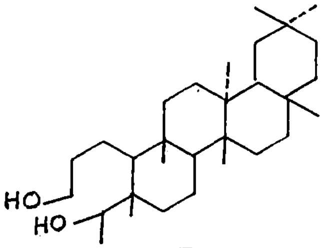
REDUCTIVE CLEAVAGE OF 3 4 SECO FRIEDELAN 3 4-OLIDE WITH LITHIUM IN ETHYLENEDIAMINE

Reaction of friedelan 3 4 olide 1, with lithium in ethylenediamine for 2 hours furnished a single compound which was subjected to column chromatography. On elution with solvents of increasing polarity benzene-chloroform (4:1) mixture gave a solid, compound A

Identification of compound A :-

The compound A was crystallised from chloroform-petrol, *M.P.*173-4^{o}*C.* Its IR spectrum (fig.1) showed a broad absorption at 3420 cm^{-1} showing the presence of hydroxyl groups indicating thereby that the lactone ring has been reduced into hydroxy groupings. The Mass spectrum (fig.2) showed molecular ion peak at m/e 428 which is due to loss of one molecule of water from the molecular ion (M-H$_2$O,0.2%)$^+$; therefore the actual molecular ion peak was to be m/e 446 (M‡), other important peaks were found at 413 (4),402 (20), 397 (8), 273 (20),219 (14), 205 (90), 191,163,149,137,123,109,95(100).

Elemental analysis and mass spectrum suggested the molecular formula to be $C_{30}H_{54}O_2$. The ^{1}H NMR (fig.3) showed the presence of seven tertiary methyl groups as singlets (3H each) between 0.87 to 1.16 ppm. and a doublet at 1.18 ppm with coupling value of 7 Hz. integrated for three protons is due to secondary methyl group at C-4 position; the AB quartet due to methine proton at C-4 probably merged with the multiplet of methylene protons at C-3 giving rise to a multiplet centred at 3.6 ppm. Thus compound A is acertained as 3,4 seco friedelan 3,4 diol-3.



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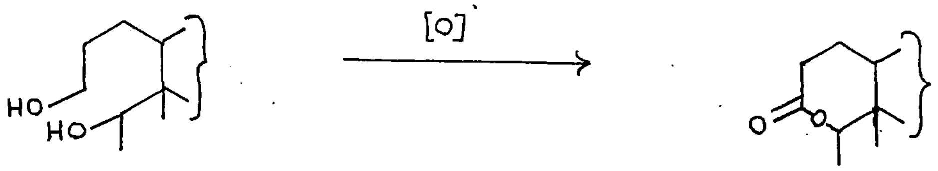
OXIDATION OF 3,4 SECO-FRIEDELAN 3→4-DIOL 3 BY JONES REAGENT.

The compound A when oxidised with Jones reagent gave back the starting material friedelan 3→4 olide 1, as identified by comparison of (m.p., m.m.p. and Co-tlc). This observation shows that the primary hydroxyl group is preferentially oxidised by Jones reagent to the carboxyl group which immediately undergoes lactonisation with less reactive secondary hydroxyl group at C-4 position.



