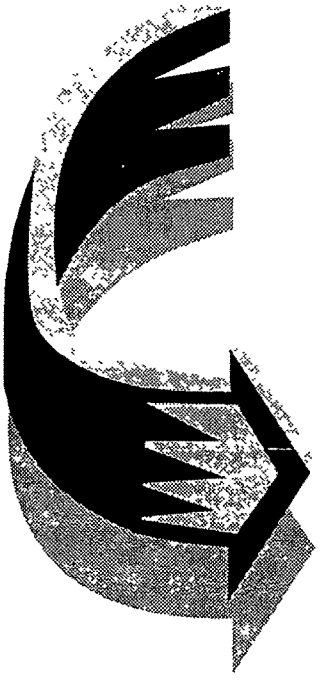
CHAPTER: V

A NEW, SIMPLE METHOD FOR OXIDATIVE ACETYLATION OF SOME SUBSTITUTED PHENOLS



V.1 ABSTRACT

A new simple method for the oxidative acetylation of some substituted phenols is described herein for the preparation of corresponding acetoxycyclohexa-3,5-dienones. A novel diacetoxycyclohexadienone has also been prepared using present method from salicyl alcohol, which can serve as a potential intermediate for the synthesis of various tricyclopentanoidal products like coriolin, capnellene and hirsutene. The structure of diacetoxycyclohexadienone were deduced from their high field PMR, ^{13}CMR, IR, mass, UV and other analytical data.

V.2 INTRODUCTION AND OBJECTIVES

Polycyclopentanoids, the compounds possessing fused cyclopentane rings, continue to receive increasing attention because of their intricate molecular framework and also owing to the diverse biological properties exhibited by some of the members.[1-3]

Presently, well over hundred such natural products are known in literature.[4] These natural products are fairly widely distributed in the nature and have been isolated from terrestrial plants,[5] marine organisms,[6] fungi and insects.[7]

Compounds containing three cyclopentane rings fused together are known as "triquinanes" and amongst the natural polyquinanes they are the most abundant.[8]

The triquinane natural products embody the two C_{11} tricyclopentanoid skeleta **1** and **2** (Figure: V.1) incorporating three linearly and angularly fused five membered rings respectively as the fundamental ring system.

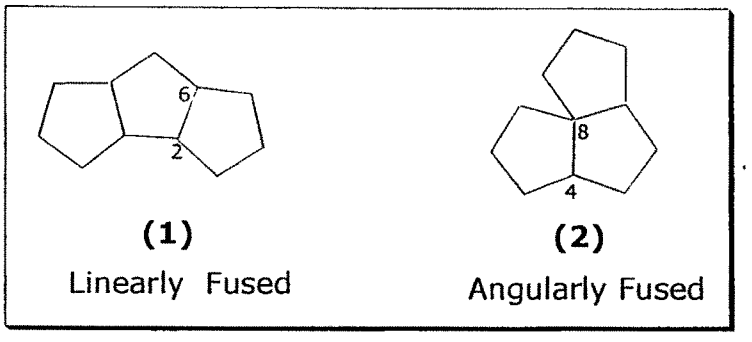


Figure: V.1

Three families of C_{11}-carbocyclic skeleta based on **1** are known, namely (i) Hirsutane family, (ii) Capnellane family and (iii) Pleurotellane family. Similarly, five families based on **2** are known. They are (i) Isocomene family, (ii) Pentalenene family, (iii) Silphinene family (iv) Silphiperfolene family and (v) Subergorgic acid family.[9]

The class of linearly fused tricyclopentanoids is further divided depending upon the mode of fusion of the third cyclopentane ring "C". The two isomers **3** and **4** (Figure: V.2) are termed as *cis-anti-cis* and *cis-syn-cis* respectively.

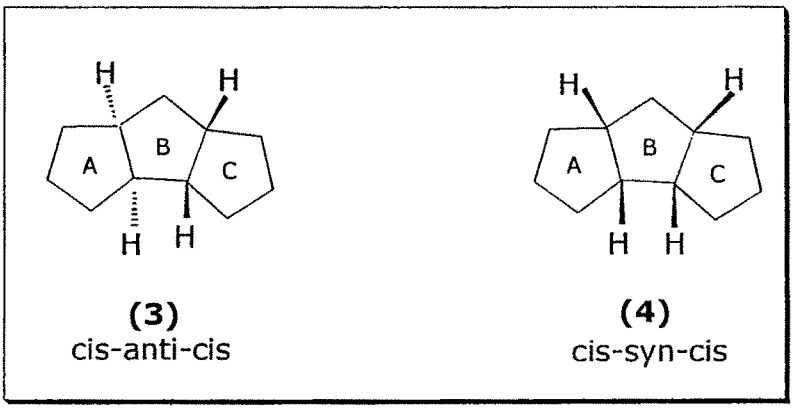


Figure: V.2

These two tricyclic parent hydrocarbons have not been characterized, but it has been shown by E. Osawa and co-workers[10] that there is only slight difference between the stabilities of **3** and the hindered fold form **4**, the *cis-anti-cis* being more stable than the *cis-syn-cis* isomer due to its chair like conformation.[11]

The *cis-anti-cis* isomer has received greater attention because it constitutes the basic carbocyclic framework of biologically important sesquiterpenoids like hirsutic acid **5**, coriolin **6**, capnellene **7** and hirsutene **8** (Figure: V.3).[12,13]

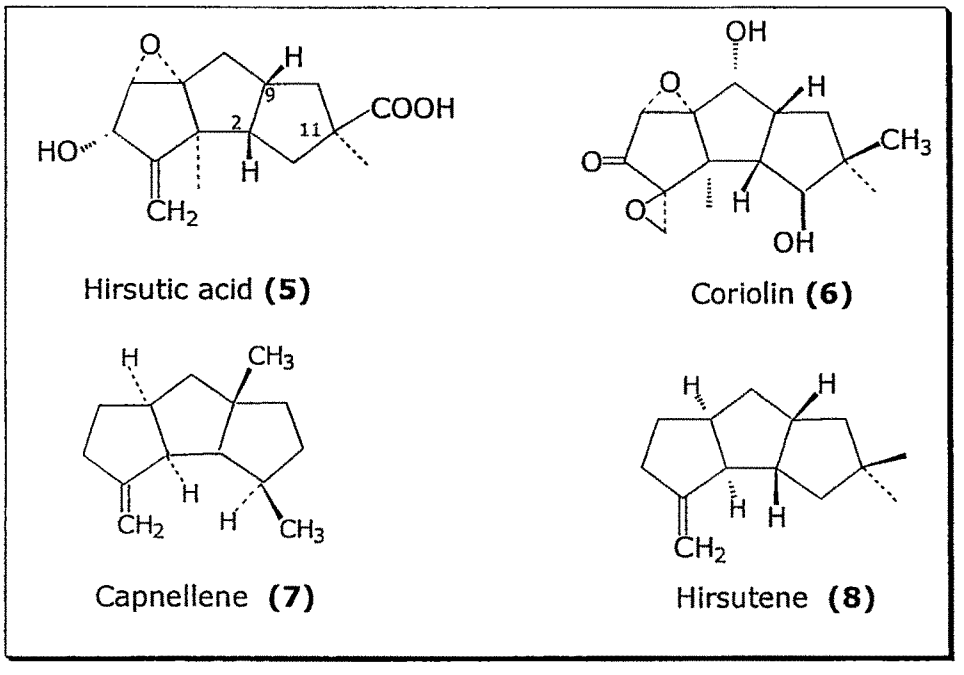
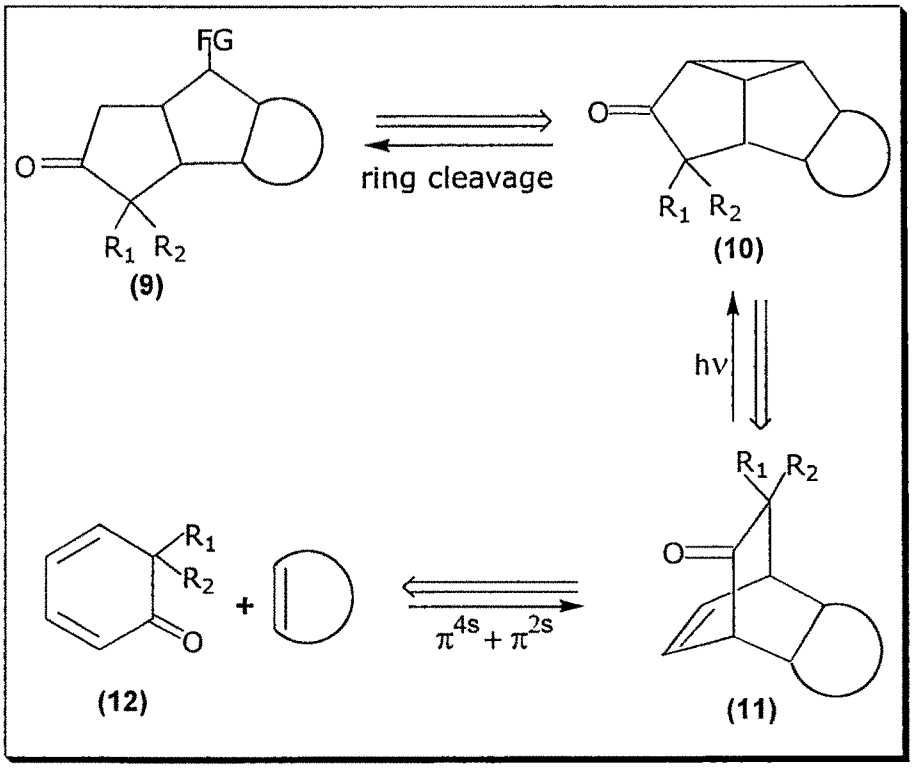


Figure: V.3

The fact that polyquinanes exhibit diverse biological activity has generated great interest in their chemistry. For example, hirsutic acid **5** is shown to possess antibiotic properties,[14] while coriolin **6** shows antibacterial and antitumour activity.[7b] Capnellene **7** and its

congeners have been suggested to act as chemical defense agents to inhibit growth of microorganisms and prevent larval settlement.[15,16] Though a variety of methods have been developed for the construction of tricyclopentanoid framework, most of them are target specific, lacking adaptability and involve multi-step sequences.[17,18] Earlier Singh *et al* reported[19] a unified approach towards the synthesis of linearly fused triquinanes of the type **9** via a peripheral ring cleavage of tetracyclic intermediate **10** which is easily obtainable from the key intermediate **11** via photochemical oxa-di-π-methane rearrangement (Scheme: V.1).[20]

The chromophoric system **11** was thought to be obtained via an inverse electron demand $\pi^{4s}+\pi^{2s}$ cycloaddition between a cyclohexa-2,4-dienone of the type **12** and a suitable dienophile (Scheme: V.1).



Scheme: V.1

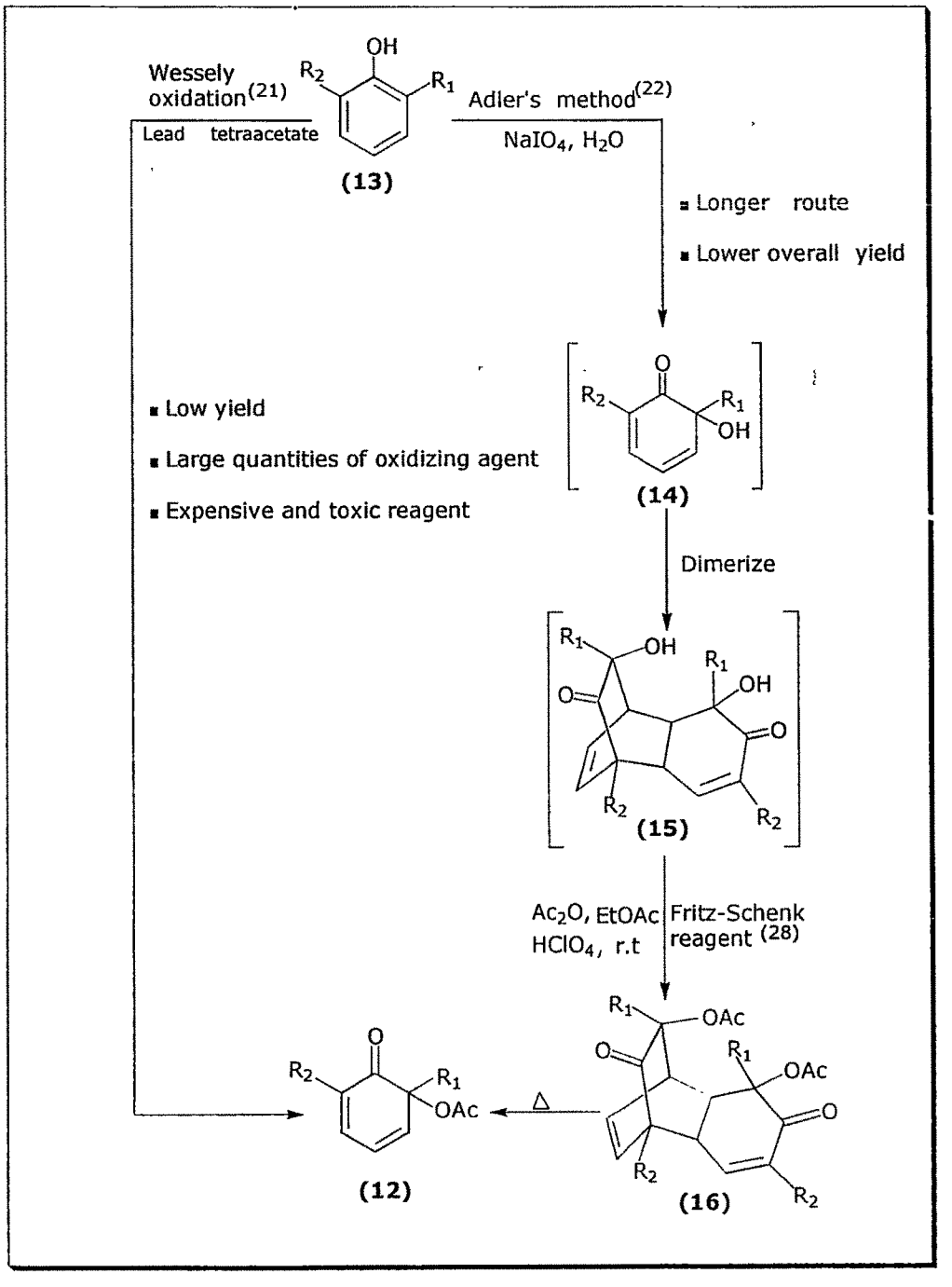
Based on the retrosynthetic plan shown in Scheme: V.1, a strategy was devised to accomplish the triquinane framework as shown in Scheme: V.2.[19a] It should be mentioned here that this approach is highly dependent on the easy availability of the cyclohexadienone **12**, via a high yielding process.

