CHAPTER-II

This chapter has been divided into four sections from Section A to Section D.

SECTION-A.

Oxidation of triterpenoid ketones[17,18,22,27] with selenium dioxide or selenium dioxide in presence of hydrogen peroxide mixture in tertiary butanol have been reported. But there is no report on the studies of oxidation of triterpenoids having double bonds in ring-A containing 4,4-dimethyl system with selenium dioxide-hydrogen peroxide in tertiary butanol. So the author carried out some reactions of that type and the results of such oxidations are being reported in this section of the thesis.

OXIDATION OF 2,3-DEHYDRO-LUPANE 71 WITH SELENIUM DIOXIDE-HYDROGEN -PEROXIDE IN TERTIARY BUTANOL.

The product obtained after refluxing a solution of 2,3-dehydro-lupane in tertiary butanol with selenium dioxide containing hydrogen peroxide for 40 hours, was subjected to column chromatography for purification. On elution with benzene-chloroform (4:1) mixture a solid material was obtained which was crystallised from chloroform-methanol, *M.P.* 245-6°C. Its IR spectrum indicated the presence of hydroxyl group and hence it was acetylated with acetic anhydride-pyridine mixture and the product on column chromatography afforded a single compound-A on elution with benzene-petrol (2:3) mixture.

Characterisation of compound A :-

Compound A was purified by crystallisation from chloroform-methanol mixture, *M.P.* 221-2°C, $[\alpha]_D$ +23.4°. Its IR spectrum (fig.1) showed peaks at 1750, 1270 and 1250 cm^{-1} showing the presence of acetate function. Elemental analysis showed the molecular formula of A to be $C_{34}H_{56}O_4$ which is in agreement with its mass spectrum (fig.2). It showed molecular ion peak at m/e 528 (M, 86%)$^+$; the other fragments of prominence appeared at m/e 513 (M $-CH_3$, 30)$^+$, 485

$(M - C_3H_7, 43)^+$, 468 $(M - AcOH, 78)^+$, 408 $(M - 2X\ AcOH, 100)^+$, 393 (88), 365 (52.5), 231 (74), 191(86), 187(98), 123(94) . The ^1H NMR spectrum (fig.3) of compound A showed the presence of two secondary methyl groups that appeared as doublet centered at (δ in ppm.) 0.77 and 0.84 (J = 7 Hz.) respectively; the six tertiary methyl groups appeared as singlet (3H each) between 0.76 to 1.08; two singlets (3H each) that appeared at 2.01 and 2.07 were due to two acetoxy methyls (2 X $-OCOCH_3$). The doublet at 5.07 that coupled with vicinal proton with coupling constant of 7 Hz. was due to coupling between equatorial C-2α-H with equatorial C-3β-H which is geminal to the acetoxyl group. The double doublet that appeared at 4.96 with coupling constant 7 & 13 Hz. were due to C-2 proton that coupled with C-3β-H and C-1β-H which caused flatness of the peaks and the latter coupling was due to the coupling of C-2 proton with C-1 axial proton. The coupling constants and their positions are in agreement with the 2β,3α- diacetoxyl derivative of oleanane/lupane as reported in literature[28] shown in the table-I.

TABLE-I.

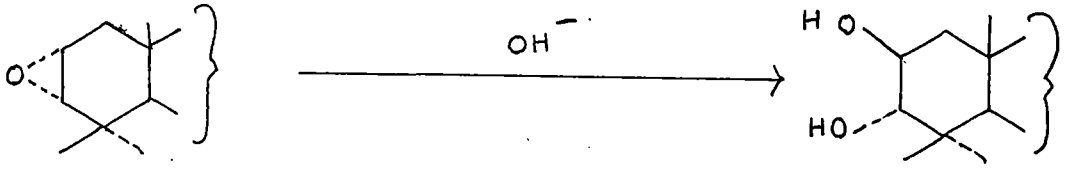
^1H NMR signals of methyl 2,3 dihydroxy Urs-12-en-28-oates and their diacetates with coupling constant in Hz. within parenthesis.

Assignments	2β,3α-$(OH)_2$,	2β,3α-$(OAc)_2$,	2β,3β-$(OH)_2$,	2β,3β-$(OAc)_2$
2-H	3.75 ddd (17, 10,2)	4.95 dd (13, 6.5)	4.08 ddd (4, 4,3)	5.31 ddd (4, 4,3)
3-H	3.63 d (10)	5.03 d (6.5)	3.20 d (4)	4.61 d (4)
Assignments.	2α,3β-$(OH)_2$,	2α,3β-$(OAc)_2$,	2α,3α-$(OH)_2$,	2α,3α-$(OAc)_2$.
2-H	3.68 ddd (11, 10, 4.5)	5.10 ddd (11,10.5,4.5)	4.00 ddd (12,4.5,3)	5.23 ddd (12,4.5,3)
3-H	2.99 d (10)	4.75 d (10.5)	3.43 d, (3)	4.96 d (3)

Thus compound A has been identified as lupan-2β,3α-diyl-acetate 73 and the original compound is therefore identified as lupan-2β,3α-diol, 72.

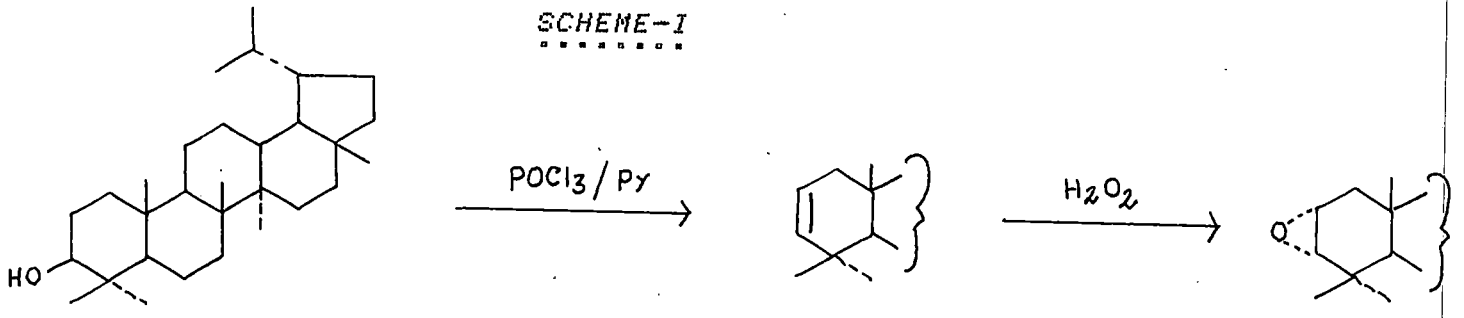
Mechanism for the formation of 2β,3α lupan-diol with selenium dioxide and hydrogen peroxide :-

The olefinic double bond at 2-3 position in ring-A of triterpenoids are much more less hindered than other position and hydrogen peroxide generally forms epoxide from the less hindered alpha side to furnish 2α,3α-epoxide. Under the acidic condition of selenic acid (P_H = 4.2) the epoxide ring cleaves to furnish the *trans* diaxial product.



The formation of such trans diol with hydrogen peroxide-formic acid etc. from cyclic olefins are well known. The formation of 73 from lupanol 69 is schematically represented in scheme-I below :-

SCHEME-I



69 70 71

72. 73

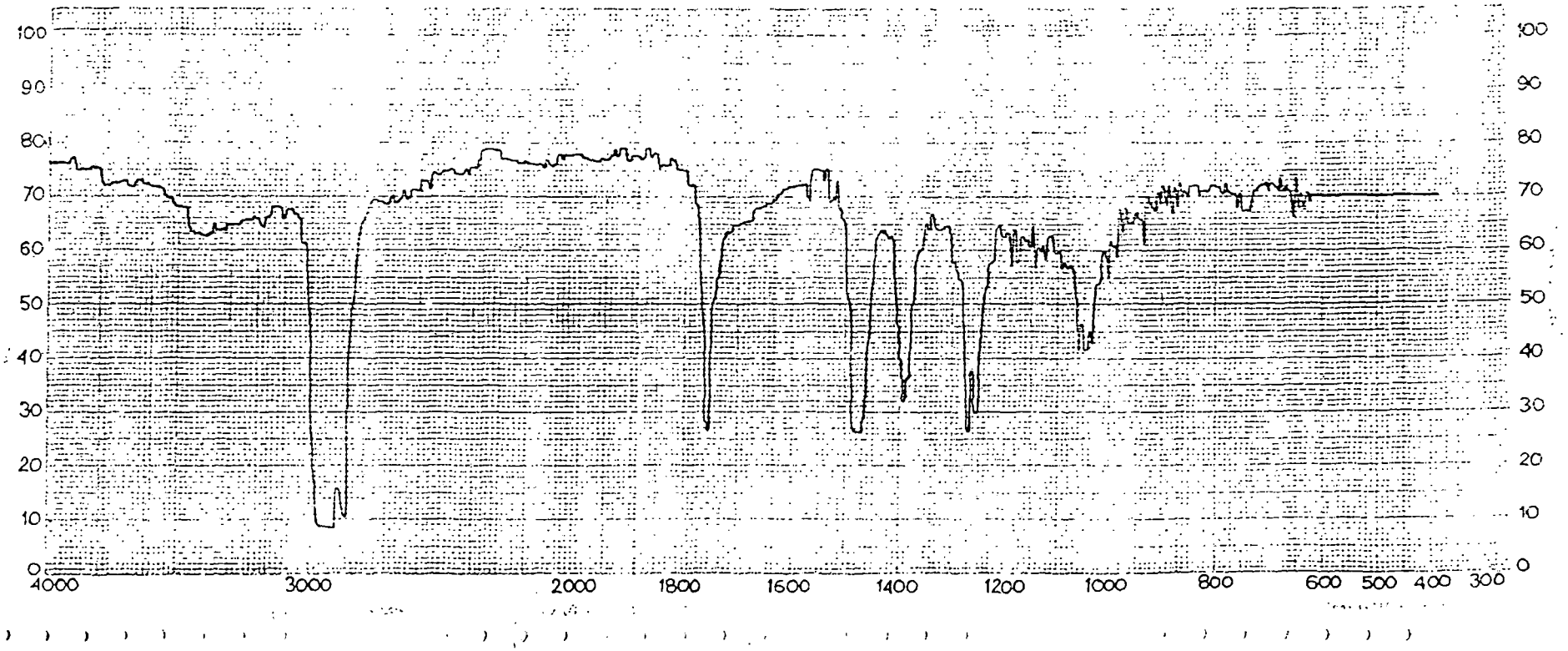


Fig. 1 : IR spectrum of lupan 2β,3α-diyl acetate, 73.

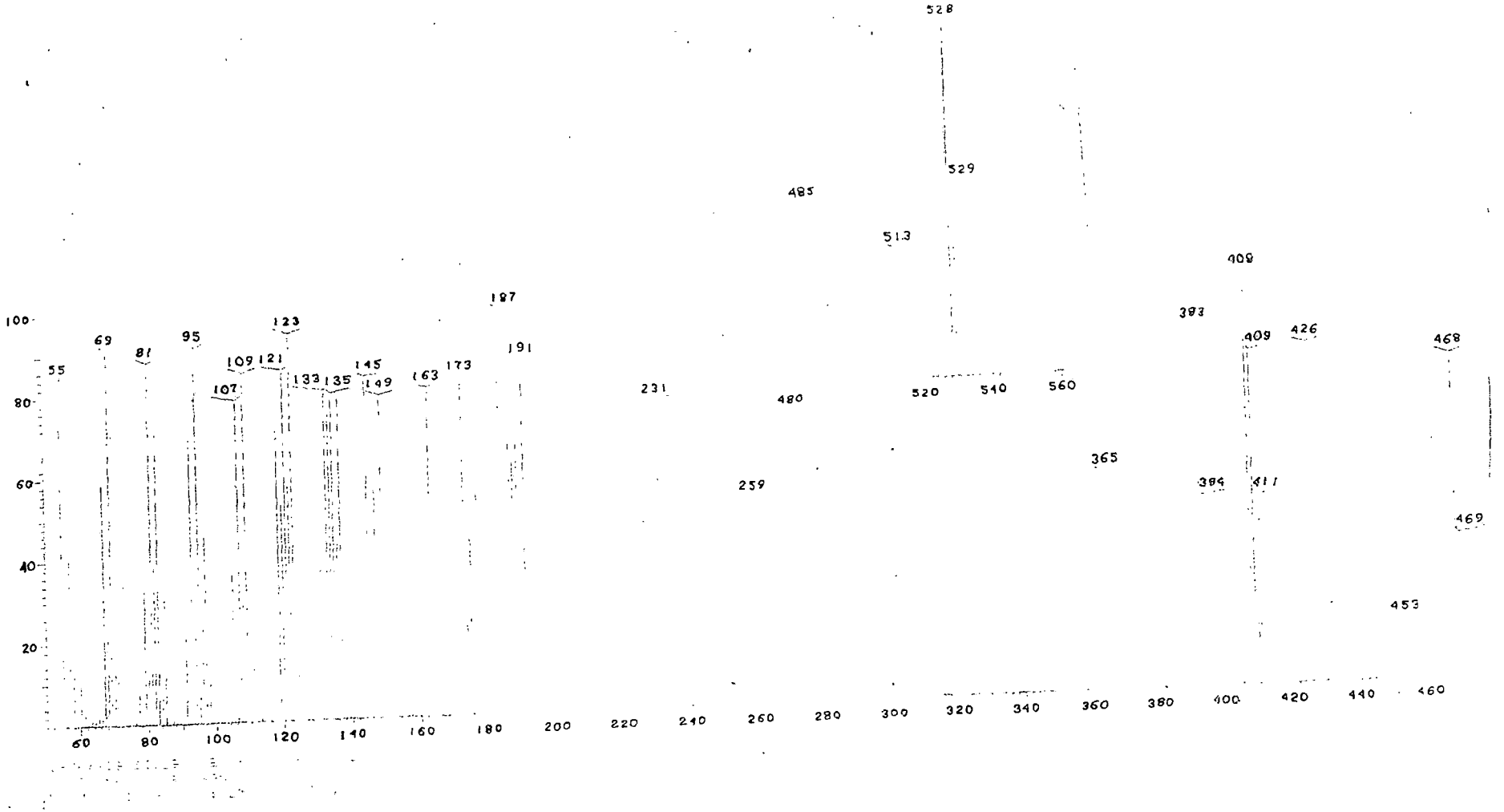


Fig. 2 : Mass spectrum of lupan 2β.3α-diyl acetate. 73.