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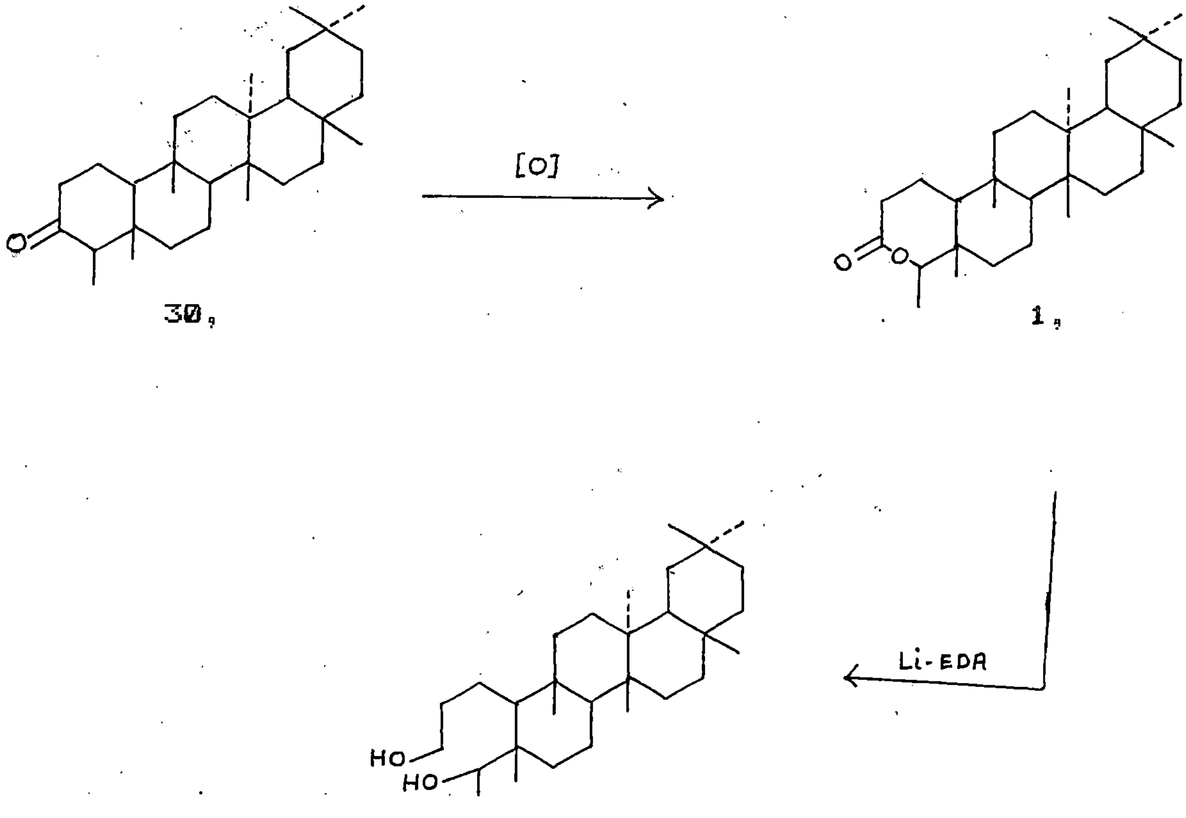
The reaction from friedelin 30 to 3,4 seco friedelin 3,4 diol 3 is schematically shown below :-