Though, 2,4-cyclohexadienones such as **12** are well known intermediates in the literature, only a few methods are reported in the literature for their preparation. The oxidation of phenols with lead tetraacetate, known, as 'Wessely oxidation'[21] is a generally used method for the preparation of 2,4-cyclohexadienones (o-quinol acetate). However, it often proceeds in low yield and furnishes a mixture of products depending upon the nature of the substituents on the aromatic rings. Furthermore, it requires rather large quantities of the expensive and toxic oxidant. Alternatively, o-quinols can also be prepared in the dimeric form by the periodate oxidation of phenols as investigated by Adler *et al.*[22] Occasionally, diacyl peroxide[23] and trifluroperoxyacetic acid[24,25] have also been used.

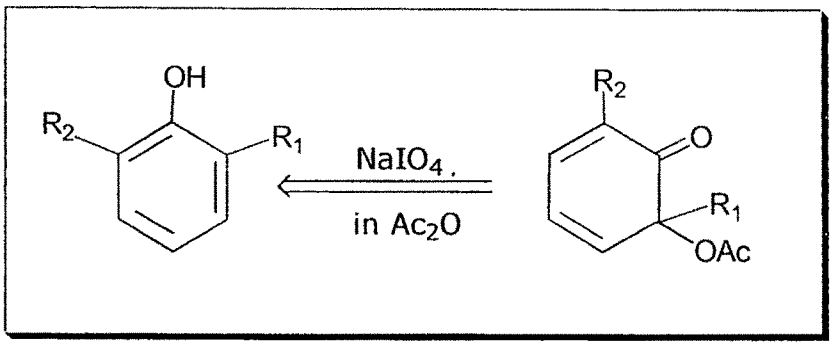
Wessely oxidation method gives acetoxycyclohexadienones **12** (Scheme: V.2) in one step albeit in low yields. On the other hand, Adler's method gives relatively better yields but results in the formation of a diol dimer of the type **15**, which had to be acetylated to the corresponding dimeric diacetate **16**, using Fritz-Schenk reagent. The dimeric diacetate was then pyrolzed to furnish the acetoxycyclohexadienone **12** resulting in lower overall yield through a longer route. A comparison of these two methods is presented in Scheme: V.2.

This prompted us to explore the reaction of substituted phenols with periodate in acetic anhydride medium. It was thought that the oxidative acetylation of phenol *in situ* would give the corresponding

acetoxycyclohexa-3,5-dienone directly in one step, as depicted below in Scheme: V.3.



Scheme: V.2



Scheme: V.3

V.3 RESULTS AND DISCUSSION

Towards accomplishing the above-mentioned objective, 2,6-dimethyl phenol **17** (Figure: V. 4) (4.0 g, 0.032 mole, excess) in acetic anhydride (20 mL) was treated with sodium metaperiodate (10.0 g, 0.046 mole) in portions, under stirring to obtain 2-acetoxy-2,6-dimethyl-3,5-cyclohexadienone **18** (32 %) and its diacetate dimer **19** (36 %).The reaction mixture was poured into a saturated solution of sodium bicarbonate (125 mL) and stirred vigorously to neutralize the excess acid. The aqueous layer was then extracted with ethyl acetate (4 × 25 mL) and the combined organic extracts were washed further with saturated sodium bicarbonate, water and brine solution followed by chromatography. All the physical and spectral characteristics of compounds **18** and **19** were in excellent agreement with those reported in the literature.[22d]

The IR spectrum of **18** (Figure: V.5) showed an absorption band at 1739 cm^{-1} diagnostic of a carbonyl group along with strong bands at 1674 cm^{-1} and 1620 cm^{-1}.[26] It showed a band at 295 nm in its UV

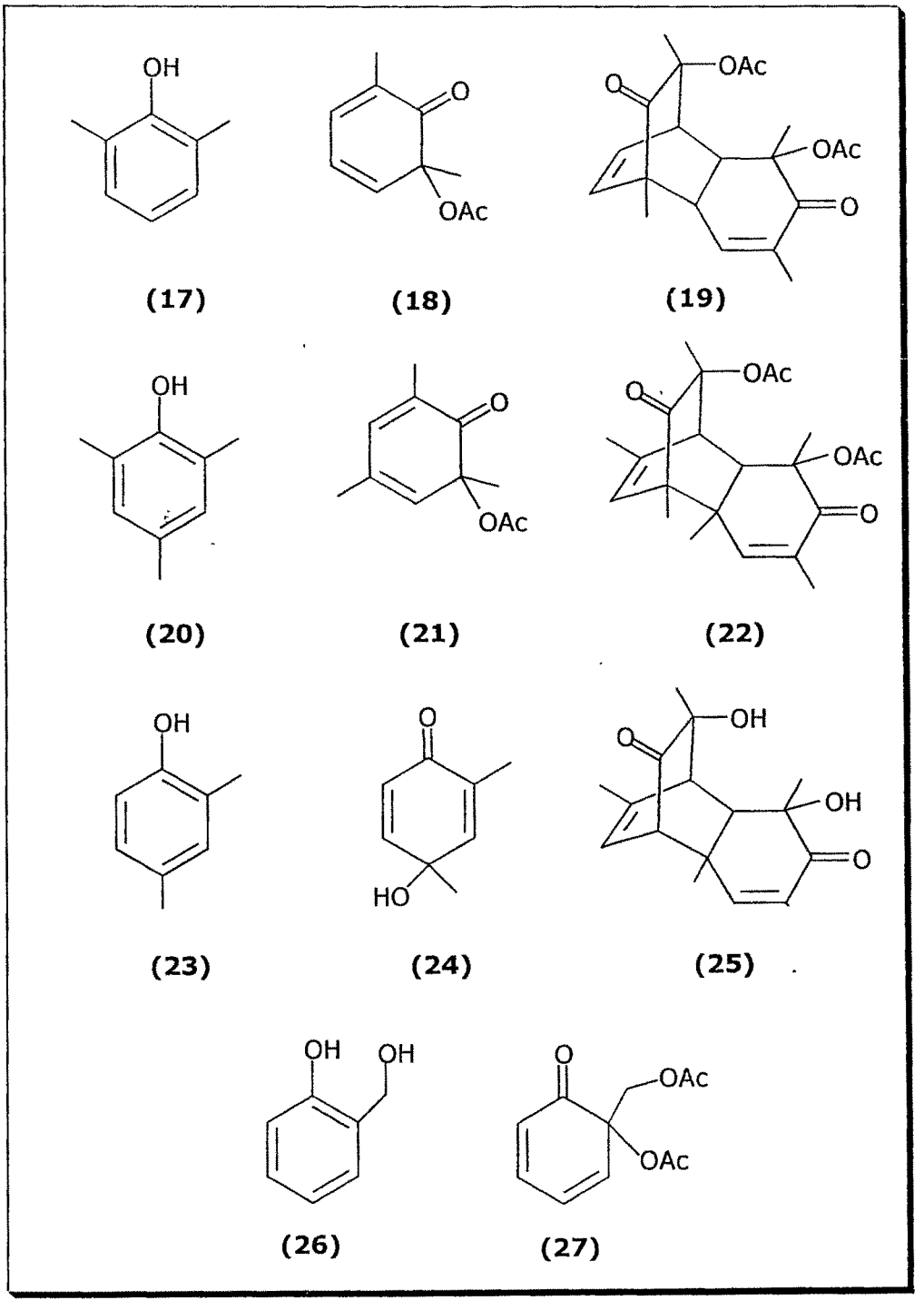

OH
O
OAc
OAc
OAc
O
O
(17)
(18)
(19)
OH
O
OAc
OAc
O
O
(20)
(21)
(22)
OH
O
HO
OH
OH
O
O
(23)
(24)
(25)
OH
OH
OAc
OAc
O
(26)
(27)

Figure: V.4

spectrum, which clearly exhibited the features of a conjugated cyclic ketone.

The compound **19** was characterized as diacetate dimer based on its PMR, UV, mass, IR and other data. The IR, UV, elemental analysis and melting point of the compound **19** were in close agreement with those reported in the literature.[22d] The analysis of the substance, m.p 158-160°C [lit.[22d] 159-160°C] indicated the composition as $C_{20}H_{24}O_6$ corresponding to a dimeric oxidation product of **17**. The compound **19** showed a band at 241 nm (calculated 237 nm) in its UV spectrum. These features were indicative of an α,β-unsaturated ketone moiety in structure **19**. The IR spectrum (Figure: V.6) showed absorption band at 1744 cm^{-1} diagnostic of carbonyl group in α-keto ester. The strong bands at 1698 cm^{-1} and 1654 cm^{-1} showed the presence of conjugated carbonyl group.

The PMR spectrum of the diacetate dimer **19** (Figure: V.7) gave signals at δ_H 6.26 (dd, 1H at C_{11}) and 5.62 (d, 1H at C_{12}) for olefinic protons, 3.72 (d, 1H at C_8) was assigned to the bridgehead proton, whereas the signal 3.44 (d, 1H at C_2) was assigned to the proton at allylic ring junction. It further gave signals at 2.17 (s, 3 H), 2.10 (s, 3 H) for acetate methyls and 1.82 (s, 3 H, CH_3), 1.71(s, 3 H, CH_3), 1.49 (s, 3 H, CH_3) and 1.39 (s, 3 H, CH_3). The mass spectrum of **19** (Figure: V.8) gave following fragmentation pattern: m/z 361(M+1), 300 (M-CH_3COOH), 241[M-(2 × CH_3COOH)], 181[(M+1)-monomer] 347, 259, 213, 139 etc and was correctly analyzed for the molecular formula $C_{20}H_{24}O_6$. It should be mentioned here that the PMR and mass spectra of compound **19** were not reported earlier.[22d]

Encouraged by these results, we attempted this method on other substituted phenols. Accordingly, 2,4,6-Trimethylphenol **20** was treated in similar way to obtain the corresponding acetoxy-

cyclohexadienone **21** (30 %) along with its diacetate dimer **22** (33 %) after usual work up and chromatography.

The IR, UV, melting point and elemental analysis of the compound **21** were also in good agreement with those reported in the literature.[22d]

The IR spectrum of the **21** (Figure: V.9) showed an absorption band at 1735 cm^{-1} for the presence of carbonyl group in a α-keto ester and strong bands at 1695 cm^{-1} and 1651 cm^{-1} for the presence of a conjugated carbonyl group.[26]

The IR, PMR and mass spectra of the compound **22** are shown in the Figures: V.10-12. The IR, UV, melting point and elemental analysis of the diacetate dimer **22** were in good agreement with those reported in literature.[22d]

The IR spectrum of the **22** (Figure: V.10) showed an absorption band at 1713 cm^{-1} for carbonyl group in a α-keto ester. The PMR spectrum of the compound **22** (Figure: V.11) displayed signals at δ_H 5.93 (s, 1H, olefinic), 5.12 (d, 1H at C_7), 3.53 (d, 1H, ring junction), 2.99 (s, 1H, bridgehead), 2.18 and 2.08 (s, 3H, CH_3 of each acetate), 1.79 and 1.75 (d, 3H, olefinic CH_3), 1.73 (d, 3H), 1.70 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.26 (s, 3H, CH_3) and 1.19 (s, 3H, CH_3). The mass spectrum of **22** (Figure: V.12) gave following fragmentation pattern: m/z 389 (M+1), 329 (M-CH_3COOH), 269 [M-(2 × CH_3COOH)] and 194 [(M+1)-monomer] and was correctly analyzed for the molecular formula $C_{22}H_{28}O_6$. It should be mentioned here that the PMR and mass spectra of compound **22** were not reported earlier.[22d]

When 2,4-dimethyl phenol **23** was treated in similar manner, we obtained the hydroxycyclohexadienone **24** (32 %) along with the dimer **25** (34 %), after usual work up and chromatography.