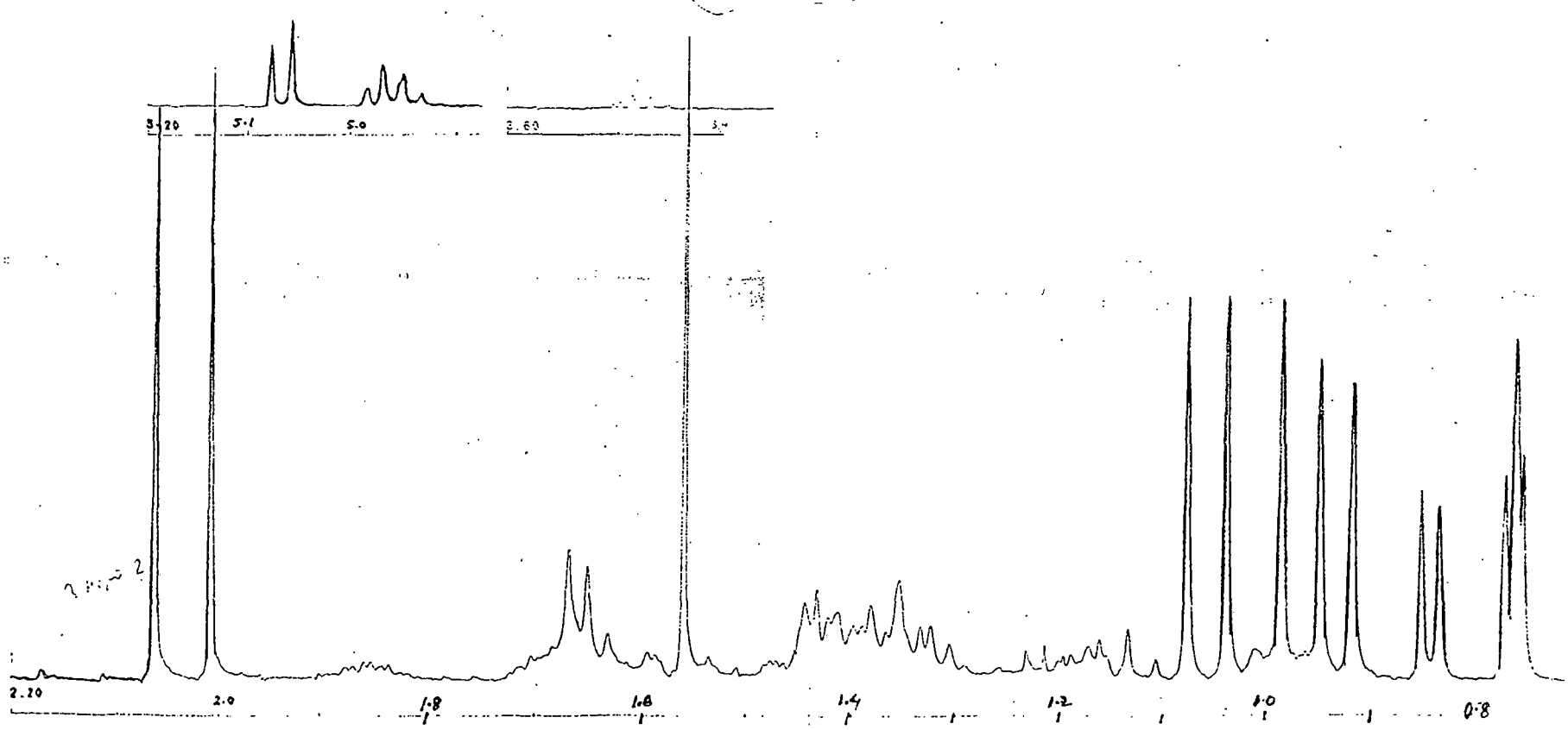


Fig. 3 : ^{1}H NMR spectrum of lupan 2β.3α-diyl acetate, 73.

OXIDATION OF 2,3-DEHYDRO-METHYL-DIHYDRO-BETULINATE 77 WITH SELENIUM-DIOXIDE IN TERTIARY BUTANOL CONTAINING HYDROGEN PEROXIDE.

The compound 2,3-dehydro-methyl-dihydro-betulinate was refluxed with selenium dioxide in tertiary butanol containing hydrogen peroxide for 40 hours over water bath. After usual workup the crude product was acetylated (as the IR spectrum showed the presence of hydroxyl group) with acetic anhydride-pyridine mixture and the product on subsequent chromatography afforded a single compound B on elution with petrol-benzene (1:4).

Identification of compound-B :-

Compound B was purified by repeated crystallisation from chloroform-methanol mixture yielding needle shaped crystals, *M.P.* 209-10^{0}C. The IR spectrum (fig.4) showed peaks at 1730,1710 cm^{-1} due to C=O stretching vibration of ester and acetate groups and 1230, 1220 cm^{-1} for -C-O- stretching vibrations of the same two functions.

Elemental analysis indicated the molecular formula to be $C_{35}H_{56}O_6$. Its mass spectrum (fig.5) showed molecular ion peak at m/e 572 (M, 4%)$^{+}$; the other fragments of importance appeared at m/e 512 (M - AcOH, 18)$^{+}$, 470 (M -[AcOH + C_3H_7],20)$^{+}$, 452 (M - 2x AcOH,68)$^{+}$ 437 (44), 411 (18), 393 (20), 377 (35), 203 (46), 191 (95), 187 (100).

From the mass spectrum and elemental analysis the molecular formula was confirmed to be $C_{35}H_{56}O_6$.

The ^{1}H NMR spectrum (fig.6) with different signals are recorded below in tabular form.

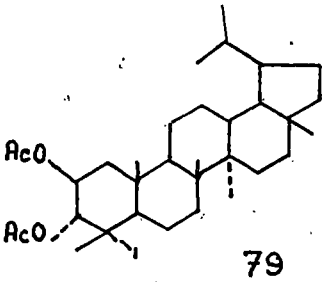
TABLE-II.

Chemical shift. (δ in ppm.)	Number of protons.	Multiplicity of signals.	Probable assignments.

0.74	3	doublet	CH_3-CH-CH_3
0.85	3	J = 7 Hz.	
0.90	2x3	singlet.	five
0.95	3	"	tertiary
0.96	3	"	methyl
1.05	3	"	groups.
2.01	3	singlet.	2x -O-CO-CH_3.
2.05	3	"	
3.64	3	singlet.	-CO-O-CH_3.
4.76	1	double doublet. J = 13, 7 Hz.	Ac-O-C_2-α H.
5.06	1	doublet. J = 7 Hz.	Ac-O-C_3-β H.

The ^{1}H NMR signals of compound B with those diacetate derivative of isomeric 2,3-diols of Oleanane and Ursane skeleton are presented in table-I in Section A for comparison.

From the spectral studies the structure of compound B is proposed to be 2β,3α-diacetoxy methyl dihydro betulinate 79.



79

The mechanism of the reaction is proposed to be same as suggested for 2,3 dehydro lupane in section-A of this chapter.

Thus, *it may be concluded that oxidation of olefinic double bond at C-2(3) position in ring-A of triterpenoids with selenium dioxide containing hydrogen peroxide exclusively produce 2β,3α - diols.*

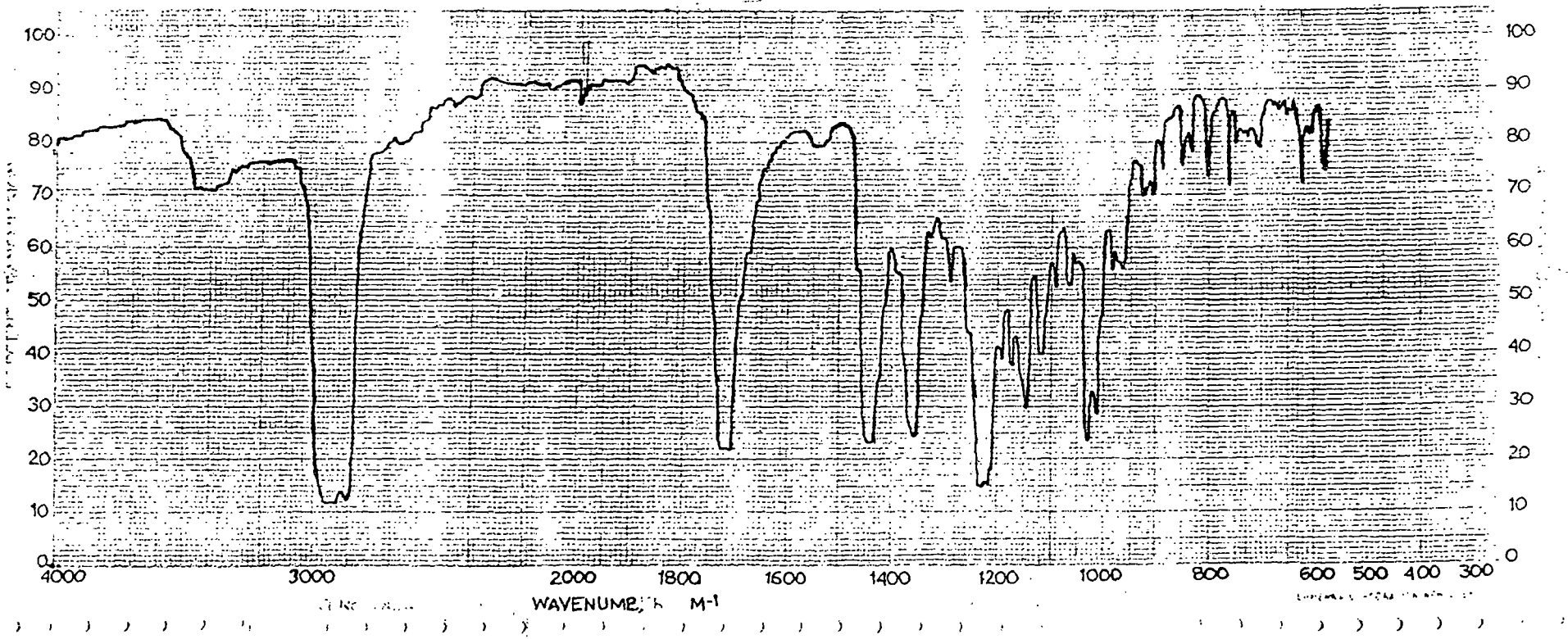


Fig. 4 : IR spectrum of 2β,3α-diacetoxy methyl dihydro betulinate 79.

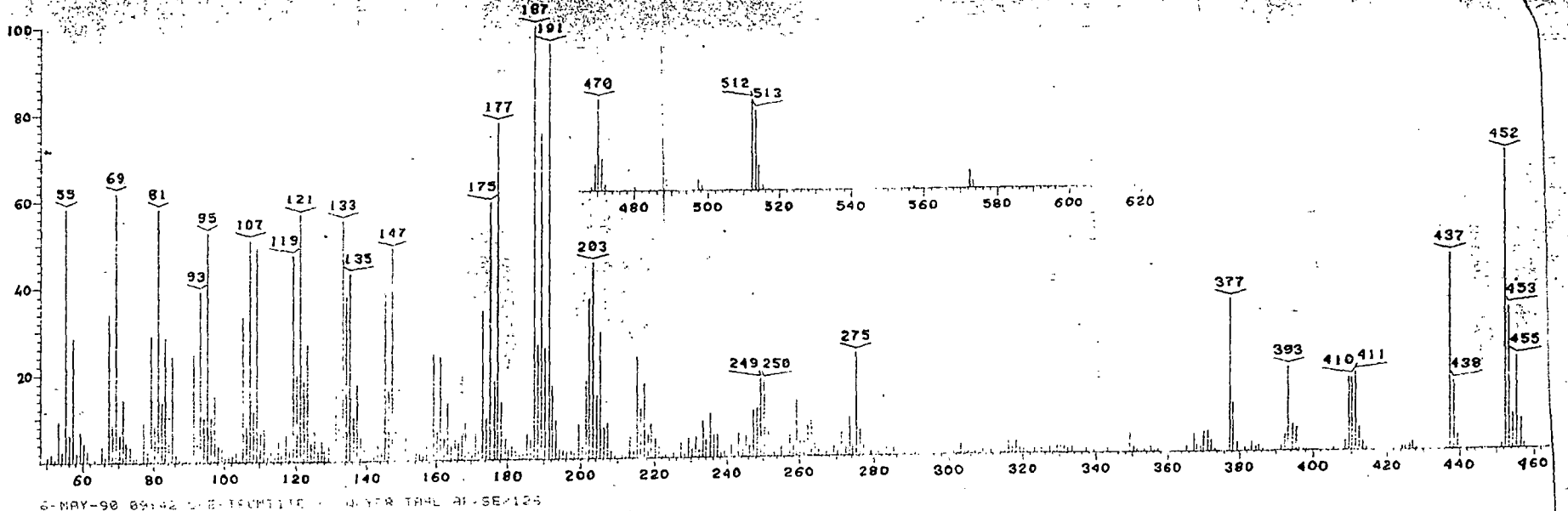


Fig. 5 : Mass spectrum of 2β,3α-diacetoxy methyl dihydro betulinate 79.

