CHAPTER III

Minor Constituents From The Roots of Ferula Jaeschkeana Vatke

MINOR CONSTITUENTS FROM THE ROOTS OF FERULA JAESCHKEANA VATKE

In Chapter II the isolation of epoxyjaeschkeanadiol and neojaeschkeanadiol, besides jaeschkeanatriol from the roots of Ferula jaeschkeana has been described. It has been possible to establish the structure of epoxyjaeschkeanadiol on the basis of spectral and chemical data and that of neojaeschkeanadiol on spectral data alone.

Epoxyjaeschkeanadiol

This new sesquiterpene alcohol, m.p. 102-103° $[\alpha]_D$+23.33°($CHCl_3$,c, 1.14) analyses for $C_{15}H_{26}O_3$ (M^+-18 at m/e 236). Its IR spectrum (Fig.I) shows a strong OH absorption (3400, 1045 cm^{-1}), but no C=O absorption. Its PMR(Fig.II) reveals the following structural features one-C-$\underline{Me}$(3H,s,1.17 ppm),-CH$\underline{Me}_2$(6H, two doublets centered at 0.86 and 0.95 ppm, J=7Hz each), a -O-C-$\underline{Me}$(3H,s,1.42 ppm) and one -C$\underline{H}$OH(1H, t, 4.12 ppm). By D-exchange (PMR) presence of two hydroxyls is inferred. Thus, two of the three oxygens are present as hydroxyls: one tertiary and one secondary. In confirmation of this acetylation (Ac_2O, pyridine) of the compound at room temperature (25°, 12 hr) furnished a hydroxy monoacetate with the expected spectral characteristics.

IR(Fig.IV): OH 3500 cm^{-1}, OAc 1735 and 1250 cm^{-1}

PMR(Fig.V): O$\underline{Ac}$(3H, s, 2.05 ppm) and C$\underline{H}$OAc(1H, t, 5.14 ppm, J=10Hz). The third oxygen atom, must then be present as an ether function.

