

PART - III

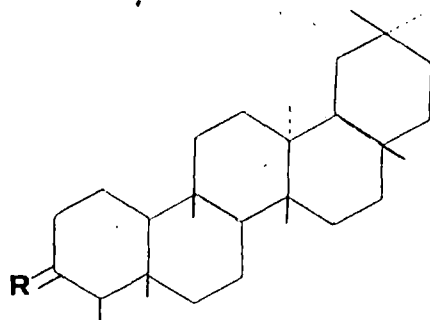
OXIDATION REACTION OF SELENIUM DIOXIDE ON OXIME DERIVATIVE  
OF FRIEDELIN

Chapter : I :

OXIDATION REACTION OF SELENIUM DIOXIDE ON OXIME DERIVATIVE OF FRIEDELIN

In continuation of studies on oxidation reaction of selenium dioxide with various triterpenoids, oxime derivative of friedelin was treated with selenium dioxide and products isolated and identified as described below.

Friedelin, 1, isolated from cork waste was converted to its oxime derivative in the usual manner (vide experimental). The identity of the product was confirmed as oxime derivative of friedelin, 2, by comparison of its physical data with those of the authentic sample (mp, IR, TLC)



1, R=O

2 R= N-OH

Oxidation of oxime derivative of friedelin, 2, by selenium dioxide and

isolation of products thereof :

The oxime derivative, 2, was refluxed with selenium dioxide in t-butanol under nitrogen atmosphere for 36 hrs. The reaction mixture was chromatographed on a silica gel column to yield two products A and B when eluted with solvents of appropriate polarity as described in Table - 1.

Table 1

Eluent	Residue on evaporation	Fractions 50 ml	Yield (mg)
1. Benzene	White solid, <u>A</u>	17-22	150
2. Benzene: EtOAc (9: 1)	White solid, <u>B</u>	32-40	110

No more product was obtained by eluting further with more polar solvent system.

Structure elucidation of compound, A :

The fractions 17-22 were combined because of their similar TLC pattern. The solid residue obtained after removal of solvent was crystallised twice from chloroform-methanol mixture to give a pure product, A, mp 295-97<sup>o</sup>,  $[\alpha]_D^{25} +60$ . It analysed for C<sub>30</sub>H<sub>45</sub>ONSe. In order to establish the identity of the compound, it was subjected to various physico-chemical methods of study.

IR spectrum (Fig 2) of compound A showed absorption peak at 1675  $\text{cm}^{-1}$  probably for a ketonic functional group with  $\alpha\beta$ -unsaturation. UV absorption (Fig. 3) was observed at 254 nm and 307 nm suggesting a ketone with a certain degree of conjugation with olefinic double bonds. Further insight was gathered regarding the structure of compound A with the help of its PMR spectrum. The resonance signals of various protons as observed in Fig. are represented in Table 2.

Table - 2

Chemical shift, $\delta$	No. of protons	Multiplicity	Probable assignment
0.93	3	Singlet	Seven tertiary methyls
0.97	3		
0.99	6		
1.04	3		
1.18	3		
1.27	3		
2.70	1	dd, (J = 12.5, 18.5 Hz)	Two protons $\alpha$ to ketone with one more proton in $\beta$ position
2.752	1	dd, (J = 18.5, 3 Hz)	
1.91	1	dd, (J = 12.5, 3 Hz)	One proton $\beta$ to a ketone
2.37	1	Doublet of a triplet (J = 13 Hz)	C - 18 proton
9.04	1	Singlet	One olefinic proton, the double bond being in conjugation with other double bonds, non-bonding electrons, ketone functional group

The PMR spectrum (Fig. 4) of compound A showed the presence of seven tertiary methyls in the region 0.9 to 1.3 ppm. The doublet of a doublet at 2.695 ppm with large coupling constants of 12.5 and 18 Hz and another doublet of a doublet at 2.753 ppm having coupling constants of 3 and 18 Hz each integrated for one proton are probably due to geminal protons  $\alpha$  to the carbonyl grouping having geminal couplings of 18 Hz showing that these protons are the methylene protons of a six membered ring. The existence of a doublet of a doublet appearing at 1.91 ppm with coupling values of 3 and 12.5 Hz that coupled with protons at 2.695 and 2.753 ppm showed that this single proton is  $\beta$  to the carbonyl group and its coupling values indicated it to be axial ( $J_{\alpha-\alpha}$  12.5 Hz and  $J_{\alpha-\beta}$  3 Hz) that has two neighbouring axial and equatorial protons. The coupling pattern of these three protons were exactly similar to that of friedelin 2, 3-dione, 3, (Fig 5). Thus a ketonic group is formed at C-2 position of ring A of friedelin derivative in compound A.

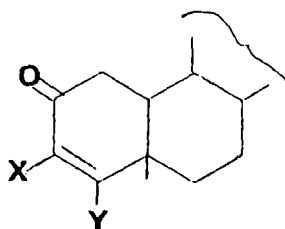
The presence of a singlet downfield at 9.04 ppm may be due to aldehydic proton or olefinic proton attached to carbon containing electron withdrawing group, having no neighbouring proton.

#### <sup>13</sup>C NMR spectrum analysis of compound A

<sup>13</sup>C NMR (Fig. 6) of compound A was recorded and compared with that of friedelin<sup>49</sup> to gather further informations on the total number of carbons and the nature of these carbons. The spectrum showed the presence of seven carbons

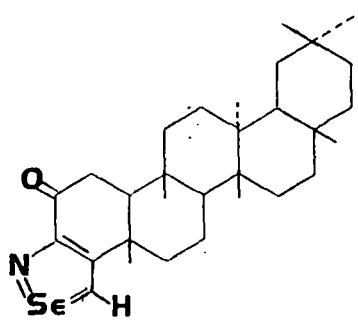
as quartets assignable to seven methyls, four carbons appeared as doublets, indicating the presence of four methine carbons, ten triplets were observed for ten methylene carbons and nine singlets for quaternary carbons were observed. Thus all the thirty carbons have been accounted for.

The existence of a singlet downfield at 193.29 ppm in conjunction with the IR absorption peak at  $1675\text{ cm}^{-1}$  indicating the presence of  $\alpha/\beta$ -unsaturated carbonyl group. So, the presence of  $\text{O}=\text{C}-\text{C}=\text{C}$  is confirmed in A. The doublet at 148.23 ppm must be the carbon bearing the olefinic proton that appears at 69.04 as singlet. The singlet carbons at 156.68 and 163.94 ppm are the olefinic carbons that are  $\alpha$  and  $\beta$  to the carbonyl group, which do account for the UV absorption at 254 nm. Thus the grouping  $\text{O}=\text{C}-\text{C}=\text{C}-$  is further confirmed. Since there is only one carbonyl group and since it has been shown also to possess  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}-$  grouping present in a six membered ring, it is obvious to contain the following partial structure :



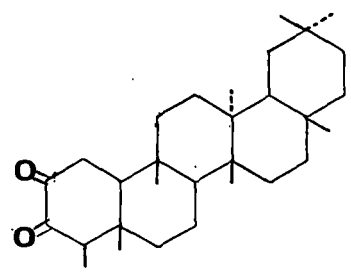
The absence of secondary methyl or methyl on a double bond indicated that C-23 is converted to  $\text{SP}^2$  carbon with a proton. Furthermore, the molecular ion at  $m/z$  515 with a cluster of ten peaks showed that there is a selenium atom and the nitrogen atom originally present as oxime. Considering that only ring A is involved in this reaction and taking account of the presence of Nitrogen and Selenium atoms and the lone  $\text{SP}^2$  carbon probably at C-23 the following structure 4

is proposed for compound A. The attachment of C-23 carbon with the selenium atom as  $SP^2$  hybrid that is in conjugation with carbonyl and the olefinic double bond as well as cumulative with the nitrogen explains the large down-field shift of the C-23-proton to 9.04 ppm. This structure also explains the large UV absorption at 307 nm.



