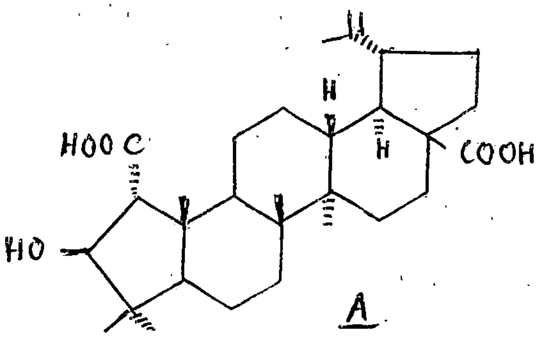
SUMMARY

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

A. PART - I :

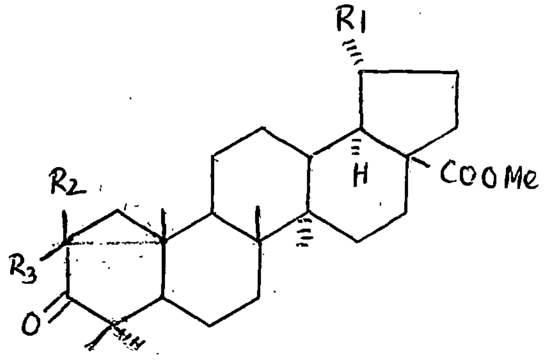
Chapter - I : In view of the fact that the present dissertation deals in part with a successful partial synthesis of dimethyl dihydroceanothate, it was felt pertinent to prepare an up-to-date survey on the isolation, structure and stereochemistry of ceanothic acid A. This constitutes the subject matter of Sections A, B and C of Chapter -I.

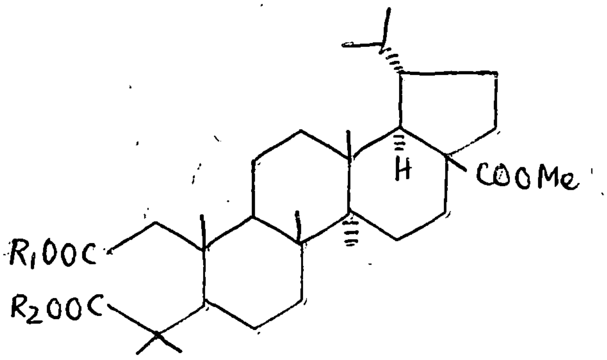


A

Chapter - II. Section A deals with a short review on previous attempts toward the partial synthesis of ceanothic acid A. Section B describes a successful partial synthesis of dimethyl dihydroceanothate III c. Autoxidation of methyl dihydrobetulonate Ia by passing a stream of oxygen in presence of K-tert.butoxide in tert.butanol gave the diosphenol Ib, m.p. 131-33°, $(\alpha)_D - 1.96^\circ$. The diosphenol on oxidation with 30% hydrogen peroxide gave the seco-acid IIa, m.p. 175-77°,

ν_{max}^{nujol} 1710 and 1690 (COOH) cm^{-1}, which on methylation with diazomethane afforded the trimethyl ester <u>IIb</u>, m.p. 146-47°, ν_{max}^{nujol} 1745, 1725 ($-CO_2Me$) cm^{-1}, identical with those reported in the literature for the trimethyl ester of the seco - A acid derived from dihydrobetulic acid (L. Ruzicka and O. Isler, Helv. Chim. Acta, <u>19</u> 506, 1936). Dieckmann condensation of the trimethyl ester in presence of K-<u>tert</u>.butoxide in benzene solution under nitrogen blanket (B. Fuchs and H. J. E. Loewenthal, Tetrahedron, <u>11</u>, 199, 1960; H. R. Nace and A. H. Smith, J.Org.Chem, <u>38</u>, 1941, 1973) gave a gummy product which on chromatography over alumina gave methyl 2α-methoxycarbonyl-3-oxo-A(1)-norlupan-28-oate <u>IIIa</u>, m.p. 191-93°, $(\alpha)_D$ 89° and its epimer <u>IIIb</u>, m.p. 175-77°, $(\alpha)_D$ 42° in the ratio of 17:1. The high yield of the β- ketoester <u>IIIa</u> with the desired stereochemistry in this reaction is significant and is at variance with the observation of Eade et al (R. A. Eade, P. K. Grant, M. J. A. McGrath, J. J. H. Simes and M. Wootton, Aust. J. Chem; <u>24</u>, 621, 1971) who stated that methyl 2α-methoxycarbonyl-3-oxo-A(1)-norlup-20(29)-en-28-oate (dimethyl dehydroceanothate) was rapidly epimerised by alkali to an equilibrium mixture containing 40% of the starting material and 60% of the isomer epimeric at C-2.