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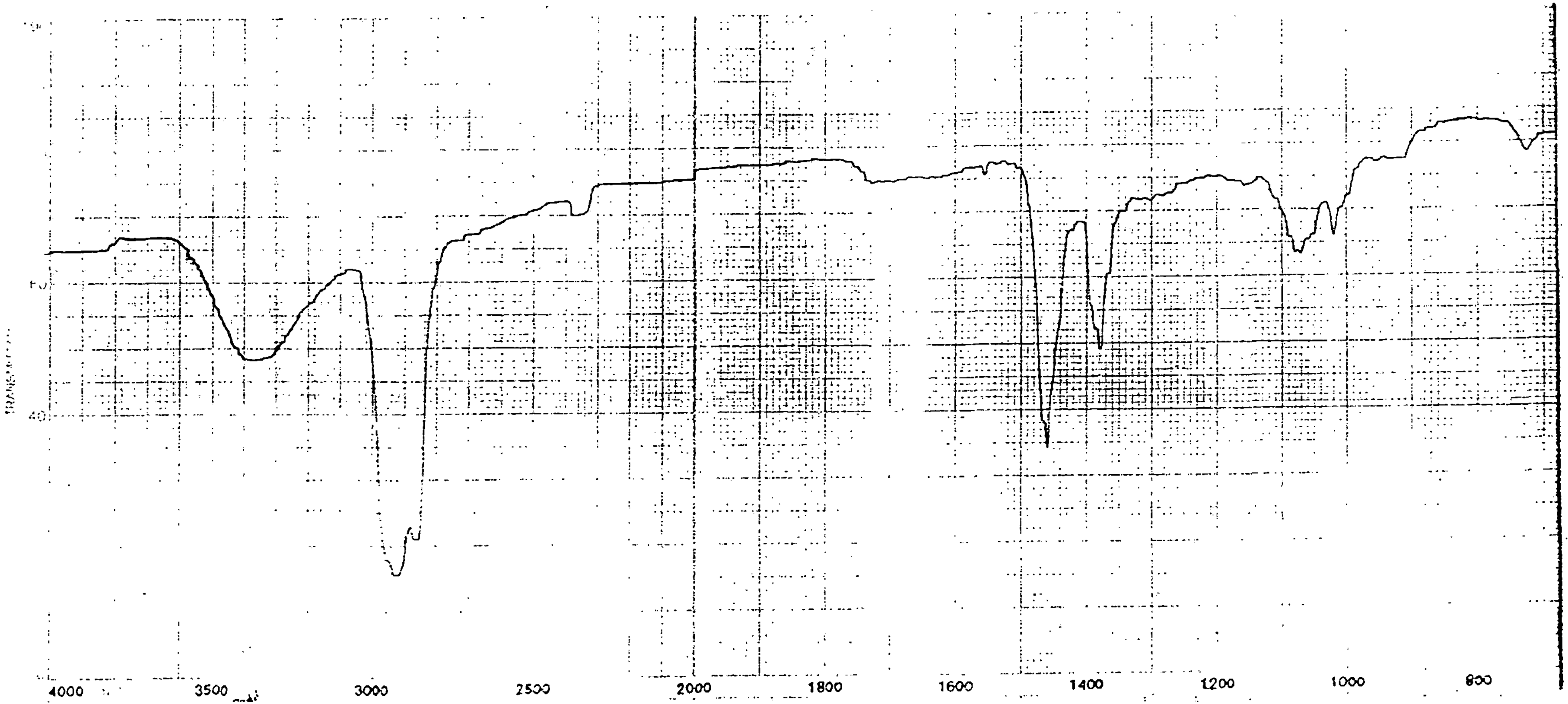


Fig. 1 : IR spectrum of 3,4 seco friedelan 3,4 diol. 3.