4

The structure 4 is further corroborated by its mass spectrum with fragments at  $m/z$  516  $[M]^+$ , 391, 362, 282, 226, 179 in conformity to fragmentation pattern reported for friedelane skeleton<sup>46</sup>. (Fig-7)



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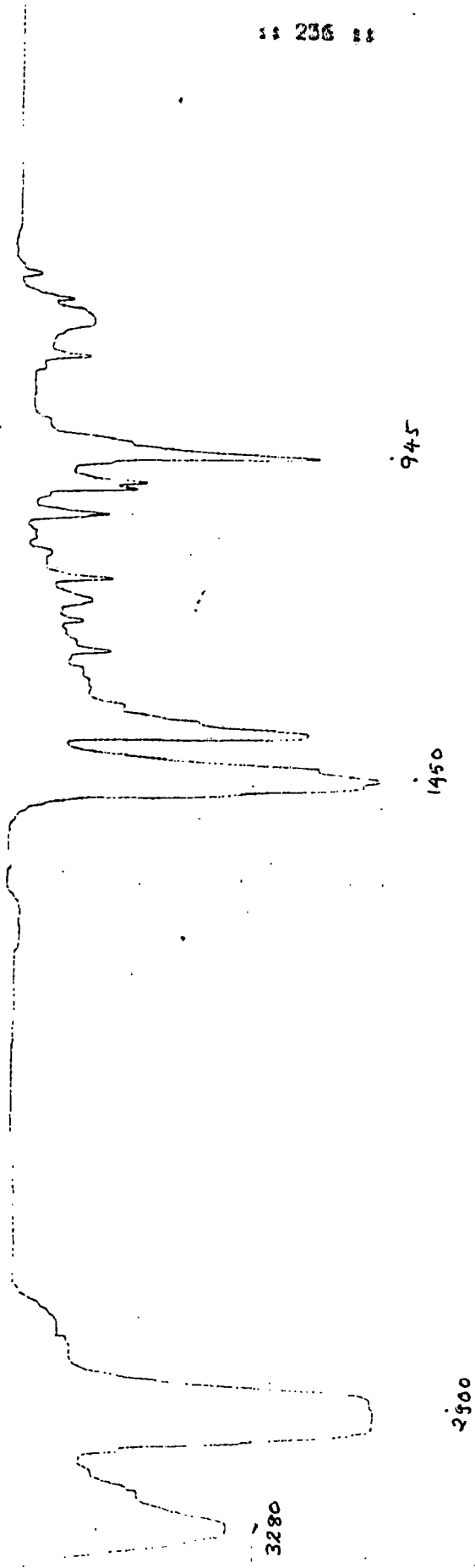


