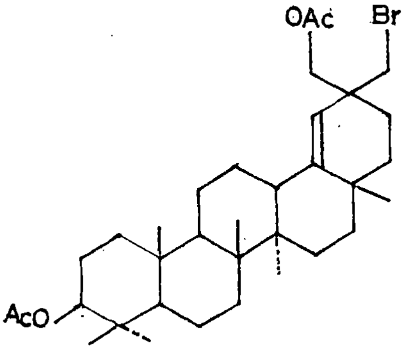


(V)

^{1}H NMR of (V) showed six tertiary methyls in the region δ 0.6-0.95 ppm. The acetoxy methyl appeared at δ 1.95 ppm.

A doublet with J value 2.5 Hz appeared at 2.44 ppm. This upfield shift of the proton in this region indicates that there is a single proton α to the carbonyl group which couples with a single vicinal proton that is β to the carbonyl group. This signal indicates that the hydroxy group in (II) is situated at C-19 position, which on oxidation gives 19-keto derivative (V) which has single α-proton at C-18 position. This α-proton would couple with C-13 proton to give the doublet. The pair of doublets that appeared at δ 3.46 (J = 3 Hz); 3.68 (J = 2.5 Hz), 3.81 (J = 2.70 Hz) ppm which indicated for four protons (1,1,2). The appearance of these doublets which appeared as two quartets in (II) must be due to anisotropic effect of the carbonyl group on the nearby $-CH_2Br$ protons.

The acetate derivative of (II) was prepared by the usual process of acetylation. Mass spectrum data gave mass peaks at 606, 604 (M^+). The existence of these peaks in 1:1 proportion indicated the presence of one bromine atom in the molecule. It showed positive to TNM test and so was also to Beilstein test. IR showed peaks at 1740, 1640, 1250 and 810 cm^{-1}. These data indicated the presence of acetoxy group and a trisubstituted double bond. ^1H NMR showed peaks in the region δ 0.7-0.9, 1.95, 2.02, 3.3-3.45, 4.38, 4.67 and 6.1 ppm. Appearance of two singlets at δ 1.95 and 2.02 ppm indicated the existence of two acetoxy methyls. Ill defined signals at 3.3 and 3.45 ppm probably indicate pair of protons geminal to bromine atoms. A multiplet at δ 4.38 ppm must be due to proton at C-3 geminal to acetoxy group. AB quartet centred at δ 4.67 ppm suggested two protons of $-CH_2$ group which is attached to acetoxy group. A singlet at δ 6.1 ppm suggested the presence of an isolated olefinic proton. This singlet vinyl proton suggested that the C-19 hydroxy group in (II) underwent dehydration to produce an olefinic double bond between C-18 and C-19 position giving rise to germanicol derivative. The mass spectrum (M^+, 606, 604) of the acetate derivative of (II) definitely proved the existence of one bromine atom in (VI). The structure of the acetate derivative of (II) has been assigned as (VI)



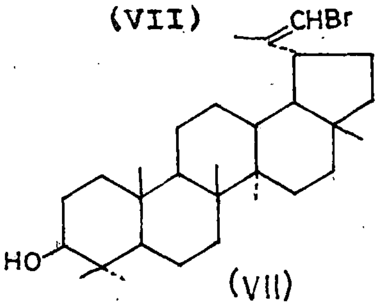
(VI)

Thus from the ^1H NMR analysis of keto and acetate derivatives of (II) it has been unequivocally confirmed to attribute structure (II) for the compound $C_{33}H_{52}O_3Br_2$.

Chapter II, Section B deals with the studies on the action of NBS and DMSO on a mixture of 29-bromo and 30-bromo lupenyl acetate in aqueous medium. The products isolated are (VII) and (VIII).

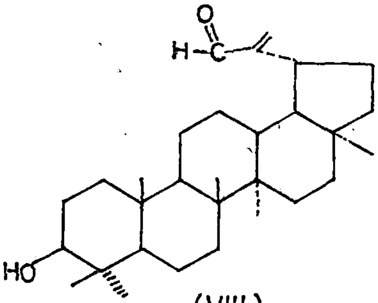
Analysis and mass spectrum value (M^+ 506, 504) showed the molecular formula of (VII) as $C_{30}H_{49}OBr$, m.p. 173-5°. IR showed peaks at 3580-3200 (-OH), 1690 ($>C = CH_2$). ^1H NMR showed peaks at δ 0.75-1.01, 3.16-3.2 and 5.89 ppm. The peak that appeared in the region at δ 3.16-3.2 ppm as quartet is due to the hydroxylic proton and the one that appeared at 5.89 as doublet indicates the presence of one olefinic proton at C-29 bearing one bromine atom $(= \underset{H}{C}-Br)$. It has been identified as 29-bromo-lup-20(29)-en-3β-ol (VII).

(VII)



(VII)

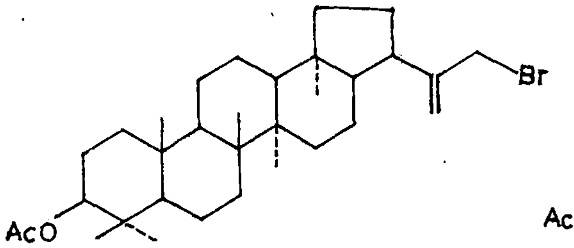
The compound (VIII) having molecular formula $C_{30}H_{48}O_2$ (from elemental analysis and mass spectrum) m.p. 235-6°, showed UV maxima at 226 nm. IR showed peaks at 3560-3100 (-OH), 1640, 810 ($C = CH_2$), 1680 ($-\overset{H}{\overset{|}{C}} = O$)$cm^{-1}$. TNM showed positive test but the compound showed negative Beilstein test. A sharp singlet that appeared in the low field region at δ 9.5 ppm indicated the presence of an aldehydic proton. A doublet appeared in the down field region at δ 5.91 and 6.28 ppm for one proton each indicate the presence of end methylene group. From these observations the compound (VIII) has been identified as 30-aldehyde-lup-20(29)-en-3β-ol.