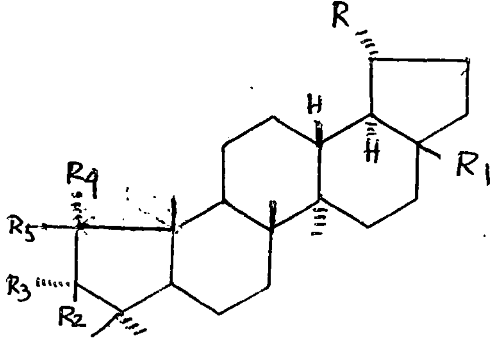


Ia, $R_2 = R_3 = H$, $R_1 = \cdots CH{<}^{CH_3}_{CH_3}$

Ib, $\genfrac{}{}{0pt}{}{R_2}{R_3}{>}{=}O$, $R_1 = \cdots CH{<}^{CH_3}_{CH_3}$

IIa, $R_1 = R_2 = H$

IIb, $R_1 = R_2 = CH_3$



IIIa, $R_1 = R_4 = COOMe$, $\genfrac{}{}{0pt}{}{R_2}{R_3}{>}{=}O$, $R_5 = H$, $R = \cdots CH{<}^{CH_3}_{CH_3}$
IIIb, $R_1 = R_5 = COOMe$, $\genfrac{}{}{0pt}{}{R_2}{R_3}{>}{=}O$, $R_4 = H$, $R = \cdots CH{<}^{CH_3}_{CH_3}$
IIIc, $R_1 = R_4 = COOMe$, $R_2 = OH$, $R_3 = R_5 = H$, $R = \cdots CH{<}^{CH_3}_{CH_3}$

IIId, $R_1 = R_4 = COOMe$, $R_3 = OH$, $R_2 = R_5 = H$, $R = \cdots CH{<}^{CH_3}_{CH_3}$

IIIe, $\genfrac{}{}{0pt}{}{R_2}{R_3}{>}{=}O$, $R_4 = R_5 = H$, $R_1 = COOMe$, $R = \cdots CH{<}^{CH_3}_{CH_3}$

The β-keto-ester IIIa on reduction with sodium borohydride in methanol-dioxan solution gave a mixture (TLC-two spots) which on chromatography over alumina first eluted (benzene : petroleum 3:2) a solid III C, m.p. 261-63°, $(\alpha)_D$ 22°, ν_{max}^{nujol} 1755, 1725 cm^{-1} identical with an authentic specimen of dimethyl dihydroceanothate supplied by Professor P. de Mayo. Further elution with the same solvent gave another solid, m.p. 140-42°, ν_{max}^{nujol} 1750, 1725 cm^{-1}. The yield of this material was not sufficient for NMR studies but by analogy with previous work (R. A. Eade, P. K. Grant, M. J. A. McGrath, J. J. H. Simes and M. Wootton, Aust. J. Chem. 24, 621, 1971) it is believed to be the C-3 epimer IIId.

Attemps were also made to prepare the β-keto ester by carbomethoxylation of the A-nor ketone IIIe at C-2. Carbomethoxylation reaction on the ketone with dimethyl carbonate was carried out in presence of sodium methoxide, K-tert.butoxide and sodium hydride in various solvents but so far the reaction did not meet with success (S. J. Rhoads, J. C. Gilbert, A. W. DeCora, T. R. Garland, R. J. Spangler and M. J. Urbighkit, Tetrahedron, 19, 1665, 1963; J. A. Marshall and N. Cohen, J. Org. Chem., 30, 3475, 1965; E. J. Corey, Rajat B. Mitra and Hisashi Uda, 86, 485, 1964; H. O. House, Modern Synthetic Reactions, W. A. Benjamin Inc. 1972, page - 546 and references cited therein).

[A preliminary account of the work was presented at the Symposium sponsored by Indian National Science Academy and Calcutta University, 1975, held at Calcutta. (Abstract No. A27).

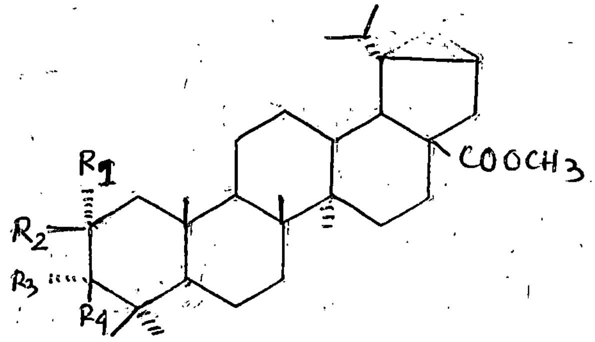
A short communication embodying the results of this work will be published in September issue, 1975 of Indian Journal of Chemistry (REPRINT NO. 4)].

B. Part - II :

Chapter - I, Sections A-D deals with an up-to-date survey of the synthesis of 2,3-diols of triterpenoids. Section E constitute a short review on autoxidation and isomerisation in ring A of triterpenoids. Section F deals with a short review on 2,3-dihydroxy triterpene acids from natural sources. Chapter -II describes an unambiguous synthesis of methyl dihydroalphitolate (Section B) and 2β, 3β-dihydroxy betulinate (Section C) starting from betulinic acid.