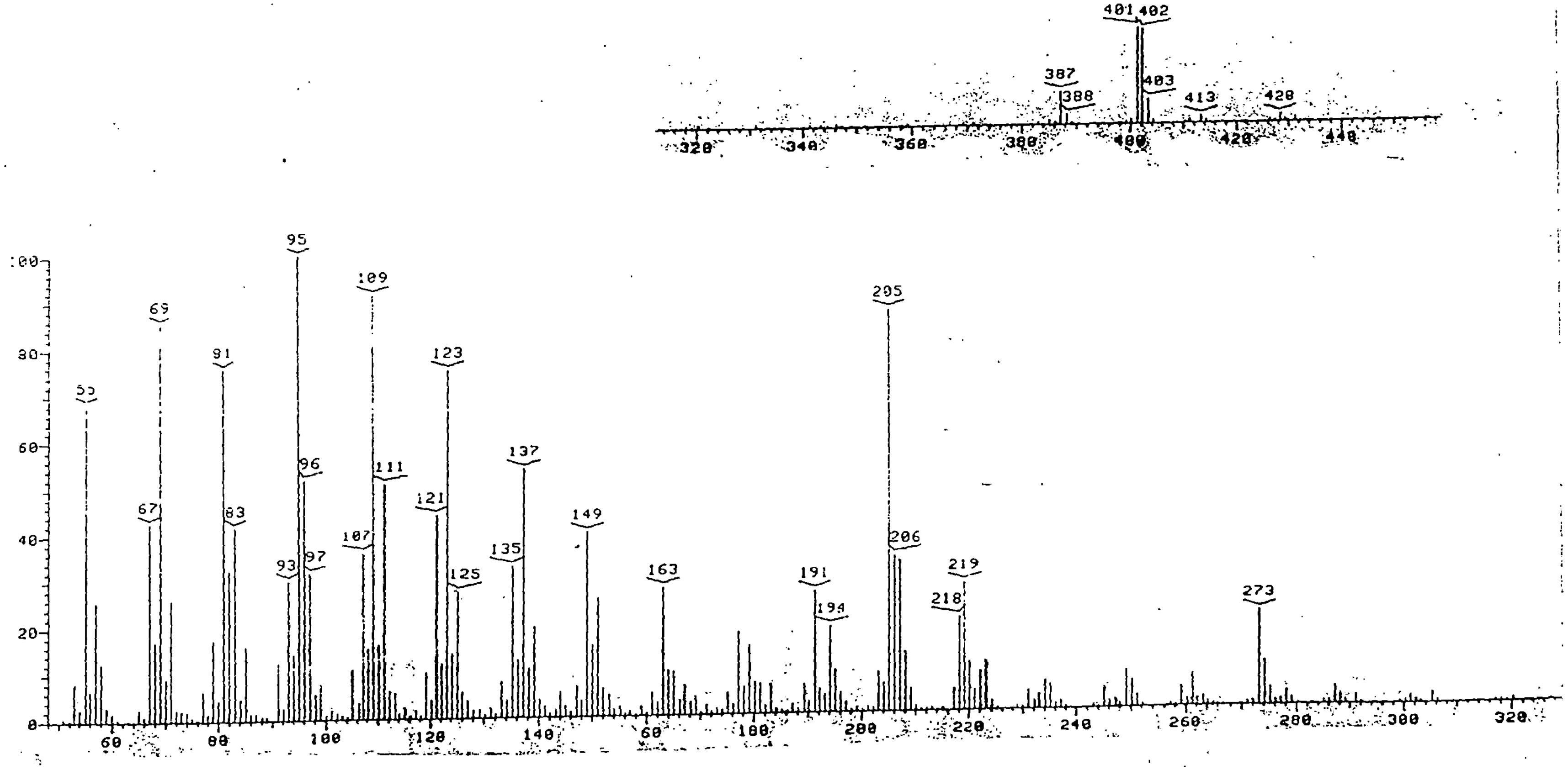


Fig.2. Mass spectrum of 3,4 seco friedelan 3,4-diol, 3.