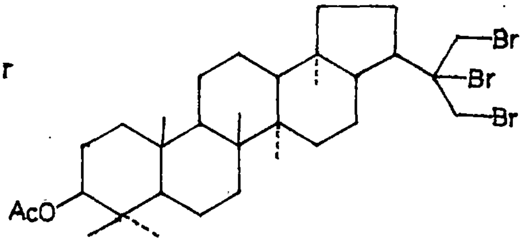
(VIII)

The formation of hydroxy aldehyde (VIII) probably takes place first through allylic bromination followed by hydrolysis and oxidation.

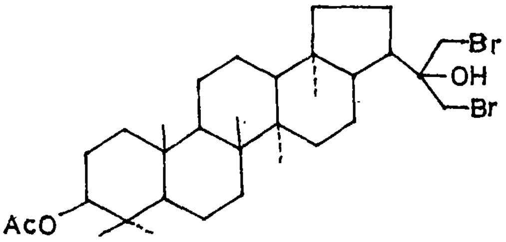
Chapter II, Section C constitutes the result and discussion of the reaction of NBS with moretenyl acetate in presence of dimethyl sulphoxide. Compounds (IX), (X),(XI),(XII) and (XIII) have been isolated and characterised.



(IX)



(X)



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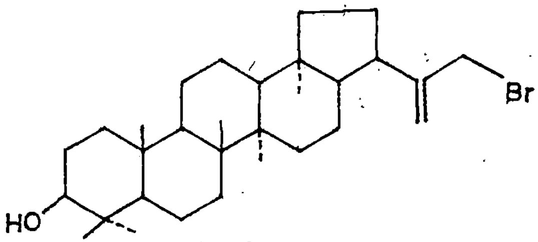
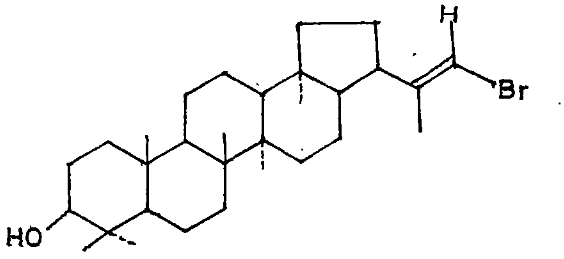


(XII)



(XIII)

Elemental analysis and mass spectral value M^+ (548, 546) showed the molecular formula of the compound (IX) as $C_{32}H_{51}O_2Br$, m.p. 222-4°. The compound showed sharp peaks in IR spectrum at 1720, 1245 cm^{-1} for the presence of acetate and other peaks at 3040, 840 cm^{-1} indicated the existence of methylenic double bond. The compound responded positive TNM test for the olefinic double bond and also positive test for bromine in Beilstein test. The compound in its ^{1}H NMR spectrum showed peaks at δ 0.69, 0.76, 0.84, 0.94, 0.97, 1.25, 2.03, 4.1, 4.45 and 4.9–5.9 ppm. The former six values (0.69–1.25) represented six tertiary methyls on saturated carbon. The peak at δ 2.03 ppm indicated the presence of acetoxy methyl at C-3. The proton geminal to acetoxy group appeared at δ 4.45 ppm as triplet. The peak at δ 4.1 ppm that appeared as AB quartet indicated two protons of methylene group containing bromine atom. The peaks in the region 5.9 and 4.9 ppm indicate the existence of two olefinic protons. From the above observations structure (IX) has been proposed for the compound $C_{32}H_{52}O_2Br$.

Mass spectrum and independent elemental analysis established the molecular formula of (X) as $C_{32}H_{51}O_2Br_3$, m.p. 241-2°, $[\alpha]_D$ + 23.14°. The compound did not respond to TNM test but responded positive Beilstein test. IR spectrum showed sharp peaks at 1725, 1245 cm^{-1} indicating the presence of C-3 acetoxy group($-O-COCH_3$) in the compound. This is supported by ^{1}H NMR. A pair of AB quartets superimposed to each other appeared in the region between δ 3.8–4.2 ppm. A plot of this region in cosy spectrum showed that this is a super imposition of two AB pairs resulting from two $-CH_2$ groups containing bromine atoms. This was confirmed by adding C_6D_6 to the solution and reducing the spectrum. The two groups were shifted differently and two separate AB pairs were seen at δ 3.89 (J = 16, 3 Hz) and 4.04 (J = 20, 3 Hz) ppm of unequal coupling constant. Peaks at δ 0.75, 0.84, 0.86, 0.87, 0.96 and 1.01 ppm clearly indicated the presence of six tertiary methyls in the compound.

^{13}C NMR of (X) showed the presence of 32 carbon atoms in the region 170-15 ppm. APT showed seven quartets inclusive of acetoxy methyl, twelve triplets for 12 $>CH_2$ two of which were for the $-CH_2Br$ (38.86, 40.2 ppm), six doublets (45.8, 48.43, 50.17, 54.17, 55.17, 80.89), the one for methine carbon (80.89) and seven singlets (36.99, 37.76, 41.52, 41.76, 45.36, 76.05, 170.99) for tertiary carbons, the one at 76.05 ppm being for carbon bearing a bromine atom. On the basis of these observations from IR, ^1H NMR and ^{13}C NMR. structure (X) has been proposed for the compound $C_{32}H_{51}O_3Br_3$.