Methyl dihydrobetulonate IVa (Section B) on autoxidation gave the diosphenol IVb, m.p. 131-33°, $(\alpha)_D - 1.96^\circ$. Acetylation of the diosphenol followed by hydrogenation gave the corresponding 2α-acetoxy - 3 Keto-dihydro-betulonate IVC, m.p. 223-25°, $(\alpha)_D + 32.56^\circ$. This compound was kept overnight on a basic column and after eluting it with benzene afforded a new product, m.p. 228-30°, which has been assigned structure IVd, methyl-

2-Keto-3-β-acetoxy Dihydrobetulinate. This is formed by migration of the acyl group from 2α-position to 3β-position. 2α-acetoxy methyl dihydrobetulonate <u>IVc</u> on sodium borohydride reduction in methanol-dioxan solution at pH 8 to reduce isomerisation gave a crystalline solid <u>IVe</u>, m.p. 259-61°, $(\alpha)_D$ - 7.14°. The latter on hydrolysis with a 15% methanolic potassium hydroxide solution afforded a product which on chromatography gave a crystalline solid <u>IVf</u>, m.p. 230-32°, indistinguishable from an authentic sample of methyl dihydroalphitolate supplied by Prof. E. Ritchie. The infrared spectra of the two compounds were found to be identical throughout the entire range.



<u>IV</u> a, $R_1 = R_2 = H$, $\genfrac{}{}{0pt}{}{R_3}{R_4}\rangle = O$

<u>IV</u> b, $\genfrac{}{}{0pt}{}{R_1}{R_2}\rangle = O$, $\genfrac{}{}{0pt}{}{R_3}{R_4}\rangle = O$

<u>IV</u> c, $R_1 = OAc$, $R_2 = H$, $R_4 = OAc$

<u>IV</u> d, $\genfrac{}{}{0pt}{}{R_1}{R_2}\rangle = O$, $R_3 = H$, $R_4 = OAc$

<u>IV</u> e, $R_1 = OAc$, $R_2 = R_3 = H$, $R_4 = OH$

<u>IV</u> f, $R_1 = OH$, $R_2 = R_3 = H$, $R_4 = OH$

<u>IV</u> g, $R_1 = R_3 = H$, $R_2 = R_4 = OH$

<u>IV</u> h, $R_1 = R_3 = H$, $R_2 = R_4 = OAc$

The diosphenol IVb (Section C) on sodium borohydride reduction in methanol solution gave a compound IVg, 261-63°, $(\alpha)_D$ 21.62°, ν_{max} 3525, 3360, 1720 cm^{-1}; diacetate IVh, m.p. 186-87°, ν_{max}^{KBr} 1745, 1720, 1258 cm^{-1}. Examination of the NMR spectrum of the diol showed a multiplet at about 3.20 ppm assigned to C3 - H and a broad unresolved multiplet at about 4.5 ppm (C2-H) which collapsed to a doublet (J =3.7 Hz) and a multiplet (ΣJ=6Hz) respectively upon exchange of hydroxyl proton with D_2O. Thus the hydroxyl group at C-3 is equatorial (Ha) and the one at C-2 is axial (He). In the NMR spectrum of the diacetate IVh these signals were shifted to a downfield to 4.8 ppm (doublet, J = 4Hz) and at about 5.4 ppm (broad multiplet). The signals for the ester group and the acetate group appeared at 3.65 ppm (3H, singlet) and at 2.06 (6H, singlet) ppm. Thus the assignment of the structure IVg for the $NaBH_4$ reduction product is consistent with NMR results. The mechanism for the exclusive for_mation of the 2β, 3β-diol has been discussed.

C. PART - III :

Chapter-I describes the morphology of the fern Polypodium juglandifolium, Don.

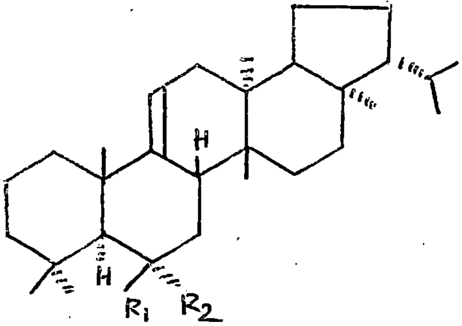
Chapter-II gives a short review on the chemical constituents of ferns of Polypodiaceae family.

Chapter - III deals on the investigation on the neutral part of the benzene extract of the fern Polypodium juglandifolium and isolation of two new triterpenes - Polypodinol A, $C_{30}H_{50}O$ and Polypodinol B, $C_{30}H_{50}O$ along with fern-9(11)-ene, filicene, cyclolaudenol, nerifoliol and β- sitosterol and detection of a new triterpene, $C_{32}H_{54}O$, in the cyclolaudenol fraction from mass-spectrometry.

Chapter - IV describes the investigations on the structure elucidation of Polypodinol A, $C_{30}H_{50}O$.