To our surprise, the corresponding hydrolyzed products were always obtained in our hands in this case. Although it is difficult to explain this result, it appears that the products might be under-going hydrolysis during the work-up.

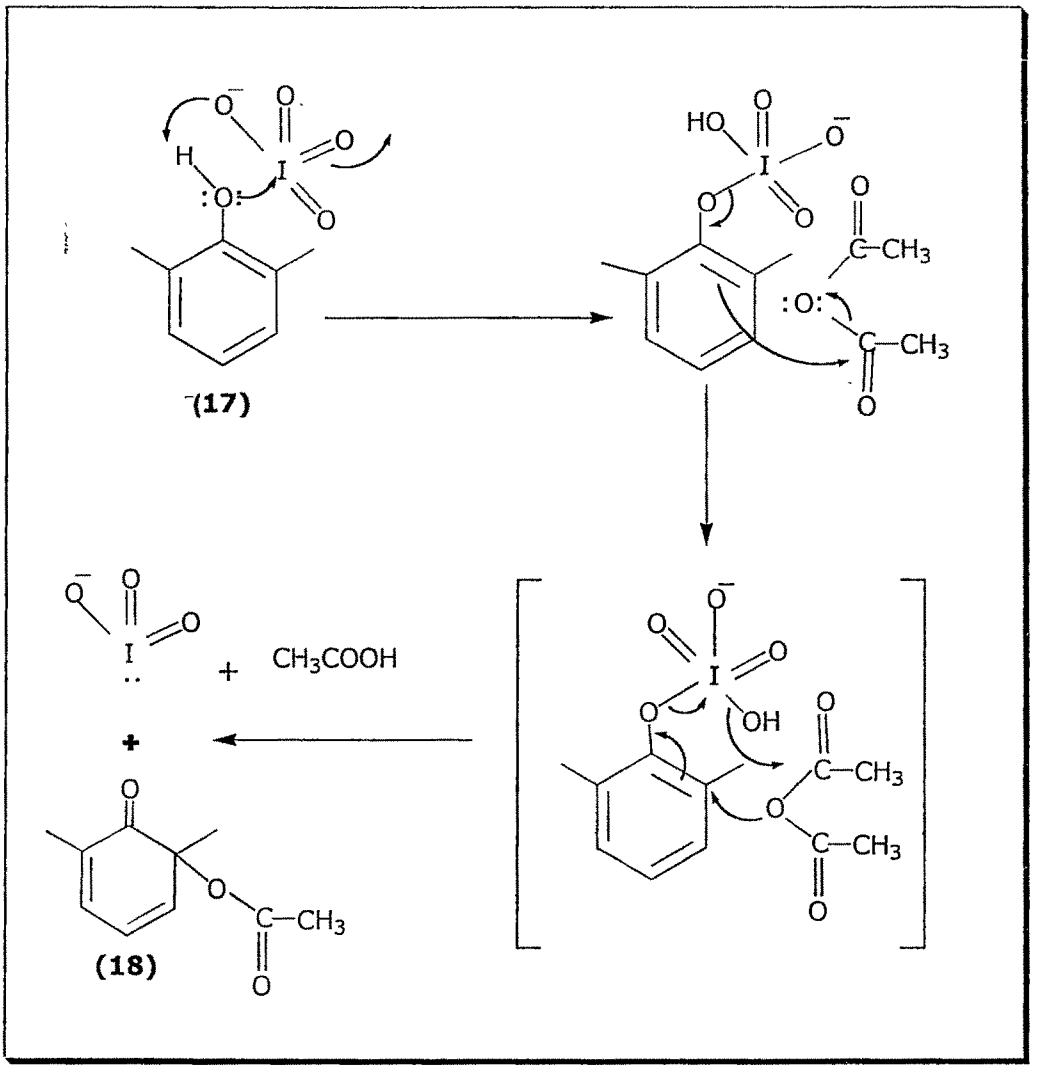
The IR, UV, melting point and elemental analysis of the compound **24** were in good agreement with those reported in the literature.[22b] The elemental analysis of the substance **24**, m.p 53-55°C (lit[22b] 53-54°C) indicated the composition as $C_8H_{10}O_2$.

The IR spectrum of the compound **24** showed an absorption band at 3456 cm^{-1} diagnostic of a hydroxyl group and a strong band at 1662 and 1631 cm^{-1} for the presence of a conjugated carbonyl group. The PMR spectrum of the compound **24** (Figure: V. 13) gave signals at δ_H 6.87 (d, 1H, olefinic-H), 6.81 (d, 1H, olefinic-H), 6.67 (m,1H at C_3, olefinic), 2.45 (s, 1H, OH), 1.89 (d, 3H, olefinic CH_3) and 1.5 (s, 3H, CH_3). The ^{13}CMR of the compound **24** (Figure: V.14) exhibited the carbonyl resonance at δ_c 186.83. The four olefinic carbons appeared at δ_c 152.67, 148.32, 134.28 and 127.61, while the carbon at OH appeared at 68.11. The olefinic methyl carbon appeared at 27.52 and methyl carbon at 16.20. It should be mentioned here that the PMR and ^{13}CMR spectra of the compound **24** were not reported earlier.[22b]

The compound **25** also gave matching spectral and analytical characteristics with those reported in the literature.[22b] Its IR spectrum showed bands at 3425 and 1681 cm^{-1}. The PMR spectrum of the compound **25** (Figure: V.15) displayed signals at δ_H 6.21 (d, 1H, olefinic-H), 6.07 (d, 1H, olefinic-H), 5.45 (d, 1H, olefinic-H), 3.85 (s, 1H, OH), 2.85 (d, 1H, bridgehead at C_1), 2.18 (s, 1H,OH), 1.74 (s, 3H, olefinic CH_3), 1.58 (s, 3H, CH_3), 1.46 (s, 3H, CH_3) and 1.26

(s, 3H, CH_3). It should be mentioned here that the PMR spectrum of compound **25** was also not reported earlier.[22b]

The probable mechanism of this oxidative acetylation is delineated in Scheme: V.4.[27]



Scheme: V.4

In continuation with this study, we have also prepared a novel diacetoxycyclohexadienone **27** from salicyl alcohol **26** using present method.

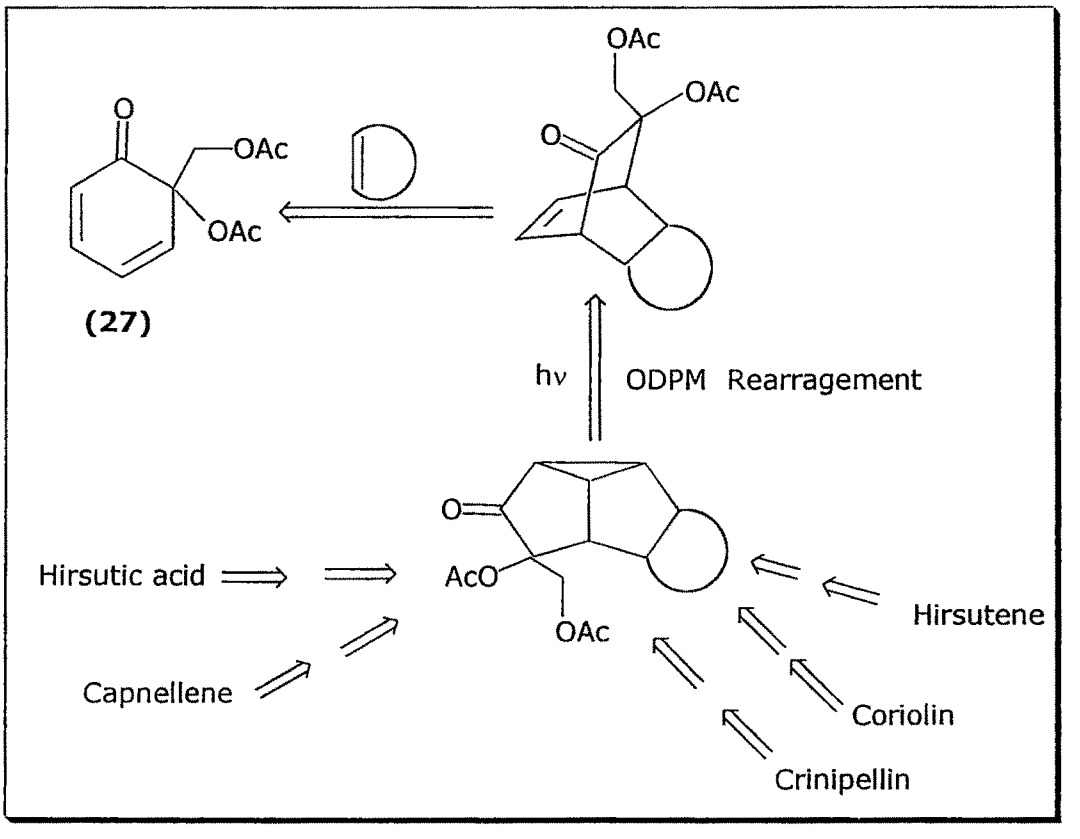
Thus, when salicyl alcohol **26** was subjected to similar oxidation, a novel diacetoxycyclohexadienone (2-acetoxy-2-acetoxymethyl-3,5-cyclohexadienone) **27** was obtained in 53 % yield after usual work-up and chromatography. The structure of the diacetate **27** was fully deduced from its IR, UV, PMR, ^{13}CMR, mass spectra and elemental analysis. It showed a strong band at 1740 cm^{-1} in addition to the characteristic carbonyl doublets at 1625 and 1570 cm^{-1} in the IR spectrum (Figure: V.16).[26] Its UV spectrum showed a band at 300 nm (calculated 302 nm[28]), indicating the presence of a 2,4-cyclohexadienone.

Its PMR spectrum (Figure: V.17) showed signals at δ 7.51(dd, J_1= $6H_z$ J_2 =$2H_z$, 1H) and 7.41 (dd, J_1= $8H_z$ J_2= $6H_z$, 1H) for δ and γ olefinic protons. The resonances observed at δ 7.35 and 7.12 were assigned to the protons at β and α positions respectively. It further gave signals at δ 5.1 (s, 2H) for methylene protons in the acetate environment and 2.3 and 2.1 (both s, 3H) for acetate methyls.

The ^{13}CMR (Figure: V.18) of **27** exhibited carbonyl resonance at δ_c 150.16, two-acetate carbonyls at δ_c 170.69 and 169.38. The olefinic carbons appeared at δ_c 130.62, 129.82, 128.45 and 126.36, the highly deshielded tetra substituted carbon at δ_c 122.98, methylene carbon at δ_c 61.90 and methyl carbons at δ_c 20.95. The mass spectrum (Figure: V.19) of **27** gave following fragmentation pattern m/z: M-43 ($CH_3C{\equiv}O^+$), M-60 (loss of CH_3COOH)[28] and was correctly analyzed for $C_{11}H_{12}O_5$. Table: V.1 summarizes the yields of various products, obtained in this oxidative acetylation method.

It should be noted that the yields by present method are found to be better than the Wessely oxidation method[21] (Lead tetraacetate) or Adler's method[22] (periodate-H_2O) followed by treatment of the resulting hydroxydienone dimer with Fritz-Schenk reagent.[29] The present method gives better yields of the cyclohexadienones (**18**, **21**, **24**, and **27**) in fewer steps from the corresponding phenols. Moreover it also avoids the use of the tedious Fritz-Schenk reagent, which selectively acetylates the 3° hydroxyl groups.[19,29]

It is worthwhile to mention here that the diacetoxycyclohexadienone **27**, can serve as a potential precursor for the synthesis of various natural products like coriolin, capnellene and hirsutene etc (Scheme: V.5).



Scheme: V.5

TABLE: V. 1

Sr. No	Phenol	**Cyclohexadienone**	(% yield)	**Dimer**	% yield
1	**17**	**18**	(32)	**19**	(36)
2	**20**	**21**	(30)	**22**	(33)
3	**23**	**24**[a]	(32)	**25**[a]	(34)
4	**26**	**27**	(53)	-	

[a]indicates corresponding hydroxy compound isolated

V.4 SUMMARY

In conclusion, we have demonstrated a new simple one-pot procedure for the preparation of acetoxycyclohexadienones, which eliminates the use of complex Fritz-Schenk reagent. A novel diacetoxycyclohexadienone **27** is also prepared by the present method from salicyl alcohol **26** that can serve as a potential precursor for the synthesis of various natural products like, coriolin, capnellene and hirsutene etc.

V.5 EXPERIMENTAL

General remarks:

Ultraviolet spectra were recorded a Perkin-Elmer Lambda-19 Spectrophotometer. IR spectra were recorded on a Perkin-Elmer PC-16 FTIR Spectrophotometer. PMR spectra (200 MHz) and ^{13}CMR (50 MHz) were recorded on a Bruker 200-FTNMR using $CDCl_3$ as solvent containing tetramethylsilane as an internal standard. Mass spectra were recorded on a Shimadzu QP-5050 A mass spectrometer. Microanalyses were performed on a Perkin-Elmer 2400 series II instrument.

Thin layer chromatographic analyses (TLC) was done on glass plates (7.8 × 2.5cm^2) using Acme's silica gel-G containing 13 % calcium sulphate as binder and the plates were prepared from the chloroform suspension. Visualization of the spots was achieved by exposure to iodine vapour. The reactions were monitored using TLC with suitable solvent systems for separation.