Analysis and molecular weight determination by mass spectrometry (M^+, 645, 643, 641) showed the molecular formula of the compound (XI) to be $C_{32}H_{52}O_3Br_2$, m.p. 258-9°, $[\alpha]_D$ + 25°. It also showed the absence of olefinic double bond. The compound showed characteristic IR peaks at 3360 (-OH), 1730, 1250 ($-OCOCH_3$)cm^{-1}. ^1H NMR of the compound showed the presence of six tertiary methyls on saturated carbons at δ 0.72, 0.84, 0.85, 0.86, 0.94 and 0.98; acetoxy methyl at 2.06 and the carbinol methine proton (C-3) at 4.45 ppm. It showed a pair of AB quartets centred at δ 3.5 and 3.72 (J = 10 Hz)ppm, two singlets at 3.48, 3.66 ppm typical of a pair of $-CH_2Br$ without restricted rotation and another set of non-resolvable peaks in the regions 3.42-3.56 ppm. The total number of protons was counted as four, an indication that the $-CH_2Br$ is in three different geometry in which one pair had restricted rotation whereas the other two pairs had free rotation. This interpretation is confirmed by ^{13}C NMR data of the compound.

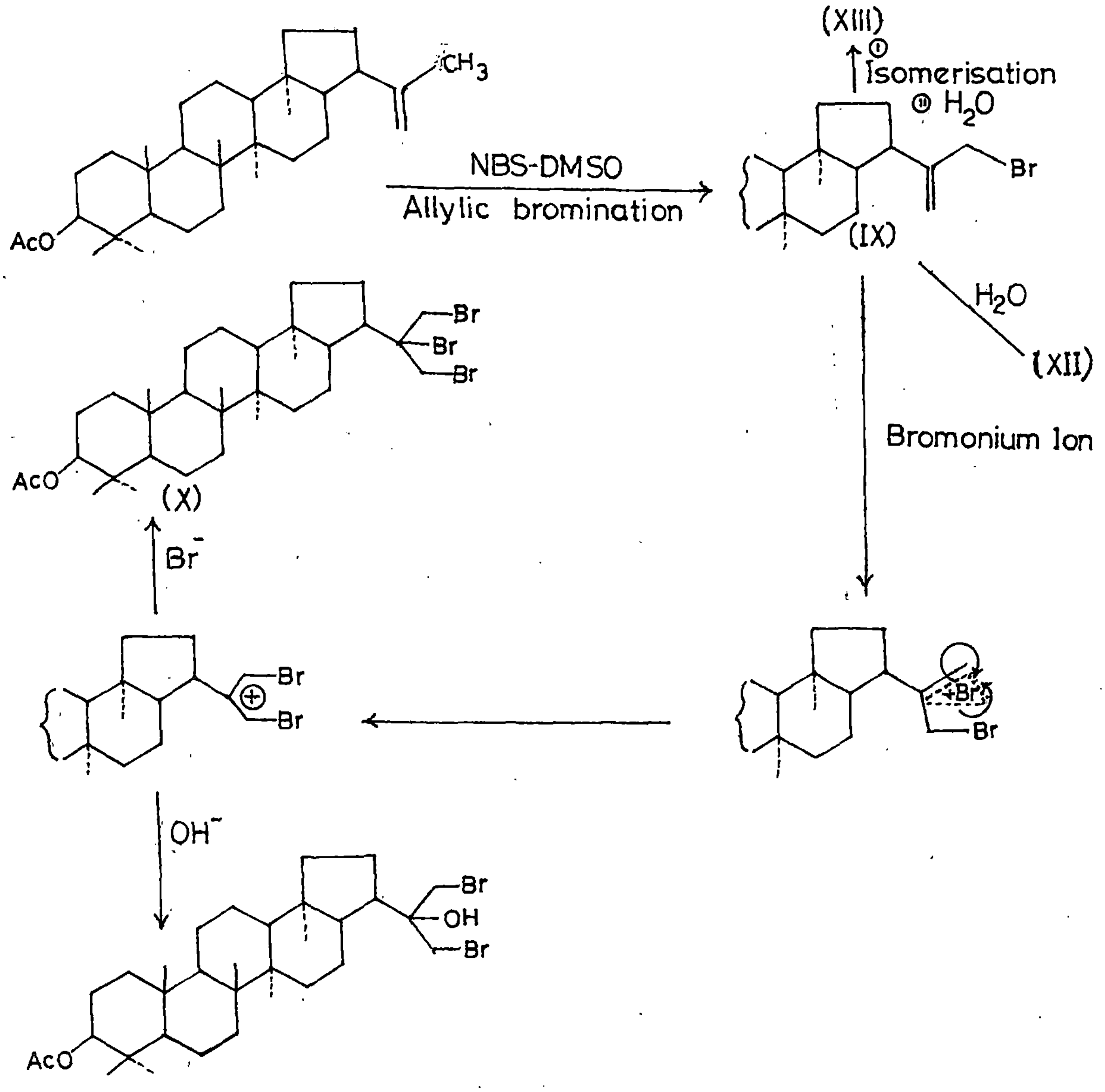
The compound (XI) in its ^{13}C NMR spectrum showed three singlets around 74.0 ppm for one carbon, showing that this carbon contains an oxygen function in three different environment. The $-CH_2Br$ carbons appeared around 21 ppm as a cluster of six peaks showing once again three isomeric $-CH_2Br$ carbons. A three lined peak for triplet carbon at 38 ppm was also observed showing that this carbon is also affected differently probably by its anisotropic effect of different stereometric $-CH_2Br$ group. Thus it must C-22-C methylene that is coupled.

Therefore from spectral data structure (XI) has been assigned for the compound $C_{32}H_{52}O_3Br_2$.

Elemental analysis and molecular weight determination by mass spectrometry (M^+, 506, 504) led to the molecular formula of (XII) $C_{30}H_{49}OBr$, m.p. 238-9°. IR spectrum of the compound showed a characteristic peak at 3320-3280 (-OH), 3040-60 (=CH_2), 1620 cm^{-1}. Thus the compound contains -OH group and a double bond. The compound is probably formed by allylic bromination and hydrolysis of the acetoxy group at C-3. From IR and mass spectra the structure of $C_{30}H_{49}OBr$ has been proposed as (XII).