Polypodinol A Va, $C_{30}H_{50}O$, m.p. 223-25°, gave a positive Libermann-Burchard test and reddish brown colour with TNM. IR spectrum of Va showed bands at 3605 cm^{-1} (-OH) and its NMR spectrum showed signals at δ 0.8 to 1.28, a multiplet centered at δ 5.40 (1H, trisubstituted double bond) and a broad diffused multiplet at δ 4.40 attributed to the proton attached to the carbon containing the -OH group. The coupling pattern indicates that this proton is attached to a carbon atom in the system $\overset{|}{-CH}-C\underline{H}OH-CH_2-$. On treatment with acetic anhydride-pyridine it furnished a monoacetate Vb, $C_{32}H_{52}O_2$ (M^+ 468), m.p. 203-4°, $(\alpha)_D$ - 83.72°, ν_{max}^{nujol} 1725 and 1245 ($-OCOCH_3$) cm^{-1}. Its NMR spectrum showed the presence of eight methyl groups between δ 0.8 to 1.16, a sharp peak at δ 2.00 (3H, $-O.CO.CH_3$), a multiplet at δ 5.40 (1H, vinyl proton) and an unresolved multiplet centered at δ 5.20 [IH, $-\overset{|}{C}H-\underline{CH}-(OAc)-CH_2-$]

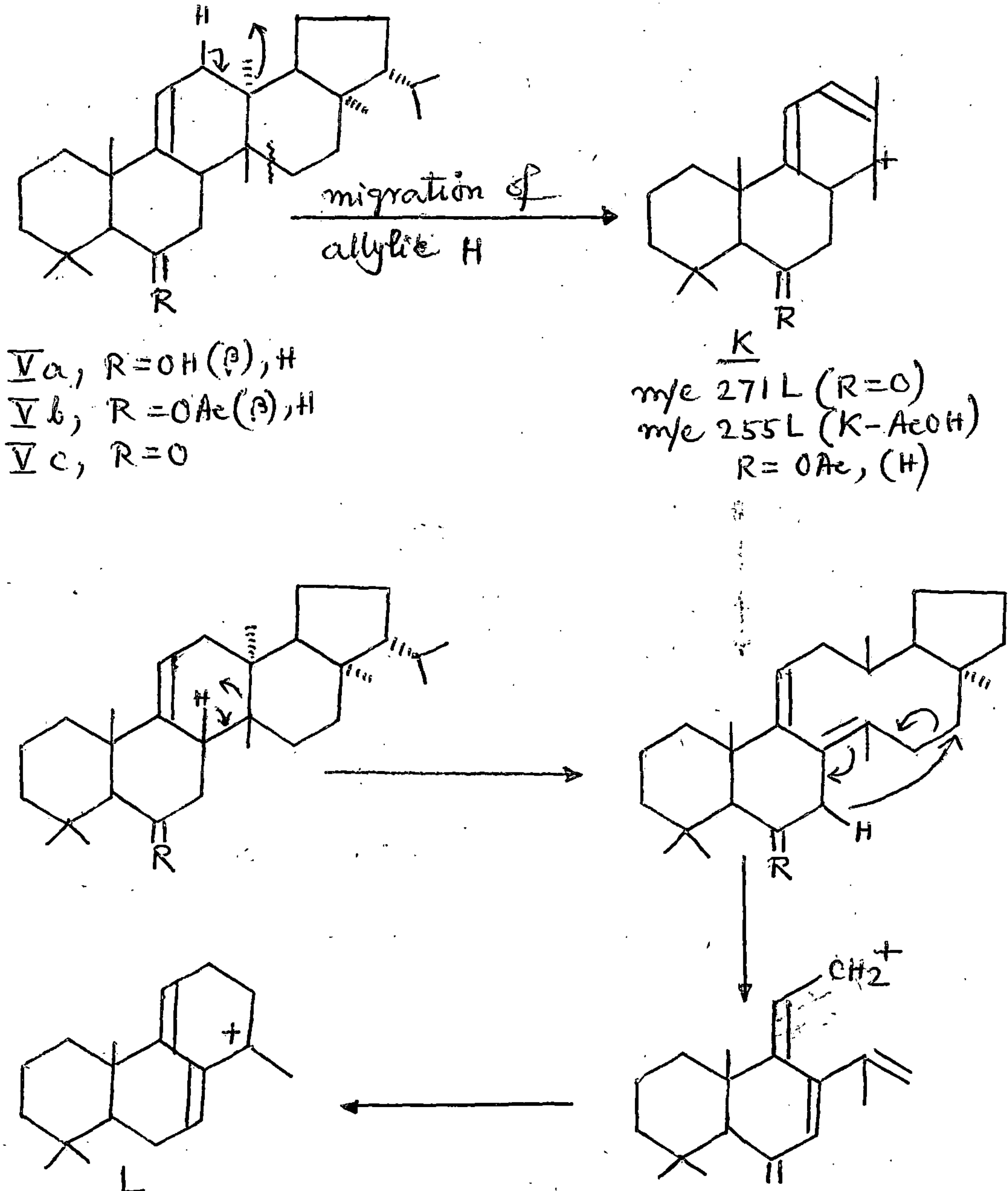
Oxidation of Va with CrO_3 - Pyridine complex gave a compound Vc, $C_{30}H_{48}O$ (M^+ 424), m.p. 221-23°, $(\alpha)_D$ + 16.66°, ν_{max}^{nujol} 1720 (six membered ring Ketone), NMR signals at δ 5.40 (IH, vinyl proton) and peaks between δ 0.8 to 1.04 for eight methyl groups. Wolff Kishner reduction of the Ketone under anhydrous condition furnished a hydrocarbon (M^+ 410), m.p. 168-69°, $(\alpha)_D$ - 16.6° and this was found to be identical with an authentic sample of fern-9(11)-ene (m.m.p., IR comparison). This experiment established that the triterpene was a hydroxy derivative of Δ^{9-11}- fernene.