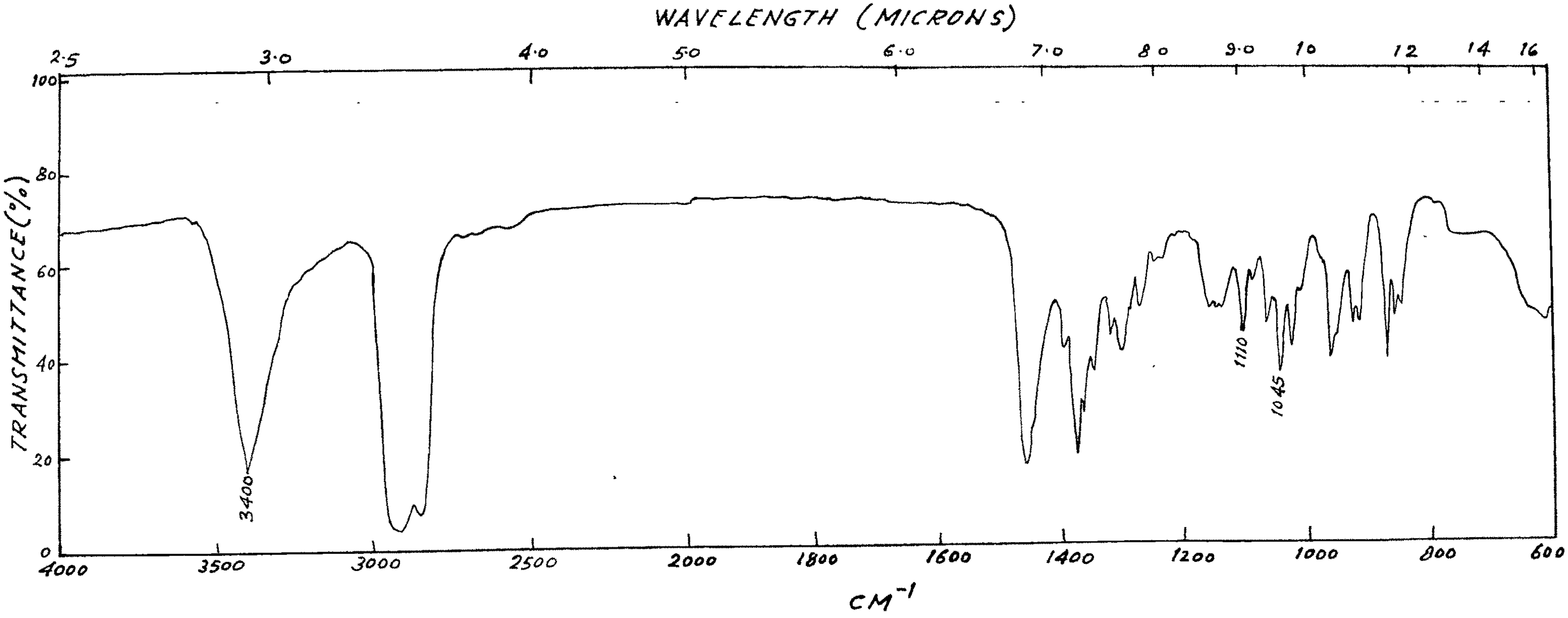


FIG. I. IR SPECTRUM OF EPOXYJAESCHKEANADIOL

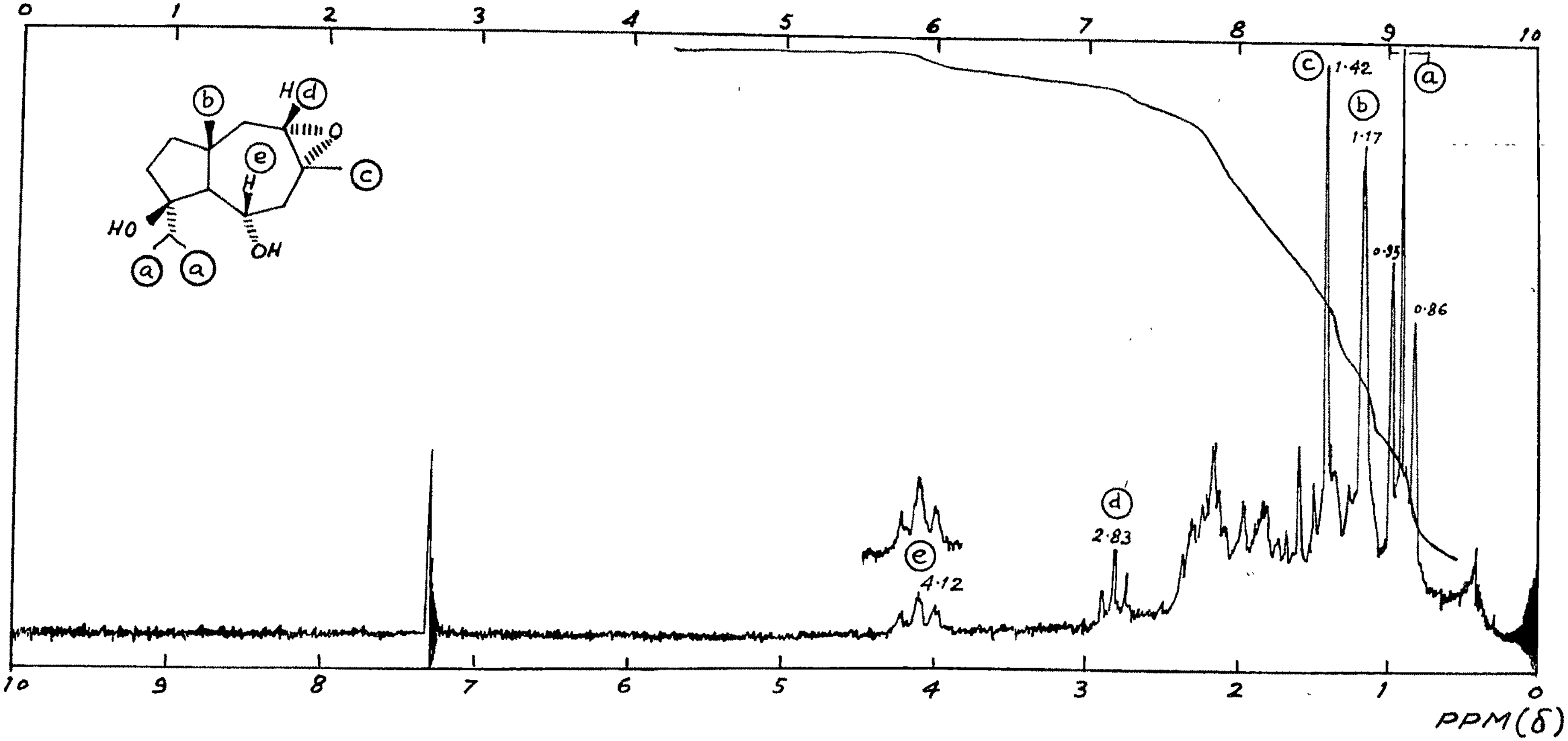


FIG. 11. PMR SPECTRUM OF EPOXYJAESCHKEANADIOL

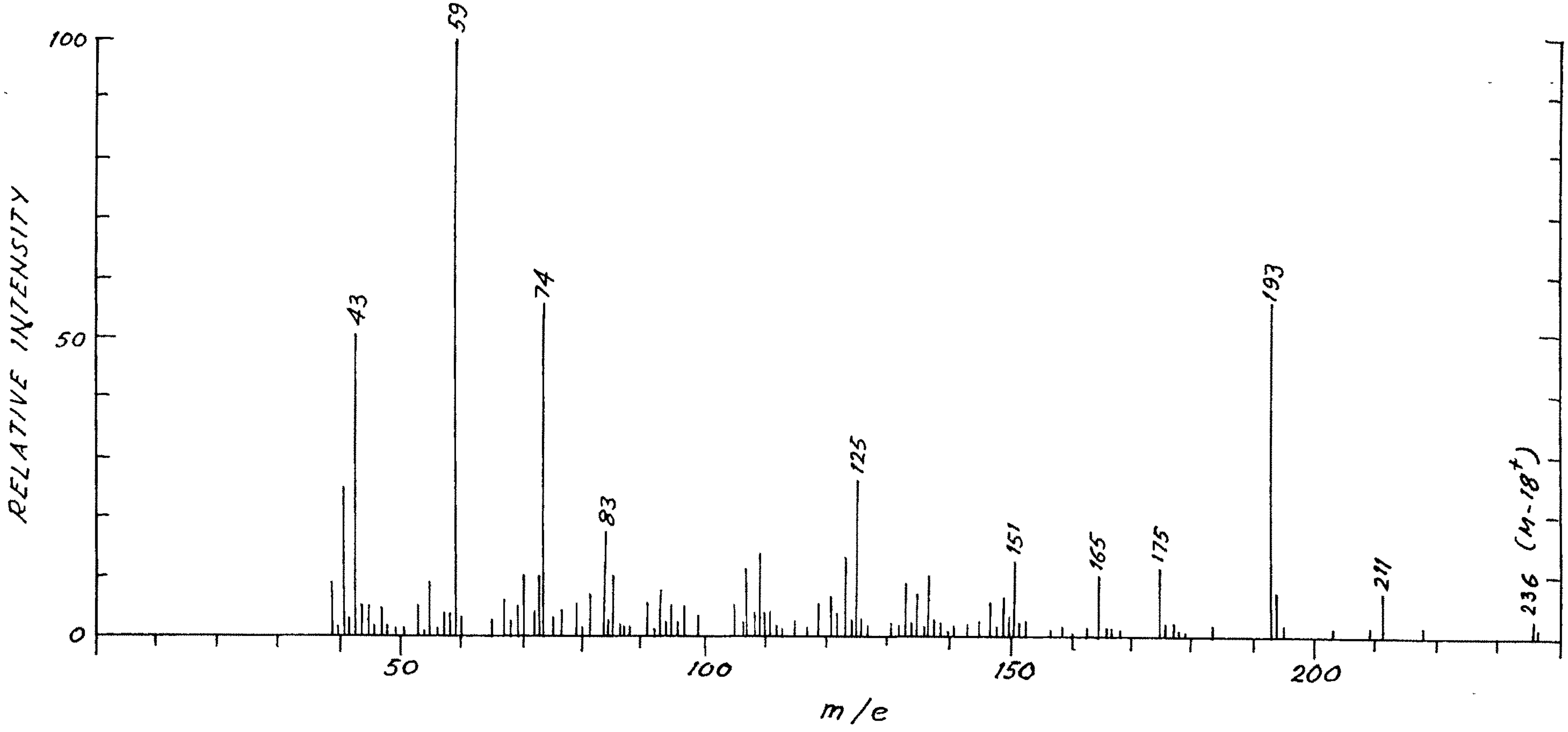


FIG. III. MASS SPECTRUM OF EPOXYJAESCHKEANADIOL

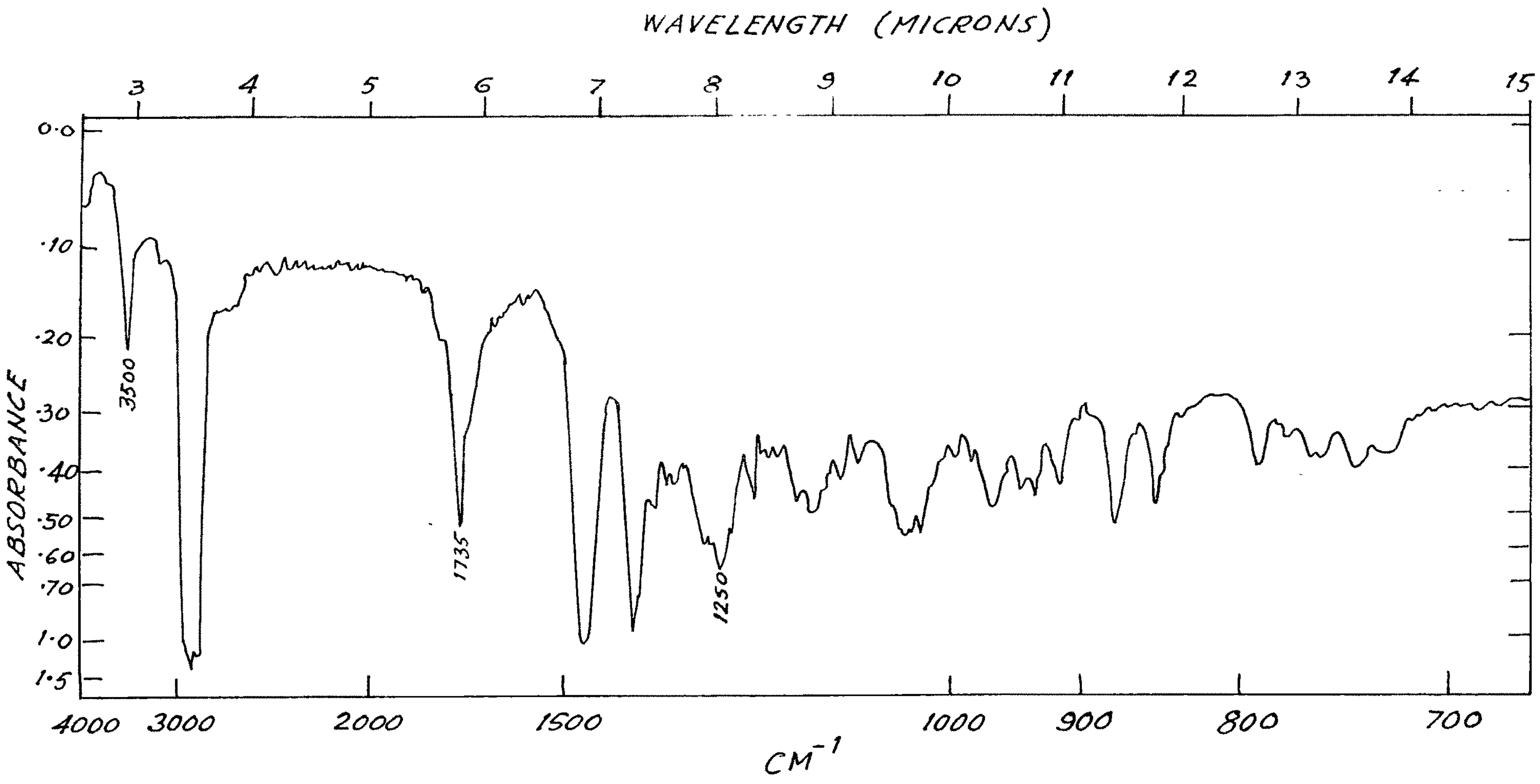


FIG. IV. IR SPECTRUM OF EPOXYJAESCHKEANADIOL ACETATE

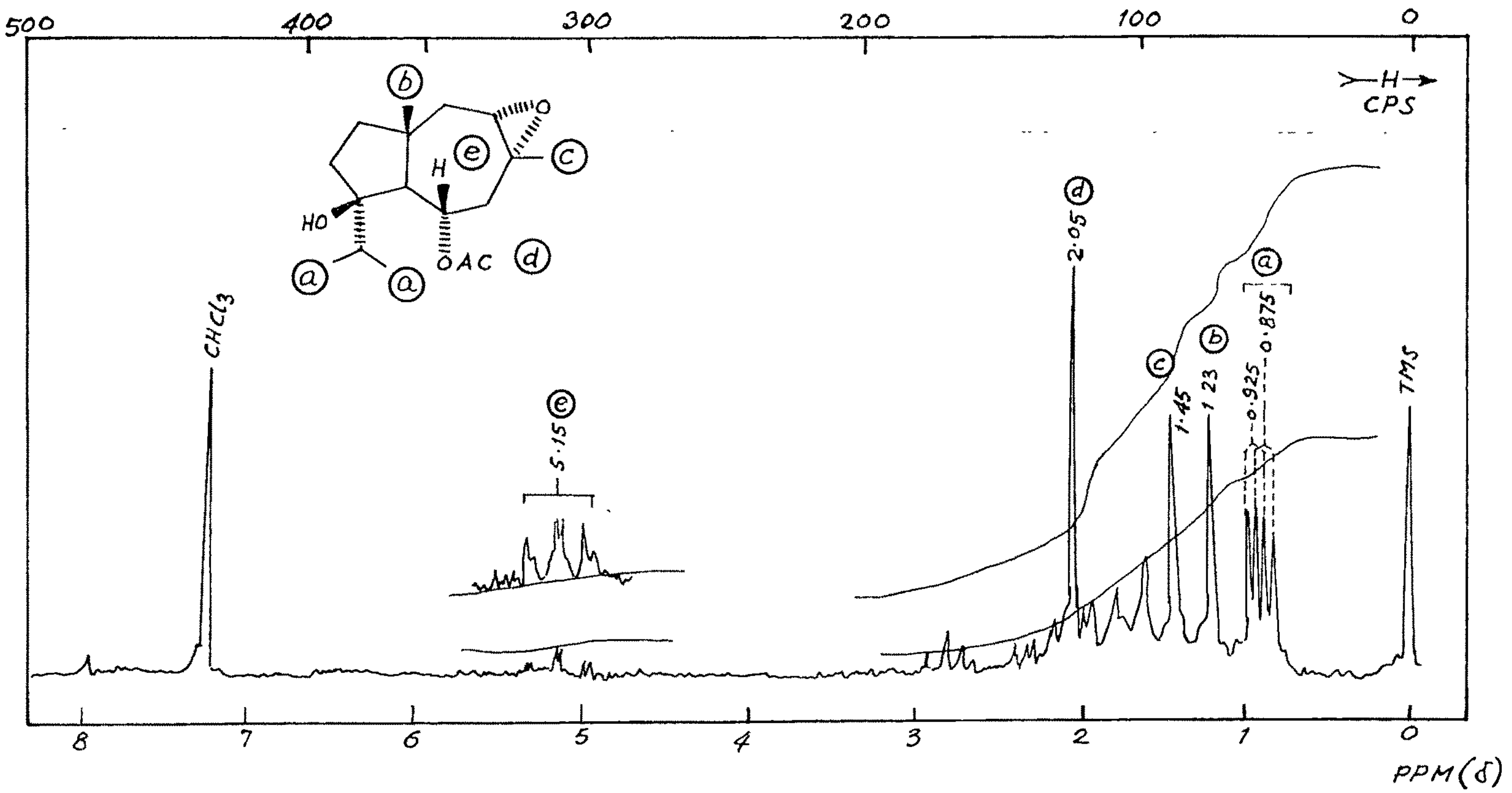
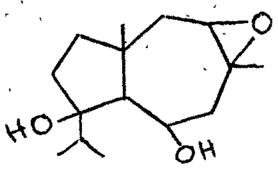


FIG. V. PMR SPECTRUM OF EPOXYJAESCHKEANADIOL ACETATE

This compound on exposure to phosgene in presence of pyridine furnished in almost quantitative yield, a crystalline cyclic carbonate, m.p.203-204°(IR: O-CO-O 1755, 1250 cm^{-1}). PMR: -C-$\underline{H}$C -O-CO-O, 1H, t,4.28 ppm). The facile formation of cyclic carbonate suggests that the two hydroxyls may be situated 1,3 to each other as in jaeschkeanadiol.

A close scrutiny of the spectral data reveals a close similarity with jaeschkeanadiol and jaeschkeanatriol suggesting possibly the same carbon framework for this alcohol. If this were so, the absence (PMR) of the grouping -C=C-$\underline{Me}$ in the new compound and the presence of possibly an oxirane linkage (IR:-C-O-C 1110 cm^{-1}; PMR: C-O-C-$\underline{Me}$, 1.42 ppm), instead suggested structure (1) for the new compound.



(1)

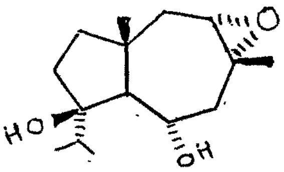
That this was indeed so could be confirmed by converting jaeschkeanadiol into its epoxide. Thus jaeschkeanadiol on epoxidation with perbenzoic acid in benzene gave, in quantitative yield, the corresponding epoxide identical in all respect (m.p, mixed m.p., GLC, IR and PMR) with the naturally occuring compound.

This establises conclusively the structure of epoxydiol as well as it's stereochemistry at all centers (with respect to jaeschkeanadiol) except those bearing the oxirane function.

Stereochemistry of the oxirane linkage

As mentioned above the conversion of jaeschkeanadiol to its epoxide apart from confirming the structure of epoxyalcohol also establishes its stereochemistry at all the centres except those bearing oxirane linkage. This was sorted out by taking advantage of syn directive effect of OH group in epoxidation of allylic alcohols. Henbest[1] was the first to establish that peracid epoxidation of allylic alcohols occurs