Elemental analysis together with mass spectrum value (M^+ 506, 504) of (XIII) led to the molecular formula $C_{30}H_{49}OBr$, m.p. 206-8°. It responded positive TNM test and showed positive Beilstein test for bromine. These observations indicated the presence of double bond and bromine in the molecule. ^{1}H NMR of the compound showed peaks at δ 0.64, 0.74, 0.79, 0.88, 0.95, 1.52, 1.70 ppm indicated the presence of seven methyls as singlet. Of the seven methyls, one methyl appeared in the lower field at 1.70 ppm. The appearance of this methyl at 1.70 is due to its position on an olefinic carbon atom. A vinyl proton appeared at δ 5.86 ppm. On the basis of these observations structure (XIII) has been proposed for the compound $C_{30}H_{49}OBr$. This is most probably formed by isomerisation followed by hydrolysis of the acetoxy group at C-3.

The probable schematic mechanism of formation of (IX), (X), (XI), (XII) and (XIII) presented as follows:



Chapter III deals with experimental details of the works contained in Chapter II.

PART II

CHAPTER I

This chapter comprises a short review of the works on autoxidation and isomerisation in ring A of some triterpenoids.

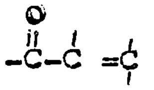
Chapter II contains isolation and characterisation of products formed during autoxidation of friedelin. A possible mode of formation of products has been suggested.

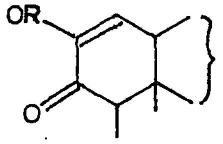
Chapter II, Section A deals with introduction and isolation of products formed as a result of autoxidation of friedelin. Compounds (XIV), (XV), (XVI), (XVII) and (XVIII) have been isolated.

Chapter II, Section B describes characterisation and structure elucidation of compound (XIV).

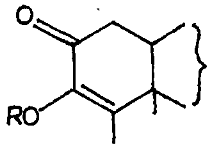
Elemental analysis and mass spectrum value (M^+ 496) established the molecular formula of the compound (XIV) to be $C_{34}H_{56}O_2$, m.p. 218°C, $[\alpha]_D$ -8.4°. The compound showed characteristic yellow colour with TNM, indicating the presence of unsaturation. It showed IR peaks at 1705, 1635, 1250, 870 and 790 cm^{-1}. The absorption at 1705 cm^{-1} could be due to a six membered ring ketone or an aldehyde or an ester carbonyl. The appearance of absorption bands at 1635, 870, 790 cm^{-1} indicated existence of tetrasubstituted double bond.

The UV absorption maxima at 235 nm seemed to be due to the presence of α,β unsaturated carbonyl group like

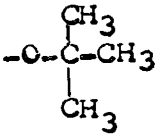

$-\overset{\overset{O}{\|}}{C}-\overset{|}{C}=\underset{|}{C}$. Two different structures could be written with such a system as A and B



(A)



(B)

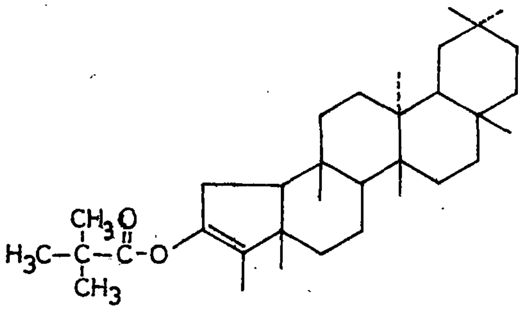
The diosphenol ether derivative of both A and B would well account for the molecular formula of (XIV), though the IR value of 1705 is of lower wave length than in the case of other simple α,β-unsaturated ketones that appear at 1660-1690 cm^{-1}. The failure to form DNP and oxime derivatives by the usual reagents indicated the absence of ketone functional group. Moreover the compound did not develop characteristic green colouration with neutral ferric chloride, showing that there is no free enol group in (XIV). Therefore two oxygen atoms in (XIV) may be present as ester group. ^{1}H NMR analysis of the compound showed peaks at δ 0.80, 0.938, 0.94, 0.965, 0.99, 1.015, 1.18, 1.48 and 1.94 ppm. Peaks in the region δ .80 -1.18 ppm indicate seven tertiary methyls. The ~~down field~~ peak at δ 1.94 ppm in the down field region indicated C-23 methyl which is situated on a double bond. The large down field shift indicated that there is large electromeric effect on C-23 methyl. Thus a double bond is proposed at 3-4 position. The absence of resonance peaks at lower field lower than 2 ppm indicated that there is no olefinic proton, thus the double bond is tetra-substituted. The absence of doublet for the C-23 methyl indicated that C-4 carbon is involved in oxidation. The sharp peak as singlet at δ 1.48 ppm integrated for nine protons appeared somewhat absurd to us initially. But considering the elemental analysis and mass spectrum value which showed an increase of 56 mass unit may partly due to introduction of three methyl groups of identical electronic property which is possible only if we take a molecule of tertiary butyl being added up in friedelin so as to have  $-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ grouping.

^{13}C NMR showed ten singlets at 166.73, 163.64, 127.92, 79.55, 50.29, 40.45, 38.22, 36.48, 29.99, 28.15; ten triplets at 39.31, 38.22, 36.49, 35.98, 35.30, 35.07, 32.77, 32.99, 30.2, 18.6, eleven -quartets at 35.05, 32.19, 31.79, 28.38, 19.86, 18.61, 18.2, 17.88, 11.32 inclusive of 3-quartets at 28.38 and 3-doublets at 62.44, 53.66, 42.87 ppm.

From ^{13}C NMR absorptions at (163.64, 127.92) ppm indicated for two olefinic carbons, the carboxyl carbonyl at 166.73 and the three additional methyl groups appearing at 28.36 must be due to tertiary butyl group which is also supported by ^{1}H NMR that gave a three 9-proton singlet at 1.48 ppm.