Fig. 1. IR spectrum of oxime derivative of friedelin



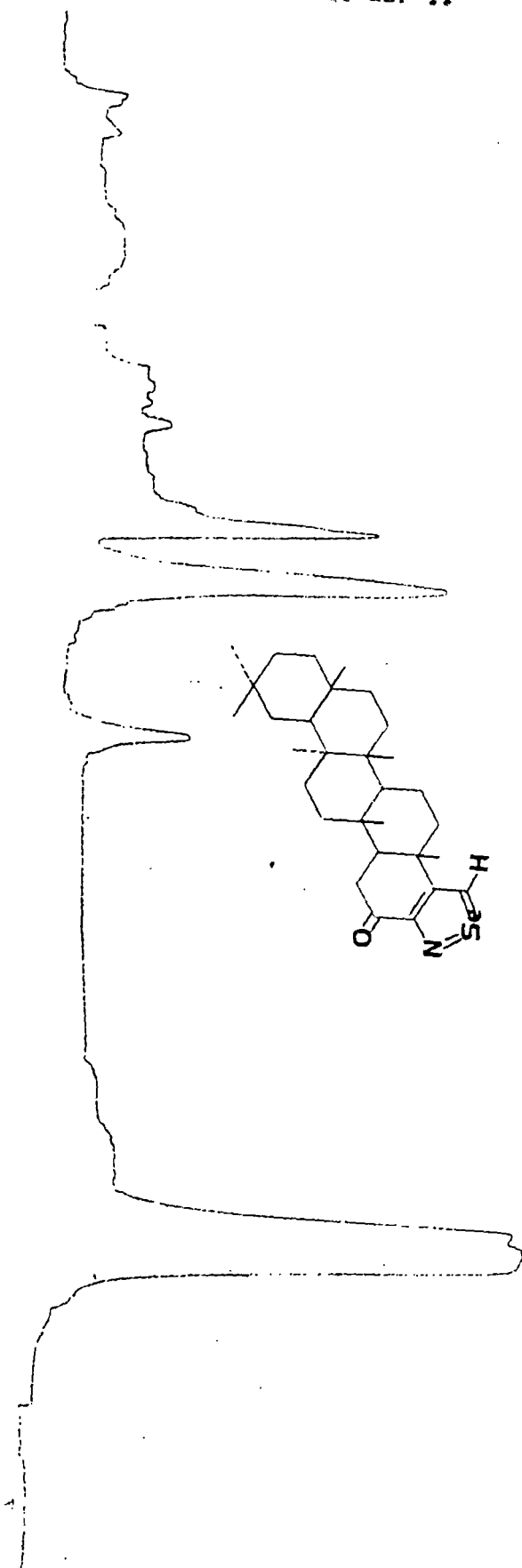


Fig. 2. IR spectrum of compound A

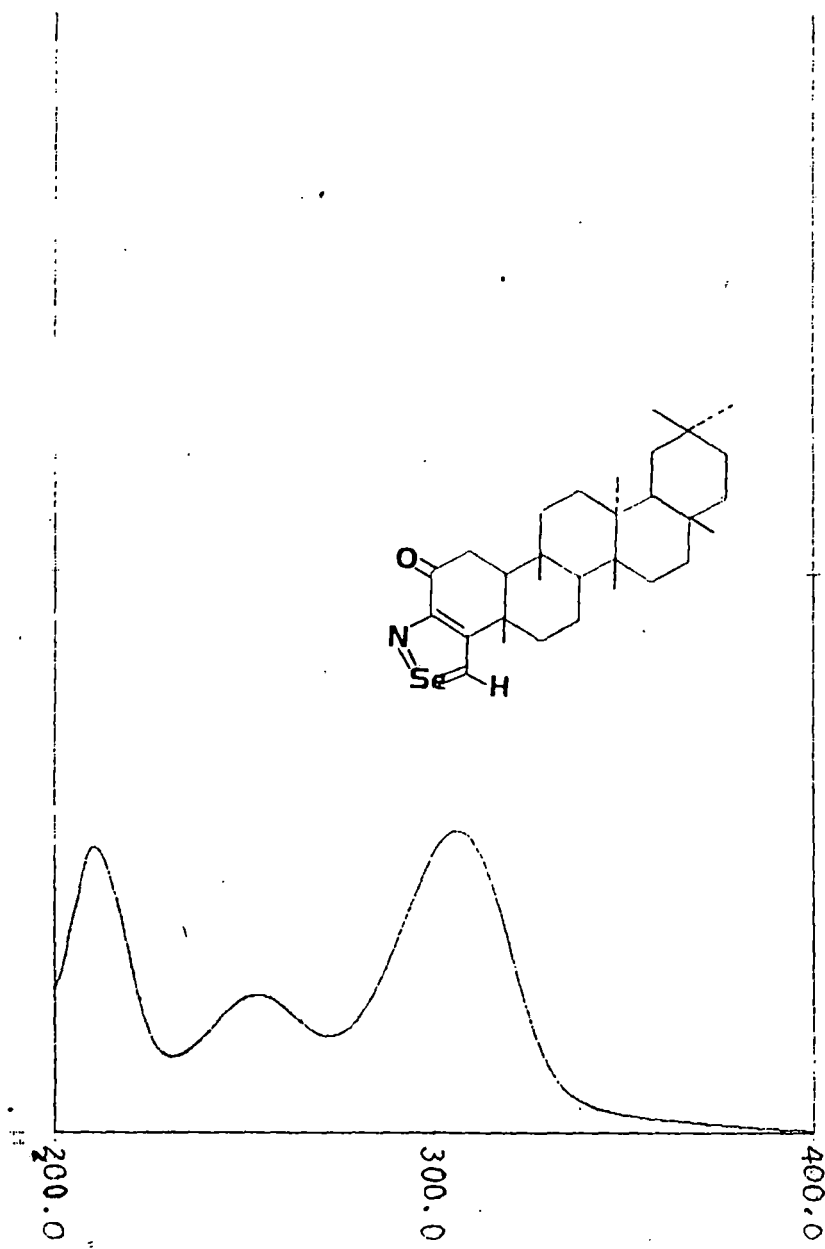


Fig. 3. UV spectrum of compound A

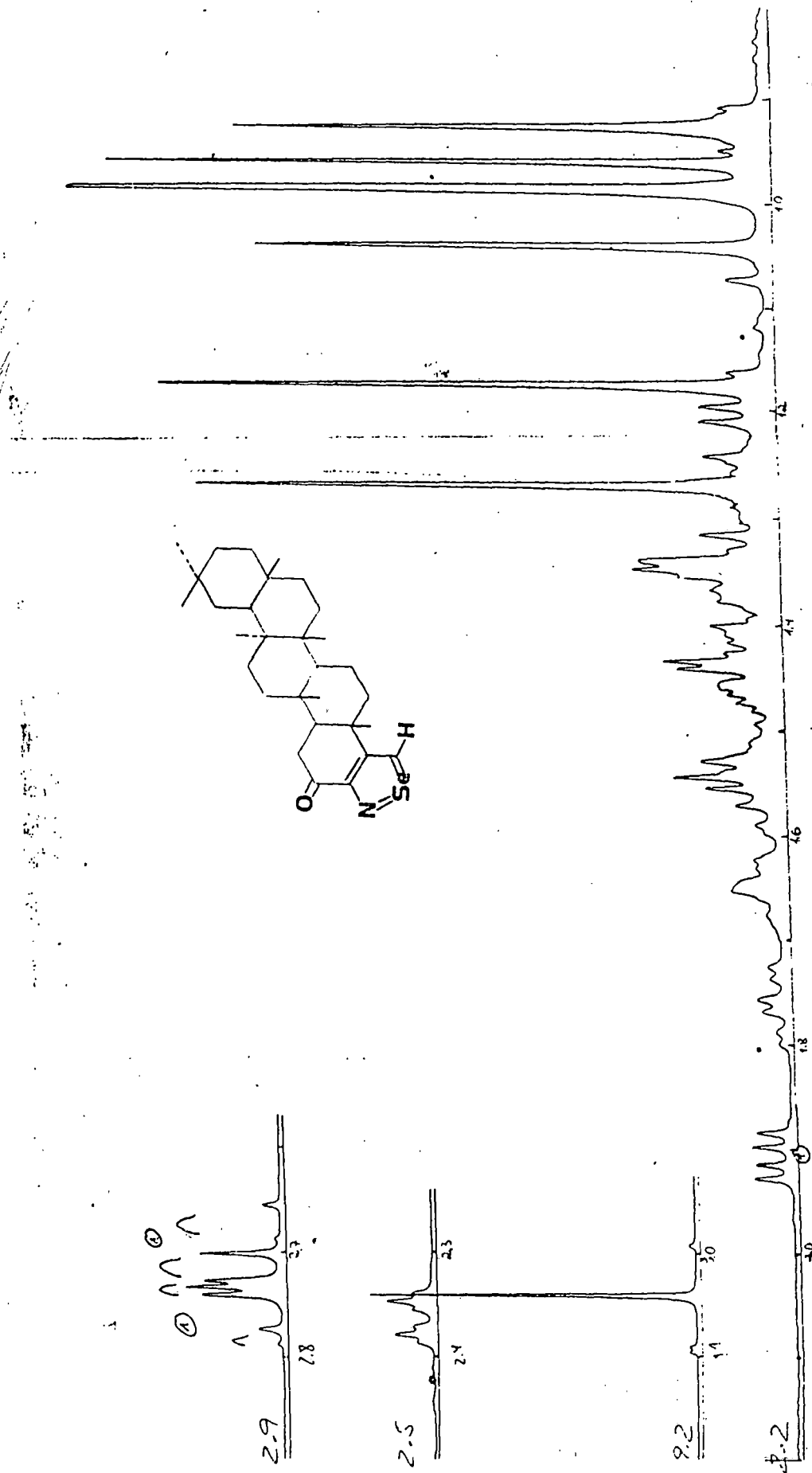


Fig. 4. PMR spectrum of compound A

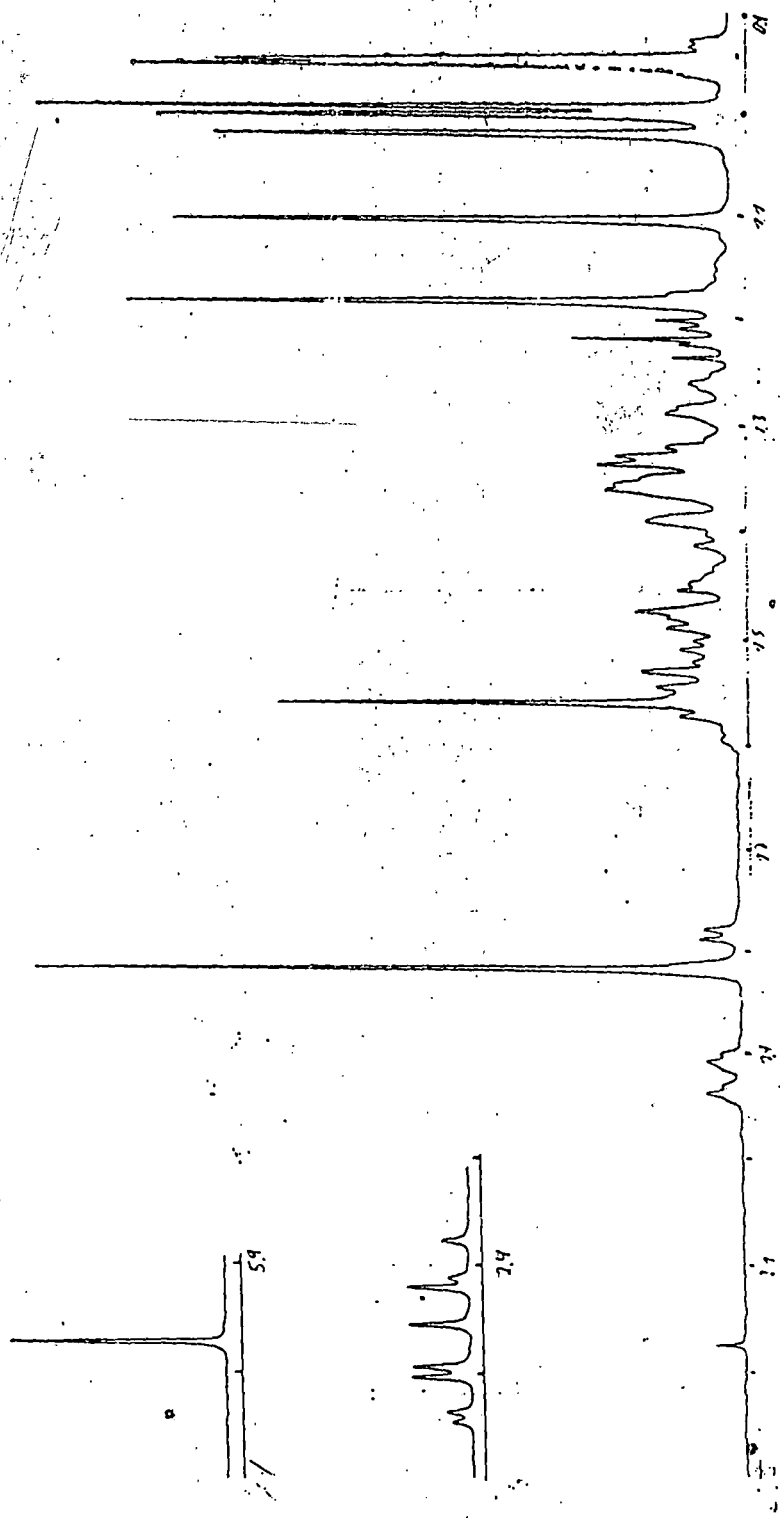