primarily cis to the OH group. Sharpless and Michaelson[2] have shown that not only allylic OH group but even homoallylic hydroxyl group also exerts syn directive influence. Thus 3-cyclohexene-1B-ol on treatment with tert. butylhydroperoxide in presence of catalytic amount of molybdenum hexacarbonyl [$Mo(CO)_6$] in benzene gave corresponding 3B-oxide. Jaeschkeanadiol was also epoxidised with tert.butylhydroperoxide using molybdenumacetylacetonate as catalyst. Although the reaction proceeded much slower than the PBA epoxidation, only a single epoxide was formed besides unreacted starting compound and other minor compounds. The epoxide was separated by chromatography (SiO_2) and it turned out to be identical with the naturally occuring epoxide (m.p., mixed m.p.,IR and PMR).

Since, in the jaeschkeanadiol, the C_5 secondary hydroxyl is α, the resulting oxide should also have α stereochemistry, Thus epoxyjaeschkeanadiol could be represented by the following stereostructure.



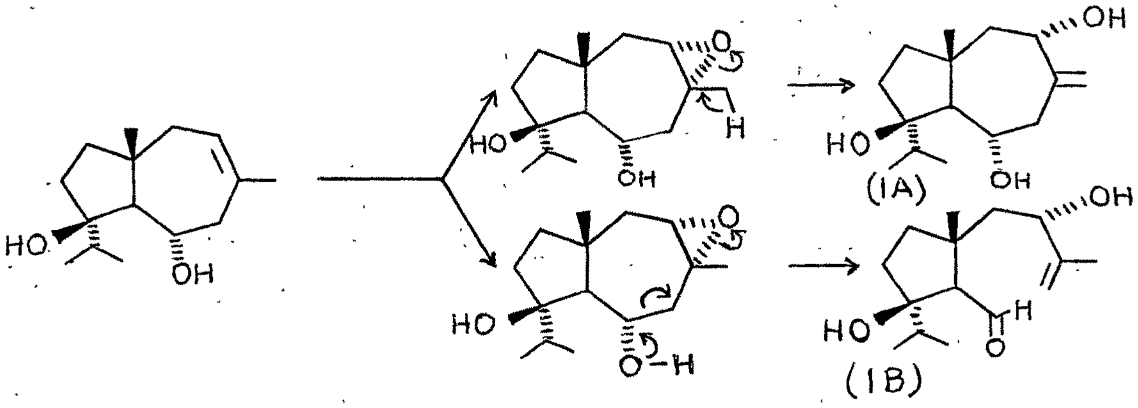
The role of directive influence of OH group in controlling the stereochemistry of the oxide linkage was confirmed by epoxidation of jaeschkeanadiol carbonate. In this case a mixture of two epimeric (TLC, solvent: light petroleum - ether) oxides was obtained, almost in 1:1 ratio. All attempts to separate them by chromatography (PLC, column) were futile. On attempting fractional crystallisation only a small quantity of the more mobile (Rf 0.35) epimer could be separated m.p. 169-170°. The less mobile epimer (Rf 0.32) corresponds to cyclic carbonate of jaeschkeanadiol epoxide (TLC).

In a separate experiment, when the epoxidation of jaeschkeanadiol was carried out using perbenzoic acid in chloroform, a complex mixture was obtained from which three compounds were separated pure by chromatography on silicagel. The major compound was identical with the natural epoxyjaeschkeanadiol. The two minor compounds designated as compounds(1A) and (1B) showed following spectral characteristic features:

Compound 1A: IR:OH 3380 cm^{-1},-C=C 1635 cm^{-1} and $>C=CH_2$ 890 cm^{-1} PMR: -C- $\underline{Me}$ (3H,s,1.06 ppm),-$CH\underline{Me}_2$ (6H,2d,centered at 0.88 and 0.93 ppm, J=7Hz), two $C\underline{H}OH$ (2H, bm, 4.14 ppm) and $-C=CH_2$(2H, d at 5.15 ppm, J=16Hz).