Therefore the two oxygen atoms in (XIV) must be present as ester group. Li-EDA reduction of (XIV) furnished a compound which was analysed for $C_{30}H_{50}O_2$, m.p. 246-7°. It showed negative TNM test and showed IR peaks at 3400-2600 (hump), 1700-1690 cm^{-1}, which are indicative of the presence of carboxyl group. Mass spectrum of $C_{30}H_{50}O_2$ showed mass peak at 442 (M^+). Thus the compound (XIV) has been proved to be an ester of tertiary butyl alcohol. Hydrolysis of the compound

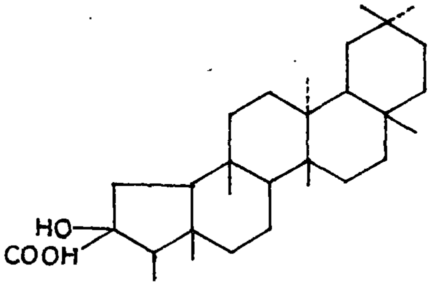
(XIV) with 20% methanolic KOH gave two products one as acid which has been analysed for $C_{30}H_{48}O_2$, m.p. 290-2° and the other as neutral compound which has been analysed as $C_{29}H_{48}$, m.p. 227-8°, $[\alpha]_D^{30}$ + 40° and was found identical with A-nor-friedelene. Thus from spectral analysis, Li-EDA reduction and hydrolysed products, the structure of the compound $C_{34}H_{56}O_2$ has been confirmed as (XIV).



(XIV)

Chapter II, Section C deals with characterisation of compound (XV).

Elemental analysis and mass spectrum value (M^+, 458) showed the molecular formula of the compound to be $C_{30}H_{50}O_3$, m.p. 242-4°. It showed negative TNM test, indicating the absence of unsaturation. IR spectrum showed bands in the regions 3600-2800 (hump), 1730-1695 cm^{-1} which are indicative of the presence of hydroxyl and carboxyl group in (XV). ^1H NMR of the compound showed peaks at δ 0.74, 0.92, 0.96, (2-CH_3), 0.98, 1.02, 1.12 (2-CH_3) ppm as singlets indicating the presence of eight methyls of which one methyl is secondary (at δ 0.98). A characteristic peak appeared in the lower field region at δ 3.86-3.89 ppm as doublet. This indicated the presence of a single proton at C-4. Peak that appeared at δ 4.51 ppm indicated hydroxylic proton and a sharp peak appeared in the very down field region at 12.0-12.1 ppm. This is for the carboxylic proton. Combination of these observations led to conclude structure (XV) for $C_{30}H_{50}O_3$.



(XV)

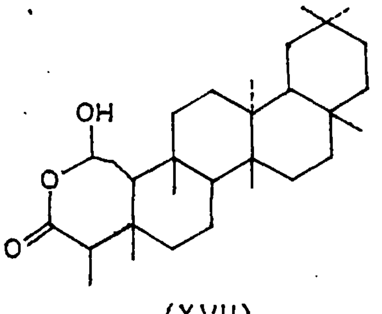
The above structure (XV) was further confirmed by acetylation. Products isolated are $C_{31}H_{50}O_2$, m.p. 235-7° and $C_{29}H_{48}$ m.p. 227-8°. $C_{31}H_{50}O_2$ has been identified as 3-nor-$\Delta^{2(4)}$-Friedelin-2-acetate. $C_{29}H_{48}$ has been identified as A-nor-friedelene.

The formation of these two products from (XV) may be that during acetylation a part of the hydroxy acid (XV) underwent decarboxylation and acetylation to give 3-nor-$\Delta^{2(4)}$-

friedelin-2-acetate and another part underwent dehydration and decarboxylation to produce A-nor-friedelene.

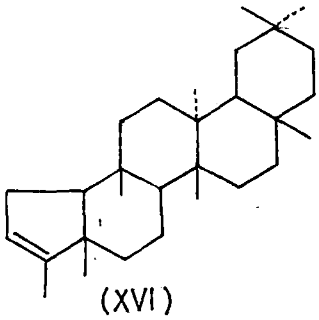
Chapter II, Section E deals with the characterisation of compound (XVII). Elemental analysis and mass spectrum value M^+ (458) showed the molecular formula to be $C_{30}H_{50}O_3$, m.p. 253-5^{o}. IR value showed the presence of lactone carbonyl group at 1730 cm^{-1} and -OH group at 3520 cm^{-1}. ^1H NMR spectrum of the compound showed a peak at δ 2.66-2.7 ppm as doublet. This was due to the hydroxylic proton. A characteristic peak appeared at δ 2.16 ppm. This peak is for the C-1 tertiary hydrogen due to the coupling of the -OH proton linked to the same carbon.

The compound has been identified as lactol, and the structure (XVII) has been proposed for $C_{30}H_{50}O_3$.



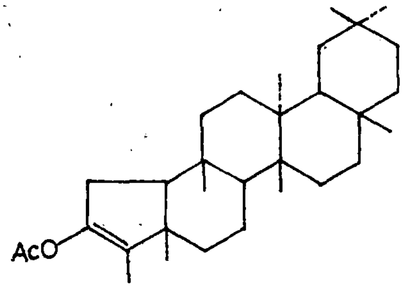
(XVII)

Chapter II, Section D comprises characterisation of compound (XVI). From elemental analysis and mass spectrum value M^+ (396) the molecular formula of the compound found to be $C_{29}H_{48}$, m.p. 227-8^{o} $[\alpha]_D^{30}$ + 40^{o}. It gave characteristic yellow colouration with TNM indicating the presence of unsaturation in the compound. IR showed peaks at 1650, 810 cm^{-1} indicating the presence of double bond. ^1H NMR showed peaks at δ 0.84, 0.94, 0.97, 1.00, 1.01, 1.02, 1.18 ppm for 7-tertiary methyls and the peak that appeared at δ 1.57 ppm indicated tertiary methyl on a double bond. A characteristic peak appeared at δ 5.30 ppm. It is for the vinyl proton. The compound (XVI) has been identified as A-nor-friedelene.