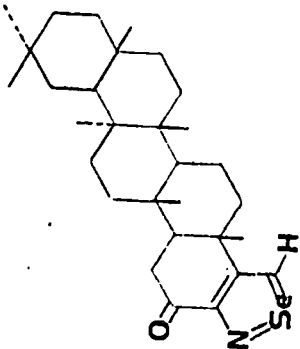
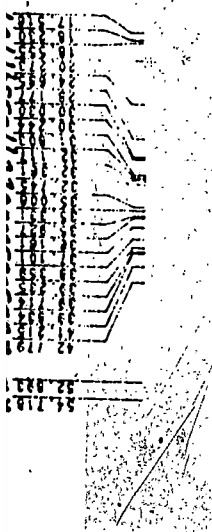


Fig. 5. PMR spectrum of friedelin-2,3-dione



198.226

156.215

102.226

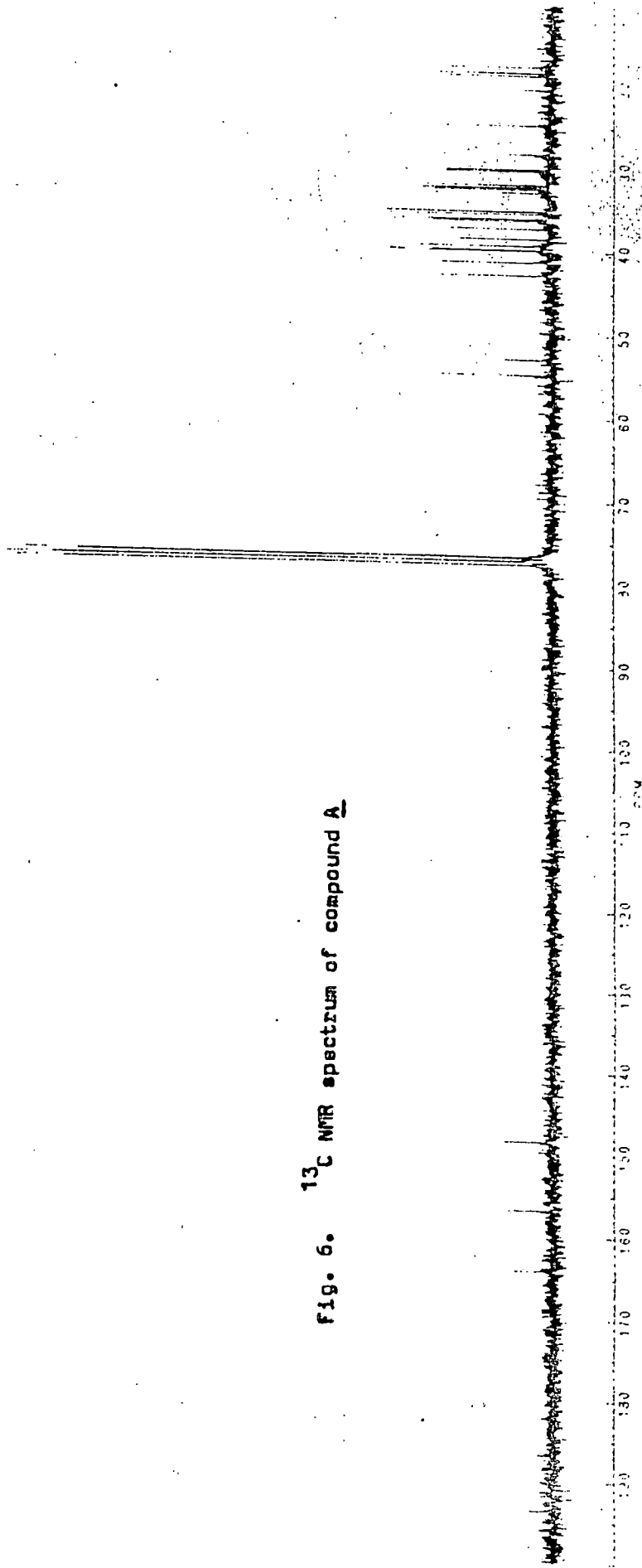
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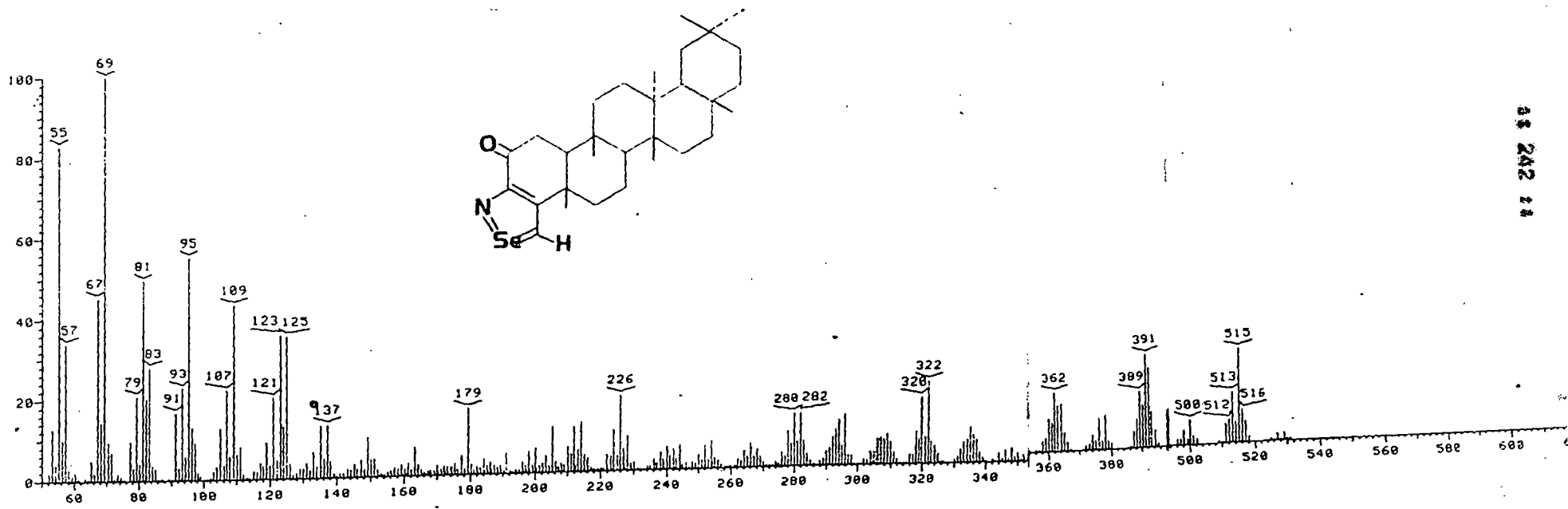
102.226