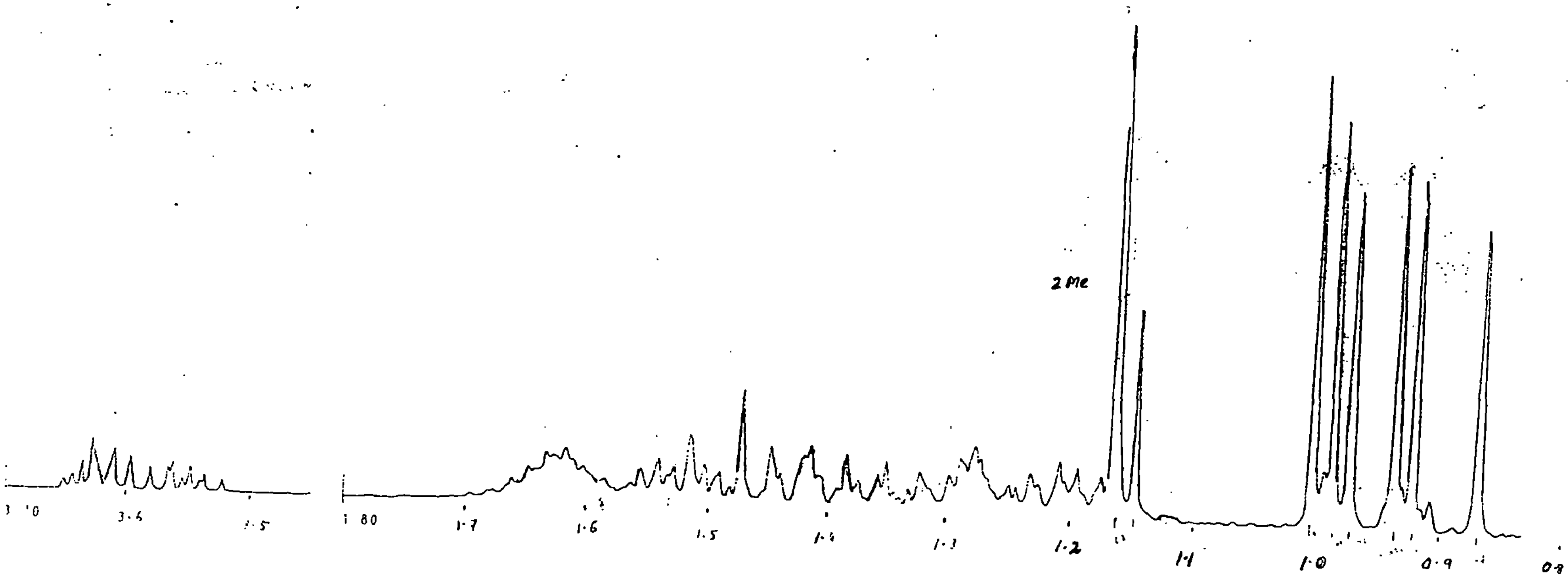


Fig. 3. ^{1}H NMR spectrum of 3,4 seco friedelan 3,4 diol, 3.

REDUCTIVE CLEAVAGE OF 3,4 SECO FRIEDELAN 3→4,27→15 DI-OLIDE WITH LITHIUM IN ETHYLENEDIAMINE.

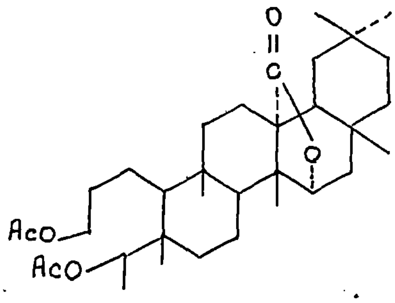
Reduction of friedelan 3→4,27→15 di-olide 2, with lithium ethylenediamine afforded a single product which was difficult to purify either by crystallisation or column chromatography. As the IR spectrum of the crude reaction product showed the presence of hydroxyl group along with the lactone carbonyl group, it was acetylated with acetic anhydride-pyridine mixture and the product was chromatographed. Elution with benzene-petrol (2:3) a solid material, compound B was obtained.

Characterisation of compound B :

The compound B was crystallised from chloroform-methanol, *M.P.* 241-2°*C*. Its IR spectrum (fig.4) showed absorption peaks at 1260 due to acetate group and 1750 cm^{-1} (broad) due to merging of lactonic carbonyl peak with acetate carbonyl peak. Mass spectrum (fig.5) showed molecular ion peak at m/e 558 $(M,0.7\%)^+$; other important peaks found were at m/e 514 $(M-CO_2)^+$, 498 $(M-AcOH,1.8)^+$, 471 (100), 425, 411, 369, 341, 315, 269. From mass and elemental analysis the molecular formula is calculated to be $C_{34}H_{54}O_6$.