Column chromatography was performed using Acme's silica gel (60–120 mesh size) and the elution was done with light petrol and ethyl acetate mixtures. The fractions eluted from the column were concentrated under reduced pressure on a Buchi-RE 111 rotary evaporator.

Oxidative acetylation of 2,6-Dimethyl phenol (17)

To a stirred solution of 2,6-dimethylphenol (**17**, 4.0 g, 0.032 moles) in acetic anhydride (20 mL) was added sodium metaperiodate (10.0 g, 0.046 moles, excess) in portions over a period of 1 hour. Stirring was continued for further 5 hours at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was then poured into a saturated solution of sodium

bicarbonate (125 mL) and stirred vigorously to neutralize excess acetic acid. The aqueous layer was then extracted with ethyl acetate (4 × 25 mL) and combined organic extracts were washed further with saturated sodium bicarbonate (25 mL), then by water (25 mL) followed by brine solution (20 mL) and dried over anhydrous sodium sulphate.

The solvent was removed under reduced pressure to obtain a bright yellow liquid, which was chromatographed over silica gel with light petrol and ethyl acetate to give **18** as a pale yellow liquid (1.80 gm, 32 %), m.p. 32-35°C (lit.[22d,30] 34-35°C).

IR ν_{max} : 3020, 1739,1674,1620,1346 and 1226 cm^{-1}.

UV λ_{max} : 295 nm.

Analysis : Found C; 65.96 %, H; 6.43 %,

Requires C; 66.66 %, H; 6.66 %, for $C_{10}H_{12}O_3$.

Further elution of the column furnished compound **19** as white crystalline solid (3.94 gm, 36 %), m.p. 158-159°C (lit.[22d] 159-160°C).

IR ν_{max} : 3007, 2982, 1744, 1698,1654,1456,1368 and 700 cm^{-1}.

UV λ_{max} : 241 nm.

PMR δ_H : 6.26 (dd, 1H at C_{11}, olefinic), 5.61(d, 1H at C_{12}, olefinic), 3.72 (d, 1H at C_8, bridgehead), 3.44 (d, 1H at C_2), 3.0 (dd, 1H at C_7), 2.17 (s, 3 H, CH_3, at $COCH_3$), 2.10 (s, 3 H, CH_3 at $COCH_3$), 1.82 (s, 3H,CH_3, olefinic), 1.71 (s, 3 H, CH_3), 1.49 (s, 3H, CH_3) and 1.39 (s, 3 H, CH_3).

MS m/z : 361(M+1), 300 (M-CH_3COOH), 241[M-(2× CH_3COOH)] and 181 [(M+1)-monomer].

Analysis: Found C; 67.12%, H; 6.67 %,

Requires C; 66.66 %, H; 6.66 %, for $C_{20}H_{24}O_6$.

Oxidative acetylation of 2,4,6-Trimethyl phenol (20)

To a stirred solution of 2,4,6-trimethylphenol (**20,** 4.0 g, 0.029 moles) in acetic anhydride (20 mL) was added sodium metaperiodate (10.0 g, 0.046 moles, excess) in portions. Stirring was further continued for 4 hours at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was then poured into a saturated solution of sodium bicarbonate (125 mL) and stirred vigorously to neutralize excess acetic acid. The aqueous layer was then extracted with ethyl acetate (4 × 25 mL) and combined organic extracts were washed with saturated sodium bicarbonate (25 mL), then by water (25 mL) followed by brine solution (20 mL) and dried over anhydrous sodium sulphate.

The solvent was removed under reduced pressure to obtain a residue, which was chromatographed over silica gel with light petrol and ethyl acetate to give **21** as a white solid (1.79 g, 30 %), m.p. 80-82°C (lit.[22d] 82-84°C).

IR ν_{max} : 3078, 2855,1735,1719,1695 and 1651 cm^{-1}.

Analysis : Found C; 67.96 %, H; 7.39 %,

Requires C; 68.04 %, H; 7.21 %, for $C_{11}H_{14}O_3$

Further elution of the column furnished compound **22** as a white crystalline solid (3.74 g, 33 %), m.p. 164-166°C (lit.[22d]162-163°C).

IR ν_{max} : 3033, 2982, 2876, 1713, 1695, 1651, 1540, 1258, 1080, 1080, 834 and 725 cm^{-1}.

UV λ_{max} : 241 nm.

PMR δ_H : 5.93 (s, 1H, olefinic), 5.12 (d, 1H at C_7), 3.53 (d, 1H, ring junction), 2.99 (s, 1H, bridgehead), 2.18 and 2.08 (s, 3H, CH_3 of each acetate), 1.79 and 1.75 (d, 3H, olefinic CH_3) 1.73 (d, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.26 (s, 3H, CH_3) and 1.19 (s, 3H, CH_3).

MS m/z : 389 (M+1), 329(M-CH_3COOH), 269 [M- (2× CH_3COOH)] and 194 [(M+1)-monomer].

Analysis : Found C; 67.89 %, H; 7.54 %

Requires C; 68.04 %, H; 7.21 % for $C_{22}H_{28}O_6$.

Oxidative acetylation of 2,4-Dimethyl phenol (23)

To a stirred solution of 2,4-dimethylphenol (**23,** 4.0 g, 0.032 moles) in acetic anhydride (20 mL) was added sodium metaperiodate (10.0 g, 0.046 moles, excess) in portions. Stirring was further continued for 5 hours at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was then worked up as mentioned above. Drying (Na_2SO_4) followed by removal of solvent under reduced pressure furnished residue, which was chromatographed over silica gel with light petrol and ethyl acetate to give **24** as a white solid (1.45 g, 32 %), m.p. 53-55°C (lit.[22b] 53-54°C).

IR ν_{max} : 3456, 1662,1631,1292, 1130 and 1095 cm^{-1}.

UV λ_{max} : 239 nm.

PMR δ_H : 6.87 (d, 1H, olefinic-H), 6.81 (d,1H, olefinic-H), 6.67 (m,1H at C_3, olefinic), 2.45 (s, 1H, OH), 1.89 (d, 3H, olefinic CH_3) and 1.5 (s, 3H, CH_3).

^{13}CMR δ_C : 186.83 (ketonic carbon), 152.67, 148.32, 134.28 and 127.61 (four olefinic carbons), 68.11(carbon at OH), 27.52 (olefinic methyl carbon), 16.20 (methyl carbon).

Analysis : Found C; 69.65 %, H; 7.96 %,

Requires C; 69.56 %, H; 7.24 %, for $C_8H_{10}O_2$

Further elution of the column furnished compound **25** as a white crystalline solid (3.25 g, 34 %), m.p. 226-228°C (lit.[22b]237-238°C).

IR ν_{max} : 3425, 1720, 1681and 1643 cm^{-1}.

UV λ_{max} : 230 nm.

PMR δ_H : 6.21 (d, 1H, olefinic-H), 6.07 (d, 1H, olefinic-H), 5.45 (d, 1H, olefinic-H), 3.85 (s, 1H, OH), 2.85 (d, 1H, bridgehead at C_1), 2.18 (s,1H,OH),1.74 (s, 3H, olefinic CH_3), 1.58 (s,3H, CH_3), 1.46 (s,3H, CH_3) and 1.26 (s,3H, CH_3).

Analysis : Found C; 69.53 %, H; 8.87 %

Requires C; 69.56 %, H; 7.30 % for $C_{16}H_{20}O_4$.

Oxidative acetylation of salicyl alcohol (25)

To a solution of salicyl alcohol (**25**, 4.0 g, 0.032 moles) was dissolved in acetic anhydride (20 mL), was added sodium metaperiodate (10.0 g, 0.046 moles, excess) portion wise and the reaction mixture was stirred at room temperature for 3 hours. The completion of reaction was monitored by TLC. The reaction mixture was then worked up as mentioned above. The organic extracts after drying (Na_2SO_4) followed by removal of solvent under reduced pressure furnished a yellowish brown liquid, which was chromatographed over silica gel. The column was eluted with light petrol and ethyl acetate to furnish a pale yellow liquid **27** (3.78 g, 53 %), b.p. (235-240°dec.).

IR ν_{max}: 1740, 1625,1570,1491,1369,1226 and 753 cm^{-1}

UV λ_{max} : 300 nm,

PMR δ_H : 7.51(dd, J_1= 6H_z J_2 =2H_z 1H, δ olefinic-H), 7.41(dd, J_1= 8H_z J_2= 6H_z 1H, γ olefinic-H), 7.35 (dd, 1H,β olefinic-H), 7.12 (d, 1H, α olefinic-H), 5.12 (s, 2H, methylene proton), 2.3 (s, 3H, CH_3 at $COC\underline{H}_3$), 2.1(s, 3H, CH_3 at $COC\underline{H}_3$).

^{13}CMR δ_c : 20.95(sp^3 carbon), 61.90 (-CH_2- carbon), 122.98 (tetra

substituted carbon), 126.36, 128.45,129.82 and 130.62 (four olefinic carbons), 170.69, 169.38 (two acetate carbonyls), 150.16 (carbonyl carbon).

MS m/z : M-43 ($CH_3C{\equiv}O^+$) and M-60 (loss of CH_3COOH)

Analysis : Found C; 57.99 %, H; 5.18 %

Requires C; 58.92,% H; 5.35 % for $C_{11}H_{12}O_5$.