PPM

Fig. 6. <sup>13</sup>C NMR spectrum of compound A



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Fig. 7. Mass spectrum of compound A

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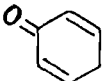
Table - 3

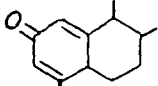
<sup>13</sup>C NMR shifts assignment ( $\delta$ ) of 1, 4, 5 and 6 (CDCl<sub>3</sub> as solvent with internal TMS)

Carbon	1	4	5	6
1	22.1 (t)	36.2 (t)	123.52 (d)	119.6 (d)
2	41.4 (t)	193.3 (s)	178.54 (s)	178.4 (s)
3	213.0 (s)	156.6 (s)	150.16 (s)	146.1 (s)
4	58.0 (d)	163.9 (s)	162.72 (s)	117.0 (s)
5	42.0 (s)	39.8 (s)	43.59 (s)	127.5 (s)
6	41.1 (t)	41.2 (t)	41.21 (t)	133.9 (d)
7	18.0 (t)	18.2 (t)	18.14 (t)	118.1 (d)
8	52.9 (d)	52.9 (d)	49.93 (d)	169.9 (s)
9	37.3 (s)	37.1 (s)	39.16 (s)	42.9 (s)
10	59.3 (d)	54.7 (d)	153.18 (s)	164.7 (s)
11	35.5 (t)	35.3 (t)	35.30 (t)	33.6 (t)
12	30.3 (t)	30.2 (t)	30.79 (t)	29.7 (t)
13	39.5 (s)	39.7 (s)	39.40 (s)	39.4 (s)
14	38.1 (s)	38.4 (s)	41.01 (s)	45.0 (s)
15	32.3 (t)	32.4 (t)	32.59 (t)	28.7 (t)
16	35.9 (t)	35.9 (t)	35.81 (t)	36.4 (t)
17	29.8 (s)	30.03 (s)	29.88 (s)	30.5 (s)
18	42.6 (d)	42.8 (d)	42.23 (d)	44.4 (d)
19	35.2 (t)	35.0 (t)	35.30 (t)	30.9 (t)
20	29.0 (s)	28.2 (s)	28.14 (s)	40.4 (s)
21	32.6 (t)	32.7 (t)	32.59 (t)	29.9 (t)
22	31.1 (t)	39.2 (t)	39.47 (t)	34.8 (t)
23	6.7 (q)	148.2 (d)	181.89 (s)	10.2 (q)
24	14.5 (q)	24.7 (q)	20.42 (q)	-
25	17.8 (q)	17.5 (q)	24.22 (q)	38.3 (c)
26	20.1 (q)	20.3 (q)	20.42 (q)	21.6 (q)
27	18.5 (q)	18.6 (q)	18.61 (q)	18.3 (c)
28	32.0 (q)	32.1 (q)	32.02 (q)	31.5 (q)
29	31.7 (q)	31.9 (q)	31.68 (q)	178.7 (s)
30	34.9 (q)	35.0 (q)	34.93 (q)	32.7 (q)
COOCH <sub>3</sub>	-	-	-	51.5 (q)

Structure elucidation of compound B

The eluted fractions (32-40) were combined after finding their TLC pattern similar. Removal of solvent resulted in appearance of white solid. This was crystallised from chloroform-methanol mixture, mp 296°. It analysed for  $C_{30}H_{44}O_3Se$ . The compound was subjected to various physico-chemical studies to establish its structure.

IR spectrum showed absorption peaks at  $1660-70\text{ cm}^{-1}$  (broad) indicating the presence of  group, a broad funnel shaped absorption around  $2700-3500\text{ cm}^{-1}$  suggest the presence of a carboxyl group. (Fig-8)

UV absorption was observed ( $\lambda_{\text{max}}$ ) at 274 and 312 nm. The calculated value<sup>50</sup> for a quione system  can be written as 215 (base) + (4 substitution) 48 + (1 exocyclic double bond) + 5 = 268.

<sup>1</sup>H NMR analysis of compound B

In an effort to clearly understand the structure of compound B, its PMR spectrum was recorded and analysed. The spectrum showed (Table - 4) for seven methyls in the region  $\delta$  0.9 to 1.6. The absence of signal from the eighth methyl infers its involvement in the reaction that has occurred. (Fig-9)



Table - 4

Chemical shift, $\delta$	No. of protons	Multiplicity	Probable assignment
0.92	3	SINGLETS	Seven tertiary methyls
0.93	3		
0.99	3		
1.12	3		
1.18	3		
1.33	3		
1.58	3		
6.42	1	Singlet	An olefinic proton $\alpha$ to a <del>ketone</del> ketone
9.26	1	Singlet(broadened)	Carboxyl proton

The signal at  $\delta$  6.42 indicates the presence of an olefinic proton on a carbon  $\alpha$  to a carbonyl group. A downfield slightly broad signal at  $\delta$  9.26 is characteristic of proton on a carboxyl group. These derivations indicate that the C-23 is converted to COOH group in compound B.