Compound 1B: IR:OH 3600,3460,1015 cm^{-1},-C=0 1706 cm^{-1} and C=C 1650 cm^{-1}, PMR: -C-$\underline{Me}$ (3H,s,1.26 ppm), -$CH\underline{Me}_2$ (3H each s at 0.88 and 0.95 ppm), -C=C$\underline{Me}$ (3H,m, between 1.68 and 1.81 ppm), -$C\underline{H}OH$ (1H,m,4.28 ppm) and $\underline{H}$-C=O(1H,d,9.96 ppm, J=2Hz)

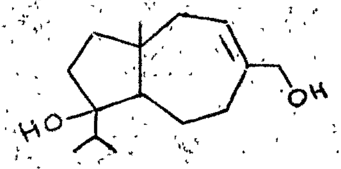
Based on the above spectral data and consideration of the mechanistic aspects[3], these compounds have been assigned following structures (1A) and(1B)



Neojaeschkeanadiol

This new sesquiterpene alcohol, b.p.150-160°(bath)/0.8mm, $[\alpha]_D$+9.85°($CHCl_3$, c, 2.03) analyses for $C_{15}H_{26}O_2$(M^+-18, m/e = 220). Its IR spectrum (Fig.VI) shows a strong OH absorption (3320, 1045 cm^{-1}). Its PMR (Fig.VII) indicates the presence of one $-C-Me$(3H, s, 0.92 ppm), $-CH\underline{Me}_2$ (6H, 2d at 0.93 and 0.97 ppm, J=7Hz), $-CH_2OH$(2H, s, 3.93 ppm) and $-C=C\underline{H}$(1H, m, 5.65 ppm). By D-exchange (PMR), the presence of two hydroxyls is inferred.

Since there is a striking similarity between the spectral data of neojeschkeanadiol and jaeschkeanadiol, it was considered reasonable to assume that the two compounds may have the same carbon framework with the placing of the tertiary hydroxyl as in jaeschkeanadiol. This assumption is further augmented by a peak at m/e 220 (M^+-18, 12.5%) in the mass spectrum of neojaeschkeandiol (Fig. VIII). This ion further fragments by loss of $CHMe_2$ to m/e 177(62.5%). Consideration of the absence (PMR) of secondary $C\underline{H}OH$ and $C=C\underline{Me}$ together with the presence of $C\underline{H}_2$ OH signal suggested structure (2) for neojaeschkeanadiol.



(2)