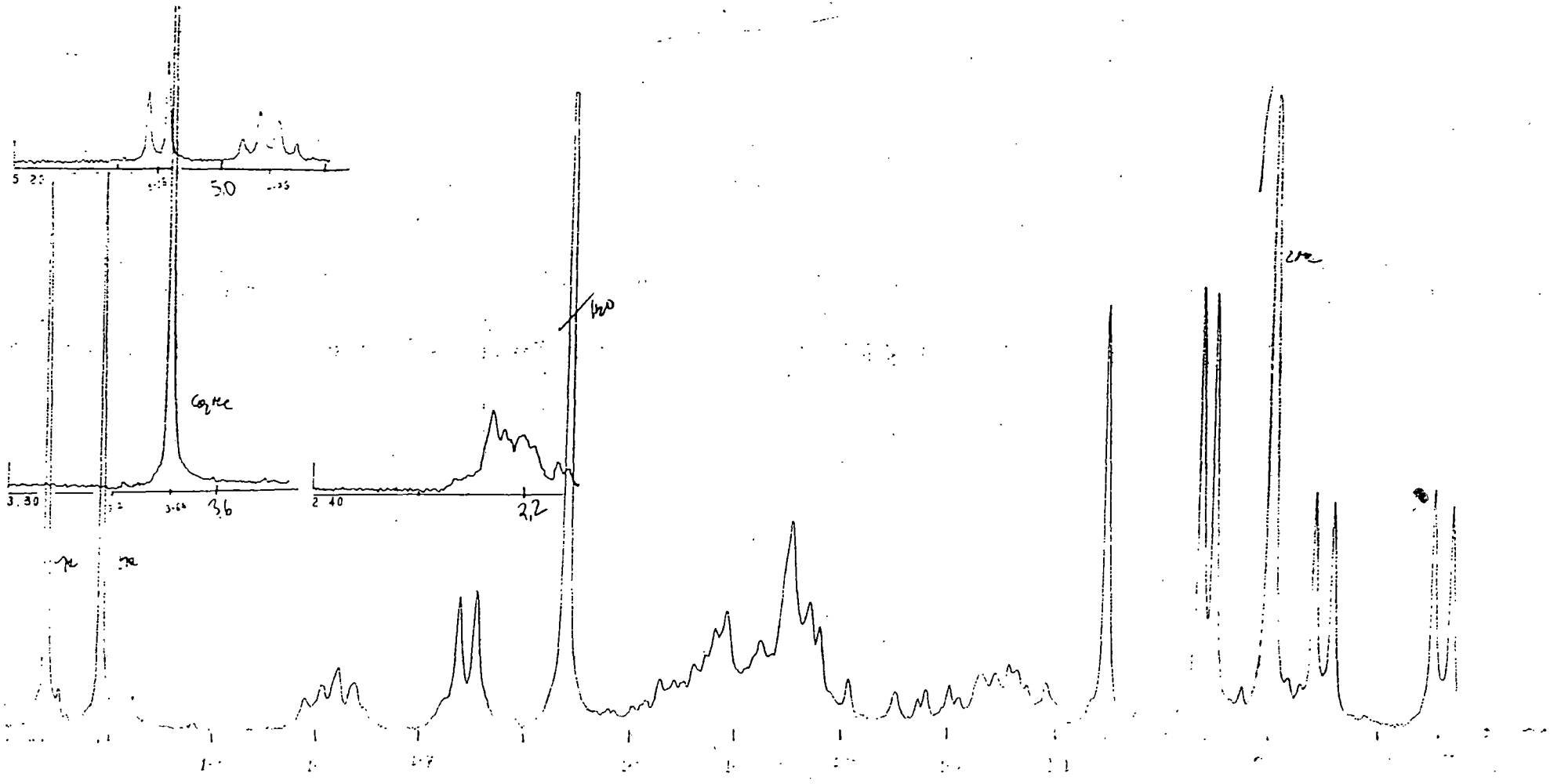


Fig. 6 : ^{1}H NMR spectrum of 2β,3α-diacetoxy methyl dihydro betulinate 79.

OXIDATION OF FRIEDEL-3(4)-ENE 82 WITH SELENIUM DIOXIDE-HYDROGEN PEROXIDE IN TERTIARY BUTANOL.

The products formed by oxidation of 2,3 dehydro lupane and 2,3 dehydro methyl dihydro betulinate with selenium dioxide in presence of hydrogen peroxide in tertiary butanol encouraged the author to extend the reaction on friedel-3(4)-ene and 3,4 dehydro friedelan 27->15α olide having 4-mono methyl system in ring-A.

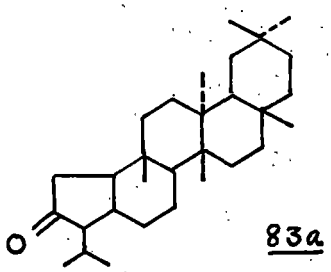
Oxidation of friedel-3(4)-ene:

Friedel-3(4)-ene 82 was refluxed with a mixture of selenium dioxide-hydrogen peroxide in tertiary butanol and the product obtained after usual work up was subjected to column chromatography - two different compounds C and D were obtained on elution with petrol-benzene (3:2) and benzene-chloroform (4:1) respectively.

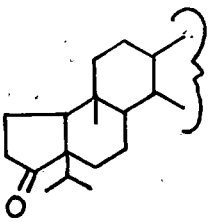
Characterisation of compound C :-

The compound C was crystallised three times from chloroform-methanol mixture to afford colourless crystals, *M.P.*207-8°C $[\alpha]_D$= +16°. In its IR spectrum (fig. 7) the presence of an absorption peak at 1715 cm^{-1} indicated that a ketone function in a six membered ring is introduced in the molecule by the reaction but the absence of absorption in the region 3200-3600 cm^{-1} showed that no hydroxyl group is formed in contrary to our previous observation. Moreover, the mass spectral and elemental analysis showed that an oxygen atom has been introduced in the molecule C making the molecular formula, $C_{30}H_{50}O$. The mass spectrum (fig.8) showed the molecular ion at m/e 426 $(M,14\%)^+$ with other fragments appearing at m/e 411 ($M-CH_3$, 12)$^+$,383 ($M-C_3H_7$, 20)$^+$, 355 (4.5),206 (21),205 (36),163 (27), 109 (38), 107 (100). The ^1H NMR spectrum (fig.9) showed presence of two secondary methyl groups centred at (δ in ppm.) 0.75 and 0.83; six other methyls as singlet in the region 0.75 to 1.07; two multiplets centred at 1.88 and 2.44 integrated for one proton each were due to α-protons to the carbonyl group which have β-protons to give multiplets. It is surprising to note that the reaction product C has two secondary

methyls which are probably in the form of isopropyl groupings. There is a gem dimethyl group as evident from the IR absorption at 1380, 1355 $cm.^{-1}$ Since the double bond is in 3(4)-position in ring-A and a ketone and isopropyl groupings are formed by the oxidising reagents, the formation of compound C having structure **83a** or **83b** could be assumed.



83a



83b

However, the structure **83a** posses a proton at C-3 carbon that would give a double doublet and the total number of α-proton to the carbonyl group would be three which is not observed. Moreover, the formation of isopropyl group at C-3 position with migration of C-5 methyl to C-4 with subsequent hydrogen addition seem to be rather difficult.Further, the fragmentation pattern of C do not follow the B:E friedelo-oleanan skeleton type.

The second possible product **83b** contains the isopropyl group at the C-5 position and the structure could explain most of the resonance peaks observed in the ^{1}H NMR spectrum of compound C. However,it may be noted that the methyl protons of the isopropyl group should appear down field due to the anisotropic effect of the nearby carbonyl group, whereas in the case of compound C this proton appear quite upfield at 0.75 and 0.83.Further, had there been any change in ring-A keeping other methyls at their original position then the protons at C-25,C-26,C-27,C-28,C-29 and C-30 should appear at positions almost same as in the case of friedelin. A comparison of the resonance peaks (δ in ppm.) of various methyl groups of compound C with that of friedelin is given in the table-III.

TABLE-III [29]

	C-23,	C-24,	C-25,	C-26,	C-27,	C-28,	C-29,	C-30.
friedelin (δ):	0.87	0.72	0.86	0.99	1.04	1.16	0.94	0.99
compound C (δ):	1.07	1.02	0.93	1.07	0.94	0.76	0.83	0.75

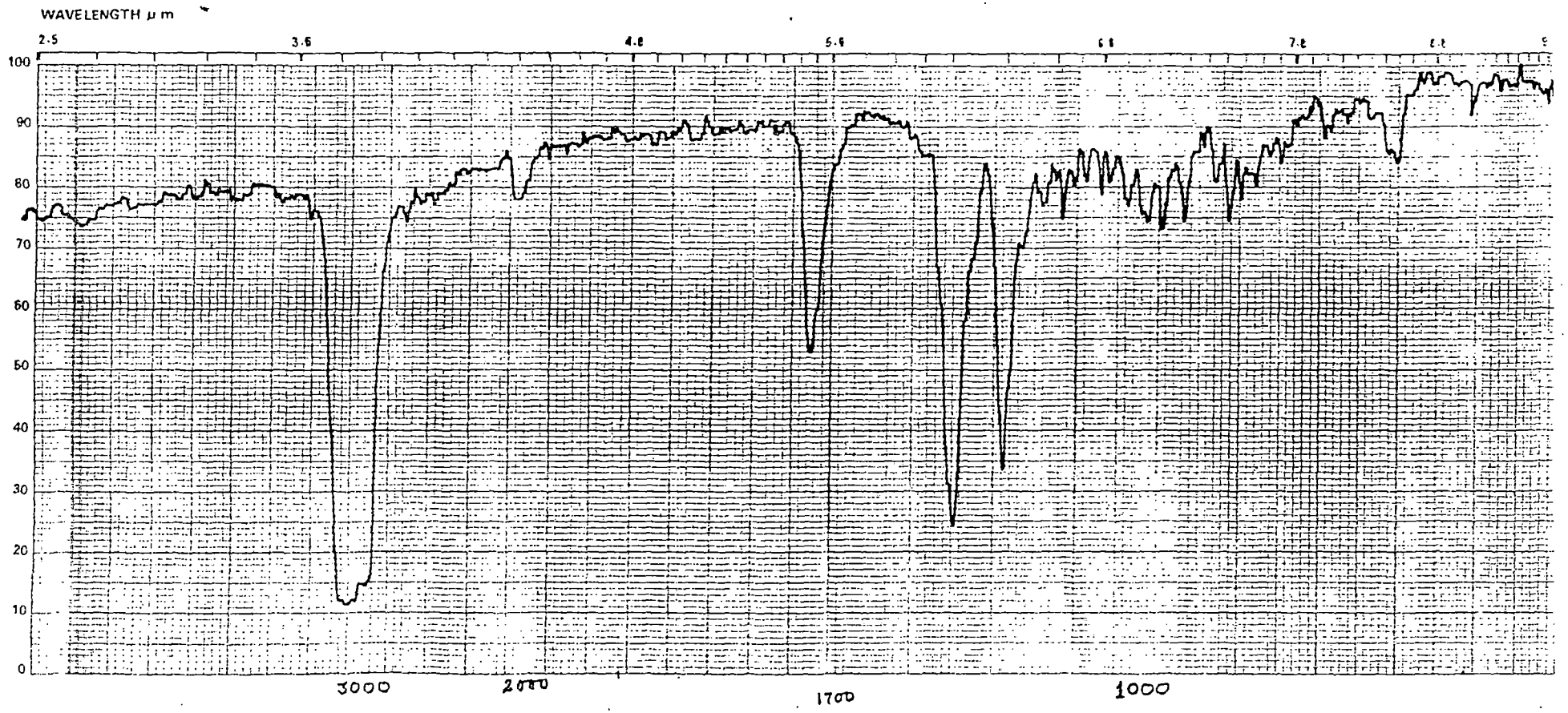


fig. 7 : IR spectrum of compound C. 83.

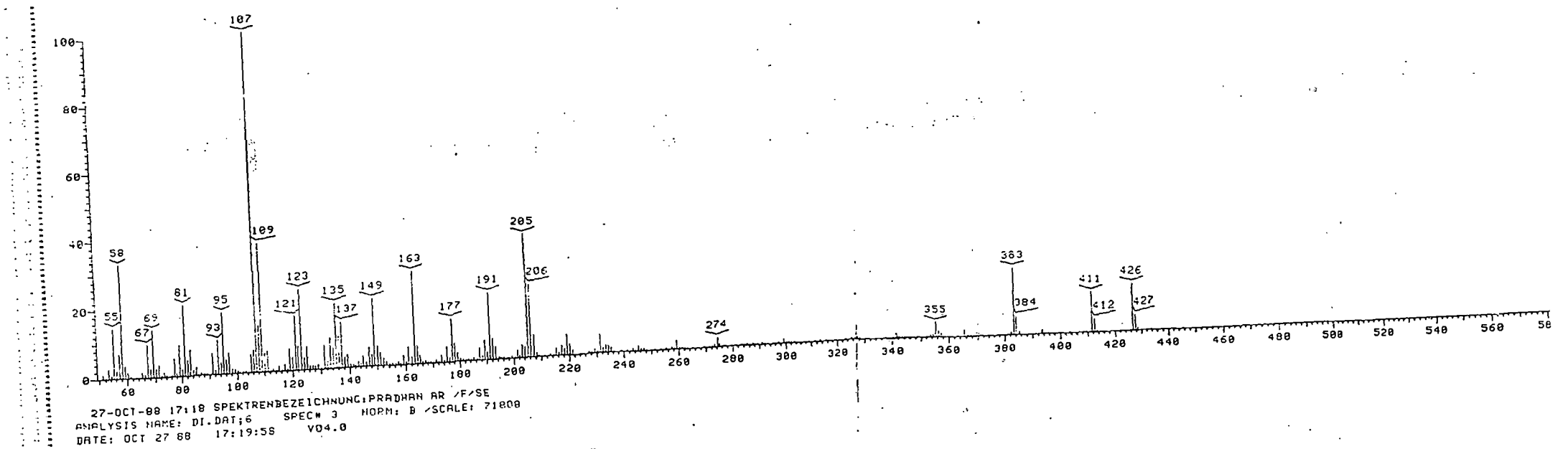


fig. 8 : Mass spectrum of compound C. 83.