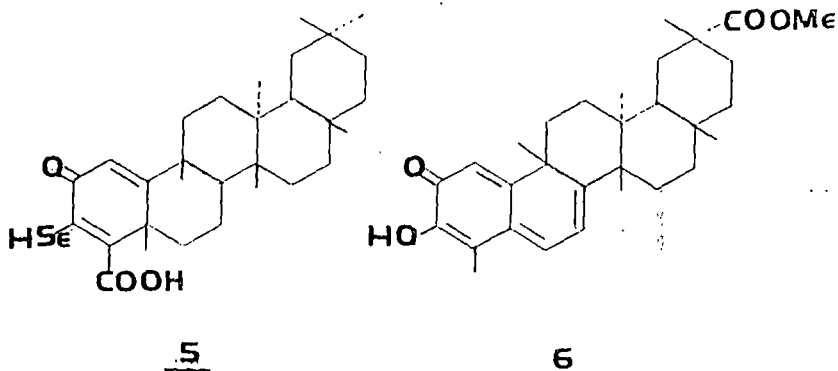
<sup>13</sup>C NMR spectrum analysis of compound B

In addition to the informations so far gathered on the basis of IR, UV and <sup>1</sup>H NMR spectra, further insight regarding the structure of compound B was made possible by recording and critically examining its <sup>13</sup>C NMR (Fig.10) spectrum.

The spectrum showed the presence of seven quartets indicative of seven methyls, nine triplets due to methylene carbons, three doublets as a result of methine carbons and eleven singlets for fully substituted carbons. Thus all the thirty carbons were accounted for. These signals values were compared with those of friedelin (Table - 3) and the position of functional groups were allotted their positions.

The existence of six carbons downfield in the region 123.5 to 181.9 ppm showed that the ring A of friedelin is highly oxidised. The existence of only seven methyls in B showed that the C-23 is also involved in the oxidation process. The most downfield singlet at 178.5 ppm is due to the quinonoid carbon<sup>51</sup> group and the next one at 181.9 ppm is due to the carboxylic carbon, the doublet at 123.5 ppm must be due to the SP<sup>2</sup> carbon possessing a proton and one at 153.2 ppm as singlet is due to the C-10 carbon. The other two singlets appearing at 150.2 and 162.7 ppm are due to carbons at C-3 and C-4 positions. The signals are in good agreement with those reported for naturally occurring compound pristimerin, 6, of friedelin skeleton having quinone type of structure as depicted in table 3.

On the basis of informations derived from the spectral data the compound B can be represented as 5.



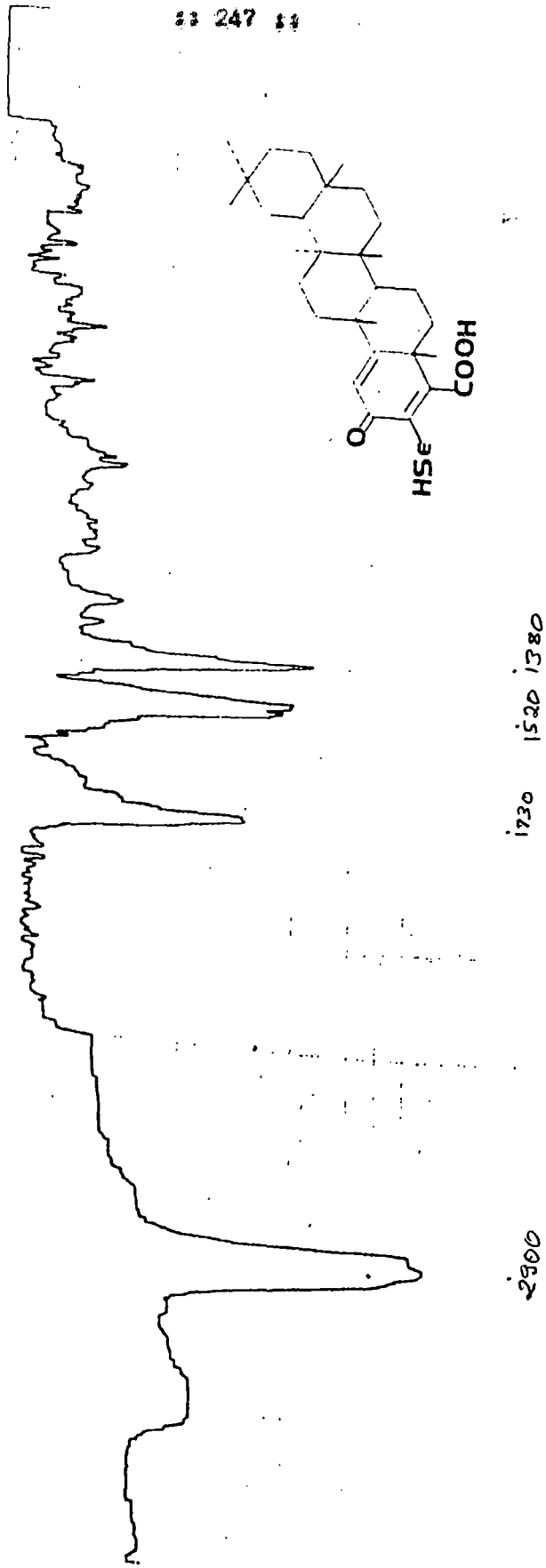


Fig. 8. IR spectrum of compound B.