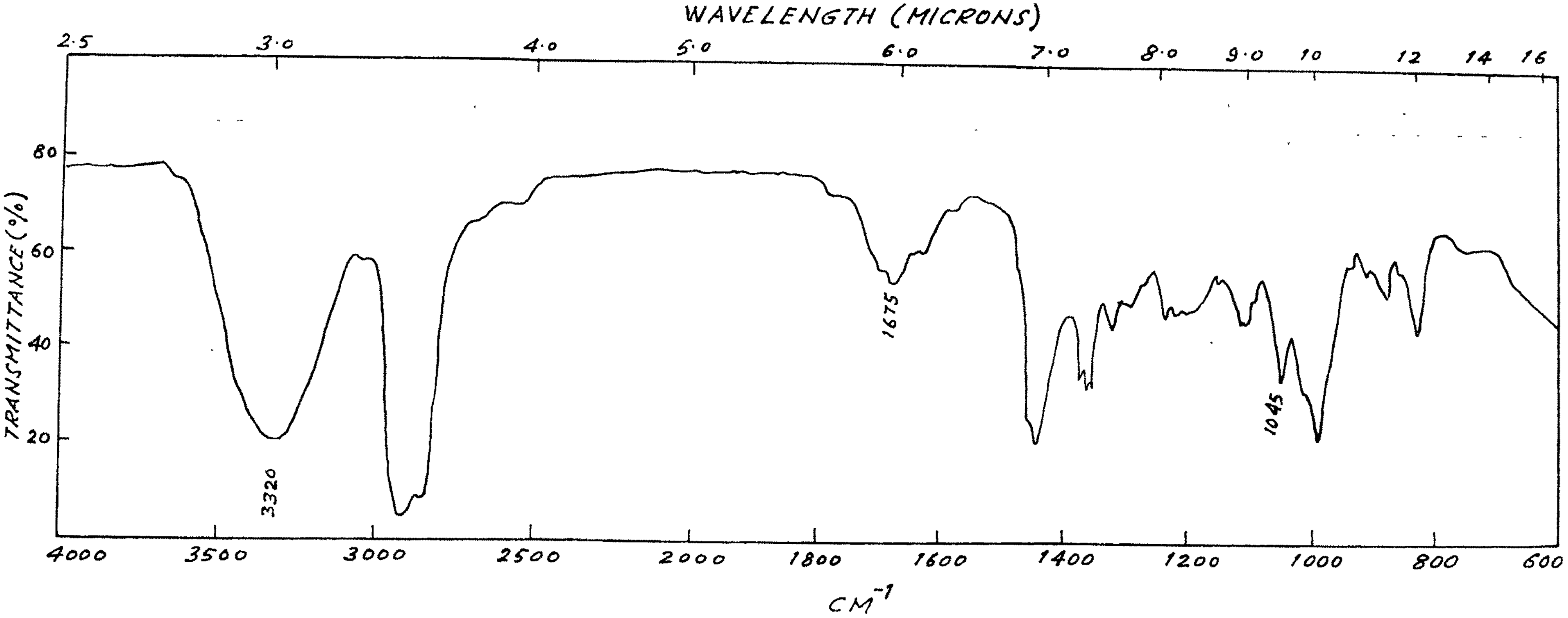


FIG. VI. IR SPECTRUM OF NEOJAESCHKEANADIOL

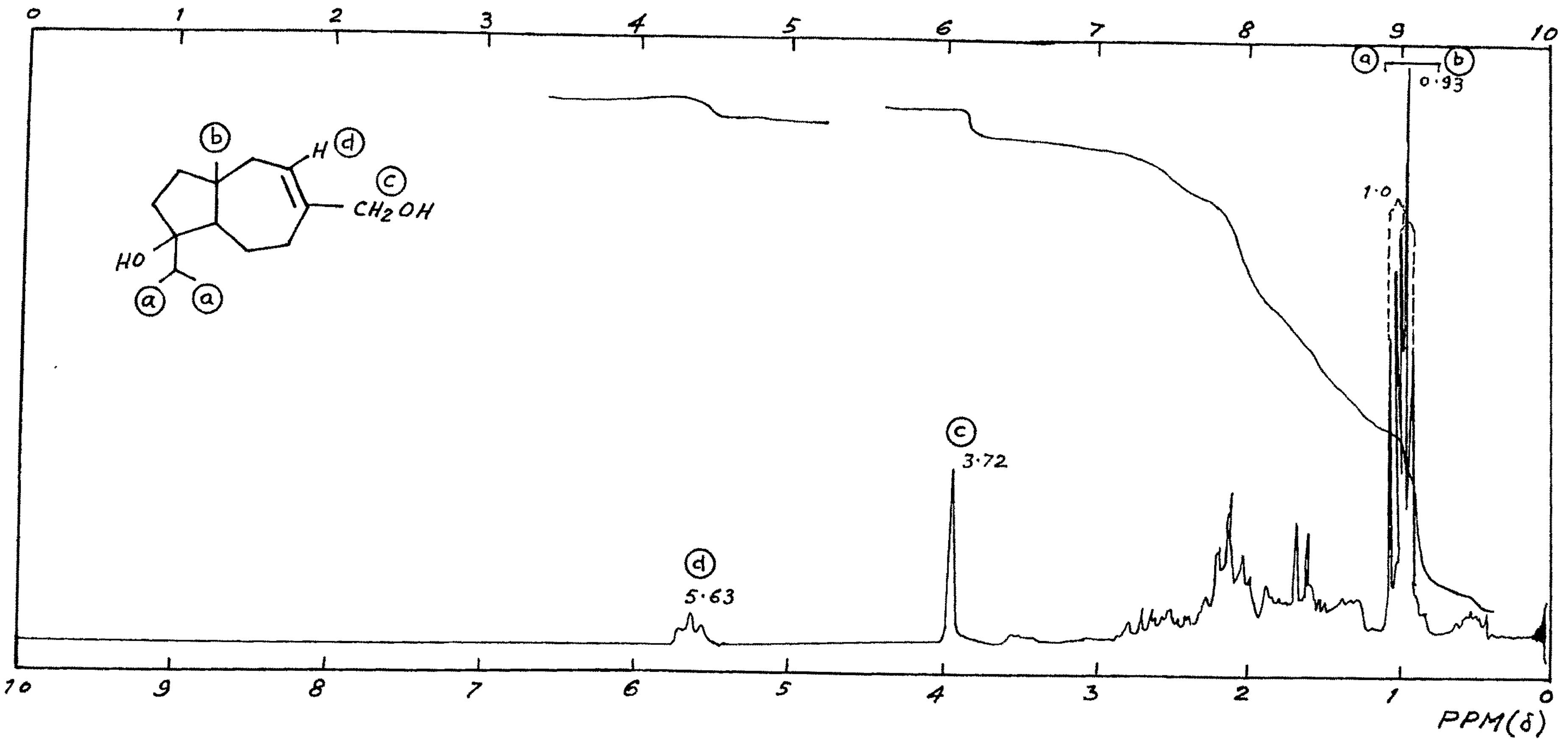


FIG. VII. PMR SPECTRUM OF NEOJAESCHKEANADIOL

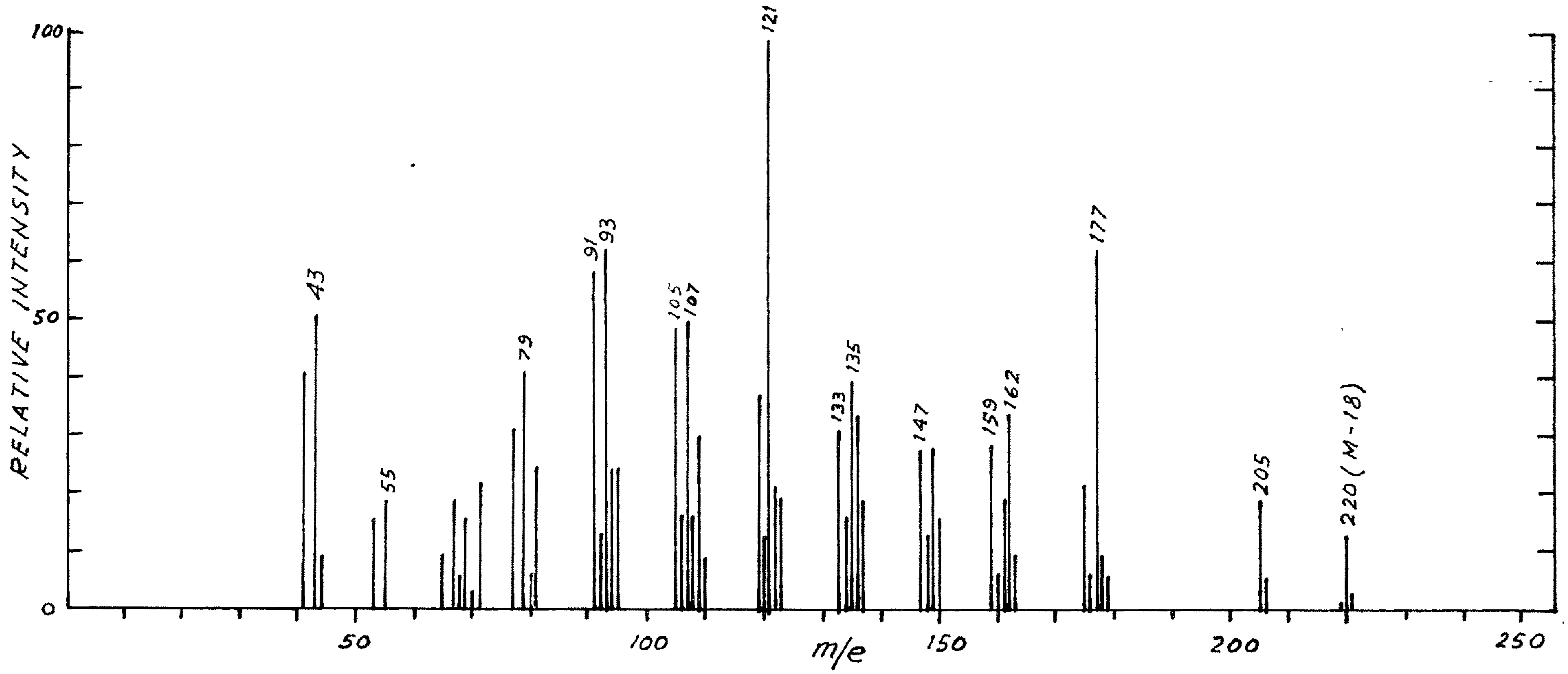
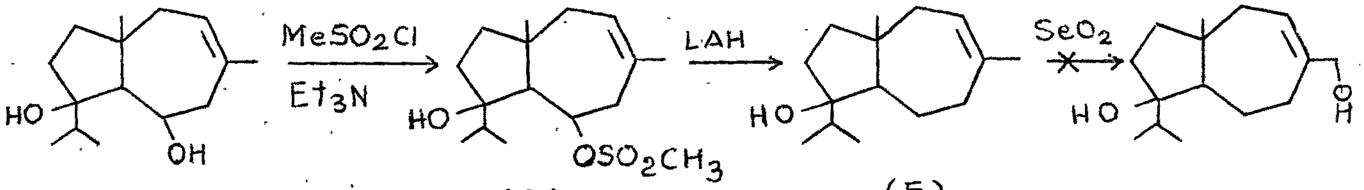


FIG. VIII. MASS SPECTRUM OF NEOJAESCHKEANADIOL

Since this compound was available in only small quantity after repeated chromatography it was not possible to carry out any chemical degradation to obtain chemical proof in favour of the structure (2). With this limitation, attention was focused on partial synthesis of (2) from the more abundant and readily available jaeshkeanadiol.



(3) (5)

FIG. IX

Jaeshkeanadiol was converted into its monomesylate (3) in quantitative yield (CH_3SO_2Cl/Et_3N), which on subsequent reduction with LAH gave a mixture from which the major compound was obtained TLC pure* by column chromatography on SiO_2 gel. However, it was found to be a mixture of atleast six compounds on GLC (20% silicone SE-30; temp 190°). Of these the major component (RT:8.4 min, 66%) and one minor compound (RT:7 min, 19%) were separated by preparative GLC. The major compound (RT:8.4) analysed for $C_{15}H_{26}O$, (M^+,m/e=222). IR: OH(3580, 1120 cm^{-1}); PMR: $-C-\underline{Me}$(3H, s, 0.96 ppm), $-CH\underline{Me}_2$(6H,2d at 0.88 and 0.95 ppm, J=7Hz each), $-C=C\underline{Me}$ (3H,s,1.77 ppm) and $-C=C\underline{H}$(1H, m, 5.42 ppm). These data fit well for the desired demesylated product(5). The minor component (RT:7,M^+ at m/e 222)analysed for $C_{15}H_{26}O$ and showed in its IR

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*This compound appears as an elongated spot on TLC and all attempts to resolve it further were fruitless.

OH absorption (3590, 1040 cm^{-1}). Its PMR showed the presence of $-C-\underline{Me}$ and $-CH\underline{Me}_2$(9H,m, between 0.88 and 1.01 ppm), $-C=\underline{Me}$ (3H,s,1.65 ppm), $-C\underline{H}OH$(1H,m,3.28 ppm) and $-C=C\underline{H}$ (1H,m, 5.34 ppm). Based on these spectral data structure (6) is suggested for this compound. There are two possibilities by which formation of (6) might have occured. If we assume an intermediacy of oxetane (4) (the stereochemical disposition of C_{10} β tert. OH group (quasi axial) and C_5 α mesylate group (quasi equatorial) is well suited for the oxetane formation), it could give alcohol (6) on reduction with LAH. However, this possibility appeared less likely from the study of molecular models. The formation of oxetane involves considerable interactions between C_7 methyl group and oxetane ring as well as C_4 β hydrogen.