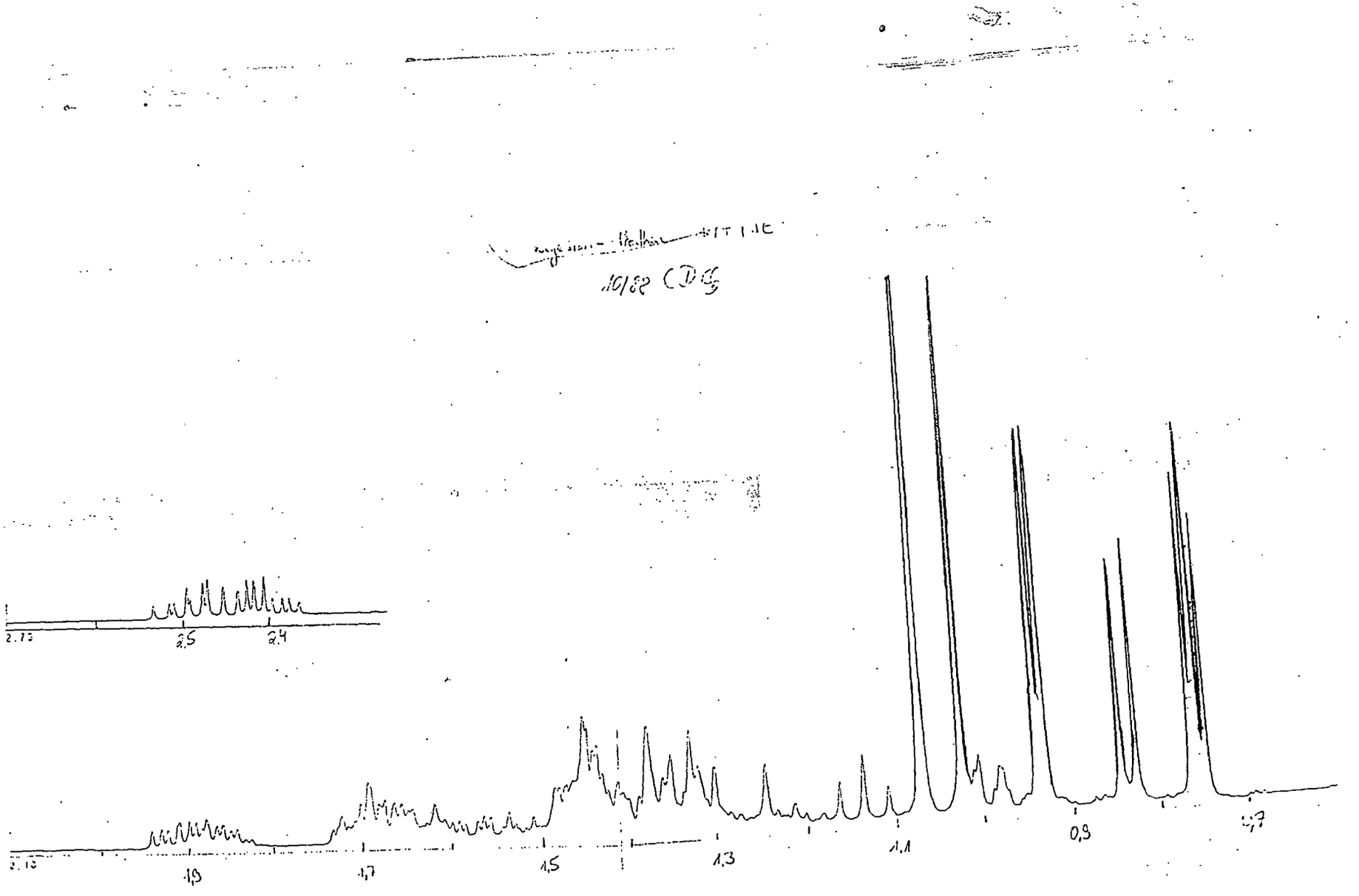


fig. 9 : ^{1}H NMR spectrum of compound C, 83.

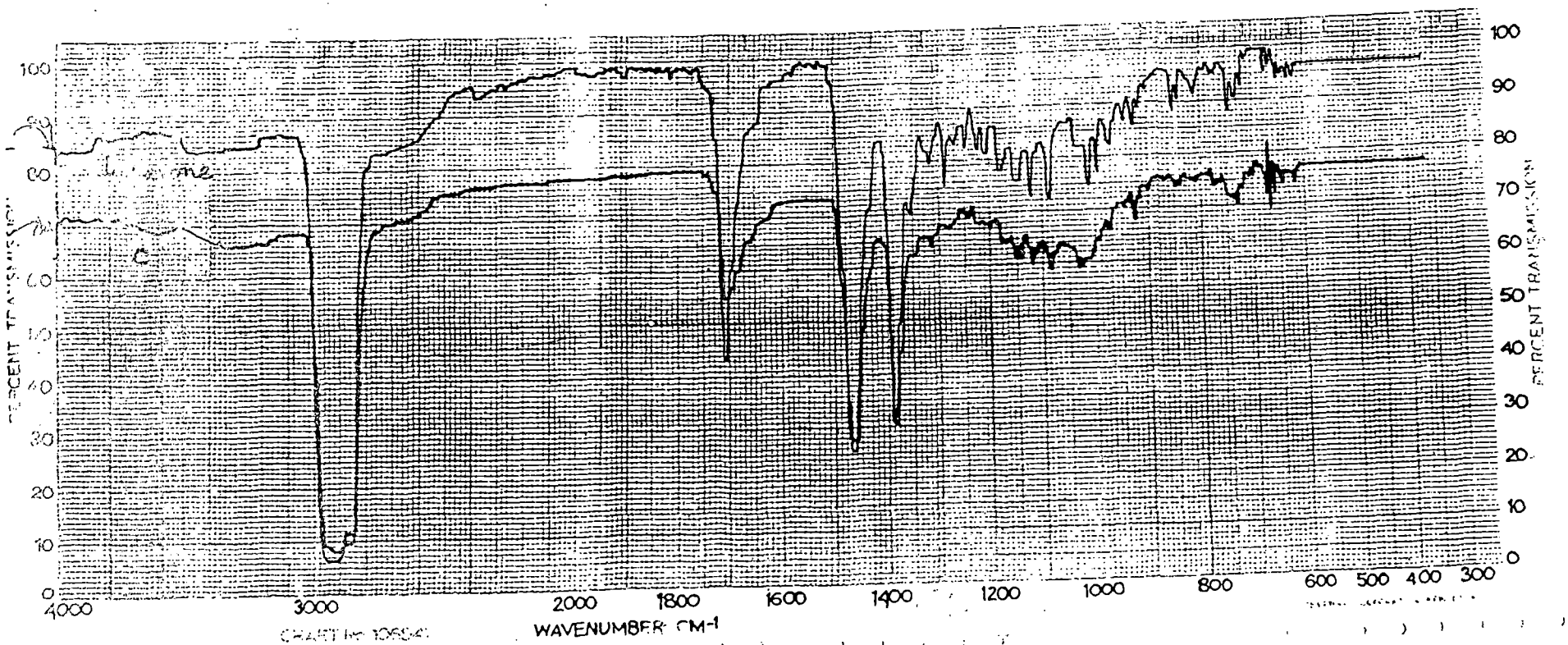


fig. 10 : Co-IR spectrum of compound C and lupanone.

The above comparison shows that compound-C is most probably having a skeleton other than friedelin.

This observation is further supported by the fact that the mass spectral fragmentation pattern of compound C do not follow the pattern of friedelane skeleton as mentioned in the foregoing statement.

A survey of literature on the fragmentation pattern of various saturated triterpenoid ketones revealed that lupanone exhibits the identical fragmentation pattern[30] with that compound C.

Compound C :	m/e	426	411	383	205	191
Lupanone :	m/e	426	411	383	205	191

A comparison of ^{1}H NMR datas of compound C with lupanone, lupenone, and lupane are given below in table-IV. Its identity was further confirmed by comparison with authentic sample of lupanone (*M.M.P.*, co-tlc,co-IR and ^{1}H NMR).

TABLE-IV.

^{1}HMR comparison of lupenone, lupane, lupanone and compound C.

Methyl group	23	24	25	26	27	28	29	30.
lupenone[36]	1.03	0.98	0.95	1.06	0.98	0.80	-	-
lupane[37]	0.84	0.78	0.83	1.03	0.93	0.76	0.84	0.76
Lupanone	1.07	1.03	0.94	1.07	0.95	0.77	0.84	0.76
Compound C	1.07	1.02	0.93	1.07	0.94	0.76	0.83	0.76

Hence, compound C is identified as lupanone **83**.

Identification of compound D :-

The compound D was crystallised from chloroform-methanol to afford white crystals, *M.P.* 235-6^{0}C, $[\alpha_D]$= +14.1^0,IR spectrum (fig.11) showed two peaks at 3340,3380 cm^{-1}indicating the presence of two hydroxyl groups; Its mass spectrum (fig.12) gave molecular ion paek at m/e 444 (M,72%)$^+$; other peaks were at m/e 429 (M-CH_3, 18)$^+$, 426 (M-H_2O, 30)$^+$,411 (10), 341 (12), 273 (14), 218 (32), 205 (57),163 (100).

From mass spectrum and elemental analysis the molecular formula is established to be $C_{30}H_{52}O_2$.

The ^{1}H NMR spectrum (fig.13) showed eight singlets in the region (δ in ppm.) from 0.88 to 1.25 for eight tertiary methyl groups; a

single proton that appeared as AB quartet centred at 3.56 with J_{ea} = 7 Hz. and J_{ee} = 3 Hz. showing that the proton is having two neighbouring protons with equatorial-equatorial and equatorial-axial coupling. Hence, the proton is equatorially oriented at C-3 and the hydroxyl group is axially oriented. The absence of a secondary methyl group and the existence of a tertiary methyl group downfield at 1.25 showed that the second hydroxyl group is attached to the C-4 position. Thus, the compound D could be friedelan 3β,4α diol. A survey of literature showed sengupta et al[31] prepared friedelan 3β,4α diol **84** using per-chloric acid as oxidising agent on friedelan 3α,4α epoxide **82a**.

Acetylation of compound D :-

Compound D **84** on acetylation with acetic anhydride-pyridine mixture gave a crystalline compound E **85**, *M.P.*245-6°C, $[\alpha]_D$ = 24°; IR spectrum showed absorption at 3500 cm^{-1} for hydroxyl group and 1720, 1280 cm^{-1} indicating acetate function. The mass spectrum showed molecular ion peak at m/e 486 (M)$^+$; other peaks were found at m/e 471, 444, 422, 408, 341, 333, 291,273, 260, 255, 247, 229, 205 (100%). The ^{1}H NMR spectrum of compound E showed eight singlets (3H each) between (δ in ppm.) 0.9 to 1.3 for eight tertiary methyl groups; a singlet appeared at 2.1 (3H) for acetate protons and the triplet that appeared at 4.75 (J = 3Hz.) is due to the methine proton that coupled with neighbouring protons and attached to the carbon atom bearing the acetate group.The inert character of the second hydroxyl group towards acetylating agent showed its attachment at the tertiary carbon (C-4). Hence, the possible structure of compound E is **85**.

The compound D on oxidation with Jones reagent gave compound E **86**, *M.P.* 253-4°C. IR spectrum (fig.**14**) showed absorption at 3470 cm^{-1} for hydroxyl group and 1715 cm^{-1} due to ketone function. Its mass spectrum (fig.**15**) showed molecular ion peak at m/e 442 (M, 10%)$^+$; other fragments of prominence appeared at m/e 436, 422, 407, 365, 281, 239, 211, 146, 111, 97, 85, 71, 57 (100). Thus, from the Mass and elemental analysis the molecular formula of compound E is found to be $C_{30}H_{50}O_2$.
^{1}H NMR spectrum (fig.**16**) of compound E showed seven singlets (3H

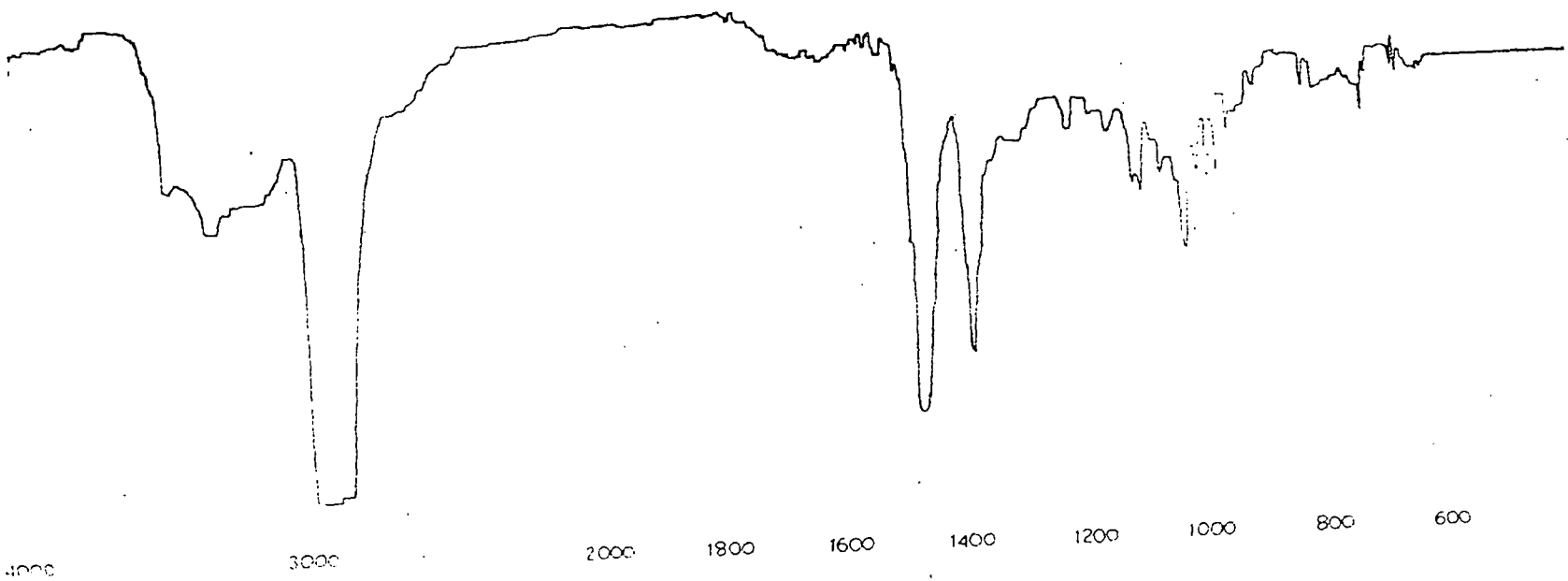


fig. 11 : IR spectrum of friedelan 3β,4α-diol, 84.