$\underline{V}a$, $R_1 = OH$, $R_2 = H$; $\underline{V}b$, $R_1 = OAc$, $R_2 = H$

$\underline{V}c$; $\begin{matrix}R_1\\R_2\end{matrix}\rangle=O$; $\underline{V}d$, $R_1 = R_2 = H$, The position of the oxygen function was established from the following observations. The position of the oxygen function may be at C-3, C-6, C-7, C-15 and C-16. Of these possibilities the first one was eliminated since the Ketone Vc did not respond to Zimmerman's colour test for 3-Keto group nor did it react with any carbonyl reagent. Moreover, it was not identical with 3-keto-fern-9(11)-ene. The study of the mass Spectra of Vb and Vc indicated that the oxygen function was most probably present in ring B either at C-6 or C-7. The compounds Vb and Vc exhibited a mass peak (Chart - A) 257 K for Vc and 241 K for Vb (formed by the loss of acetic acid from the ion K). In addition to species K and its further decomposition products the spectra V b and Vc showed a very abundant fragment at 271 L for Vc and 255 L for Vb. This type of fragmentation pattern and other evidences discussed earlier can be explained by assuming the presence of hydroxylic function at ring B either at C-6 or at C-7. A careful examination of the circular dichroism curve of Vc established the position of oxygen function at C-6. 300 MHz NMR of Vc was also taken which is also in conformity with the structure Va for the new triterpene.

CHART - A

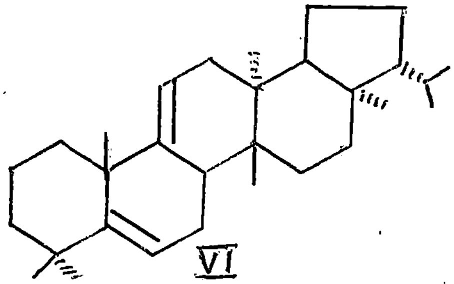


$\underline{V}$a, R = OH(β), H
$\underline{V}$b, R = OAc(β), H
$\underline{V}$c, R = O

$\underline{K}$
m/e 271 L (R=O)
m/e 255 L (K-AcOH)
R = OAc, (H)

$\underline{L}$
m/e 257 K (R=O)
m/e 241 K (L-AcOH)
R = OAc, (H)

Dehydration of Va with $POCl_3$ - Pyridine afforded a single product VI, m.p. 157-58°, no UV



VI

absorption above 220 nm. NMR spectrum showed the presence of two vinyl protons (two multiplets, one centered at δ 5.28 and the other at δ 5.44). Compound VI on acid isomerisation afforded an oily compound which did not show any UV absorption above 220 mμ. The formation of a single product VI during the process of dehydration indicated the β-axial orientation of the hydroxylic function at C-6. $NaBH_4$ reduction of the Ketone Vc gave the epimeric alcohol, m.p. 200-1°; acetate, m.p. 177-79°. Oxidation gave back the original Ketone. This also established that the reduced alcohol has the 6α-equatorial conformation.

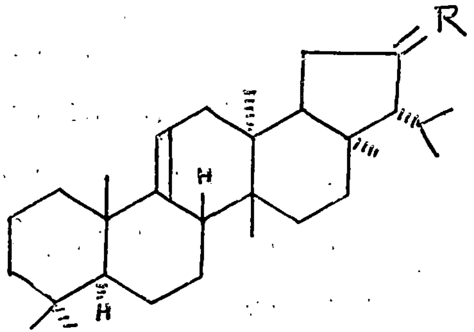
Chapter - V deals with investigation on the structure of the new triterpene polypodinol B, $C_{30}H_{50}O$.

In addition to Polypodinol A, a new triterpene Polypodinol B, $C_{30}H_{50}O$, m.p. 164-66° has been isolated. It gave a monoacetate $C_{32}H_{52}O_2$ (M^+468), m.p. 207-8°, $(\alpha)_D$ 38.00°.

Oxidation of Polypodinol B gave a Ketone, $C_{30}H_{48}O$ (M^{+} 424), m.p. 174-75° which on W.K. reduction gave a hydrocarbon, m.p. 168-69° identical with fern-9(11)-ene. Thus Polypodinol B is also a hydroxy derivative of $\Delta^{9(11)}$-fernene.

Mass spectrum of the Ketone showed the molecular ion peak at M^{+} 424 in addition to peaks at m/e 409 (M^{+}-15), m/e 243 and m/e 231 characteristic of a $\Delta^{9(11)}$- fernene system. The mass spectrum of the monoacetate was more informative and exhibited a mass fragmentation pattern having the following peaks : M^{+}468, m/e 453 (M^{+}-15), m/e 393 (M-15-HOAc) in addition to peaks at m/e 231 and m/e 243. The fragmentation pattern revealed that it was similar to that of $\Delta^{9(11)}$- fernene system. The presence of the base peak at m/e 243 in both the Ketone and the acetate indicated that there is no substitution in rings A and B.