The other possibility involves intramolecular transfer of mesylate group (trans mesylation) giving (7), which on reduction with LAH could furnish alcohol (6; α OH)(Fig.X)

Having obtained the desired compound (5), the next step was to oxidise the vinylic methyl to the primary alcohol function. SeO_2 in dioxane was inevitably the reagent of choice [5]. When compound (5) in dioxane was treated with freshly sublimed SeO_2, a fairly complex mixture was obtained after the usual work up. The TLC of the product did not show the presence of the desired neojaeshkeanadiol. Oxidation was also attempted using

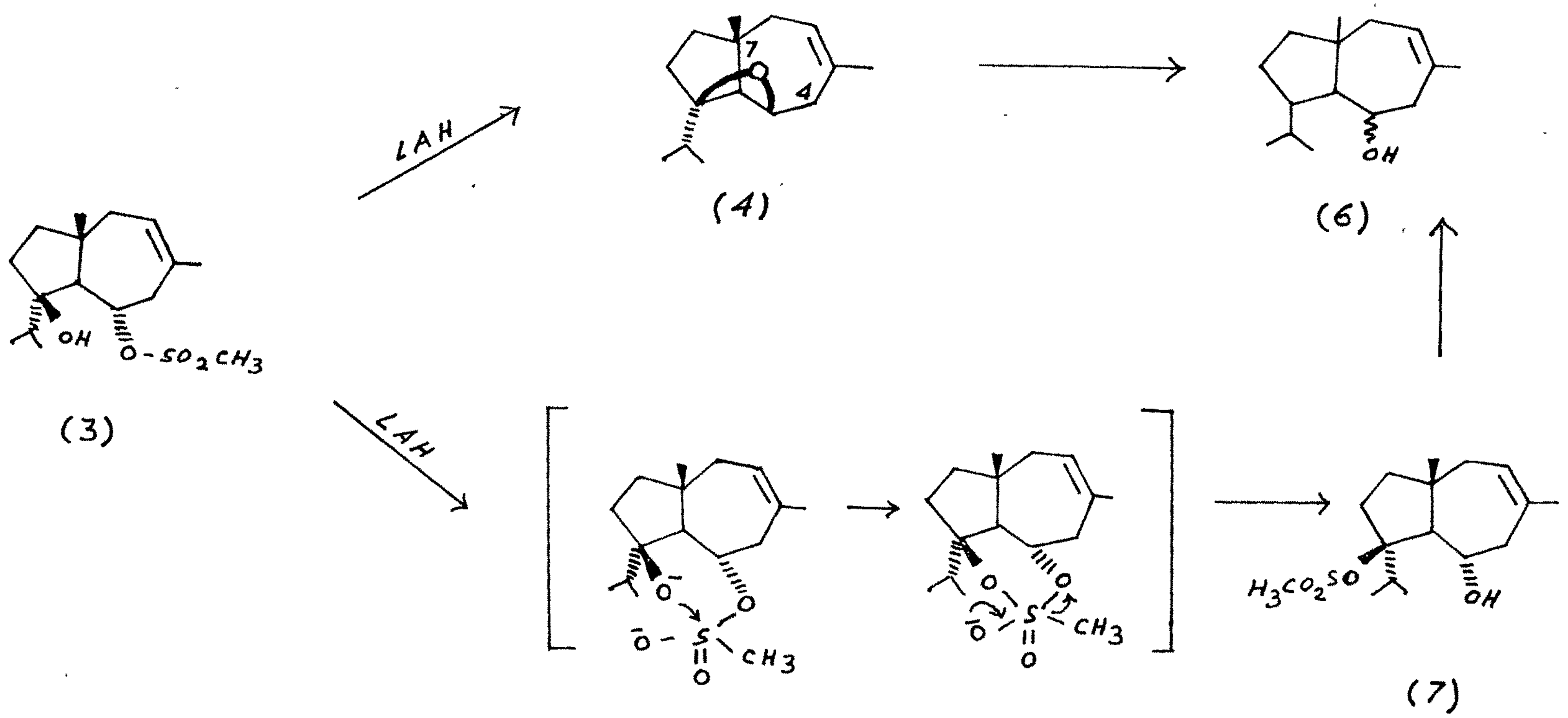


FIG. X

SeO_2 in DMSO [6], but in this case too, a complex mixture was obtained, the TLC of which was identical to that obtained using SeO_2 in dioxane. No attempt was made to investigate these complex mixtures.

In view of the difficulties encountered in our earlier transformation, we planned a new route for the conversion of jaeschkeanadiol to neojaeschkeanadiol which did not involve the oxidation step utilising SeO_2. (Fig. XI) It was conceived that if we could convert jaeschkeanadiol into the alcohol of the type (8), then the allylic rearrangement followed by subsequent selective removal of C_5 hydroxyl function should give neojaeschkeanadiol.

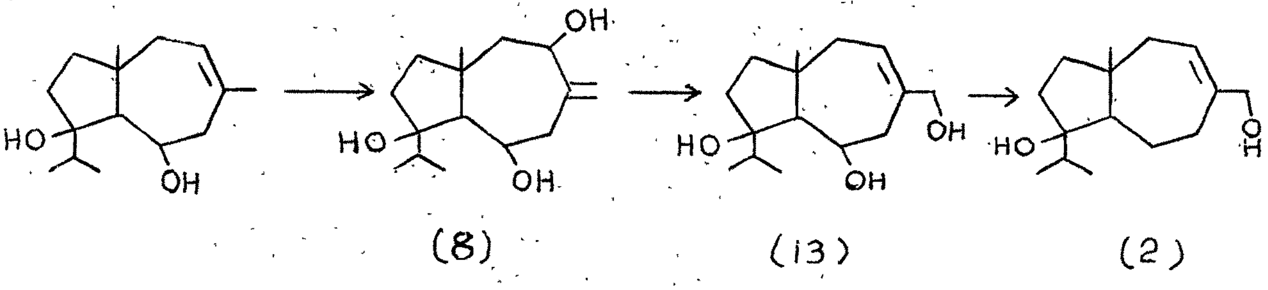


FIG. XI

Accordingly, jaeshkeanadiol was converted into the corresponding epoxide (7). Treatment of this epoxide with lithium diethylamide[7] in ether furnished a complex mixture from which the required alcohol (8) was obtained pure by chromatography over SiO_2 gel. IR (Fig. XII) OH 3380, 1045 cm^{-1} and $-C{=}CH$ 1635, 900 cm^{-1}; PMR(Fig.XIII) $C{=}C\underline{H}_2$(2H, d, at 5.16 ppm, J=16Hz). However, the rather low yields (18%) of the desired alcohol(8) prompted us to look for an alternative method. Neutral alumina (gr.I) is employed[8] to obtain allylic alcohol from an epoxide. When jaeshkeanadiol epoxide was isomerised over alumina, the desired allylic alcohol was obtained in 59% yield. To see whether the yields could be further improved by using alkali doped alumina[9], epoxide was treated with basic alumina. No change in the product composition was found.

Having thus obtained alcohol(8), next step was to protect hydroxyl functions at C_{10} and C_5. With a view to protecting these two hydroxyls, the allylic alcohol was treated with phosgene. The product obtained from this reaction analysed for $C_{16}H_{23}O_3Cl$ (M^+ at m/e 298). Its IR (Fig.XIV) showed absorption due to $-O-CO-O$ (1750 and 1250 cm^{-1}), but no OH absorption. Its PMR (Fig.XV) revealed the presence of $-C-\underline{Me}$(3H, s, 1.08 ppm), $-CH\underline{Me}_2$ (6H, 2d, 1.0 and 1.07 ppm, J=7Hz each)-$C\underline{H}-O-CO-O$(IH, triplet of doublets, 4.33 ppm, $J_1=J_3=5$Hz and $J_2=11$ Hz)

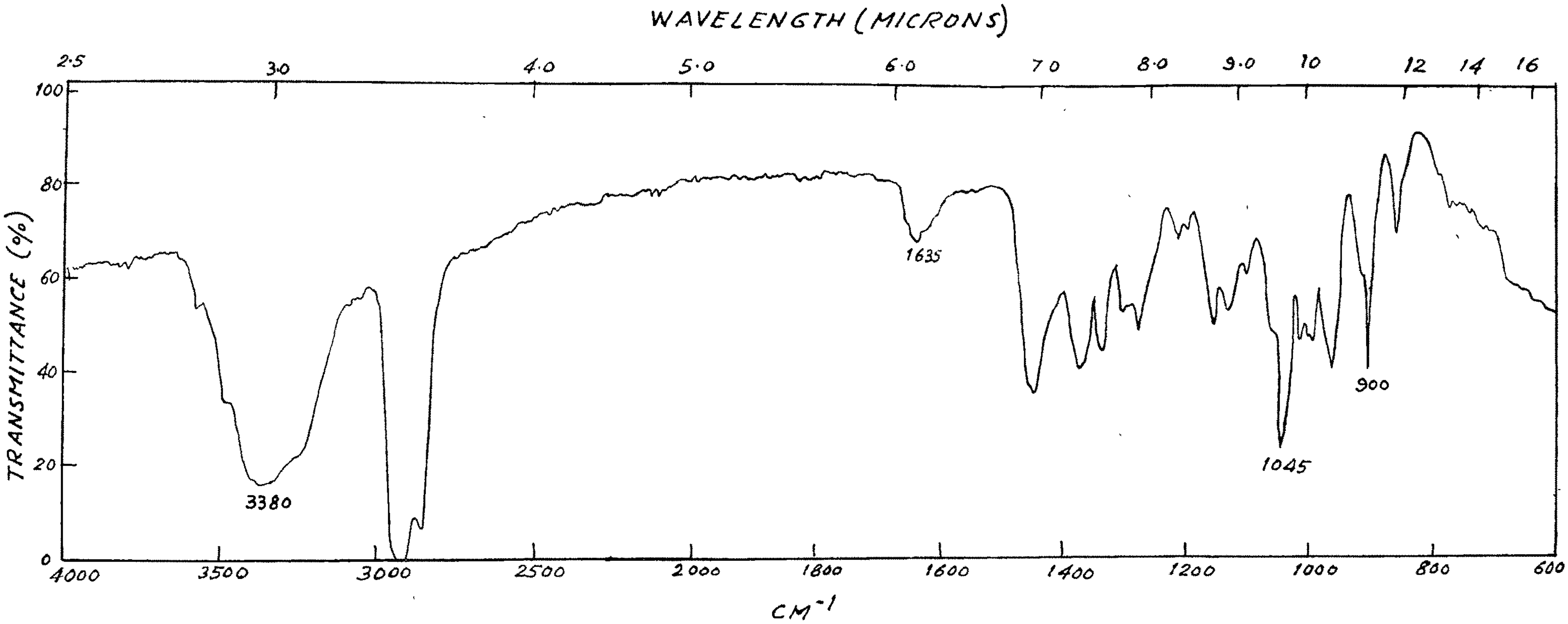


FIG. XII. IR SPECTRUM OF ALLYLIC ALCOHOL (8)