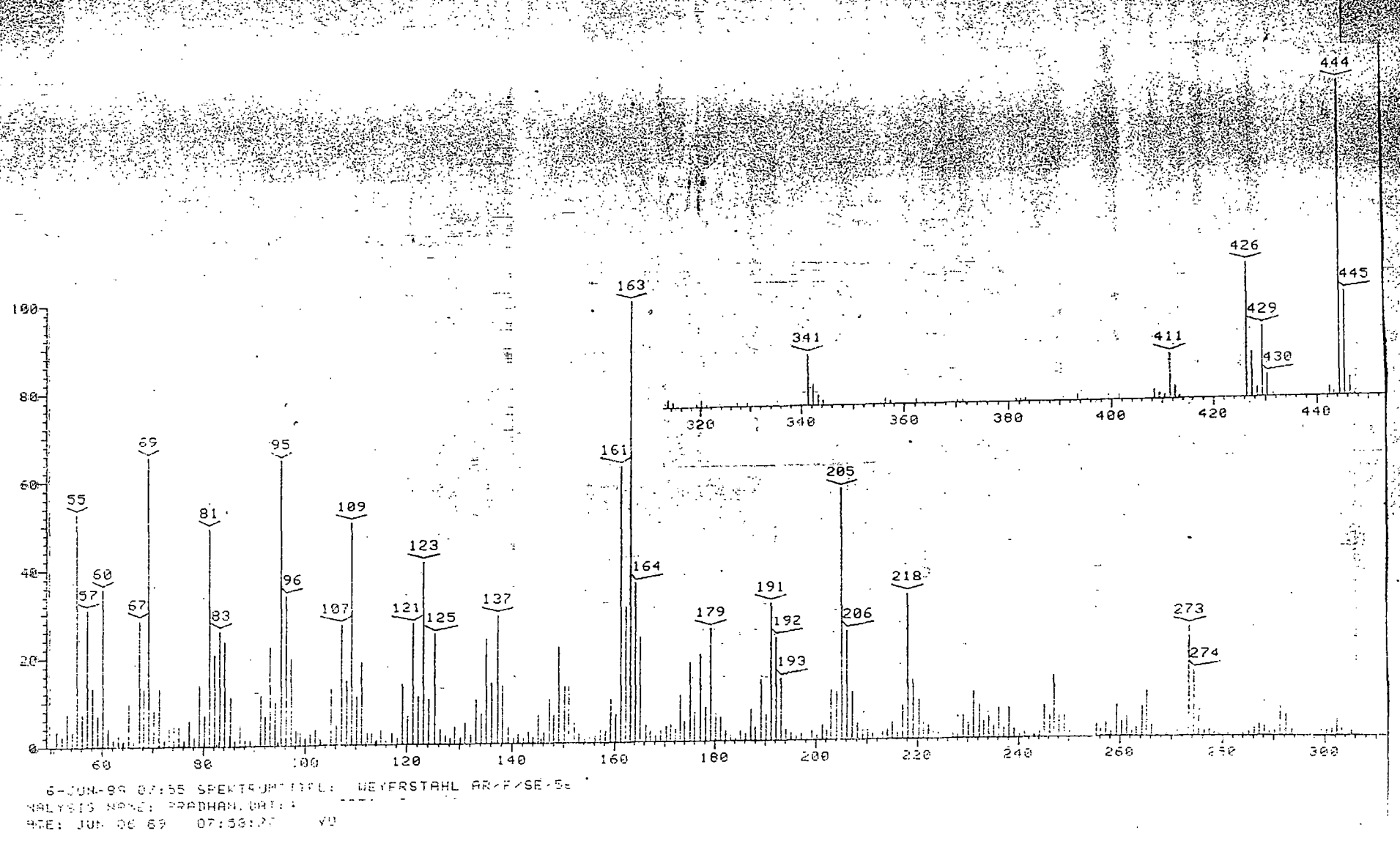


fig. 12 : Mass spectrum of friedelan 3β,4α-diol, 84.

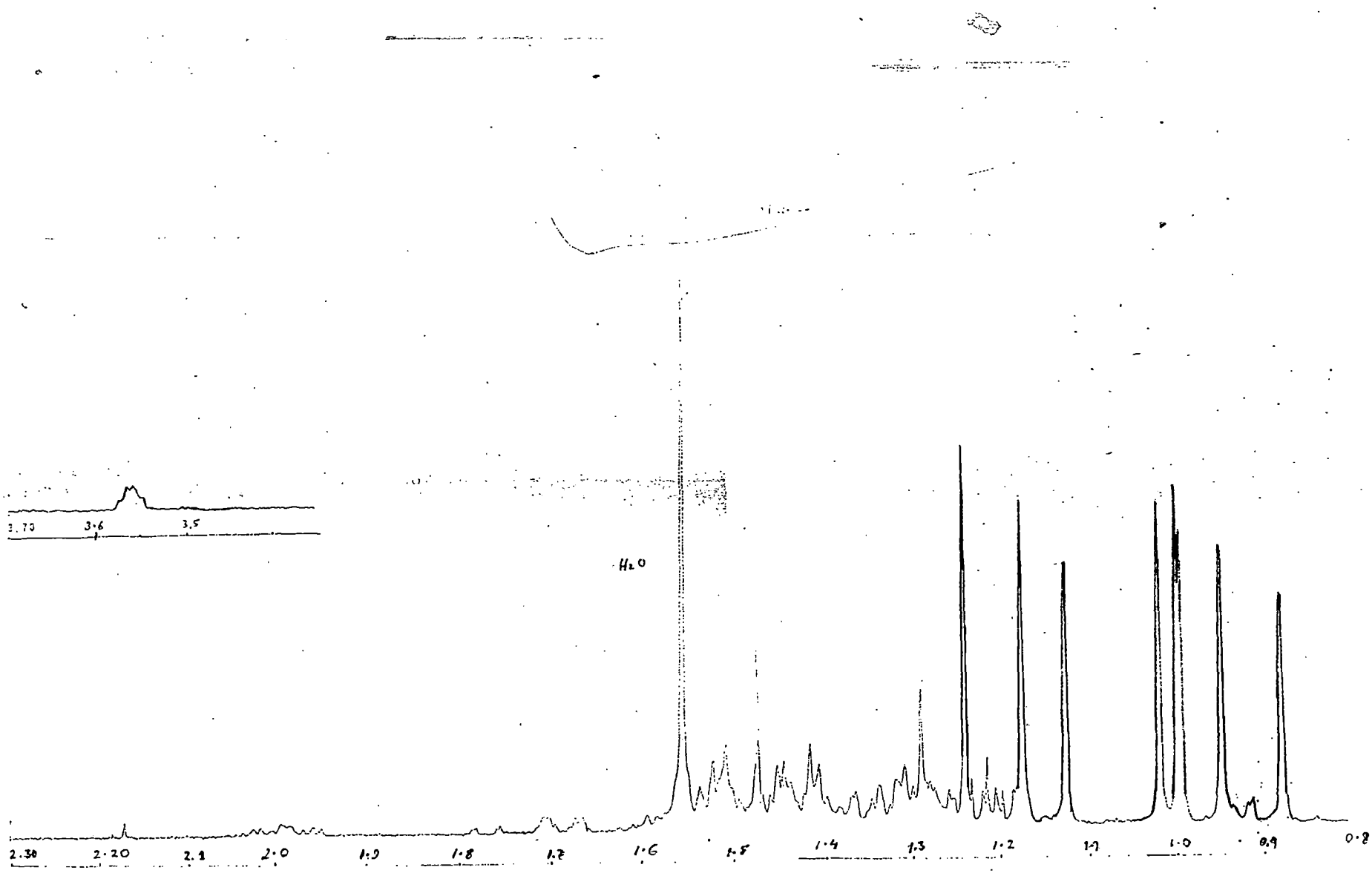


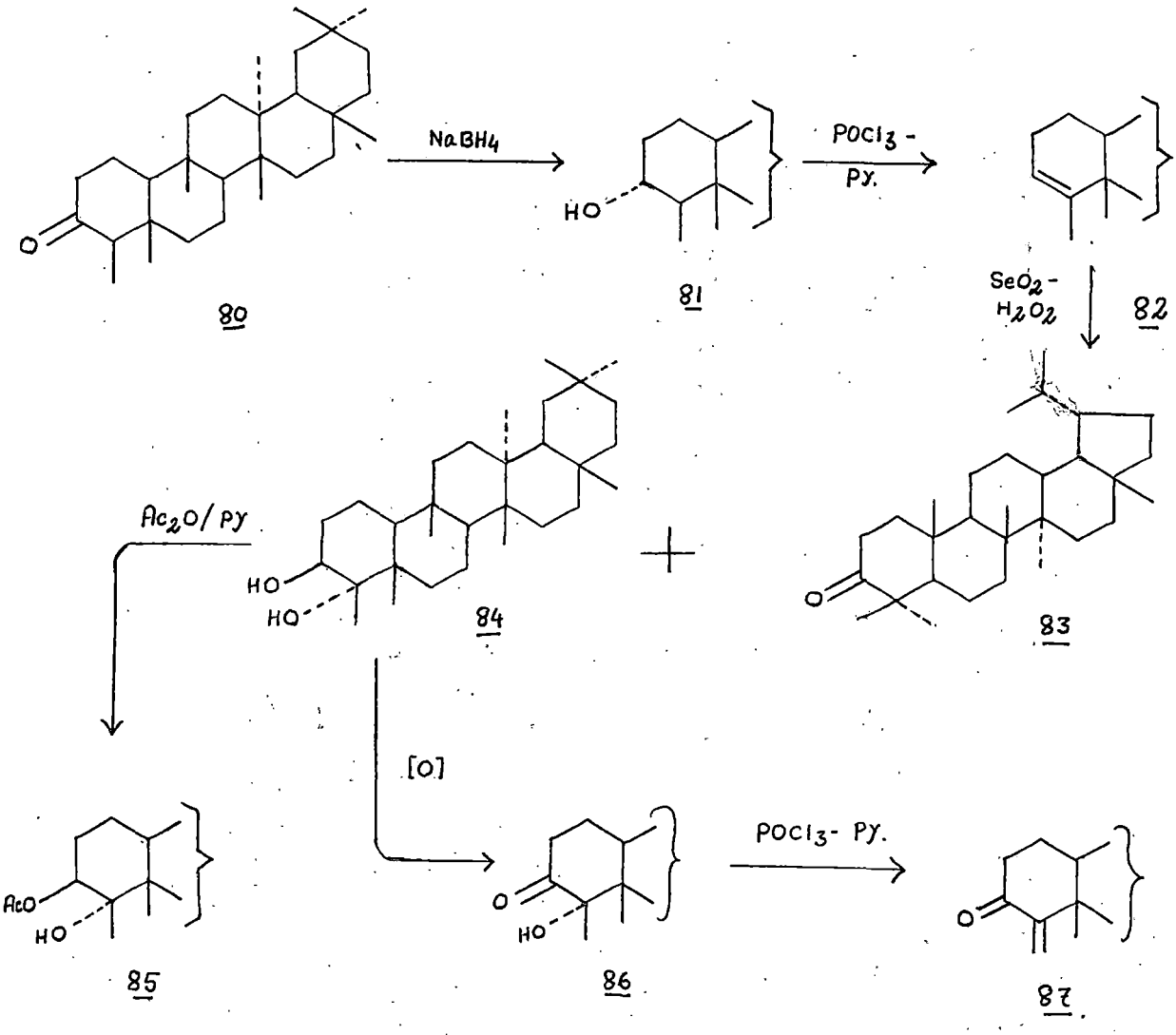
fig. 13 : ^{1}H NMR spectrum of friedelan 3β,4α-diol, 84.

each and one 6H) beteen (δ in ppm.) 0.8 to 1.17 ; one doublet of doublet (J= 3 and 8 Hz.) centred at 2.105 is probably due to methine proton at C-18; The two multiplets centred at 2.23 and 2.96 are accounted for axial and equatorial protons at C-2. Thus,compound E is proposed to be friedelan 3-oxo,4α-ol **86**.

The compound E was dehydrated with phosphorus oxychloride in pyridine when it afforded compound G, **87** *M.P.*208-9^{o}C. It gave UV (methanol) absorption at (λ_{max}) 220 nm. (fig.17) showing the presence of α,β unsaturated ketone. Further, IR spectrum showed peaks at 1690,1650 cm^{-1} confirming the presence of conjugated ketone moiety.

Hence, compound G was identified as friedelan-3-oxo,4(24)-ene, **87**.

The conversion of friedlin **80** to friedelan-3-oxo,4(24)-ene **87** is depicted in the following scheme:-