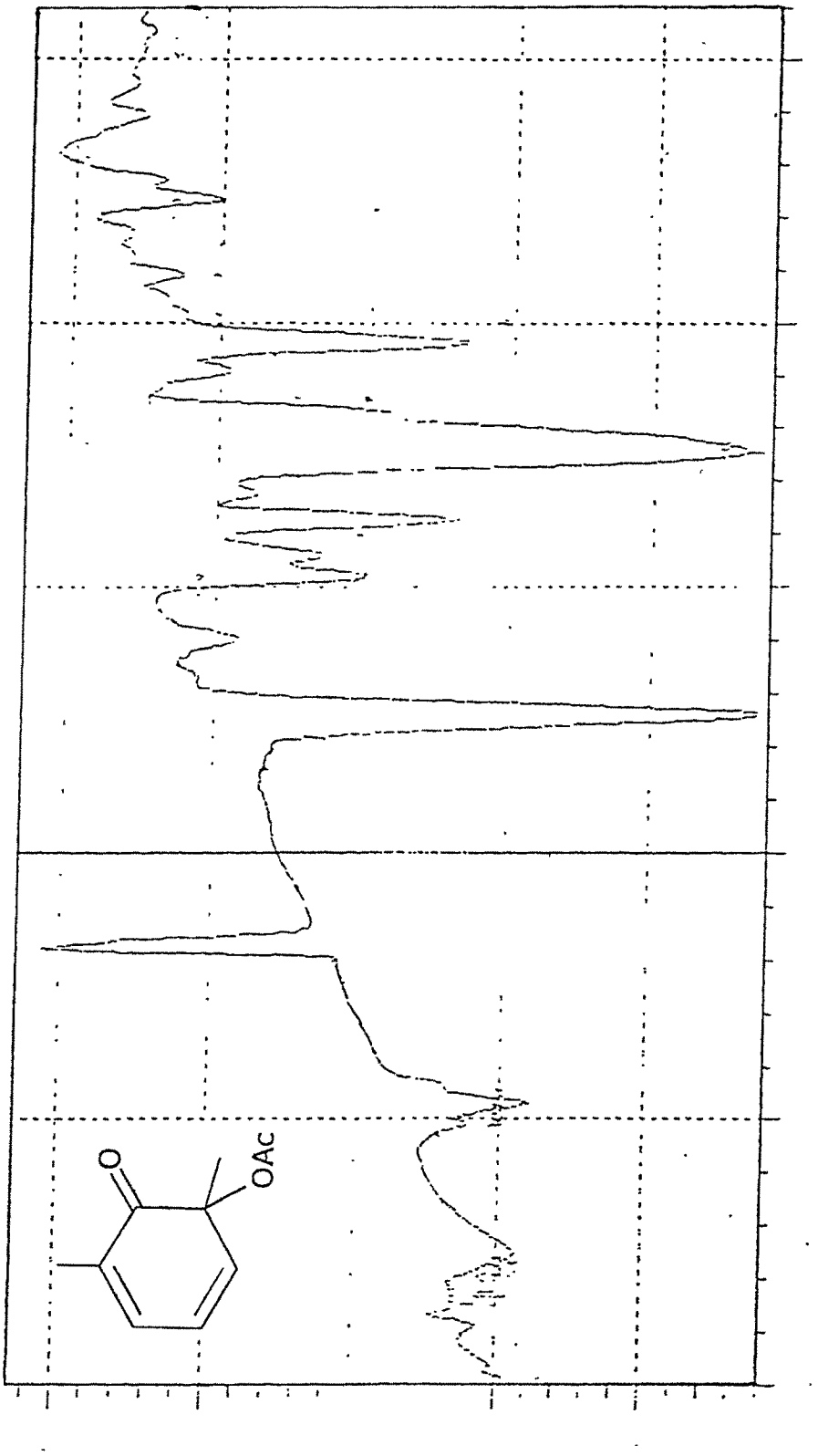


Figure V. 5 : IR Spectrum of the compound **18**

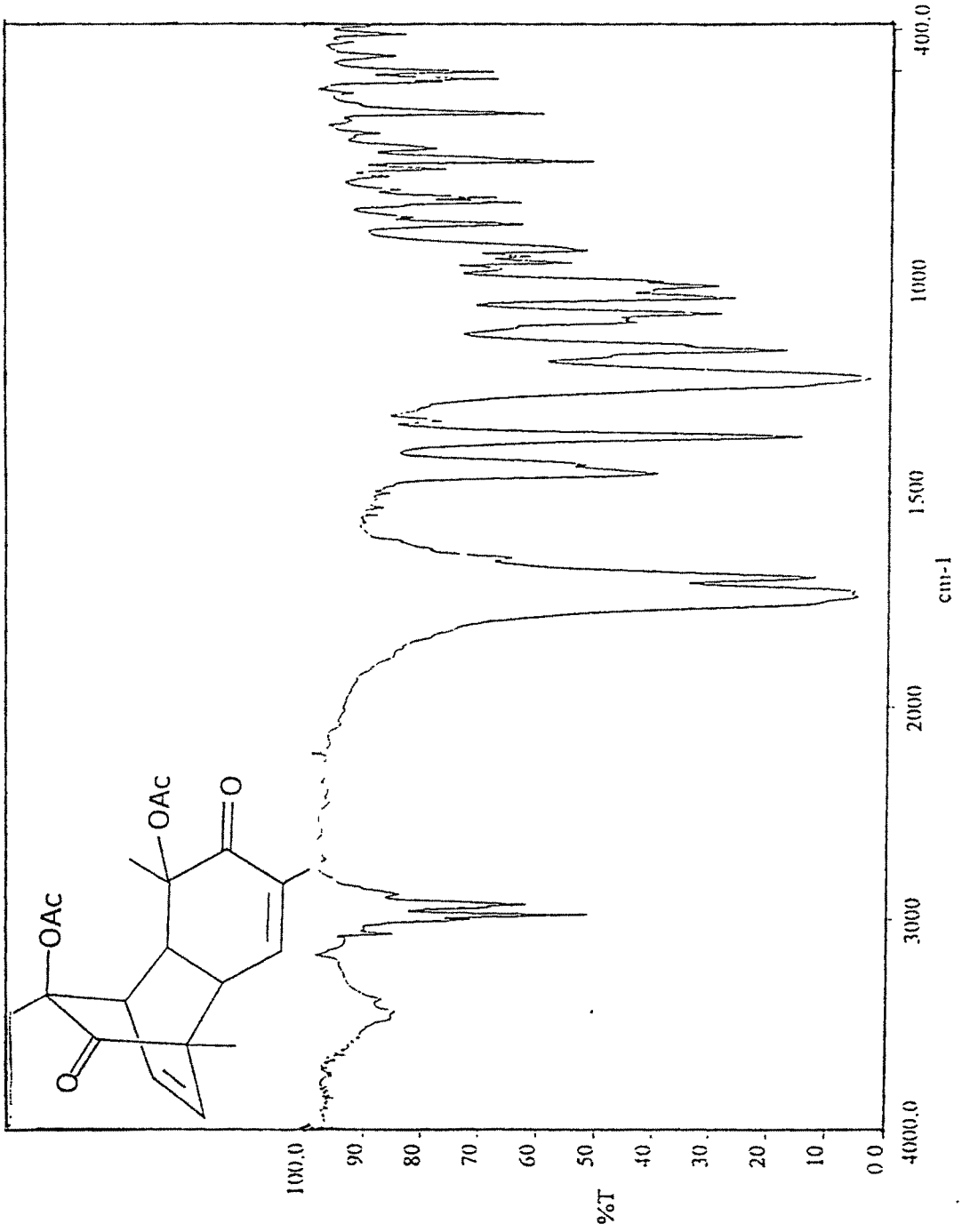


Figure V. 6 : IR Spectrum of the compound **19**

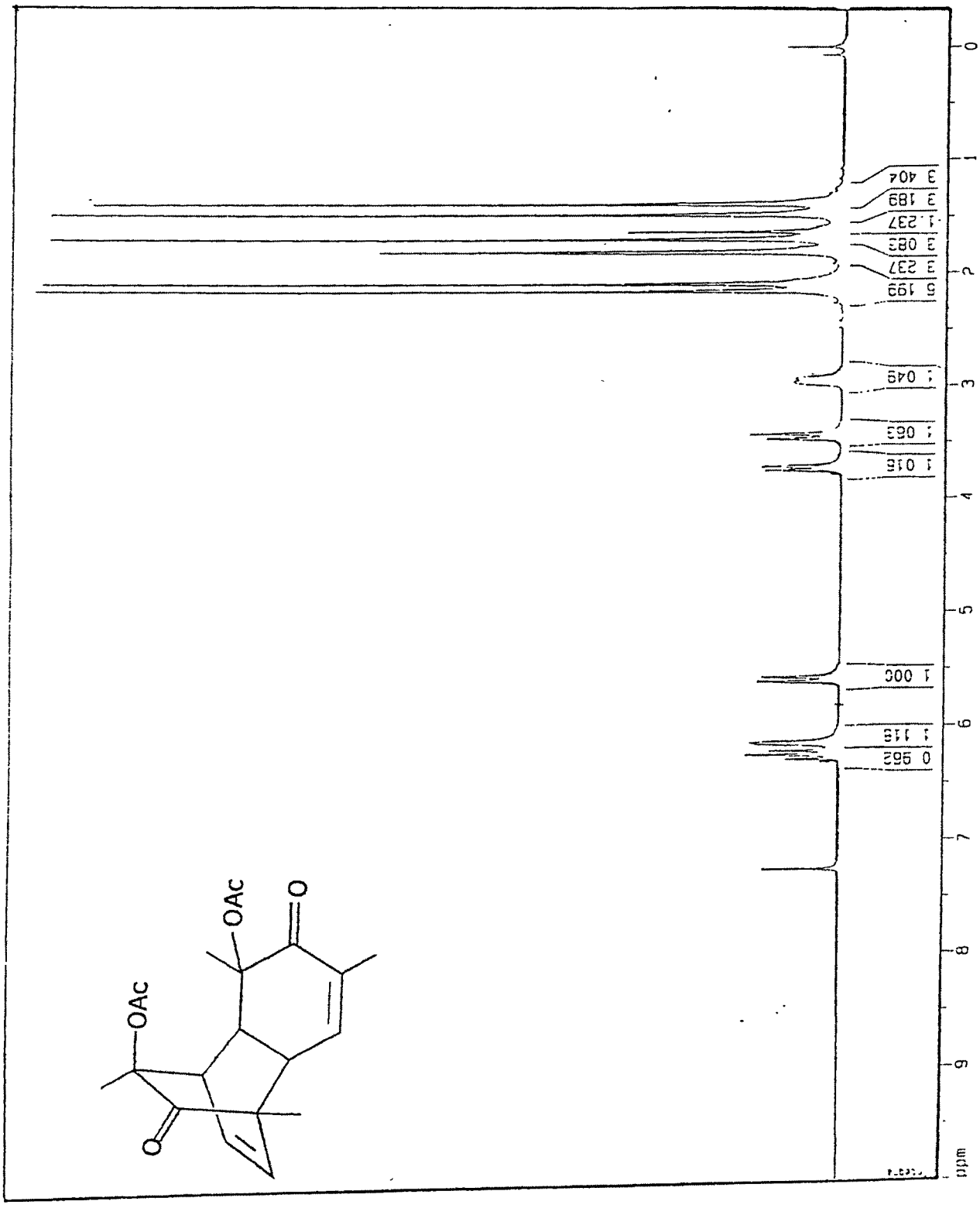


Figure V. 7 : PMR Spectrum (200 MHz) of the compound **19**

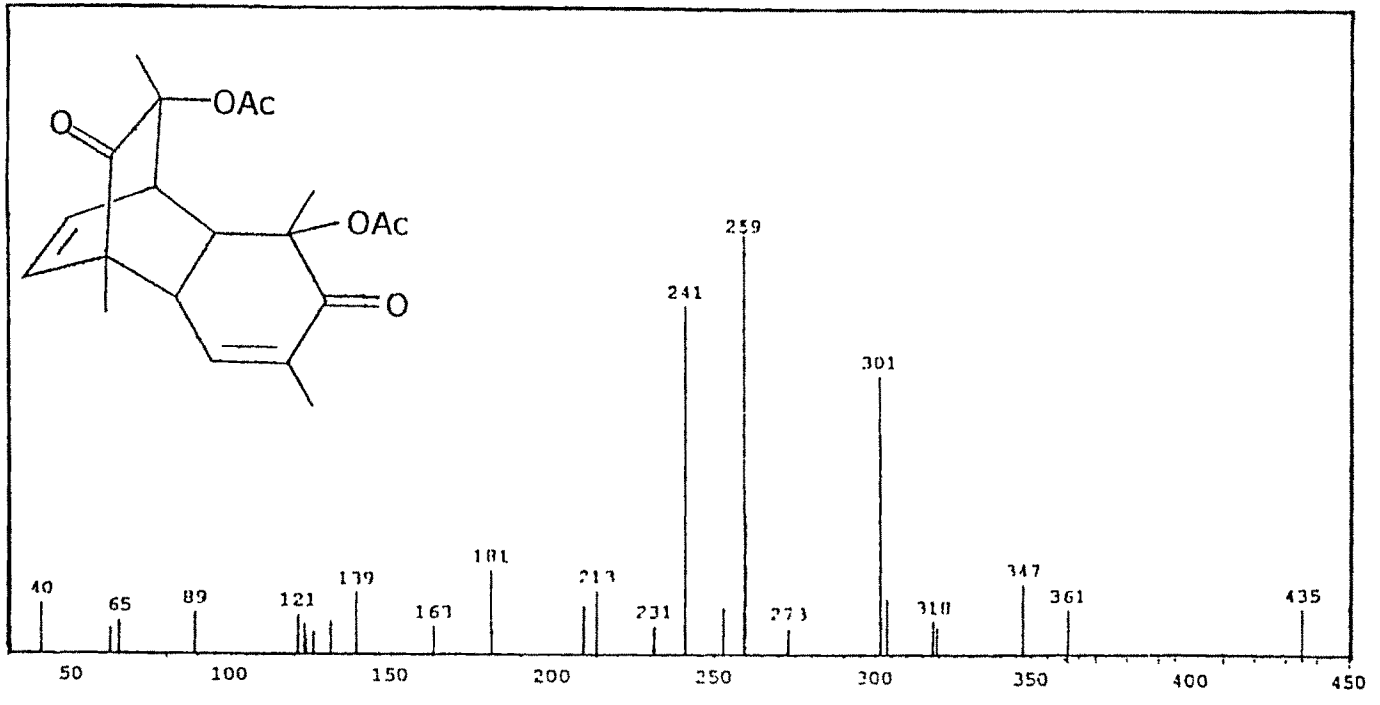


Figure V. 8 : Mass Spectrum of the compound **19**