The ^1H NMR (fig.6) showed (δ in ppm.) six singlets between 0.83 to 1.16 and one doublet centred at 1.14 (J= 7Hz.) which are accounted for seven methyl groups of which one at C-4 that coupled with the geminal methine proton giving rise to the doublet observed; two sharp singlets (3H each) that appeared at 2.02 and 2.05 indicates the presence of two acetate functions; one AB quartet that centred at 4.83 is due to the methine proton at C-4. The multiplet centred at 3.96 is accounted for the methylene protons at C-3 which coupled with the neighbouring protons. The methine proton at C-15 coupled with adjacent protons giving rise to the triplet at 4.34 (J= 3 Hz.).

Hence, from the spectral studies the structure of compound B is proposed to be 3,4 seco friedelan 3,4 dio-acetoxy 27→15 olide 5



5,

The formation of dihydroxy lactone from the dilactone during reduction with lithium-ethylenediamine indicated that the ε-lactone ring at $3\rightarrow4$ is much more exposed to the reagent and the γ-lactone ring at $27\rightarrow15$ is sterically hindered, is well documented from this observation; the parent lactone at $27\rightarrow15$ in odollactone forms acid and small amount of triol.[5]

Mechanism of lactone cleavage :-

The reductive action of lithium in ethylenediamine is stereoselective as evident from this reaction. The ring-A lactone is very much sterically exposed than the lactone at C_{27} — C_{15} which is crowded. Thus there is a strong competition of these two lactones for reaction with the reagent and the lactone at C_3–C_4 undergoes Bouveault Blanc reduction by protonation of the lactone radical-anion concerted with the second electron transfer. This allows the acyl oxygen fission to take place with the formation of alkoxide ion and aldehyde group in the same molecule. Further reduction and protonation of the aldehyde group than affords the diol.

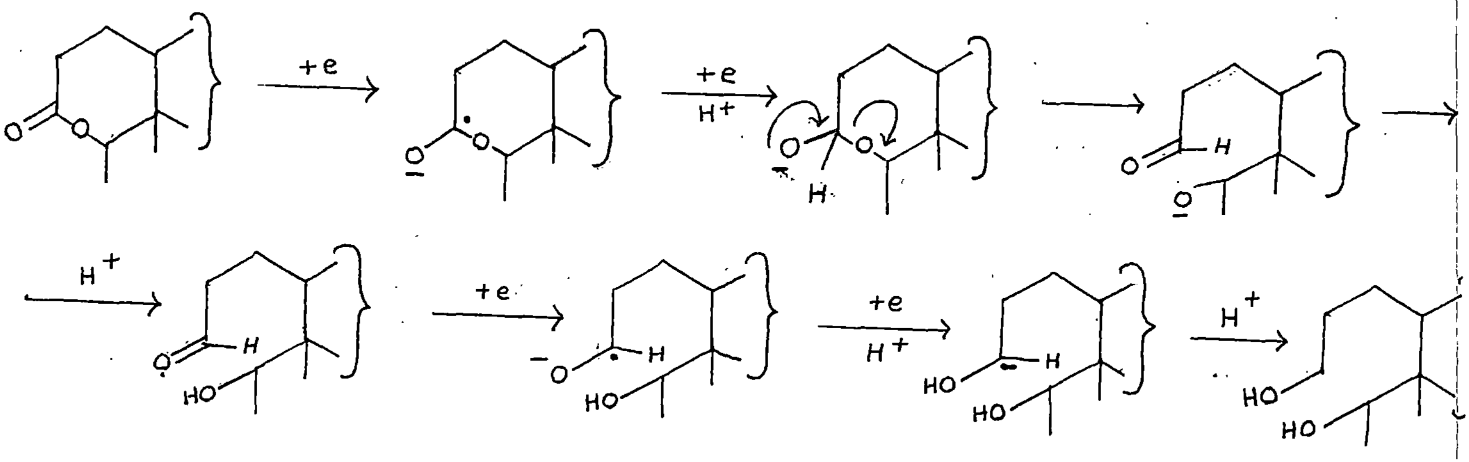


Fig.4. IR spectrum of 3,4 seco 3,4 dio-acetoxy friedelan 27→15-Olide,5.