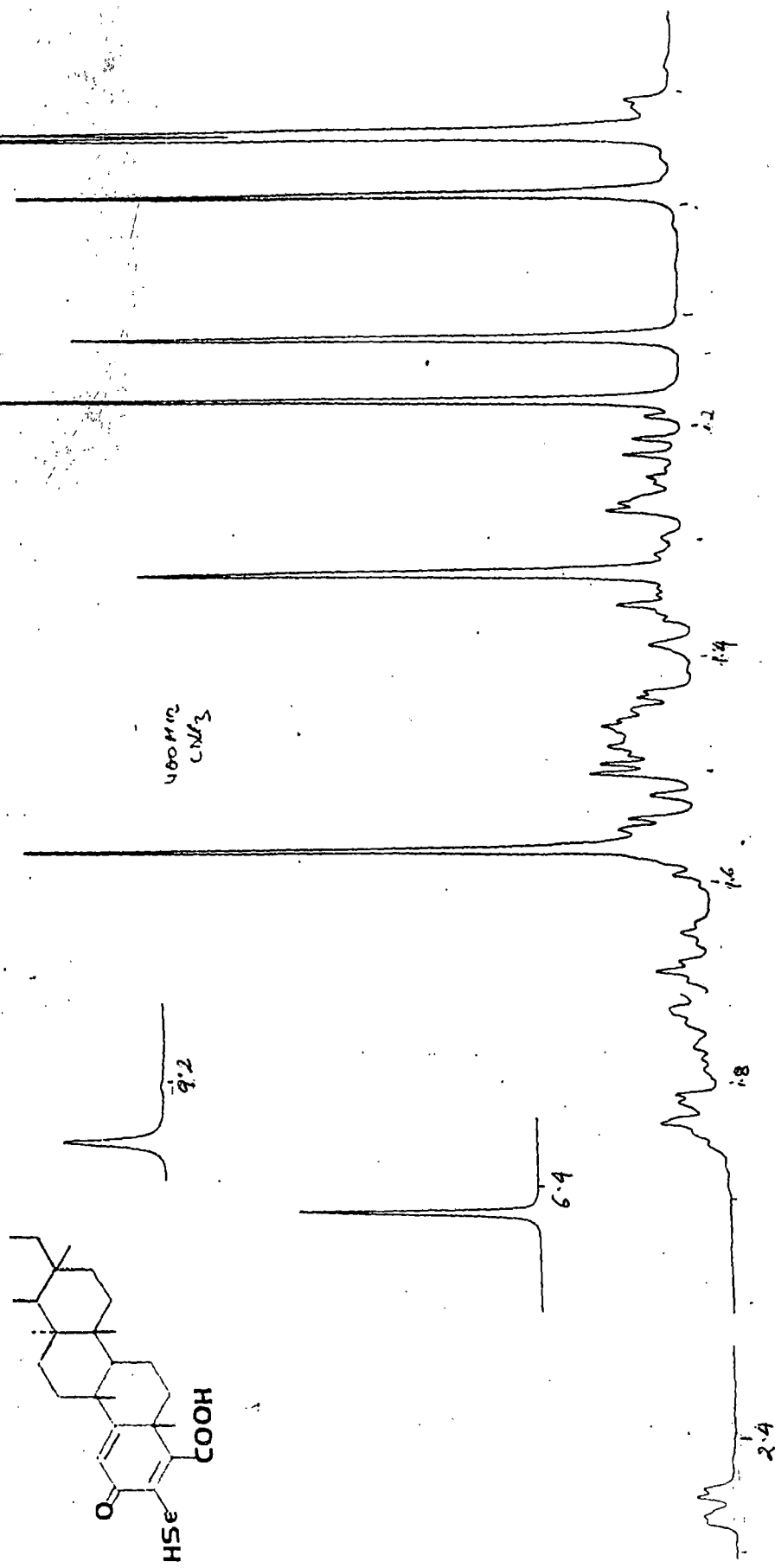


Fig. 9. PMR spectrum of compound 9.

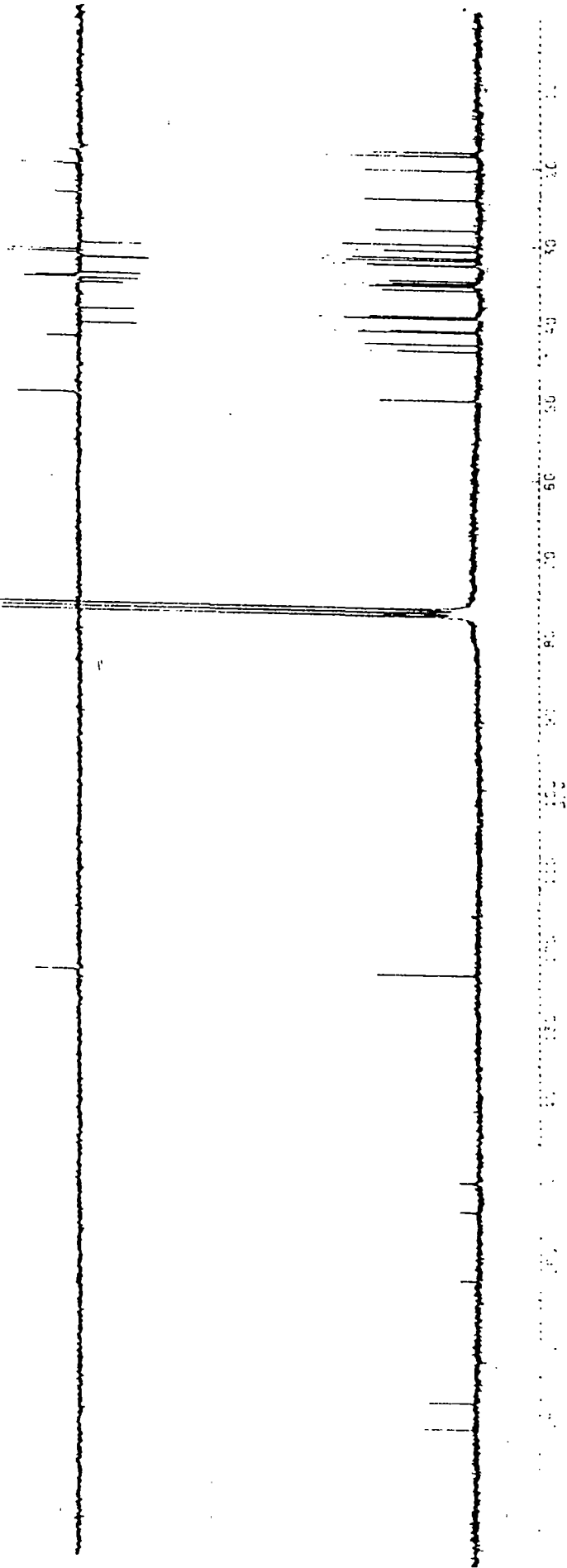
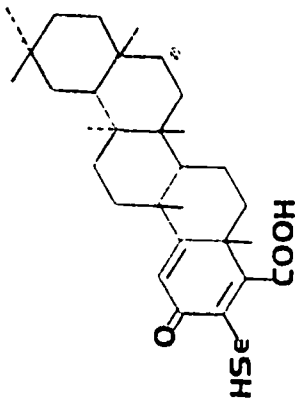


Fig. 10. <sup>13</sup>C NMR spectrum of compound B

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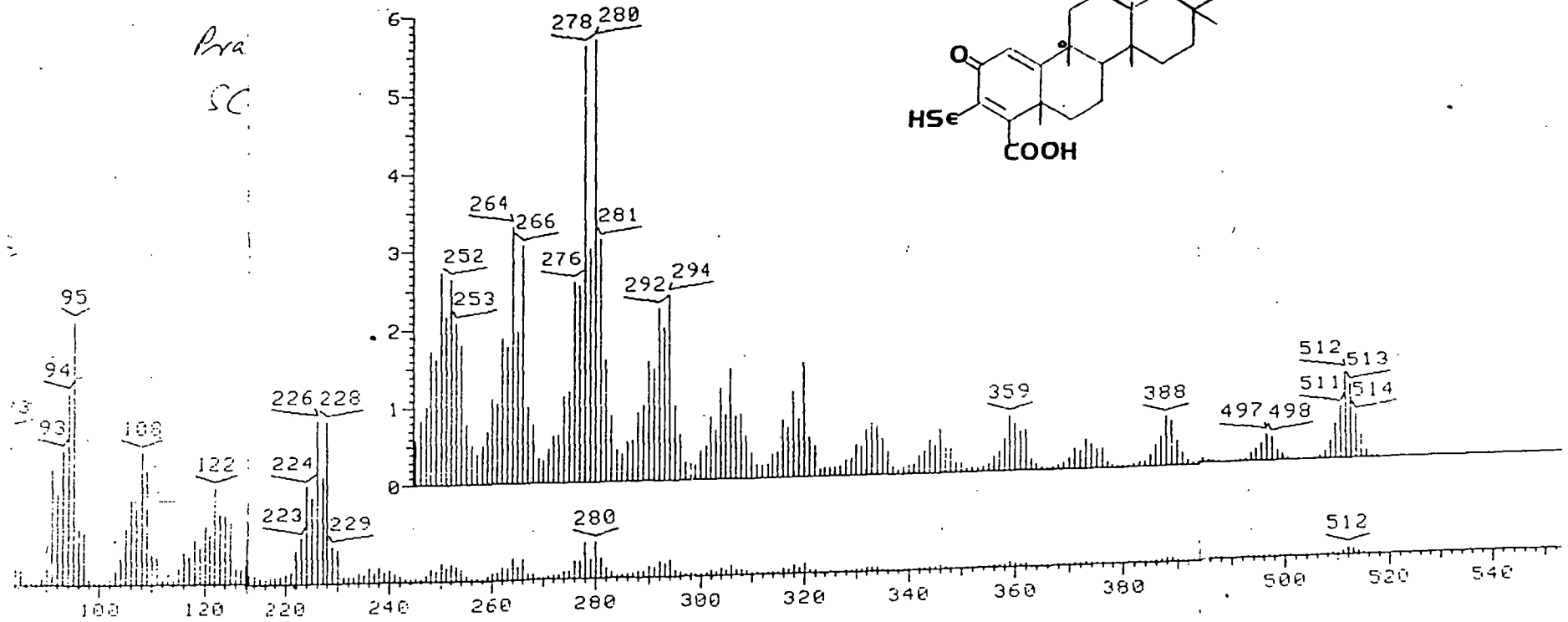
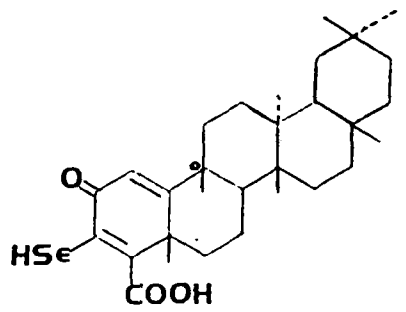