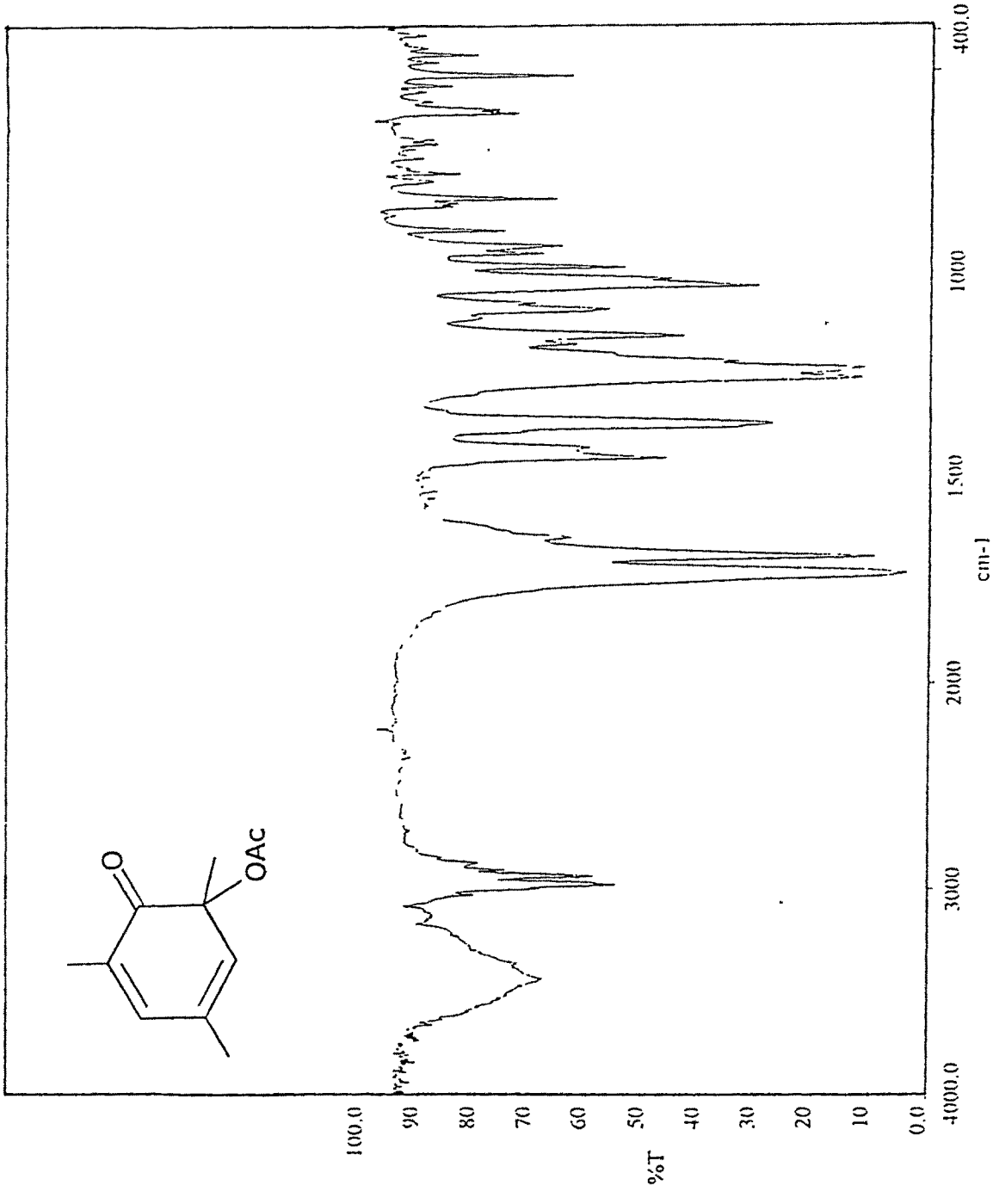


Figure V. 9 : IR Spectrum of the compound **21**

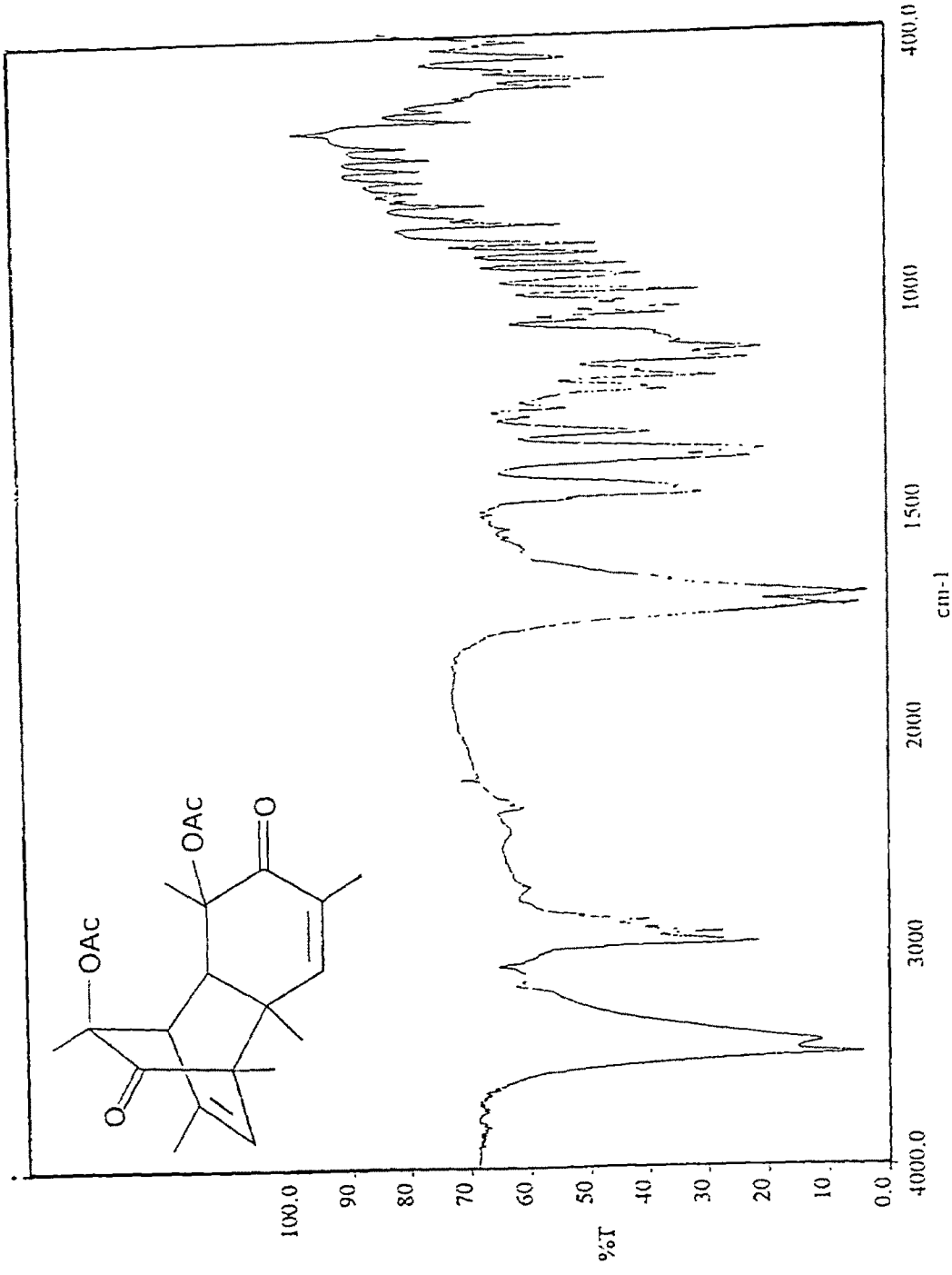


Figure V. 10 : IR Spectrum of the compound **22**

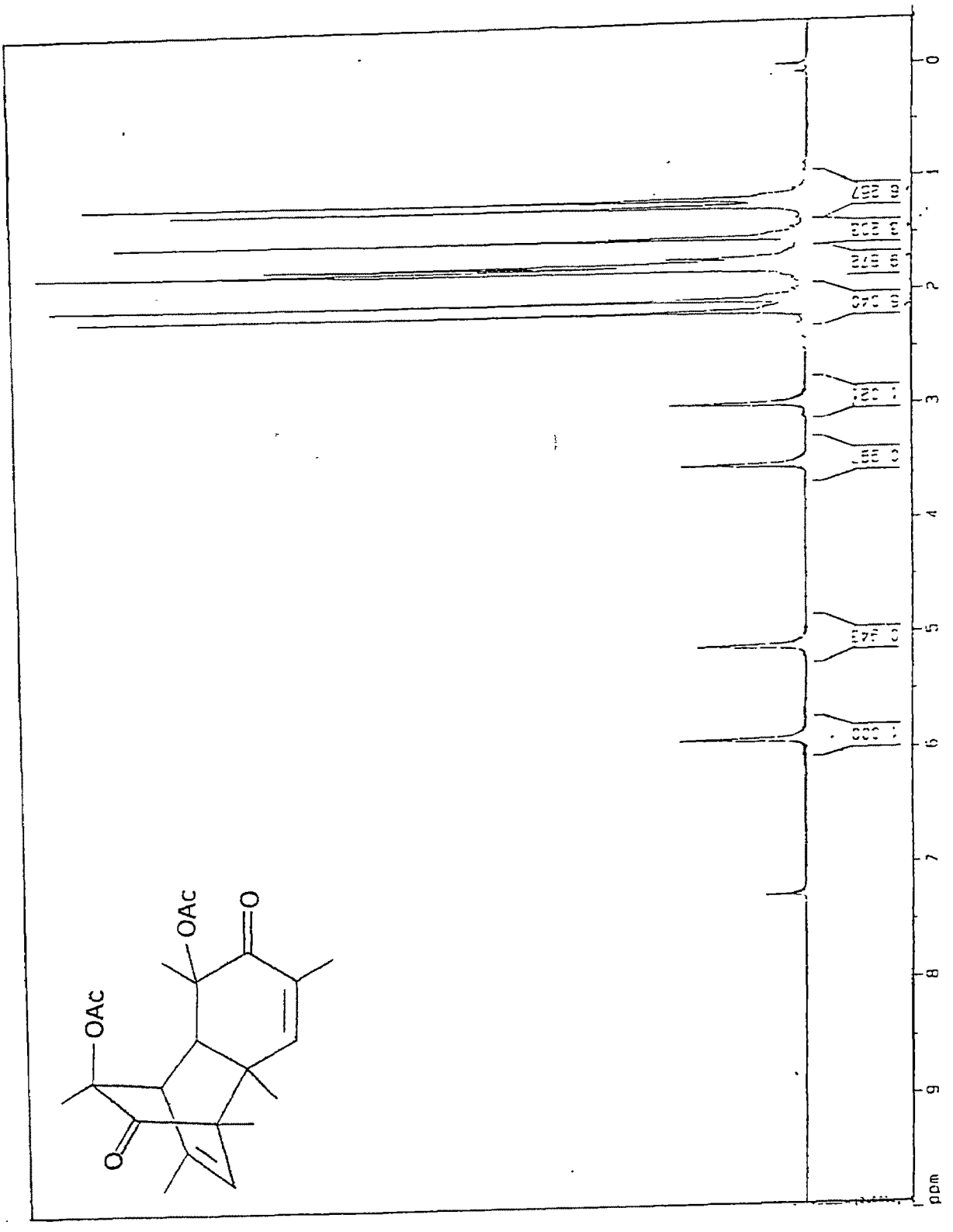


Figure V. 11 : PMR Spectrum (200 MHz) of the compound **22**

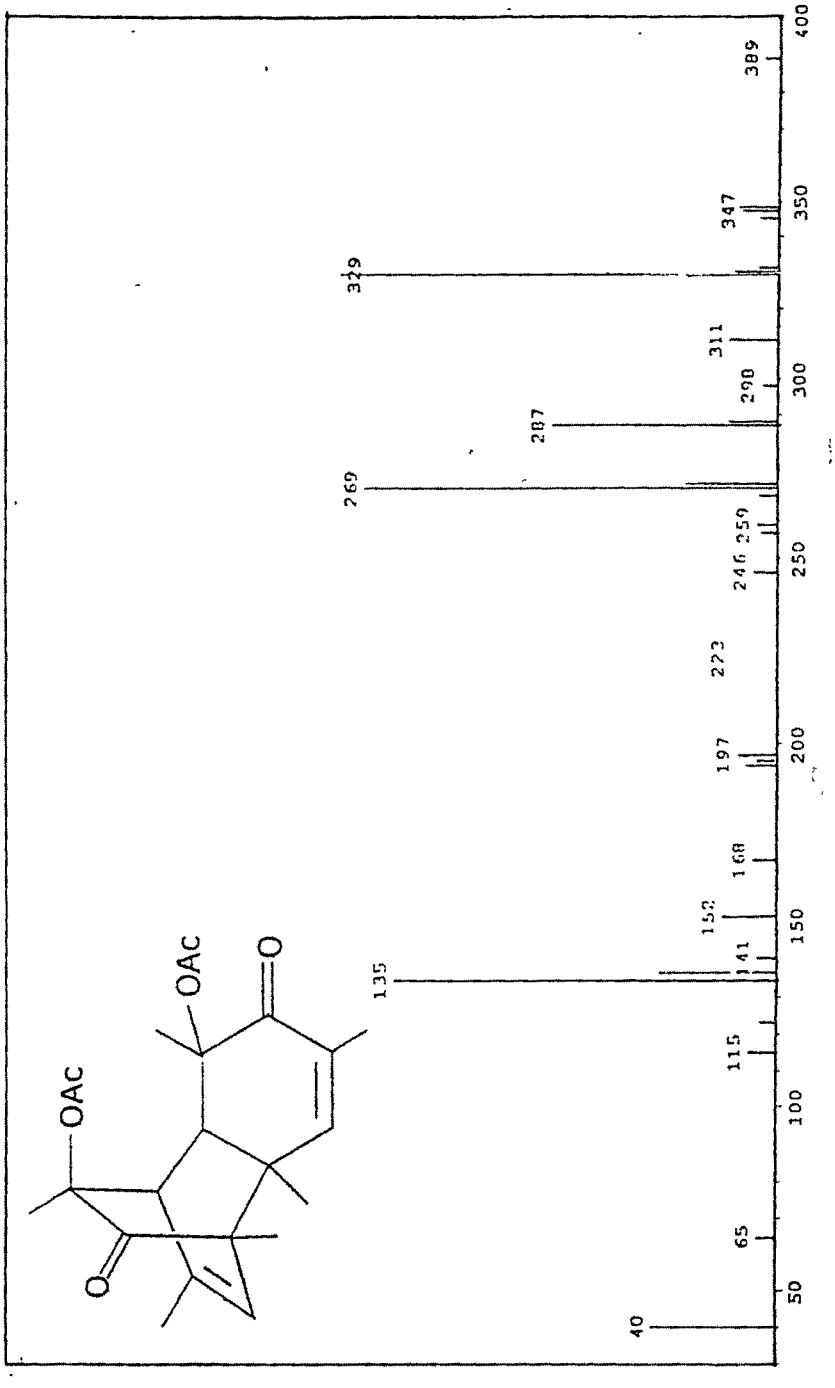


Figure V. 12 : Mass Spectrum of the compound **22**