The other possible alternative positions for the (OH) group are at C-15, C-16 in ring D or some other position in ring E. CD curve of the Ketone showed a negative Cotton effect. Inspection of Drieding models of C-15 Ketone and C-16 Ketone suggested that both would show a positive Cotton effect. Since a negative Cotton effect is actually observed for the Ketone, positions C-15 and C-16 are ruled out. Therefore, we believe that the carbonyl group is most probably situated at some position in ring E. From an examination of the 300 MHz NMR spectrum of the Ketone we have proposed a tentative structure VIa for the Ketone and VIb for the triterpene Polypodinol B.



VI a), R = O

VI b), R = $<^{H}_{OH}$

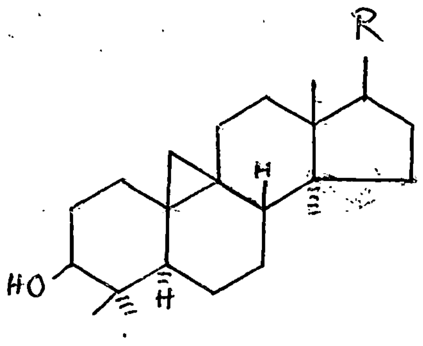
The stereochemistry of the -OH group has not been settled. CD curve and 300 MHz NMR spectrum of the Ketone has been discussed. Further work is in progress to arrive at a firm conclusion about the position of the (OH) group.

[A preliminary account of this work was presented at the "Science Congress Association" held in Nagpur, India (1974)]

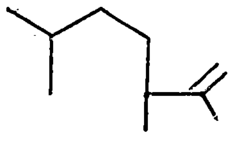
Chapter - VI describes the detection and structure determination of a new triterpene - a cyclolaudenol homologue $C_{32}H_{54}O$ by mass spectrometry.

In Chapter - III isolation and identification of cyclolaudenol has been mentioned. It has been shown that the cyclolaudenol fraction was a mixture of two compounds (TLC). But by careful fractional crystallisation of their benzoates, one of the components was isolated as cyclolaudenol benzoate.

The original mixture (A) on acetylation gave an acetate (B), m.p. 107-8°, $(\alpha)_D$ 55.17°. Hydrogenation of the mixture gave a compound (C), m.p. 132-33°, which on acetylation gave an acetate (D), m.p. 127-28°. Oxidation of the original mixture gave a mixture of Ketones (E), m.p. 107-8°. Mass spectra of the original mixture (A), its acetate (B), the dihydro-compound (C) and its acetate (D) were measured and it was observed that along with cyclolaudenol (M^+ 440) a second component having M^+ 454, that is, a new triterpene alcohol was present. The mass spectrum of this new compound has been found to correspond very closely to that of Cyclolaudenol VIIa and are in agreement with earlier findings (P.Benveniste, L.Hirth and G.Ourisson, Phytochem., 5, 31, 1966; H.E.Audier, R.Bengelmans and B.C.Das, Tetrahedron Letters, 4341, 1966; R.T.Aplin and G.M.Haruby, J.Chem.Soc.(B), 1077, 1966)



VII a, R =



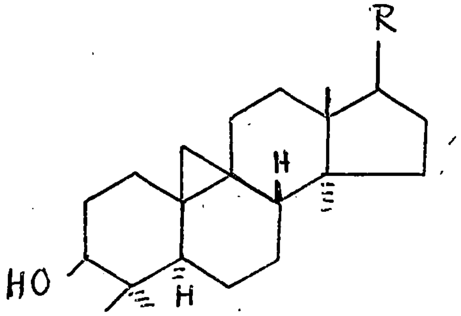
VII b, R = $C_{10}H_{19}$

VII c, R = $C_{10}H_{21}$

The unusual feature of the spectrum (Chart B) of Cyclolaudenol <u>VIIa</u> is the intense fragment (a) at m/e 300 and have the composition $C_{22}H_{36}$ and corresponds to the loss of ring A plus one hydrogen atom since it remains at m/e 300~~0~~ in the spectra of the corresponding Ketone. This is formed from the molecular ion m/e 440 by a one step process. The other fragments, besides the loss of a methyl group (m/e 425), water (m/e 422) and methyl-plus-water (m/e 407) arise from M-18 fragment and involve cleavage of the side chain - (b) m/e 379 ($M-18-C_3H_7\cdot$), (C) m/e 353 ($M-18-C_5H_9\cdot$). A further fragment (e) m/e 175 common to all spectra, corresponds to the loss of both ring A and the side chain. Another significant peak (d) m/e 315 ($M-R\cdot$) is common to Cyclolaudenol <u>VIIa</u>, its homologue <u>VIIb</u> and its dihydroderivative <u>VIIc</u> which arises by elimination of R group from M. The most plausible mechanism (McLafferty, Chem. Commun., 78, 1966) for the formation of these fragments is depicted (path A) where initial ionisation of 9-10 bond relieves the strain imposed on ring B, fission of the activated 5-6 bond followed by transfer of one of the activated C-11 hydrogen via a "Mc Lafferty" type of rearrangement.