Fig. 11. Mass spectrum of compound 8

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EXPERIMENTAL

Isolation of Friedelin :

Air-dried milled cork (500 g) was extracted exhaustively with petrol in a soxhlet apparatus for 20 hrs. On concentration of the solvent, the extract afforded a solid residue (A) which was collected by filtration. Complete removal of solvent from the filtrate portion yielded a gummy solid residue (12 g). It was taken up in minimum amount of chloroform and then chromatographed in a column (48 cm x 4 cm) of silica gel (300 g) and eluted with petrol followed by solvents of increasing polarity. Fractions of 200 ml of each were collected and monitored by TLC.

Table - 5

Fraction numbers	Eluent	Residue on evaporation	Yield(mg)
1-5	Petrol	Waxy residue	200
6-10	Petrol : benzene (1 : 1)	Gummy residue	100
11-20	Petrol : benzene (1 : 1)	White solid	600 mp 258-64 IR $\nu_{\text{max}}$ 1700

Further elution did not afford any friedelin.

The residue 'A' and the white solid were indentical (Rf) on TLC and therefore mixed together and treated with chloroform (200 ml) and filtered. The filterate on concentration and cooling afforded white solid which was crystallised from chloroform-methanol to give needle shaped crystals (2.5 g) of pure friedelin mp  $265^{\circ}$ , IR :  $1700\text{ cm}^{-1}$ .

Preparation of friedlin oxime, 2 :

To friedlin, 1, (2.0 g) dissolved in pyridine (20 ml) was added hydroxylamine hydrochloride (1.2 g) and absolute alcohol and the mixture was refluxed for three hours. After the reaction was over the alcohol was ~~for~~ evaporated off and diluted with cold water. The precipitated solid was collected, washed with methanol and dried under suction. The solid (1.8 g) was crystallised from chloroform to afford friedlin oxime, 2, mp  $290-93^{\circ}$  identical with the authentic sample (TLC, IR, mp).

	% C	%H
Found :	81.52	11.1
Calculated for		
$\text{C}_{30}\text{H}_{50}\text{NO}$	81.82	11.36



OXIDATION OF FRIEDELIN OXIME WITH SELENIUM DIOXIDE IN TERTIARY BUTANOL

Isolation of compound A and B :

A mixture of friedelin oxime, 2, (1.5 g), selenium dioxide (2 g) and tertiary butanol (200 ml) was refluxed for 36 hours under nitrogen atmosphere. The solvent was distilled off under reduced pressure and the residue was extracted with ether. The ether extract was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue (1.3 g) obtained after removal of ether was dissolved in minimum amount of benzene and loaded on top of a silica column (60 g) developed in petrol. The column was then eluted with petrol followed by solvent of increasing polarity. The result has been tabulated (Table 6) as shown.

Table - 6

Eluent	Fractions 50 ml	Residue on evaporation	Yield (mg)
1. Petrol	1-4	Nil	Nil
2. Petrol: benzene(4:1)	5-7	Nil	Nil
3. Petrol: benzene(3:2)	8-10	Nil	Nil
4. Petrol: benzene(2:3)	11-13	Nil	Nil
5. Petrol: benzene(1:4)	14-16	Nil	Nil
6. Benzene	17-22	White solid, <u>A</u>	150
7. Benzene:EtOAc(19:1)	23-31	Nil	Nil
8. Benzene:EtOAc(9:1)	32-40	White solid, <u>B</u>	110

Further elution with more polar solvents did not afford any solid.

EXAMINATION OF FRACTIONS, 17-22 : ISOLATION OF COMPOUND, A

Fractions 17-22 were found to be identical on TLC, hence combined and solvent removed to yield a white solid A, which was crystallised twice from chloroform-methanol mixture to give a pure product, 4, mp 295-97<sup>o</sup> identified on the basis of its physical data.

Analysis report :

	% C	% H
Found	68.8	7.9
Calculated for	70.04	8.77
$C_{30}H_{45}ONSe$		
UV ( $\lambda_{max}$ )	254, 307 nm	
IR (Nujol) $\nu_{max}$	1675 $cm^{-1}$	
MS	m/z 514, 391, 362, 282, 226, 179	
PMR (CDCl <sub>3</sub> )	$\delta$ 0.93, 0.97, 0.99, 1.04, 1.18, 1.27, (7 s, 21H, 7 Me); 2.70(dd) + 2.752(dd) (J = 19.5 Hz, 12.5 Hz); 1.91(dd) (J = 12.5 Hz, 3 Hz) (H-C-C-C = O); doublet of a triplet (J = 13 Hz) (C-18 proton); 9.04 (one olefinic proton, the double bond being in conjugation with other double bonds, non-bonding electrons, ketone functional group)	

EXAMINATION OF FRACTIONS, 32-40 : ISOLATION OF COMPOUND, B

Fractions 32-40 were combined after finding them to be identical on TLC. Removal of solvent under reduced pressure yielded a solid B which was crystallised from chloroform-methanol mixture to give a pure product, 5, mp 296<sup>o</sup> identified on the basis of its physical data.

Analysis report :

	% C	% H
Found	: 64.5	8.15
Calculated for	: 67.8	8.28
$C_{30}H_{44}O_3Se$		
UV ( $\lambda_{max}$ )	: 274, 312 nm	
IR (Nujol) $\gamma_{max}$	: 1660-70 $cm^{-1}$ , 2700-3500 $cm^{-1}$	
MS	: m/z 512, 388, 359, 294, 280, 228, 122	
PMR ( $CDCl_3$ )	: $\delta$ 0.92, 0.93, 0.99, 1.12, 1.18, 1.33, 1.58 (7 s, 21H, 7 Me); 6.42 (an olefinic proton $\alpha$ to a lactone); 9.26 (Carboxyl proton)	

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