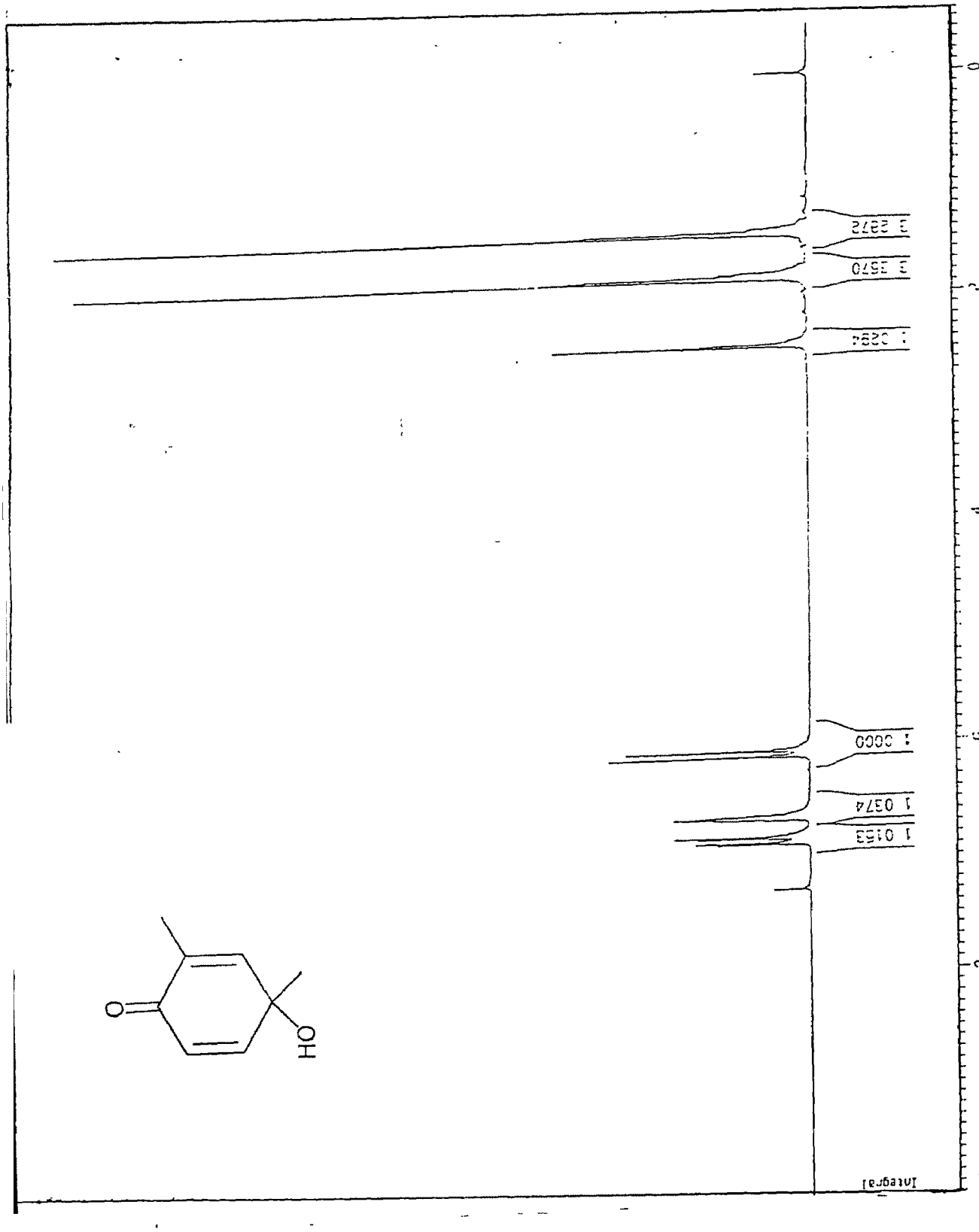


Figure V. 13 : PMR Spectrum (200 MHz) of the compound **24**

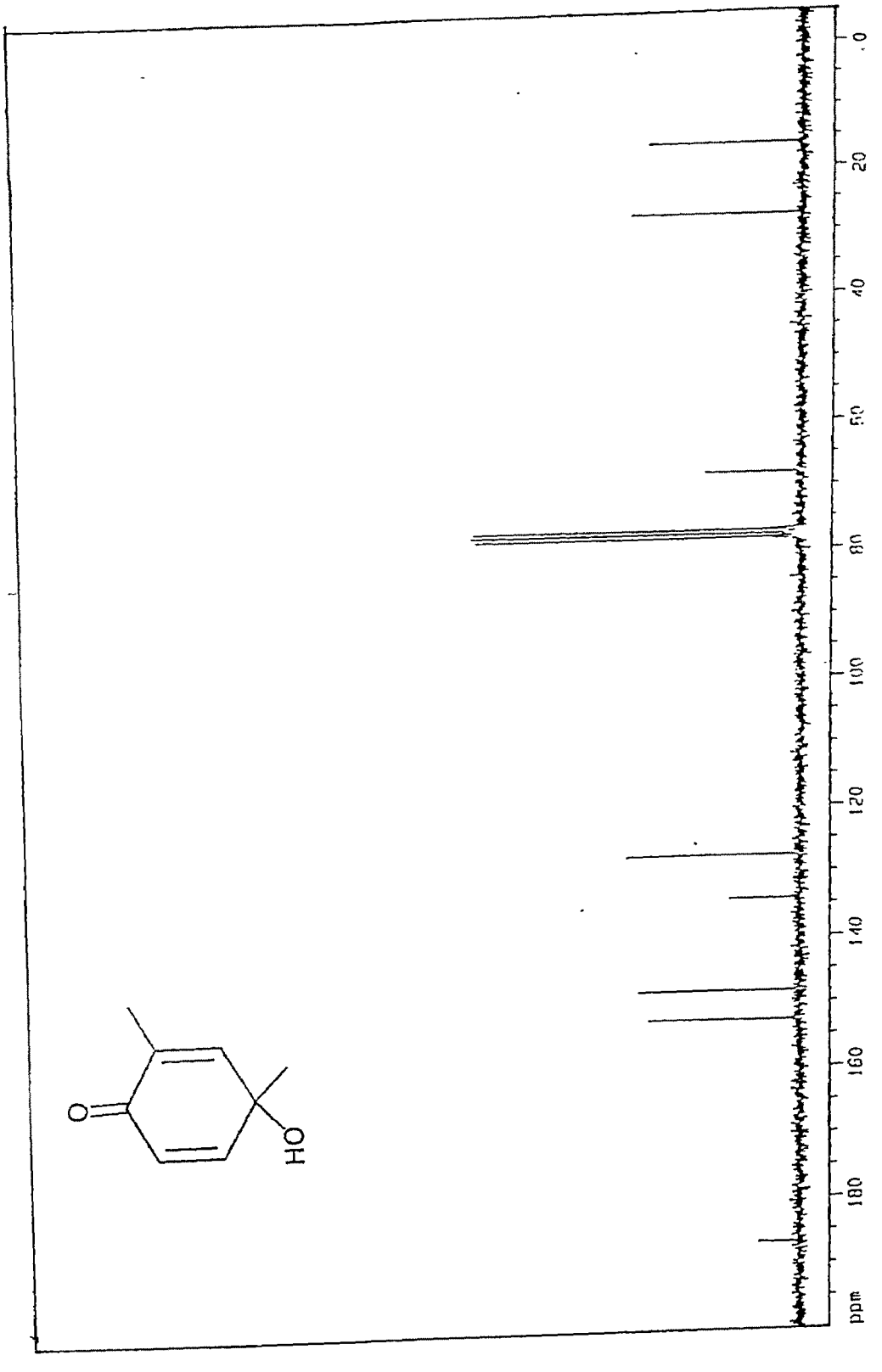


Figure V. 14 : ^{13}CMR Spectrum (50 MHz) of the compound **24**

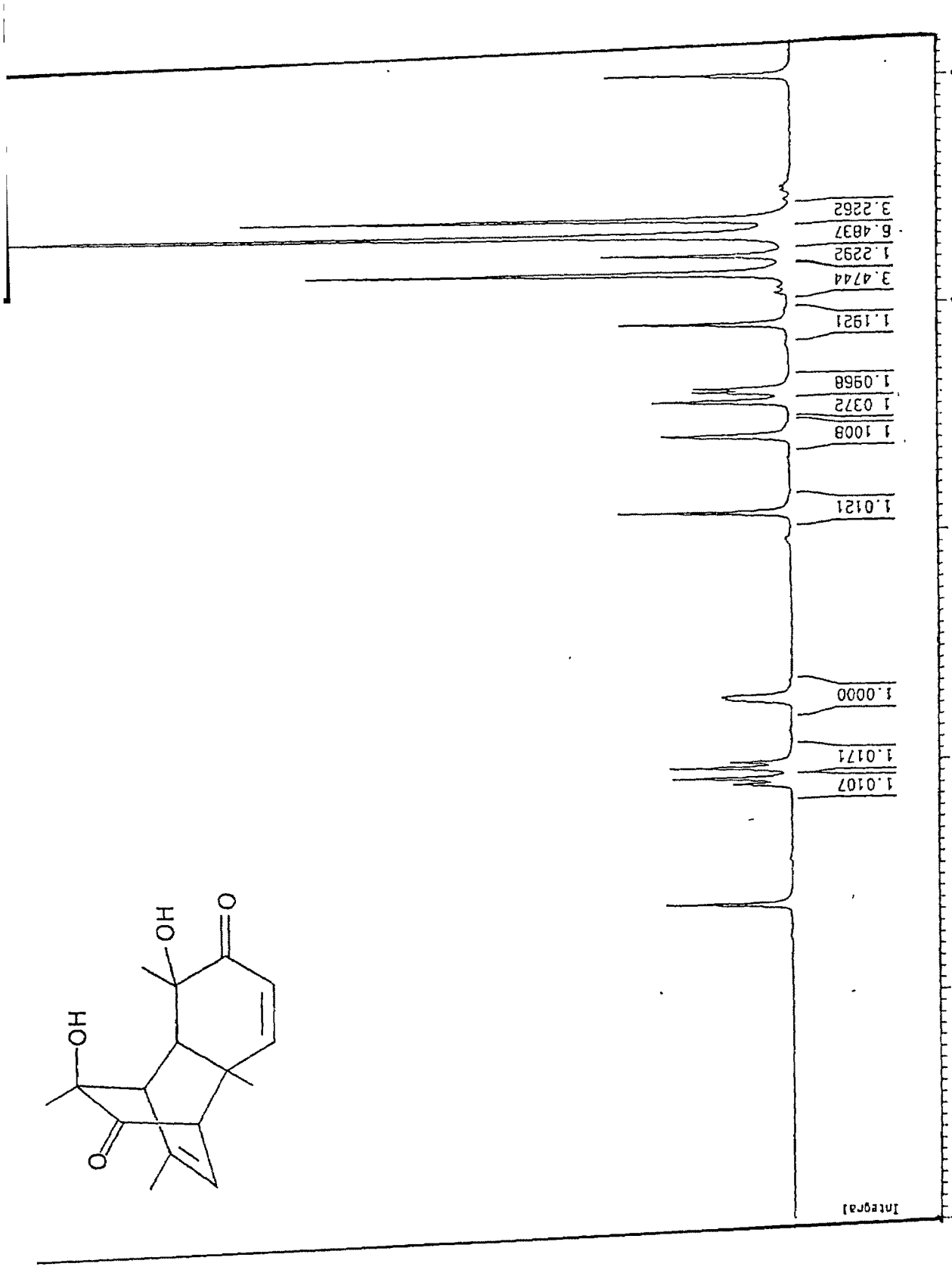


Figure V. 15 : PMR Spectrum (200 MHz) of the compound **25**

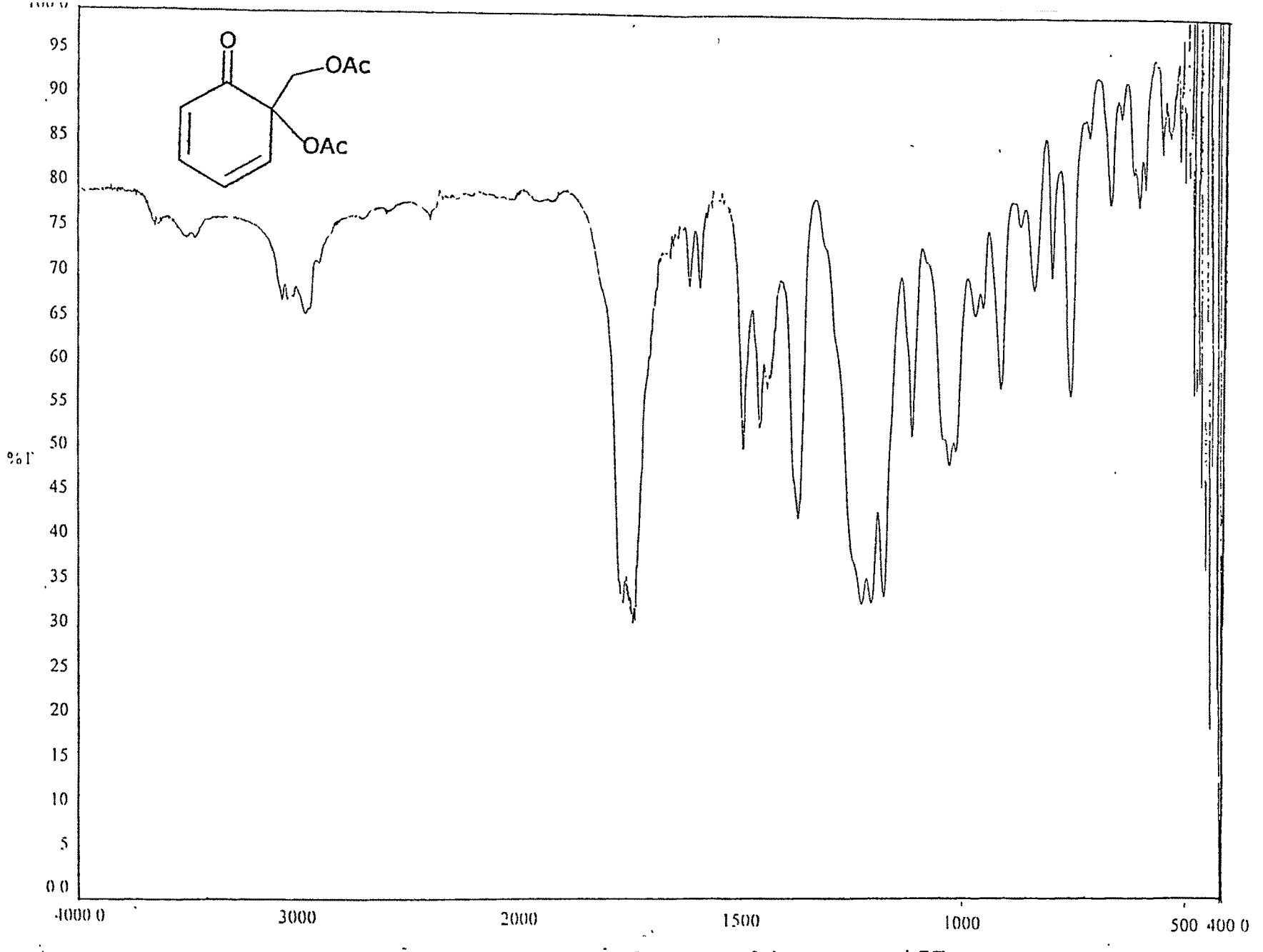


Figure V. 16 : İR Spectrum of the compound **27**