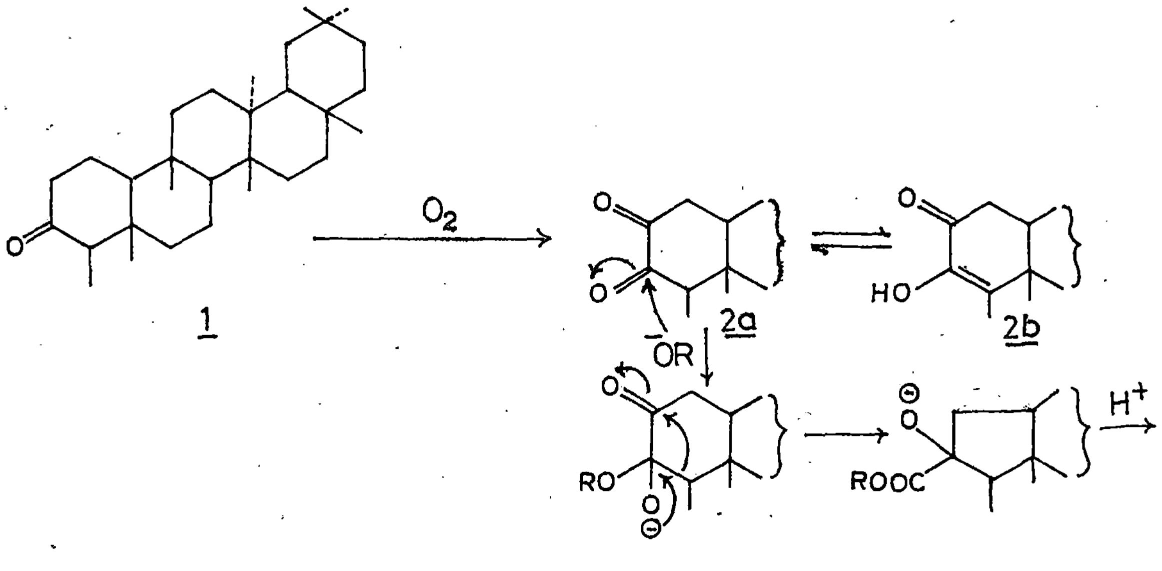
(XVI)

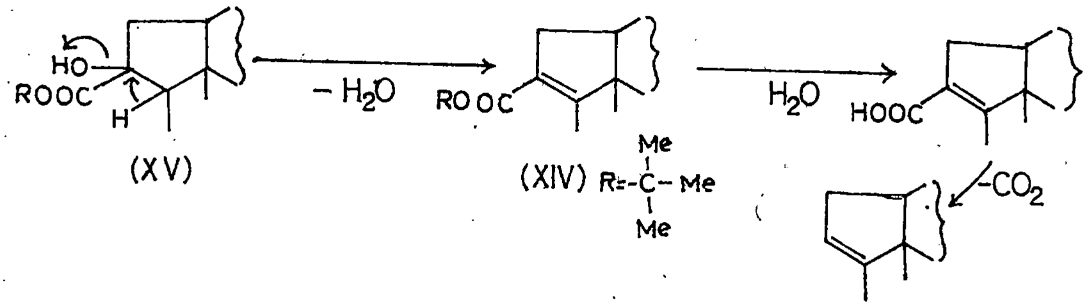
Chapter II, Section F deals with characterisation of compound (XVIII) which has been discussed. It has been established to be 3-nor-Δ^2-friedelin-2-acetate by IR, mass and ^1H NMR spectral analysis. Analysis and mass spectrum value M^+ (454) indicated the molecular formula $C_{31}H_{50}O_2$. Appear of peak at δ 1.55 in ^1H NMR spectrum indicates the presence of methyl on a double bond at C-4 and the absence of carbinol proton showed the acetoxy group is attached to a carbon without having proton. Combination of these observations led to conclude structure (XVIII) for $C_{31}H_{50}O_2$.



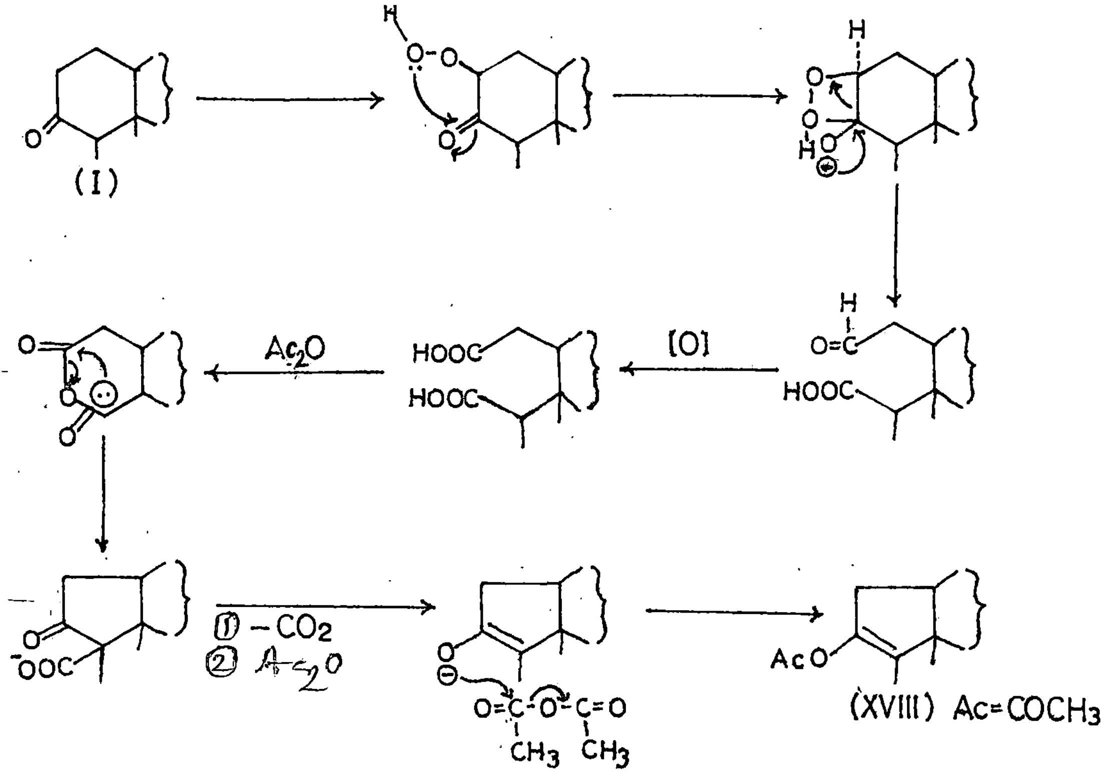
(XVIII)