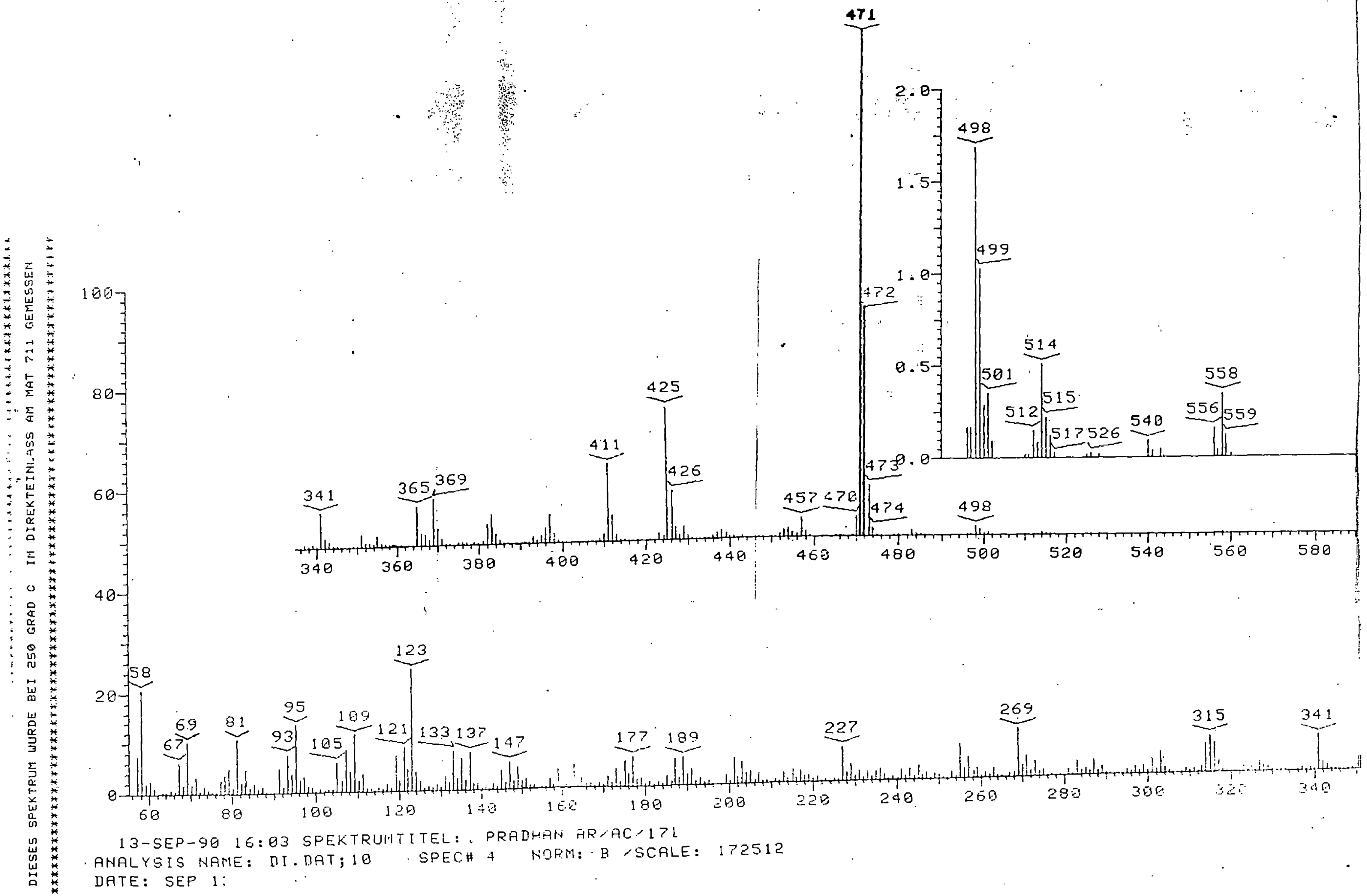


Fig.5. Mass spectrum of 3,4 seco 3,4 dio-acetoxy friedelan 27→15-olide,5.