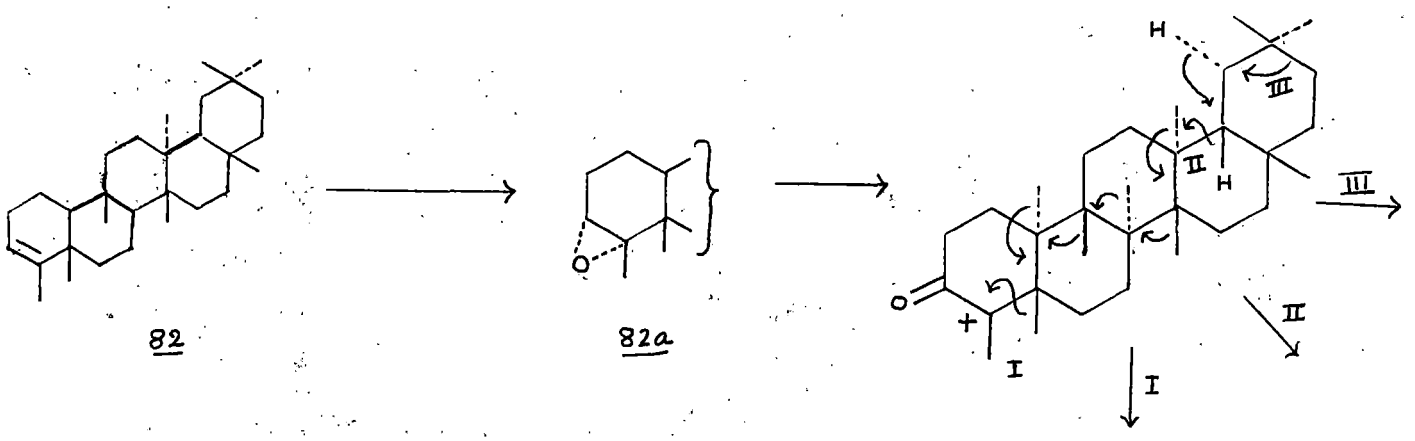


The mechanism suggested for lupanone formation is shown below :-

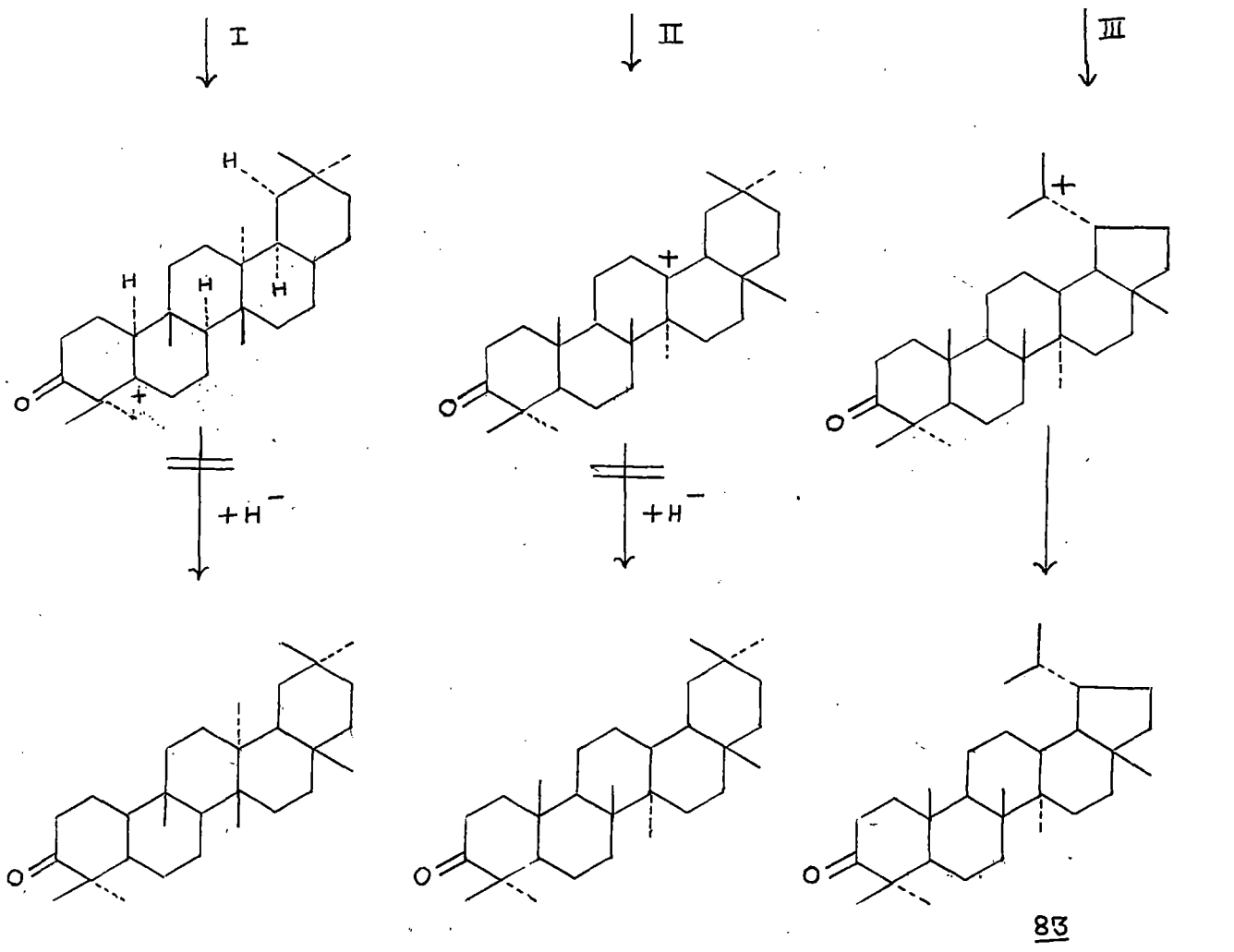
It is well known that unsymmetrical epoxide on treatment with Lewis acids like boron triflouride-ethearate causes epoxide ring opening with the formation of carbocation at the more substituted carbon atom to furnish a ketone by hydride transfer rearrangement[38].

In the present case the epoxide formed by the reaction with hydrogen peroxide at C_3-C_4 position of friedelene (82) probably undergoes this sort of ring opening to give a carbocation at C-4 position. Than there may undergo a backbone rearrangement which may involve 1,2 shifts of methyl groups and hydrogen atoms leading to the shift of the carbocation from C-4 to C-20 carbon. Since a hydride ion is produced during the formation of a ketone, this hydride ion attacks the C-20 carbocation to give lupanone (83).

It is reported [34,39] that friedel-3(4)-ene (and 3-hydroxy friedelane after dehydration) undergoes isomerisation of double bond in acidic medium to give glut-5(6)-ene /glut-5(10)-ene or β-amyrin / δ-amyrin which involve 1,2 shift(s) accompanied by loss of a proton whereas in the present case the epoxide ring rearrangement causing formation of hydride ion and a ketone, favours addition of this hydride ion but the addition of this hydride ion to the carbocation at C-5 or C-13 is not favoured energetically. Hence, further isomerisation of the carbocation at the extreme position is probably most favoured energet--ically to form the carbocation at C-20. The probable steps are represented in the following scheme :

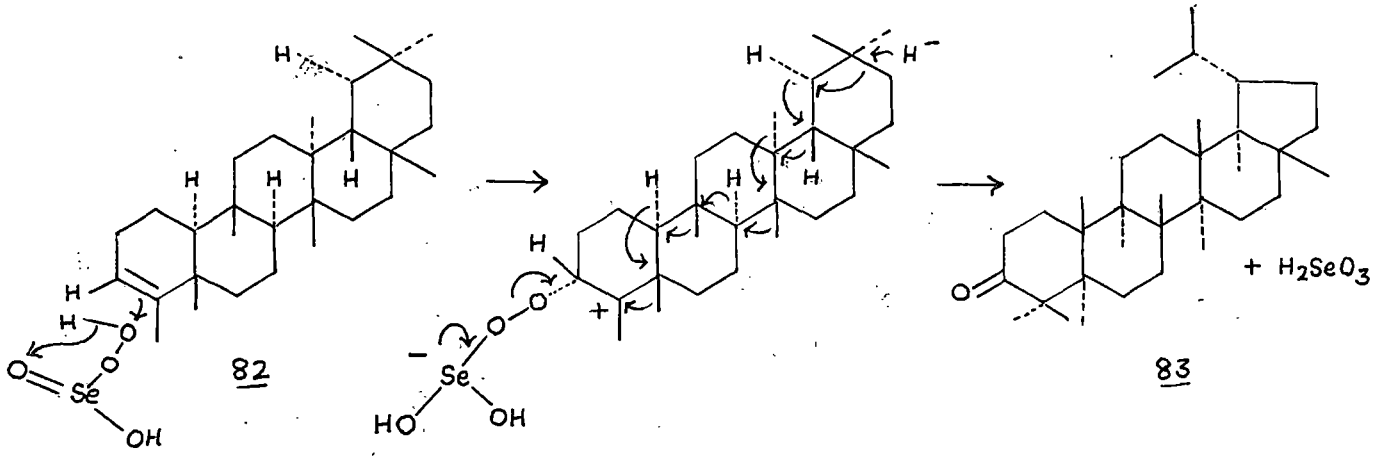


82 82a



83

The other possibility may involve the attack of olefinic double bond of friedel-3(4)-ene (82) by the peroxyselenic acid at C-3 position generating a peroxy organo selenious di-ion. This di-ion forms the ketone by the loss of a hydride ion and the carbocation at C-4 undergoes a series of 1,2 shifts leading to the formation of carbocation at C-20. The C-20 carbocation than accepts the hydride ion giving lupanone (83).



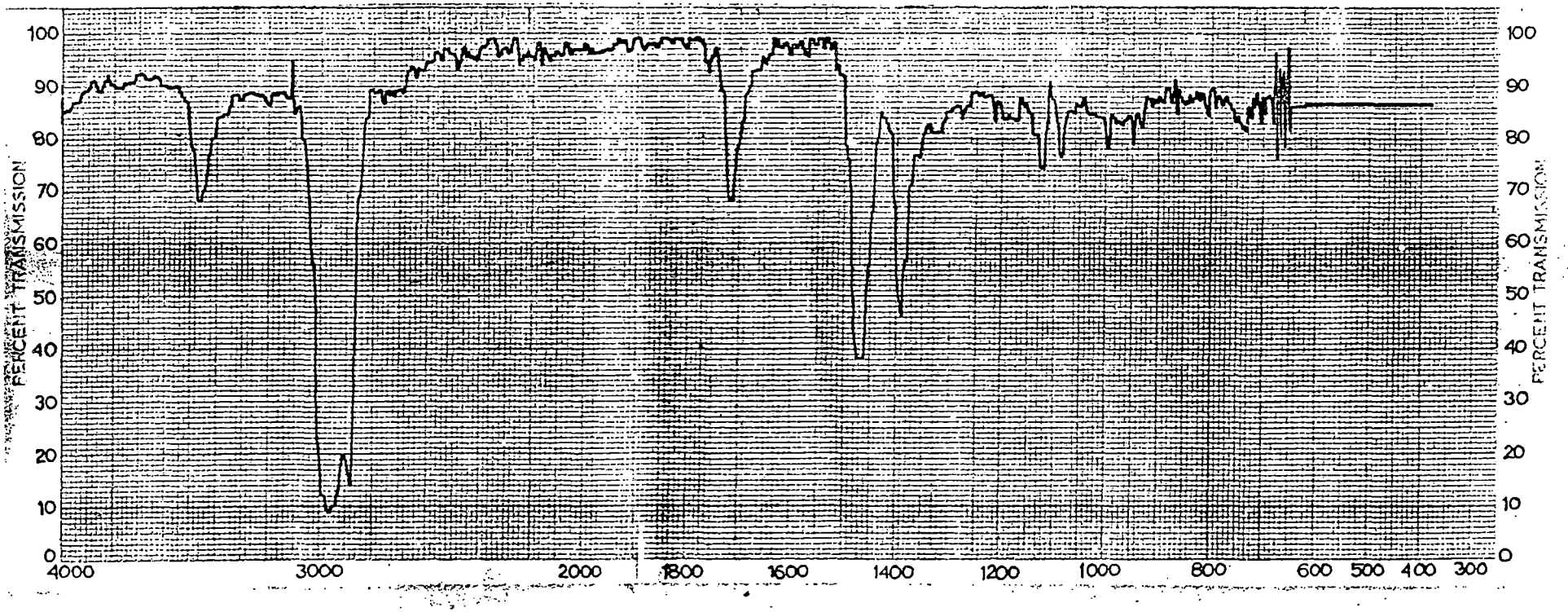


fig. 14 : IR spectrum of friedelan 3-oxo,4α-ol, 86.

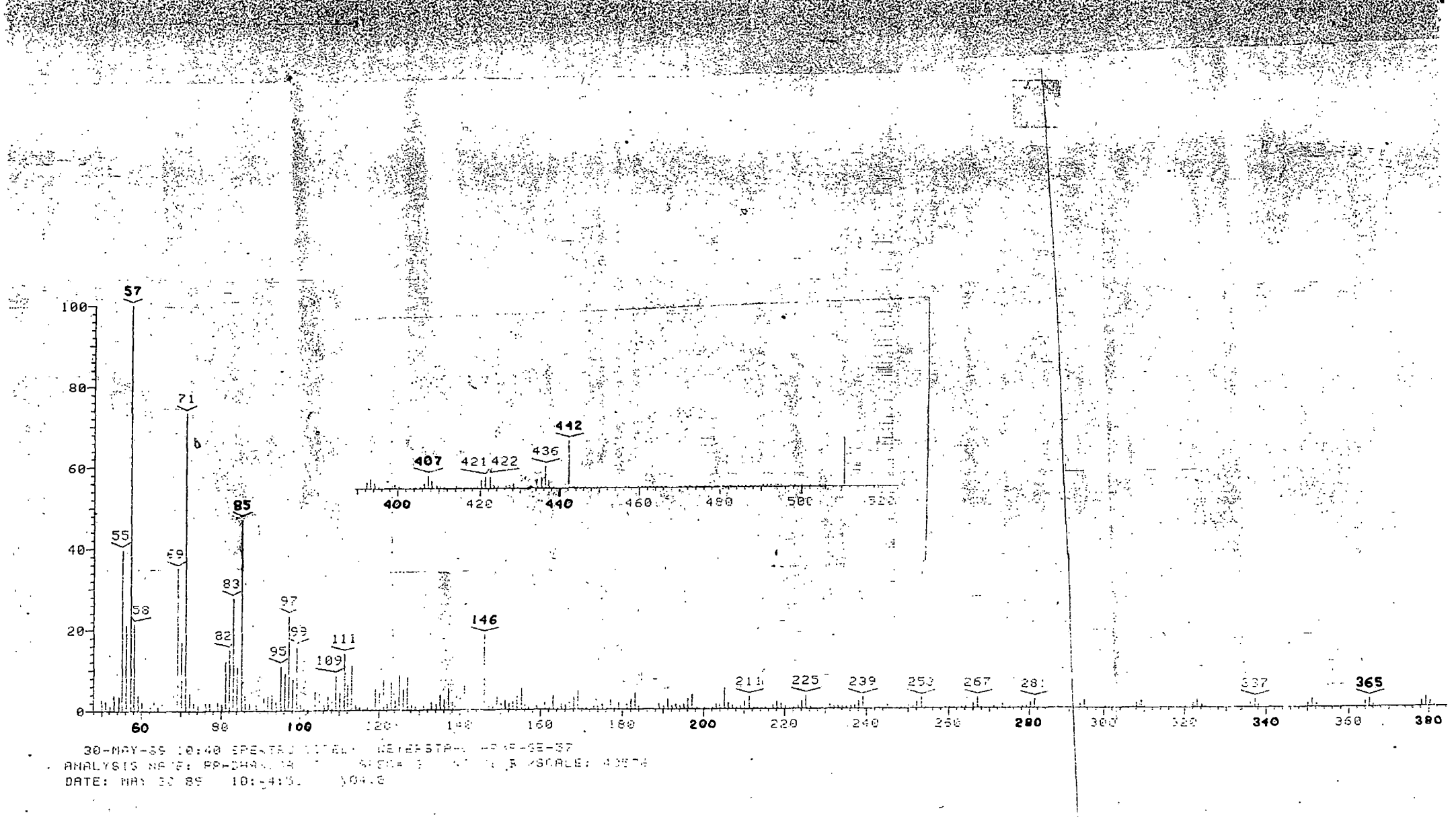


fig. 15 : Mass spectrum of friedelan 3-oxo,4α-ol, 86.