The formation of (XIV), (XV), (XVI) has been proposed to proceed through the following mechanism. In presence of oxygen friedelin 1 undergoes oxidation to form the diketo 2a compound which is in equilibrium with its enol 2b. Under the influence of base (K-t-BuO), the diketo compound 2a undergoes benzil-benzilic acid rearrangement to give the hydroxy ester which subsequently eliminates water to give α,β unsaturated ester (XIV). Hydrolysis of the ester would give hydroxy acid, which subsequently eliminates water to give α,β-unsaturated acid. This α,β unsaturated acid may also be formed by hydrolysis of the ester(XV)A part of the α,β unsaturated acid under the reaction condition may undergo decarboxylation to give the unsaturated hydrocarbon A-nor-friedelene.





The formation of 3-nor-$\Delta^{2(4)}$-Friedelin-2-acetate (XVIII) has been proposed to proceed through the formation of α-hydroperoxy ketone, which subsequently cleaved to form seco-2-aldehyde-3-carboxylic acid. This undergoes further oxidation to form 2,3 seco-dicarboxylic acid under basic condition which upon cyclization forms the anhydride. The anhydride under basic medium rearranges to form the anion of keto acid, which undergoes decarboxylation followed by acetylation to afford the compound (XVIII).



Chapter III describes the experimental details of Chapter II.

Part III has been divided into four Chapters.

Chapter I, Section A contains the morphological features of the plants of Flacourtiaceae family, while some previous works on the plants of the same family have been reported in Section B.

Chapter II, Section A deals with terpenes and their classification while in Section B the diterpenes and their main skeletons have been discussed.

Section C comprises a brief review on lactones and hydroxy lactones of diterpenoids. Special emphasis on the lactones and hydroxy lactones particularly of the Kaurane skeleton has been given in this section.

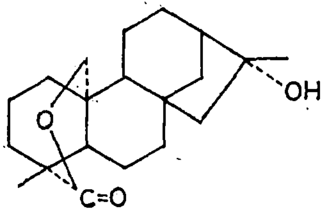
Section D comprises of the works done on the constituents of neutral part of benzene extract of the root of Gyno Cardia Odorata R.Br., a plant of flacourtiaceae family. Three new diterpene lactones have been reported in this section. The names hydroxy odolide, Odolide and iso odolide have been proposed by the author since they have been isolated for the first time from the species.

Chapter III deals with the preliminary investigation on the root of Gyno Cardia Odorata R. Br. Extraction and isolation of different materials have been described in brief. This chapter again has been divided into five Sections, viz. A, B, C, D and E.

Chapter III, Section A deals with elemental and spectrometric analysis of hydroxy Odolide. Elemental analysis of hydroxy Odolide suggested the molecular formula to be $C_{20}H_{30}O_3$, m.p. 218^o, $[\alpha]_D$ - 50^o. The mass spectrum of the compound showed the mass peak at 318 (M^+). So combination of elemental analysis and mass spectrum value led to the molecular formula $C_{20}H_{30}O_3$, which indicated that the compound belongs to diterpene group. The compound in its IR spectrum showed peaks at 3320-3240 (broad), 1730, 1720 and 1140 cm^{-1}. The broad peak in the region 3320-3240 cm^{-1} indicated the presence of hydroxy group and peaks in the region 1730, 1720 and 1140 cm^{-1} indicated the presence of lactone carbonyl moiety. ^{1}H NMR of hydroxy odolide showed two tertiary methyls at δ 0.87 and 1.33 ppm as singlet, two protons centred at δ 4.01 and 4.12 ppm as doublets. The peak that appeared in the region at δ 2.10-2.14 ppm probably as AB quartet indicated methylenic protons (2H) at C-15 which is typical of kauranoids. ^{13}C NMR spectrum along with APT of the compound showed two tertiary methyls at 23.58, 24.30, ten $>CH_2$ at 18.72, 20.54, 22.48, 23.90, 35.24, 39.10, 39.66, 40.57, 56.55, 76.51, three $-\overset{|}{\underset{|}{C}}H$ at 49.19, 49.66, 53.14 and five non-protonated carbons at 32.89, 44.66, 47.65, 79.25, 174.78 ppm. The triplet at 76.51 ppm is due to a methylene carbon which bears oxygen. The singlet at 174.78 ppm is due to lactone carbonyl carbon and the singlet at 79.25 ppm is attributed for carbon bearing another oxygen. This establishes the formula $C_{20}H_{30}O_3$ for hydroxy Odolide which is in good agreement with results of elemental analysis and mass spectrum.

Chapter III, Section B deals with the investigations on the elucidation of the structure of hydroxy Odolide from spectral analysis.

From spectral analysis the structure of hydroxy odolide has been proposed as (XIX).