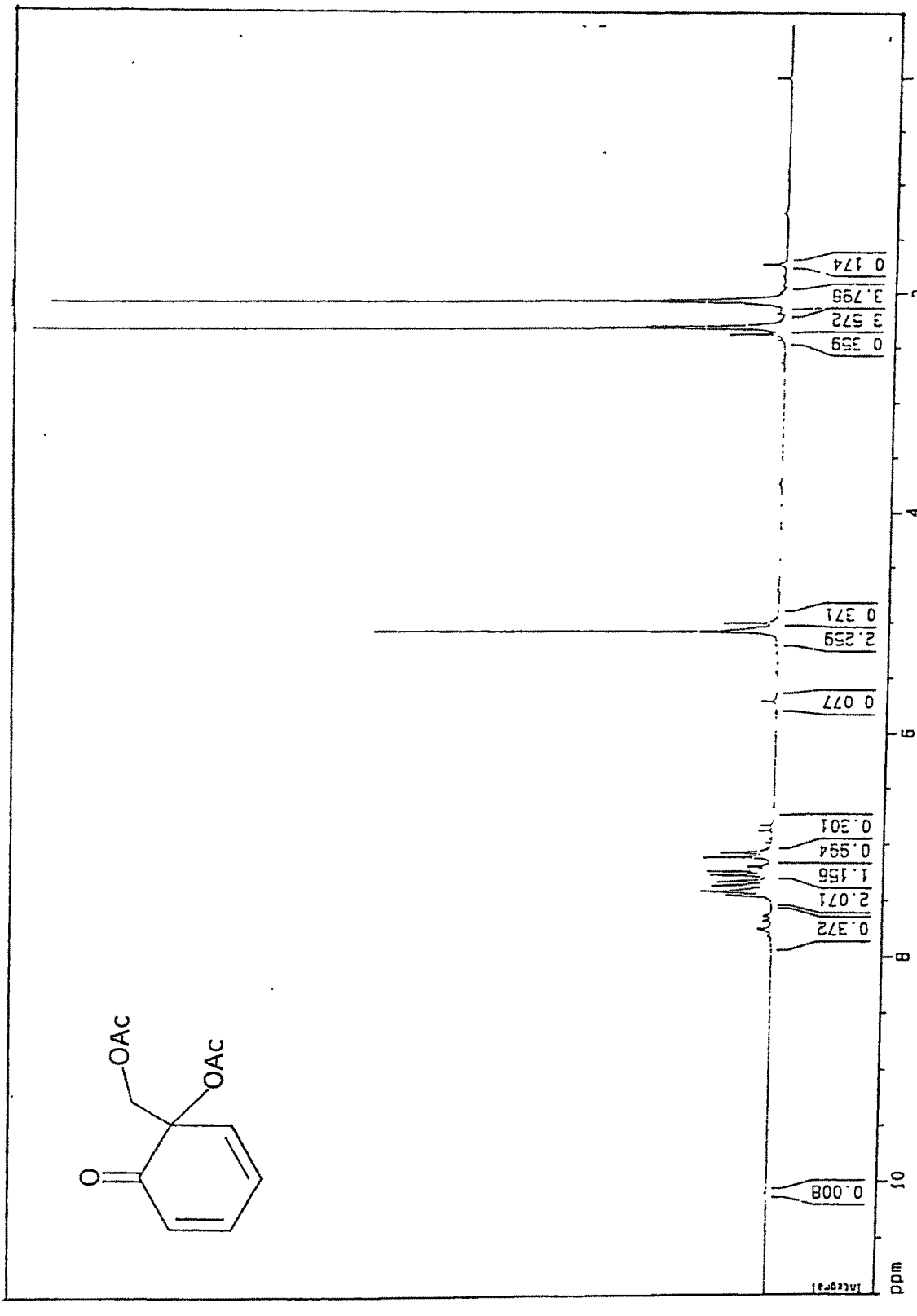


Figure V. 17 : PMR Spectrum (200 MHz) of the compound **27**

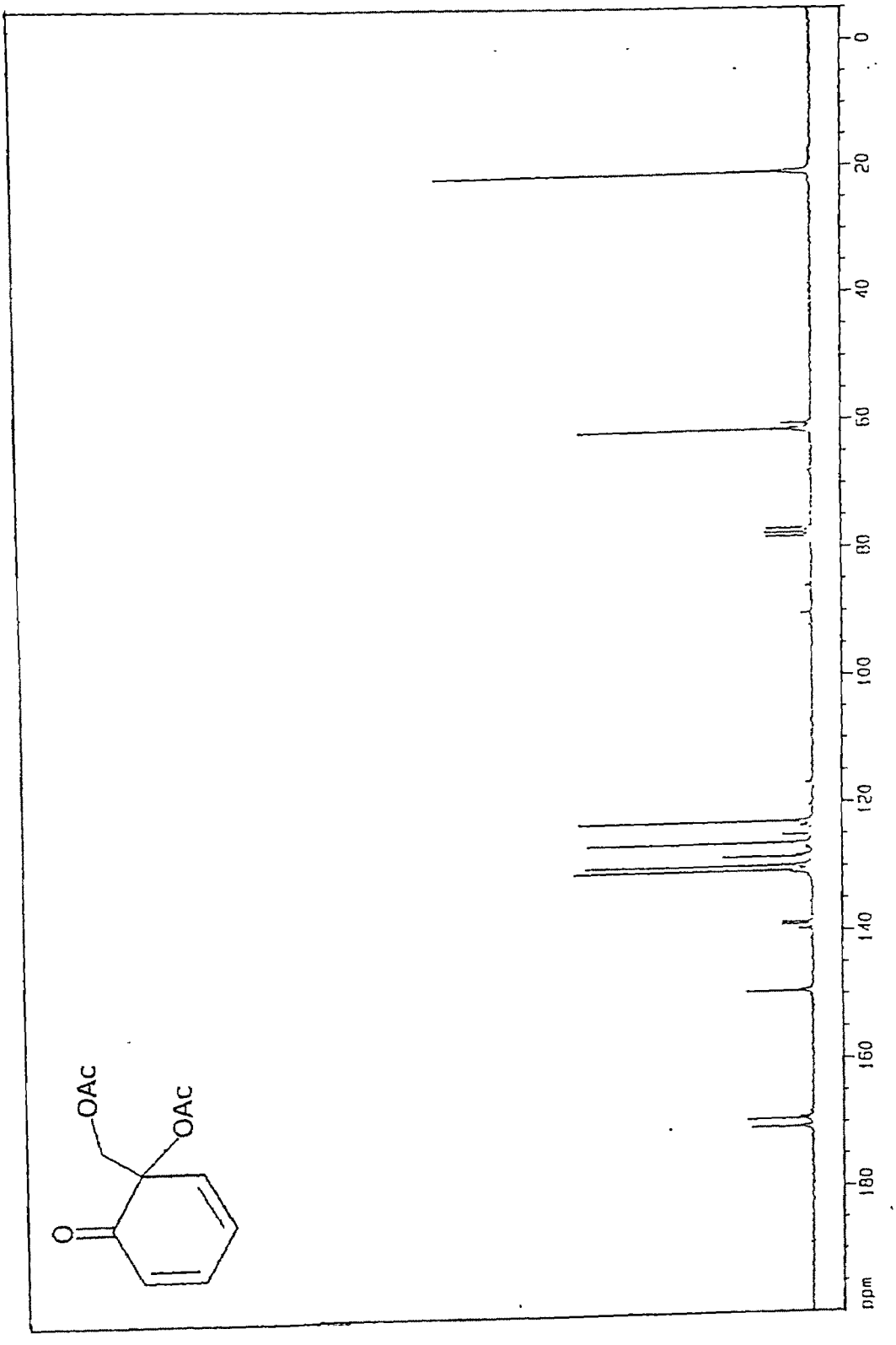


Figure V. 18 : ^{13}CMR Spectrum (50 MHz) of the compound **27**

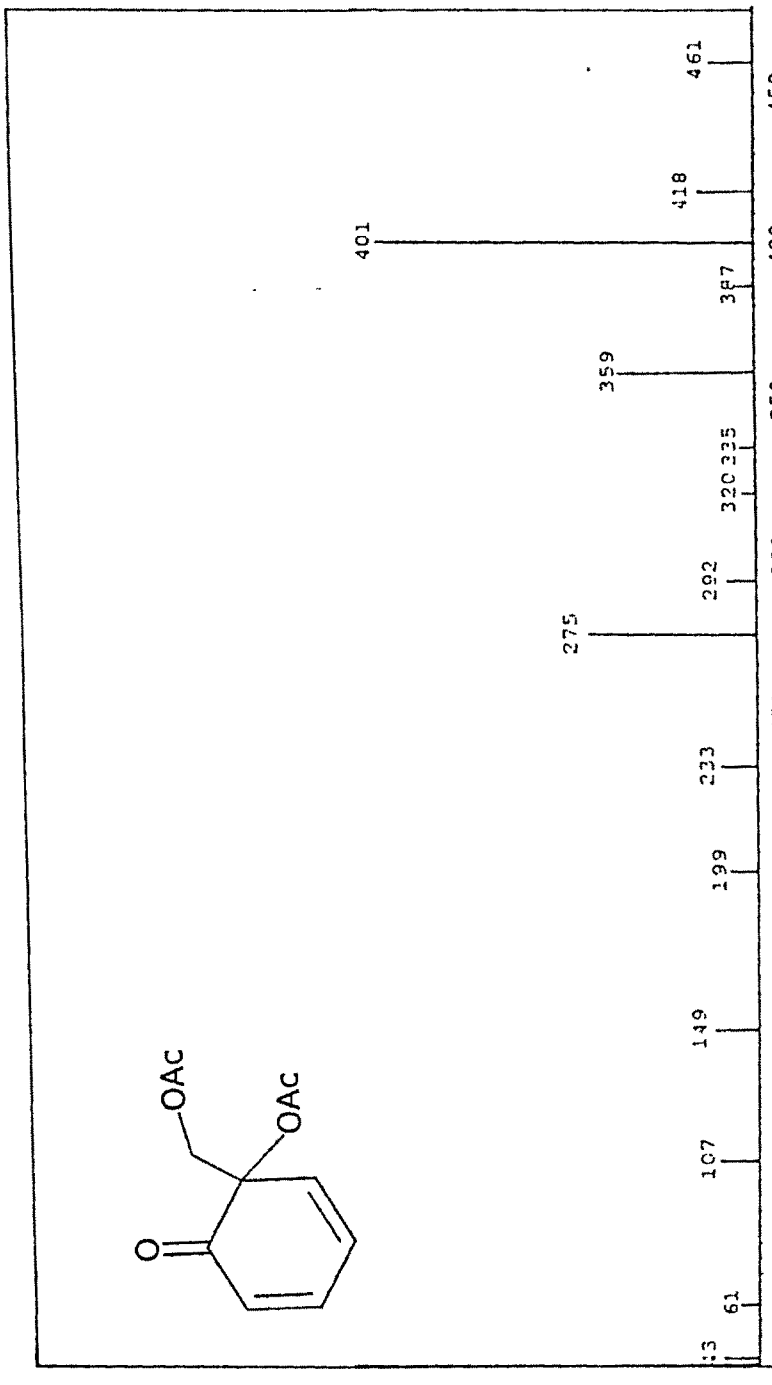


Figure V. 19 : Mass Spectrum of the compound **27**

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