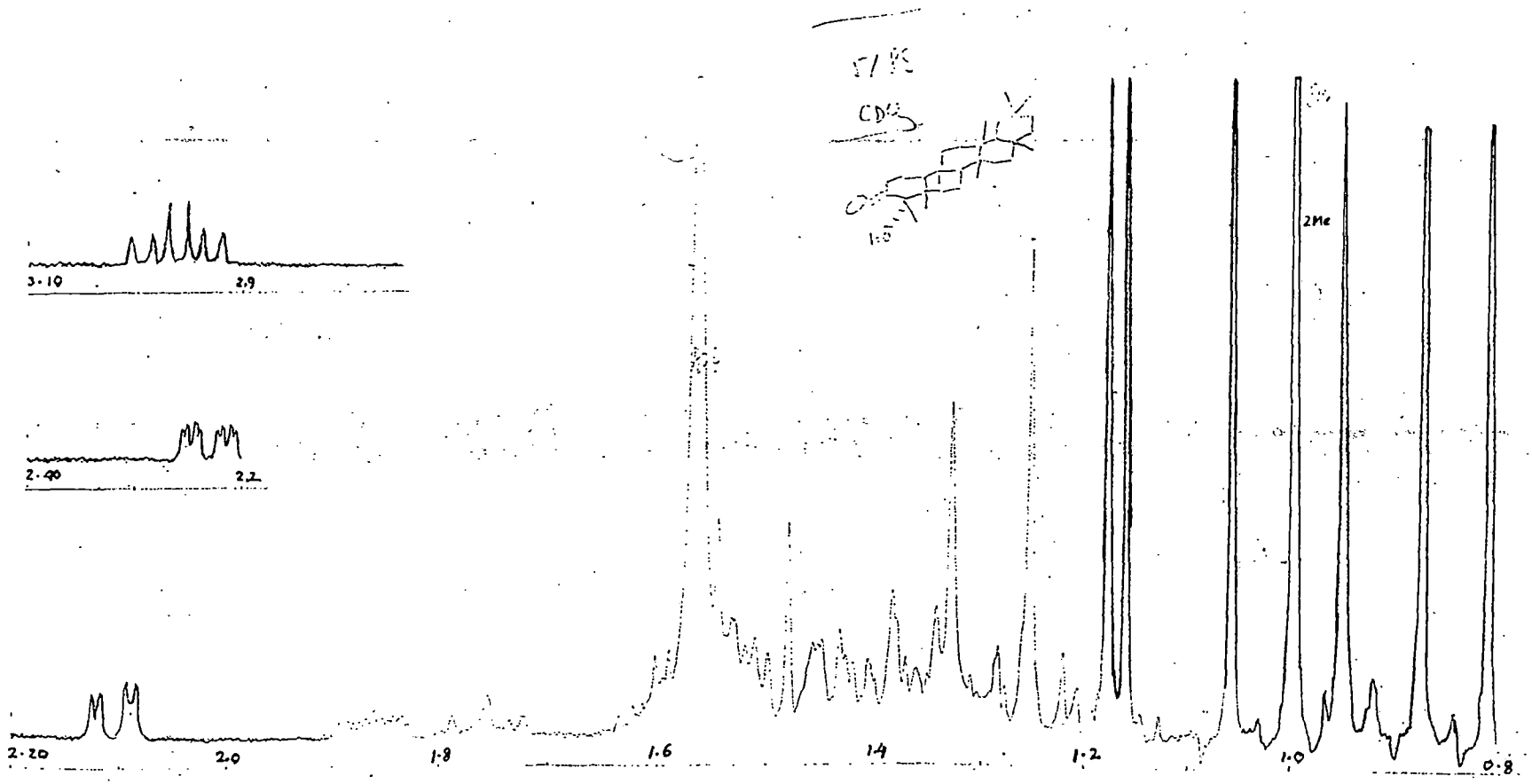


fig. 16 : ^{1}H NMR spectrum of friedelan 3-oxo,4α-ol, 86.

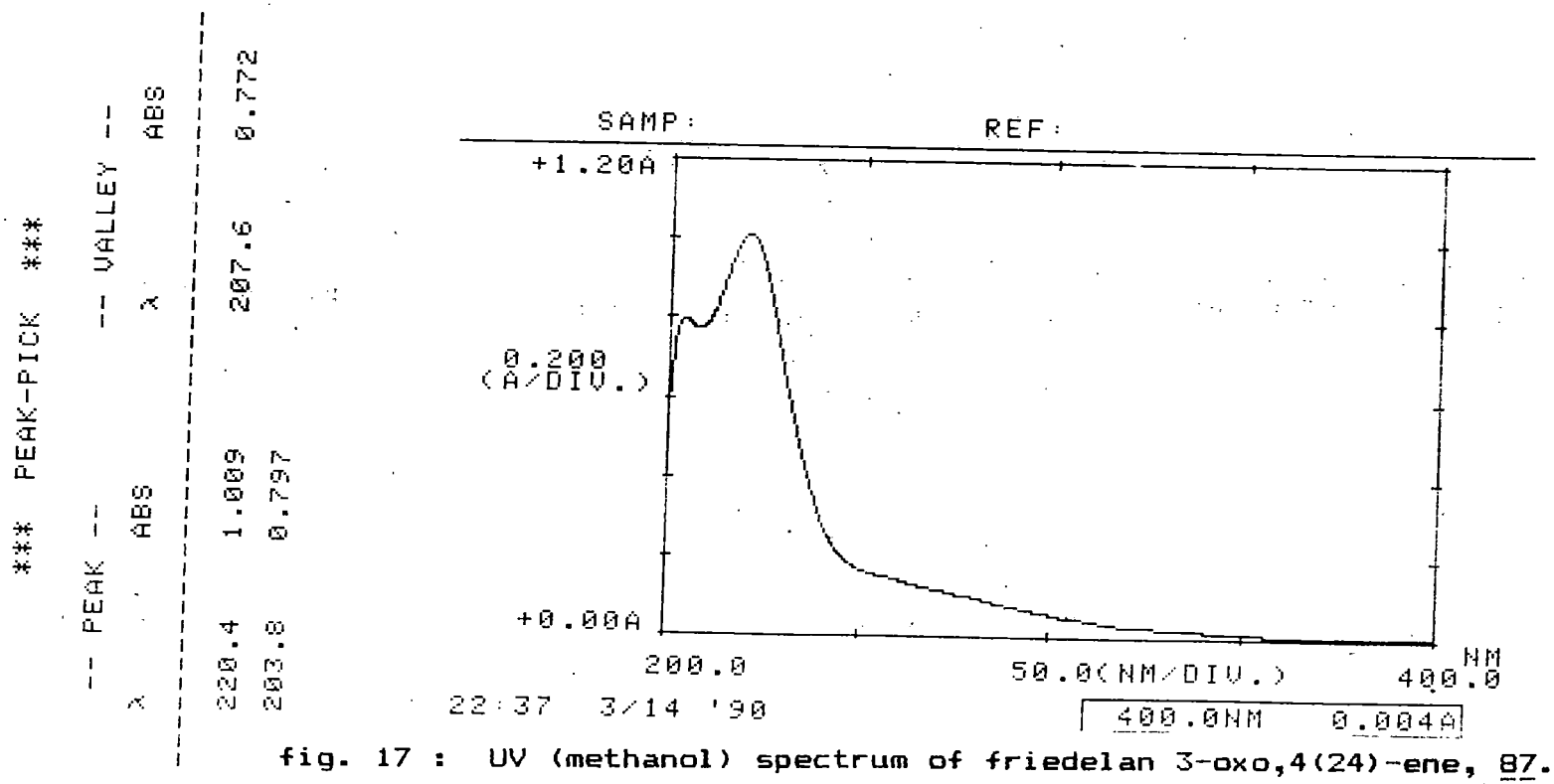


fig. 17 : UV (methanol) spectrum of friedelan 3-oxo,4(24)-ene, 87.

OXIDATION OF 3,4 DEHYDRO FRIEDELAN-27→15α OLIDE WITH SELENIUM DIOXIDE IN TERTIARY BUTANOL CONTAINING HYDROGEN PEROXIDE.

The compound 3,4-dehydro-friedelan 27 → 15α olide **91**, prepared from friedelan-3-oxo, 27→15α olide **88** (see experimental) was dissolved in tertiary butanol and refluxed with selenium dioxide in presence of hydrogen peroxide. After usual workup, the crude product was subjected to column chromatography and a single compound H was obtained on elution with benzene-chloroform (1:1).

Characterisation of compound H : Isolation of friedelan-3β,4α diol, 27→15-olide 92:

The compound H was crystallised from chloroform-methanol to furnish needle shaped crystals, *M.P.* 270-71°C; Its IR spectrum (fig. **18**) showed peaks at 3500 and 3440 cm^{-1} indicating the presence of two hydroxy groups and at 1760 cm^{-1} for carbonyl group of γ-lactone moiety. The mass spectrum (fig.**19**) indicated the molecular ion peak m/e at 472 (M,22%); other important peaks appeared at m/e 436 (M $-2H_2O$ 28)$^+$, 386 (33), 385 (100), 133 (66). Elemental analysis and mass spectral data showed the molecular formula to be $C_{30}H_{48}O_4$.

^1H NMR spectrum (fig.**20**) signals for different protons are recorded in tabular form as shown in table-V.

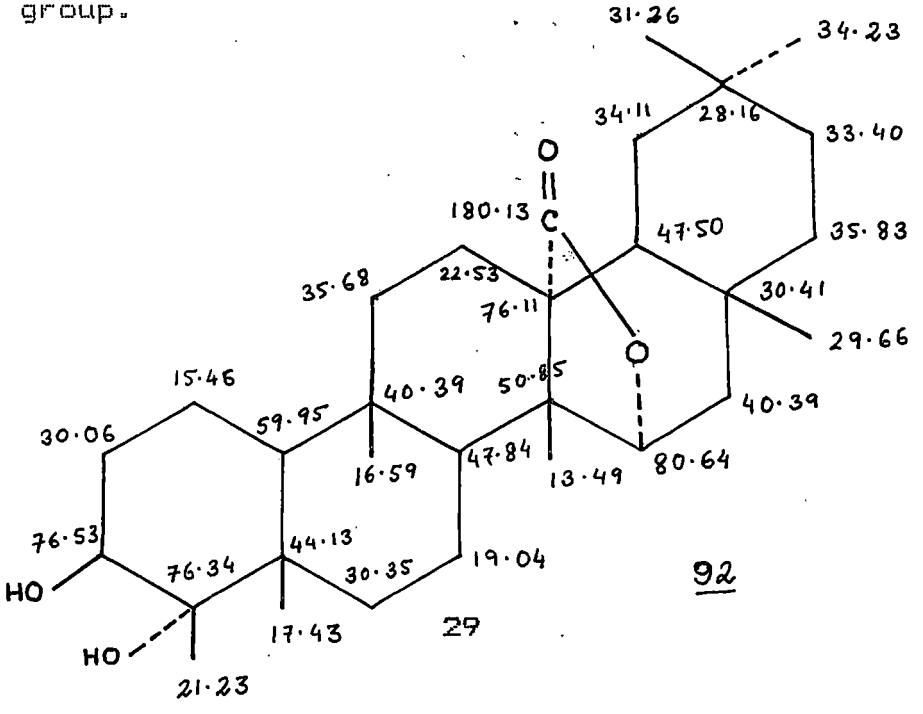
TABLE-V.

Chemical shifts. (δ in ppm.)	No.of protons.	Multiplicity of signals.	Probable assignment.
0.86	3	singlet	seven
0.94	3	"	tertiary
0.96	3	"	methyls.
0.99	3	"	
1.02	3	"	
1.05	3	"	

1.21	3	"	
2.02	1	triplet of doublet. (J = 3 & 13.5 Hz.)	methine proton (18α-H)
3.54	1	triplet. (J = 3 Hz.)	3α-H geminal to 3β-OH.
4.34	1	triplet. (J = 3 Hz.)	A methine proton geminal to lactonic O-atom.

The ^{1}H NMR signals of compound H was compared with friedelan 3β,4α diol 84 as discussed in Section C. The position and coupling values of the two protons attached to the C-2 and C-3 carbons are exactly similar and have the stereochemistry which is shown to be 3β,4α for the hydroxyl groups in compound H also.

The ^{13}C NMR spectrum (fig.21) accounted for 30-carbon atoms. APT experiment showed the existance of 7 $-CH_3$ as quartets, 10 $-CH_2-$ as triplets, 5 -CH- as doublets and 8 -C- as singlets. Among them the doublets that appeared downfield at 76.34 and 80.64 ppm. are due to carbon atoms bearing -OH group at C-3 and lactonic O-atom at C-15 respectively. The two downfield singlets at 180.13 and 76.11 ppm. are accounted for carbonyl carbon of the lactone moiety and C-4 bearing another -OH group.

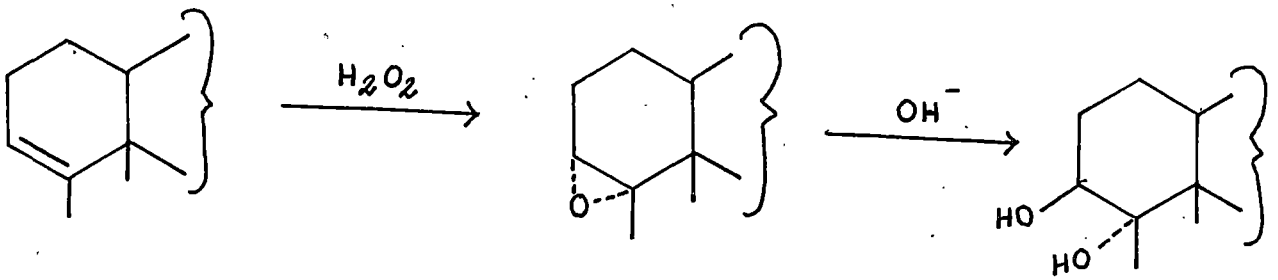


92

Thus from, ^{1}H NMR, Mass and ^{13}C NMR spectral studies the structure of compound H is proposed to be friedelan-3β,4α-diol 27→15α olide 92.

Mechanism proposed for the reaction :-

The formation of friedelan-3β,4α-diol 84 and friedelan-3β,4α-diol 27->15α olide 92 from 3(4)-dehydro-friedelan 82 and 3(4)-dehydro-odolactone 91 on oxidation with selenium dioxide containing hydrogen peroxide indicated that 3,4-epoxide is first formed with hydrogen peroxide. The epoxide is definitely formed at the less hindered alpha side to furnish 3α,4α-epoxide compound 91a which then undergoes epoxide ring cleavage by the attack of perhydroxy selenic acid from the β-phase to generate the trans diol D and H respectively.