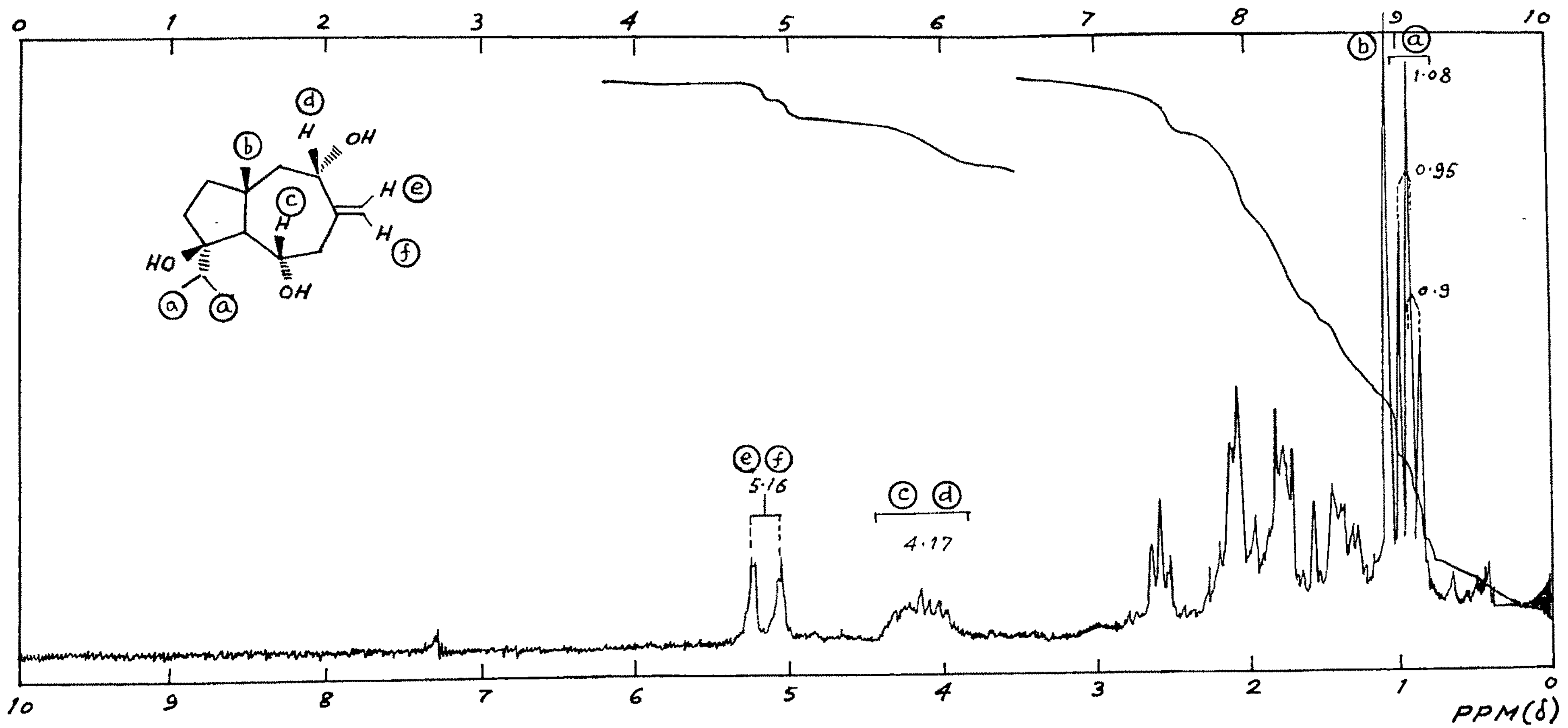


FIG. XIII PMR SPECTRUM OF ALLYLIC ALCOHOL (8)

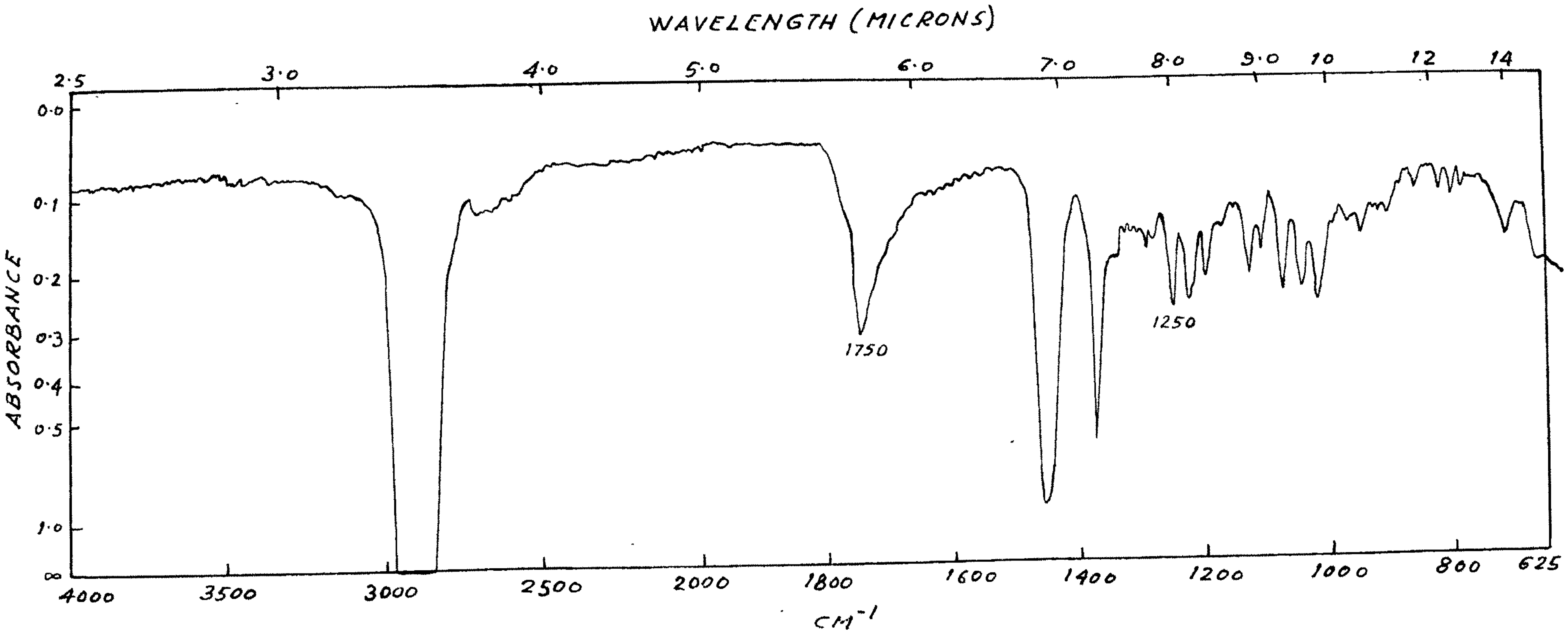


FIG. XIV. IR SPECTRUM OF CHLORIDE (10)