The mass spectra of the new C-32 triterpene <u>VIIb</u> ($M^{+}454$) and its dihydrocompound <u>VIIc</u> has been found to contain all the peaks (Chart B) characteristic of Cyclolaudenol but in this case

CHART - B

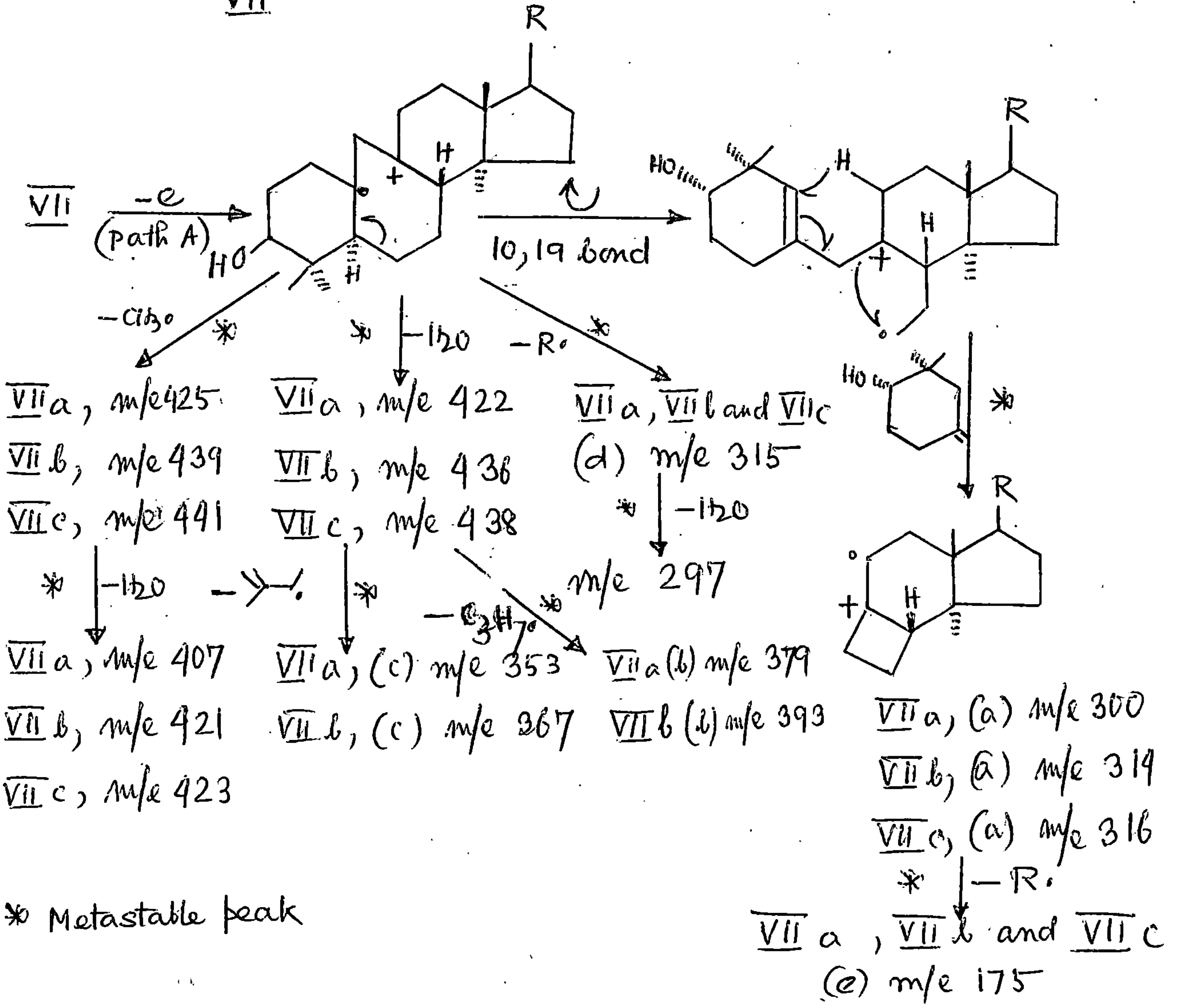


VII

VII a, R =  (M+ 440)

VII b, R = $C_{10}H_{19}$ (M+ 454)

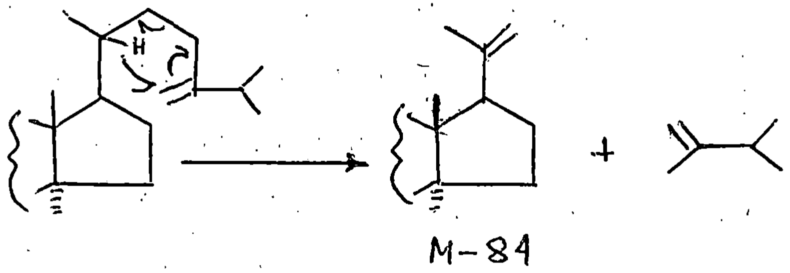
VII c, R = $C_{10}H_{21}$ (M+ 456)