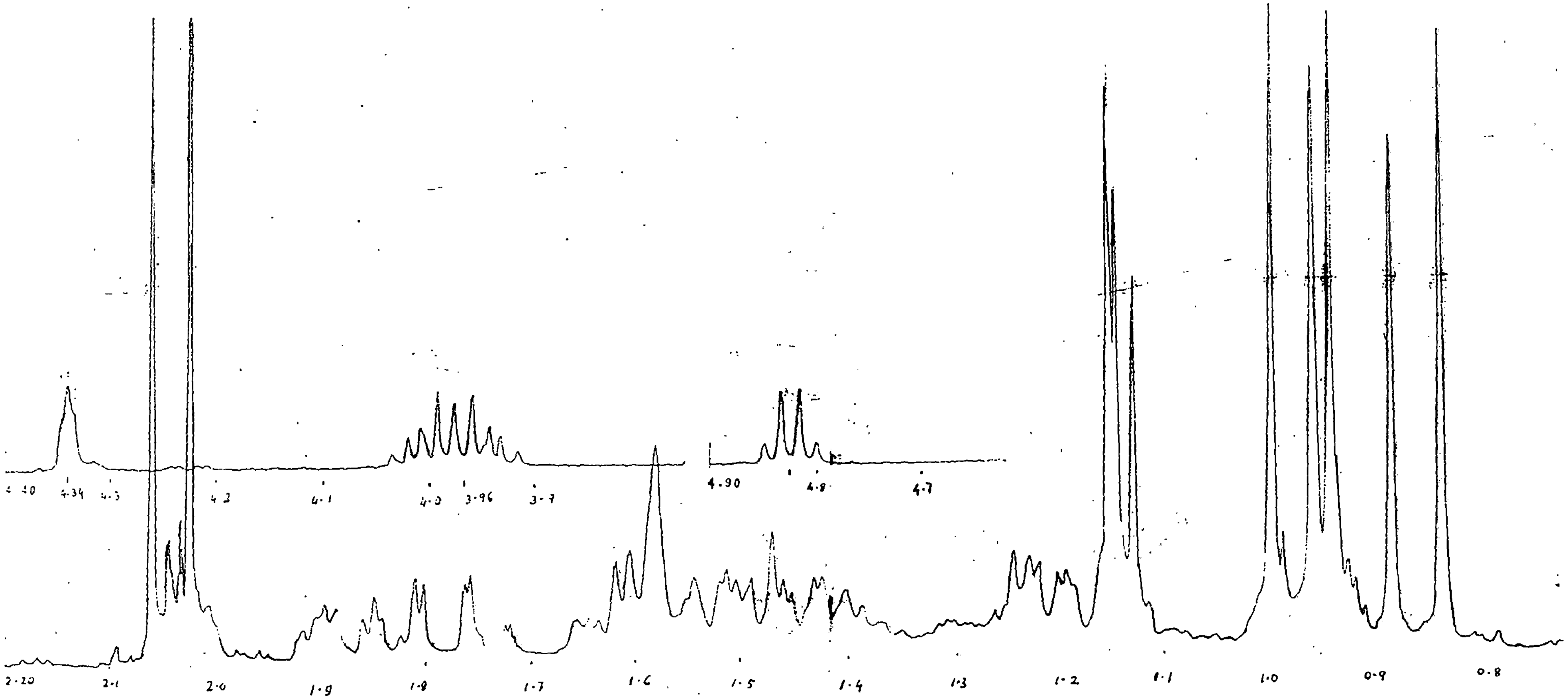


Fig.6. ^{1}H NMR spectrum of 3,4 seco 3,4 dio-acetoxy friedelan 27→15-olide,5.