82 or 91 — a — 84 or 92

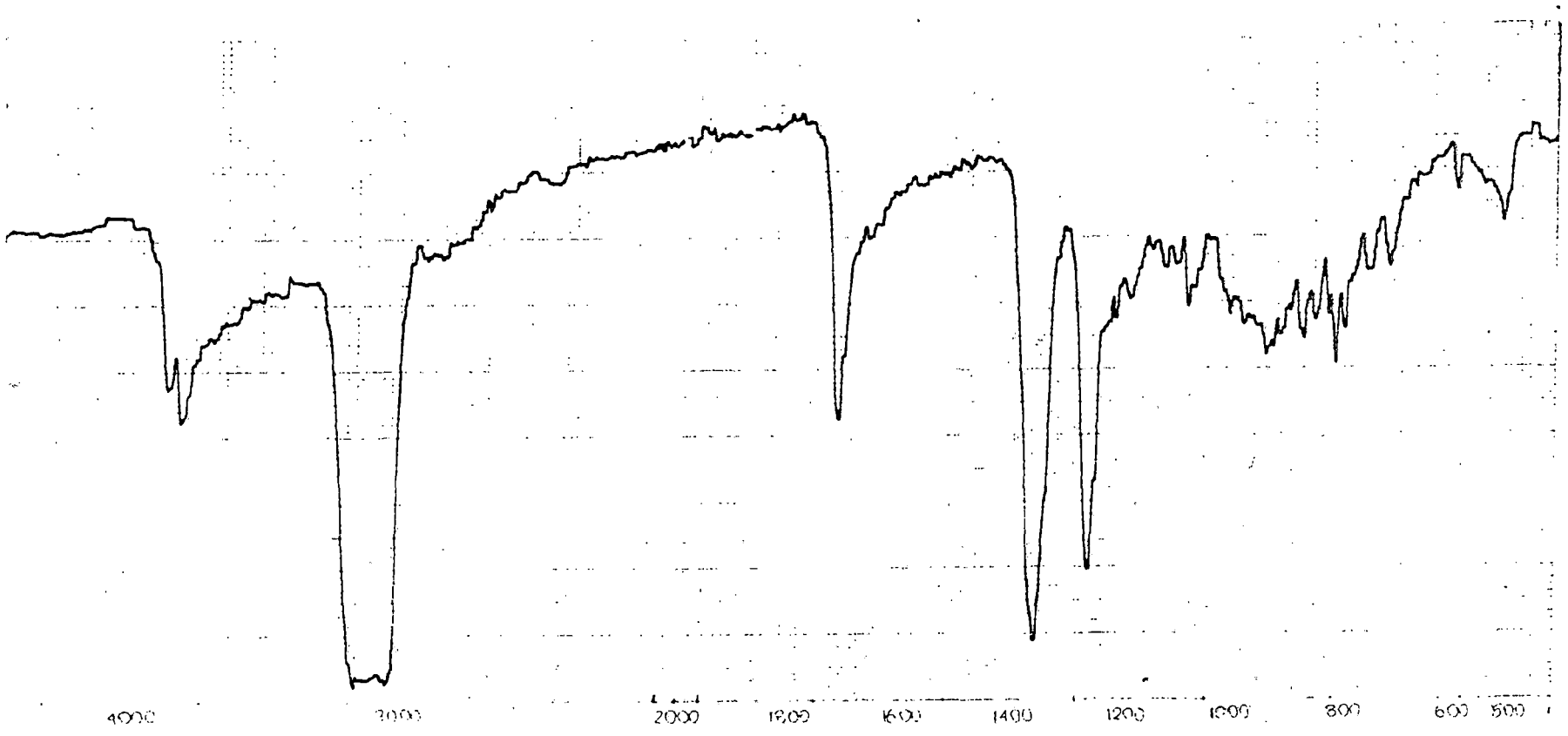


fig. 18 : IR spectrum of friedelan 27→ 15α-olide,3β,4α-diol, 92.

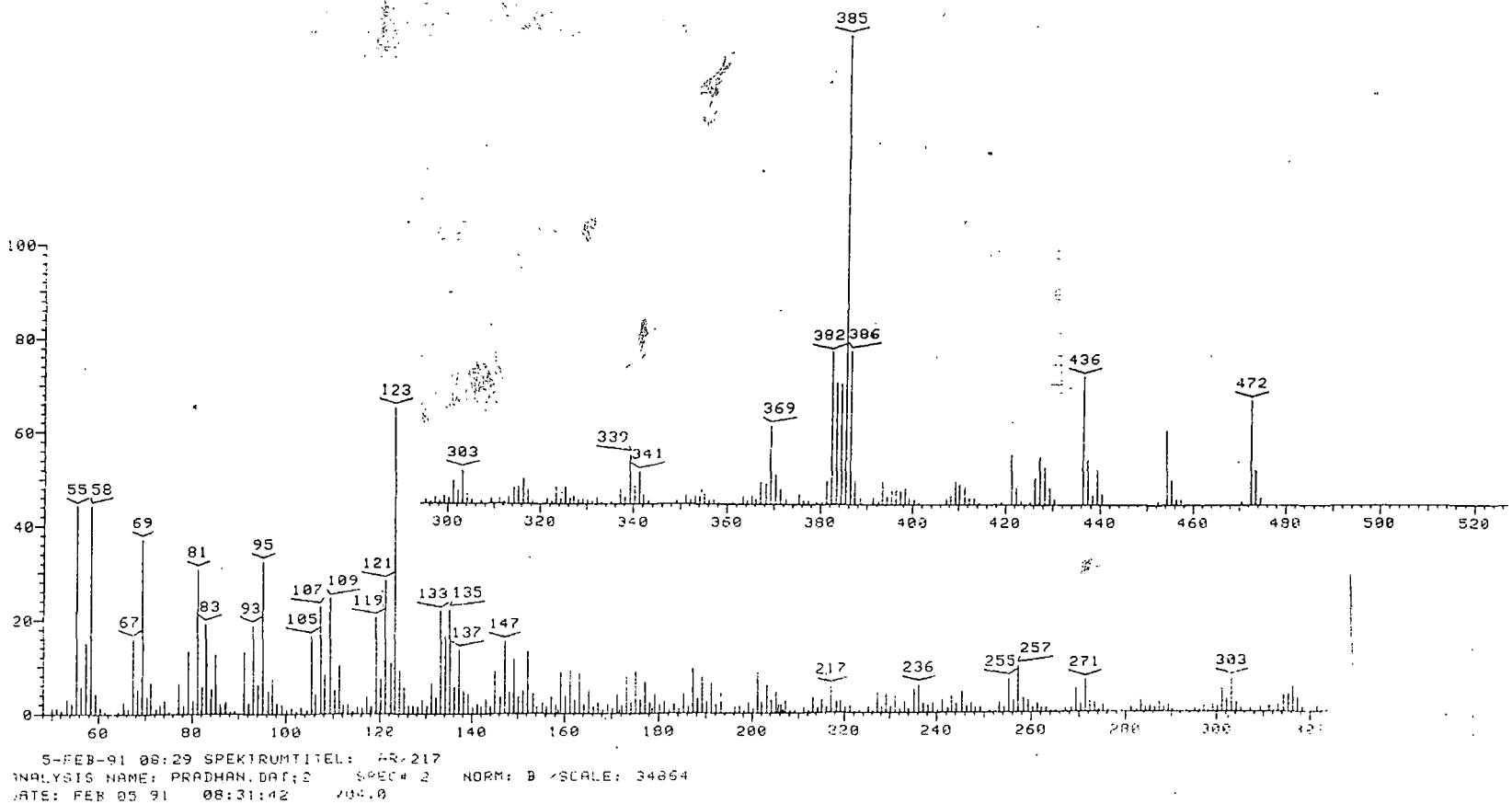


fig. 19 : Mass spectrum of friedelan 27→15α-olide,3β,4α-diol, 92.

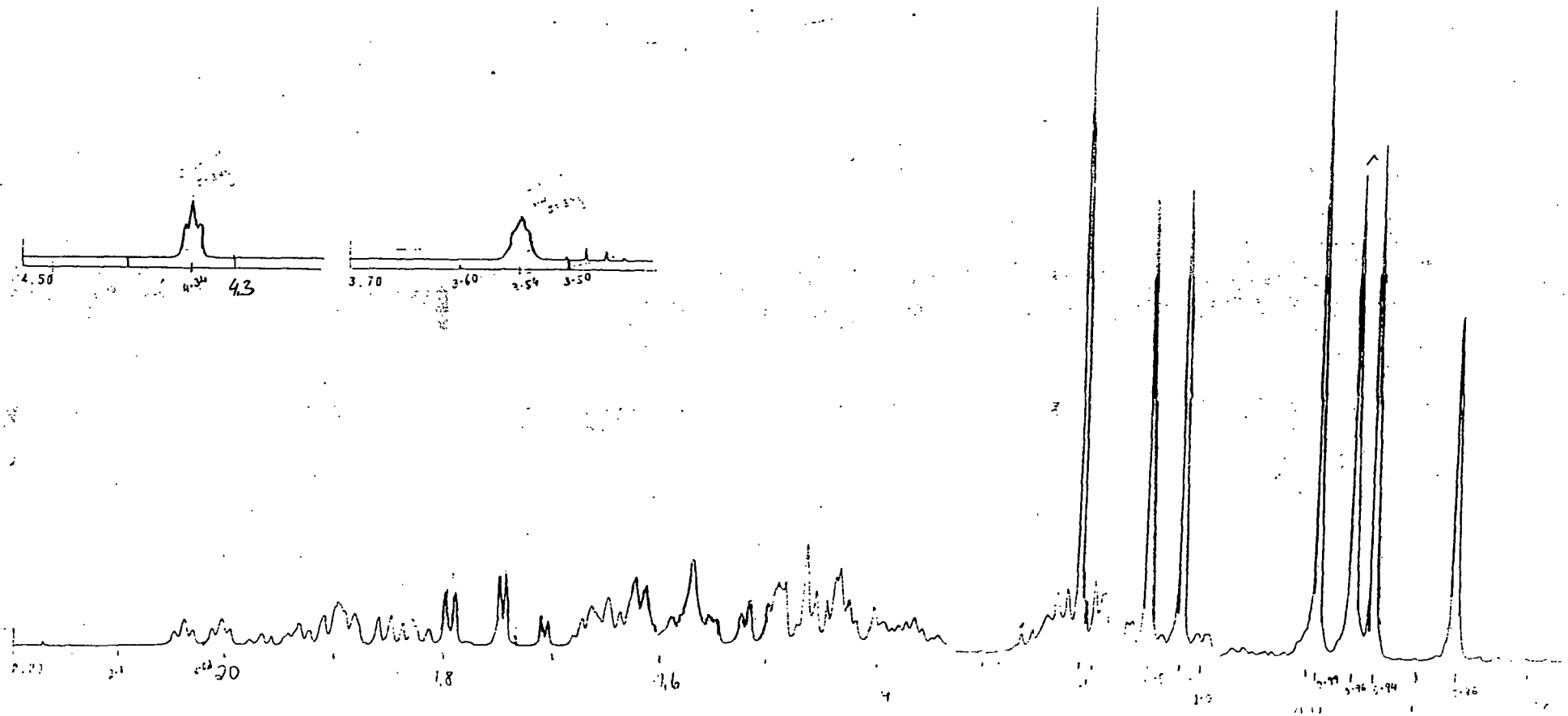


fig. 20 : ^{1}H NMR spectrum of friedelan 27→15α-olide,3β,4α-diol, 92.

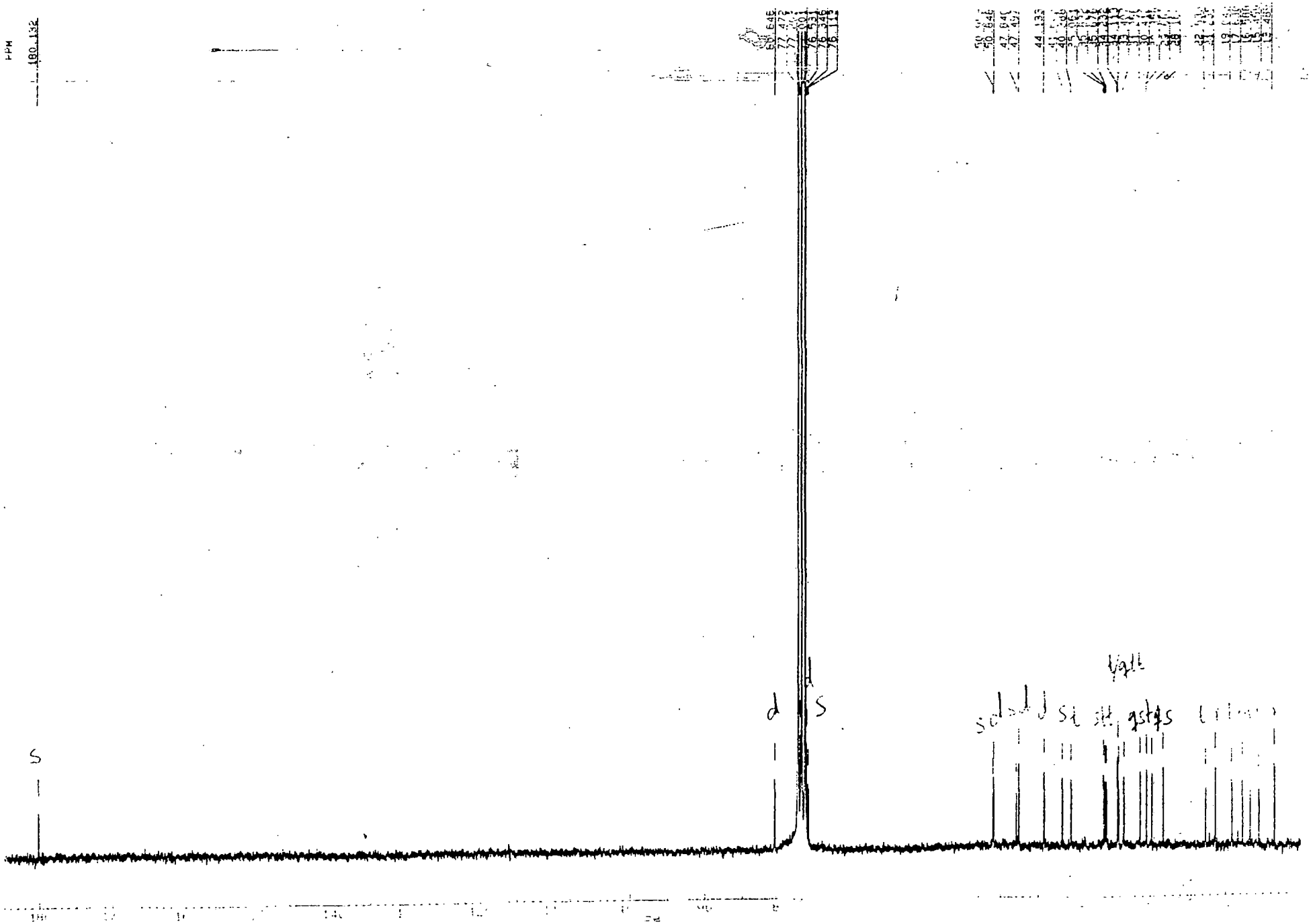


fig. 21 : ^{13}C NMR spectrum of friedelan 27→15α-olide,3β,4α-diol, 92.