* Metastable peak

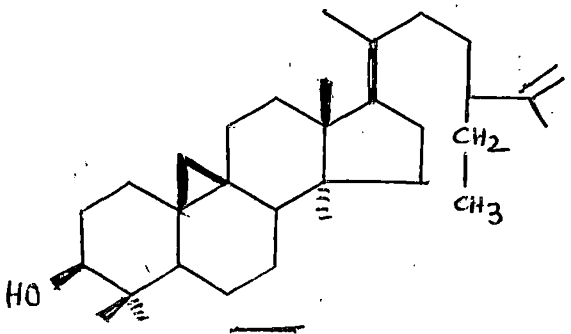
the peak found by loss of side chain $M^{+}-R$ for compounds VIIb and VIIc was at 315 indicating the presence of an extra carbon atom in the side chain. The intense fragment at m/e 314 for VIIb have the composition $C_{23}H_{58}$ and corresponds to the loss of ring A and one hydrogen atom since it remains at 314 in the mass spectra of the corresponding acetate and is moved to m/e 316 in the spectrum of the corresponding dihydrocompound VIIc . A further fragment gave a sharp peak at m/e 175 due to loss of ring A and side chain. This also corrobrates the presence of the extra carbon atom in the side chain. In addition to these peaks, the peak at m/e 315 ($M^{+}-R$) for VIIb and VIIc and at m/e 357 for the acetates of VIIb and VIIc again established the presence of the extra carbon atom in the side chain (R) of the cyclolaudenol nucleus. The other major fragments, besides the loss of methyl radical (m/e 439), water (m/e 436) and methyl-plus-water (m/e 421) are from M-18 fragment and involve cleavage of the side chain. These peaks are exhibited at m/e 393 ($M-18-C_3H_7\cdot$) and m/e 367 ($M-18-C_5H_9\cdot$). The appearance of these mass peaks has been explained.

The position of the double bond ($=CH_2$, NMR) in the side chain at 25 (26) position may be tentatively assigned from the mass spectrum of VIIb and its acetate as the M-84 fragment observed in the "McLafferty" rearrangement involving 24-28 double bond and the C-20 hydrogen has been found to be absent in the spectra of VIIb and its acetate (J. Bergman, B.O. Lindgren and C.M. Svahn, Acta. Chem. Scand., 19, 1661, 1965)



All these facts has been discussed in detail in Chapter - VI and established beyond doubt that the C-32 compound contains a cycloIaudenol nucleus with the extra carbon atom in the side chain.

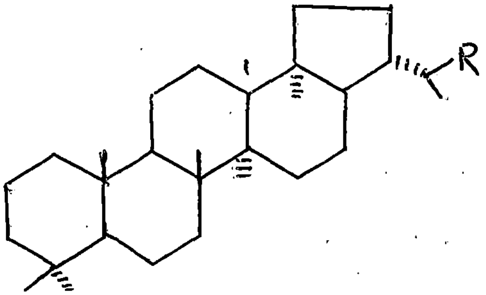
On biogenetic grounds the new triterpene has been tentatively assigned structure VIII. A mechanism for the biosynthesis of this new triterpene in the fern Polypodium juglandifolium has been proposed.



VIII

[A preliminary account of this work was presented at the "Convention of chemists, CSIR, India, 1974 held at Madurai, (REPRINT NO. 3)]

Chapter - VII : Mitra et al (G.N.Pandey and C.R.Mitra, Tetrahedron Letters, 1353, 1967) converted neriifoliol IXa to the corresponding aldehyde by Sarret oxidation and recorded its m.p. as 76°. They reduced this aldehyde by Wolff - Kishner reduction and obtained a hydrocarbon m.p. 190-92°, $(\alpha)_D$ + 36° which they reported was same as hopane . We repeated their experiment with hydrated CrO_3- Pyridine complex and the product obtained after chromatography was found to be identical with isoadiantone. The mother liquor after crystallisation showed the presence of both adiantone and isoadiantone (TLC). However, Sarret oxidation with anhydrous CrO_3- Pyridine complex according to the procedure of Ratcliffe and Rodehorst (Ronald Ratcliffe and Ronald Rodehorst, J.Org.Chem., 35, 4000 1970) afforded a single compound, m.p. 205-6°, ν_{max}^{nujol} 2720, 1730 cm^{-1}; M^+ 426. NMR spectrum of the compound showed a peak at δ 9.65 (IH) characteristic of one aldehydic proton. Wolff-Kishner reduction of the aldehyde IXb gave hopane, m.p. 218-19° identical with an authentic sample (IR).



IX a, $R = CH_2OH$

IX b, $R = CHO$

IX c, $R = CH_2OTs$

IX d, $R = CH_2Cl$

The above observations are quite at variance with those reported by Mitra et al and suggest that the oxidation proceeds by different mechanisms depending on the reaction conditions. This reaction is being studied in detail to arrive at the correct mechanism of the reaction.

We had also planned to prepare nerefoliol tosylate IXc by the usual procedure with highly purified p-toluene sulfonyl chloride and pyridine at room temperature and then convert the tosylate to hopane by LAH reduction. But during this preparation we failed to isolate the desired tosylate but instead obtained a compound, m.p. 221-22°, which gave a positive test for halogen. Structure IXd has been assigned to it from elemental analysis, IR, NMR and mass spectral studies. In this case we find that the normal reaction is retarded and instead a different reaction takes place giving a product by substitution. A probable mechanism for the formation of IXd has been suggested.

D. PART - IV :

Part - IV describes chemical investigation on some Indian plants.

[REPRINT NO.1 and REPRINT NO.2]