(XIX)

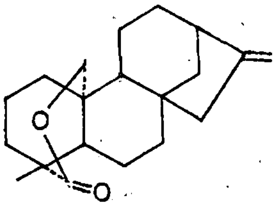
The presence of δ-lactone moiety and hydroxyl group has been established from the IR spectrum. The nature of oxygen functions is also established by the appearance of three peaks in the low field region of ^{13}C NMR at 174.18 ppm (six membered lactone carbonyl carbon), 79.78 ppm (for a carbon bearing the OH group) and 76.51 ppm (for a carbon bearing the lactone oxygen). The resistant to oxidation by Jones' reagent indicates that the hydroxyl group attached to a carbon atom may be a tertiary one.

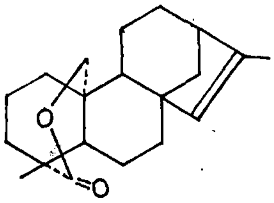
The non protonated Carbon that appeared at 79.25 ppm in the ^{13}C NMR has been attributed for carbon carrying hydroxyl group. Thus the tertiary nature of hydroxyl group has been established. The appearance of doublets in ^1H NMR spectrum at δ 4.01 and 4.12 ppm indicated two protons coupling with each other with geminal coupling constant 14 Hz attributed for the protons on the same carbon bearing the lactone oxygen. The position of lactone carbonyl and lactone oxygen at C-19 and C-20 has been settled from the analysis of ^{13}C NMR.

Chemical proof of the structure of hydroxy Odolide has been described in Section C of this Chapter. Li-EDA reduction of hydroxy odolide produced hydroxy acid of known structure which on esterification with diazomethane furnished methyl ester of 16α-hydroxy(-)-kuran-19-oic acid of known structure. The structure of hydroxy ester was confirmed from elemental analysis IR , mass and ^1H NMR spectra. IR spectrum showed peaks at 3340-3240 (-OH) and 1720 cm^{-1} for ester group. Mass spectrum showed mass peak at 334 (M^+). Combination of elemental analysis and mass spectrum value led to the molecular formula of the ester to be $C_{21}H_{34}O_3$. ^1H NMR of the hydroxy ester exhibited peaks for three tertiary methyls at δ 0.738, 0.896 and 1.360 ppm as singlet. The down field shift of the methyl proton at δ 1.360 ppm indicated the methyl group to be situated on a tertiary carbon atom at C-16 carrying the hydroxyl group. A characteristic peak appeared in the region at δ 2.23-2.30 ppm as AB quartet indicated methylenic protons (2H) at C-14 was also typical of kauranoids. In the down field region at δ 3.67 ppm there appeared a sharp peak as a singlet. This was for the three protons of $-COOCH_3$ group. The position of hydroxyl group is thus confirmed at C-16.

Section D describes the results of investigation on the neutral part of Gyno Cardia Odorata from which two isomeric new lactones $C_{20}H_{28}O_2$, m.p. $131-2^{\circ}$, $[\alpha]_D$ -72° have been isolated. TNM gave characteristic yellow colouration indicating the presence of unsaturation. From the high resolution mass spectrum, the molecular formula was found to be $C_{20}H_{28}O_2$ (M^+ 300). The IR spectrum showed peaks at 3010, 1725, 1600, 1150, 870, 810 cm^{-1}. The presence of six membered ring ketone (δ-lactone) was indicated by the appearance of peaks at 1725, 1150 cm^{-1}. Peaks at 870, 820 cm^{-1} indicated the presence of exocyclic methylenic double bond ($=CH_2$) which is supported by the appear of peak at 3010 cm^{-1} along with another olefinic double bond at 1600 cm^{-1} which is tribubstituted. ^1H NMR spectrum showed a sharp singlet at δ 0.904 ppm that was due to the presence of tertiary methyl group at C-4. Two singlets that appeared at δ 1.703 and 1.720 ppm that was integrated for three protons indicated that both the peaks belonged to the same methyl group, down field shift of which indicated it to be situated on a double bond. Appearance of doublet at 4.703 and 4.881 ppm and a singlet like at 5.015 ppm was indicated by ^1H NMR. The former two values represented methylenic protons and the latter vinylic proton. The nature of these protons arrived at by irradiation experiments.

Irradiation experiments showed that a vinyl methyl group is present in the molecule but the integration of the vinyl methyl and olefinic protons suggested that there is at least a mixture of two isomeric compounds. This was found to be true by gas-liquid chromatography. GLC showed that this fraction contains a mixture of two isomeric compounds in the ratio 80:20 . Therefore the structure suggested for the compounds are


(XX)


(XXI)

The convincing proof of the structures (XX) and (XXI) was forthcoming from the ^{13}C NMR analysis. ^{13}C NMR indicated a sharp triplet at 76.71 ppm which suggested that this carbon is connected with an oxygen that carries two protons with it. The protons probably appeared as AB quartet in the ^{1}H NMR spectrum at δ 4.1 ppm. The appearance of two singlets at 175.2 and 174.7 ppm were the lactonic carbonyl carbon and the peaks at 156.2 and 144.1 ppm as singlet indicated olefinic carbon. The doublet at 132.6 and the triplet at 102.5 ppm showed the presence of vinyl carbon and methyl carbon. A survey of the literature showed that a kaurane nucleus probably fit in the above compounds to explain the above observation with C-19 carbon being the lactonic carbonyl attached to C-20 carbon. The 15, 16 and 16, 17 carbons possessing olefinic double bond as isomeric mixture. It is to be mentioned in this connection that the total carbon shift assignment has been made by comparison with the ^{13}C shift values of potamogetonin, (-)-ent-kaur-16-ene and (-)-ent-16-kauren-19-oic acid. Therefore structures (XX) and (XXI) have been proposed for Odolide and iso Odolide.

Section E comprising of biogenesis of Odolide, iso odolide and hydroxy Odolide with reference to biogenesis of tetracyclic diterpenes has been discussed.

Chapter IV describes the experimental details of the works contained in Chapter III.