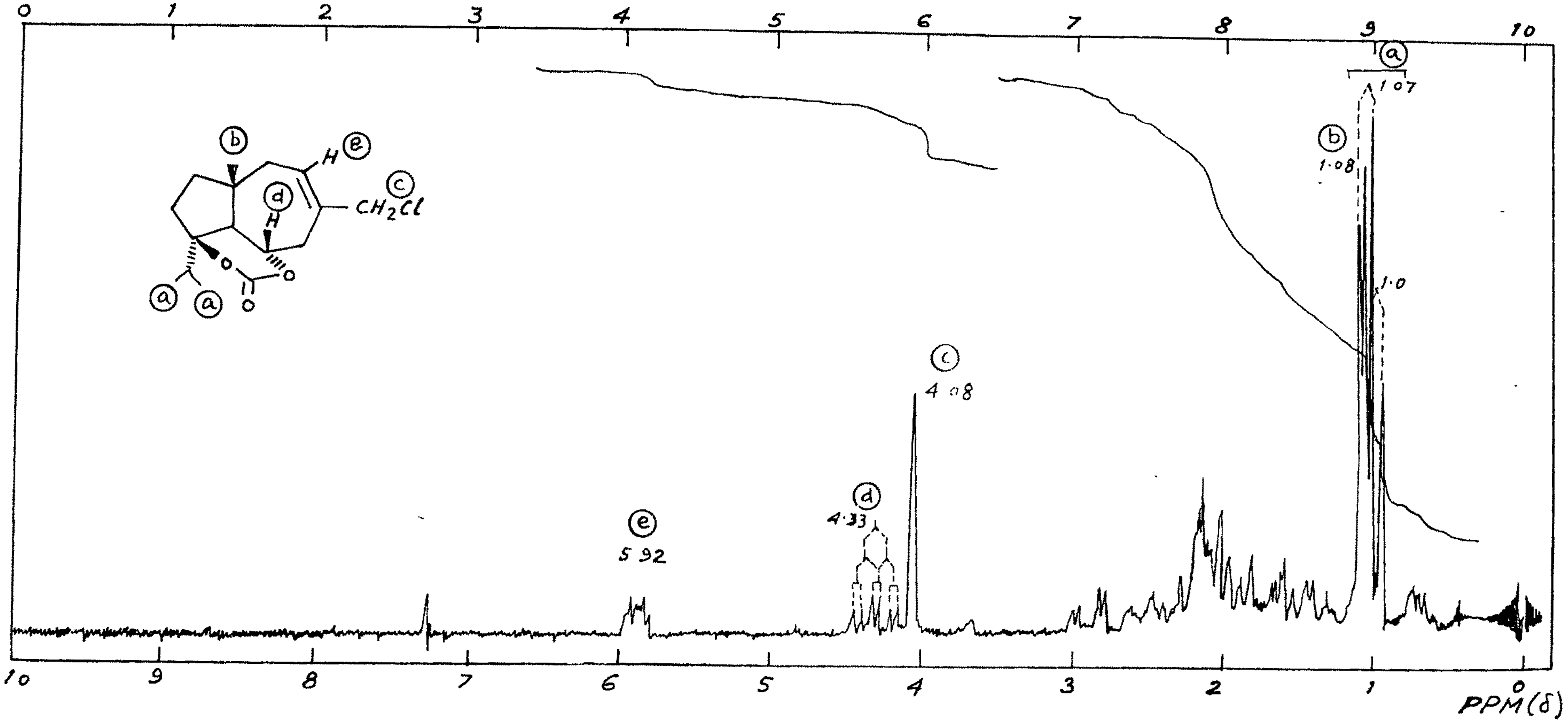
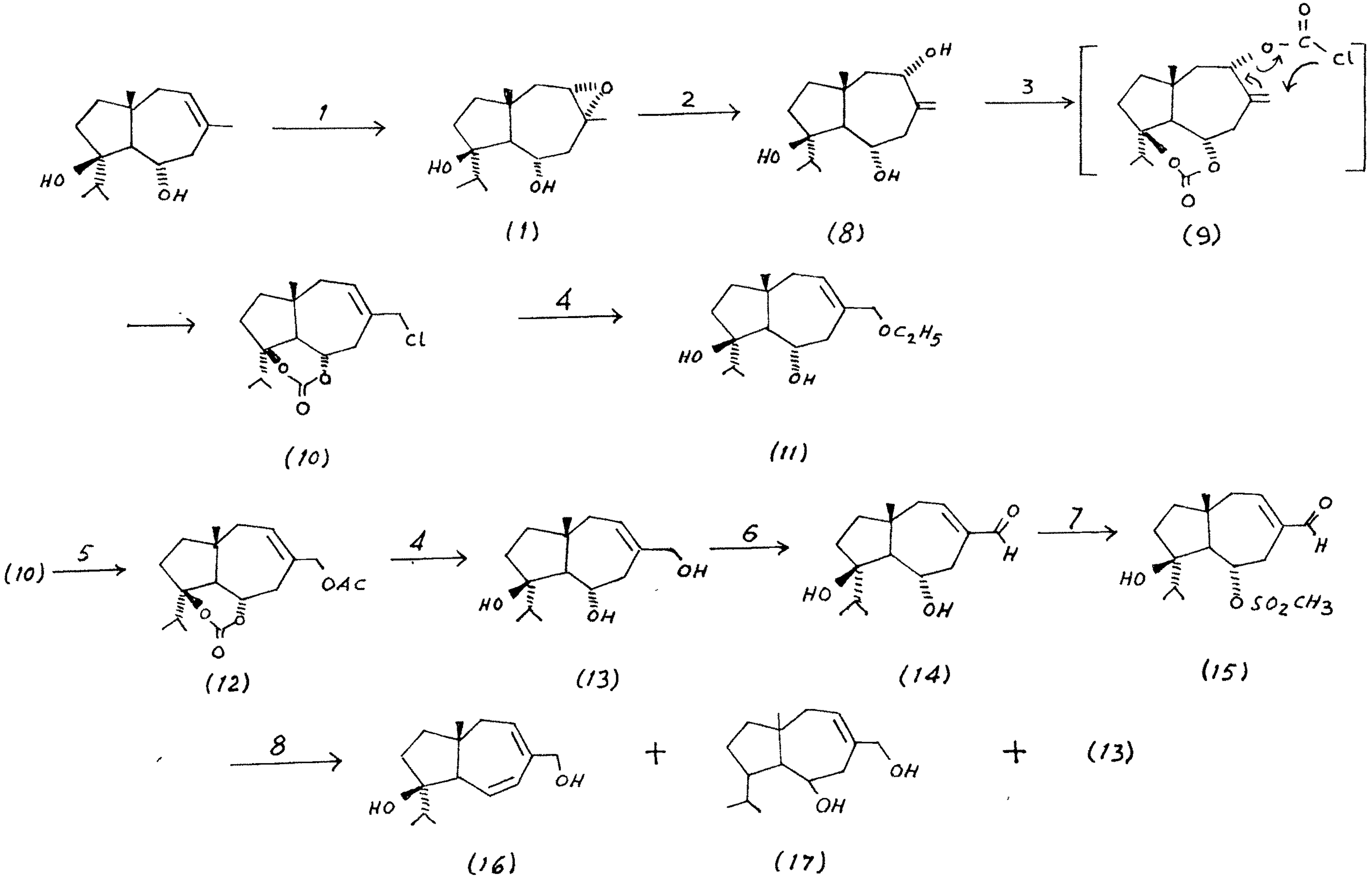


FIG. XV. PMR SPECTRUM OF CHLORIDE (10)

-C=C$\underline{H}$(1H,m,5.92 ppm) and a sharp singlet at 4.08 ppm integrating for two protons. On the basis of these spectral data, this compound is assigned structure(10). The formation of this compound can be visualised through the intermediacy of chloroformate (9) (Fig.XVI) with the concomitant allylic rearrangement to furnish (10)[10].

In order to get the corresponding hydroxy derivative (13), the allyl chloride was solvolyzed with aq ethanolic KOH. The PMR of the crude mixture indicated it to be a mixture rich in ether (11). No attempt was made to separate individual component and instead an alternative approach was planned. It was thought worthwhile to displace chloride by acetate function and hydrolyse the resulting acetate with alkali to get triol (13). The displacement reaction proceeded smoothly using NaOAc in AcOH in presence of catalytic amount of cuprous chloride[11] giving acetate(12). IR(Fig.XVII):-O-CO-O 1747, 1220 cm^{-1}; OAc 1722, 1250 cm^{-1}; PMR (Fig.XVIII):-C$\underline{H}$-O-CO-O-(IH,m, 4.28 ppm),-OA$\underline{c}$(3H,s,2.08 ppm),-C$\underline{H}_2$OAc(2H,s,4.5 ppm).

The acetoxy carbonate on subsequent treatment with 5% ethanolic KOH[12] gave the desired triol(13). IR(Fig.IXX): OH 3590, 3390 and 1035 cm^{-1}, no C=O absorption. PMR(Fig.XX): -C$\underline{H}$OH and -C$\underline{H}_2$OH(3H, m, 3.91 ppm). Having successfully functionalised C_3 methyl, the next step was the selective removal of secondary hydroxyl at C_5. The allylic primary hydroxyl group in (13) was selectively oxidised



REAGENTS-

1. PBA/BENZENE
2 Al_2O_3
3. $COCl_2$/PYRIDINE
4. 5% ETHANOLIC KOH
5. NaOAc/AcOH
6. DDQ/DIOXANE
7. CH_3SO_2Cl/Et_3N
8. LAH

FIG. XVI

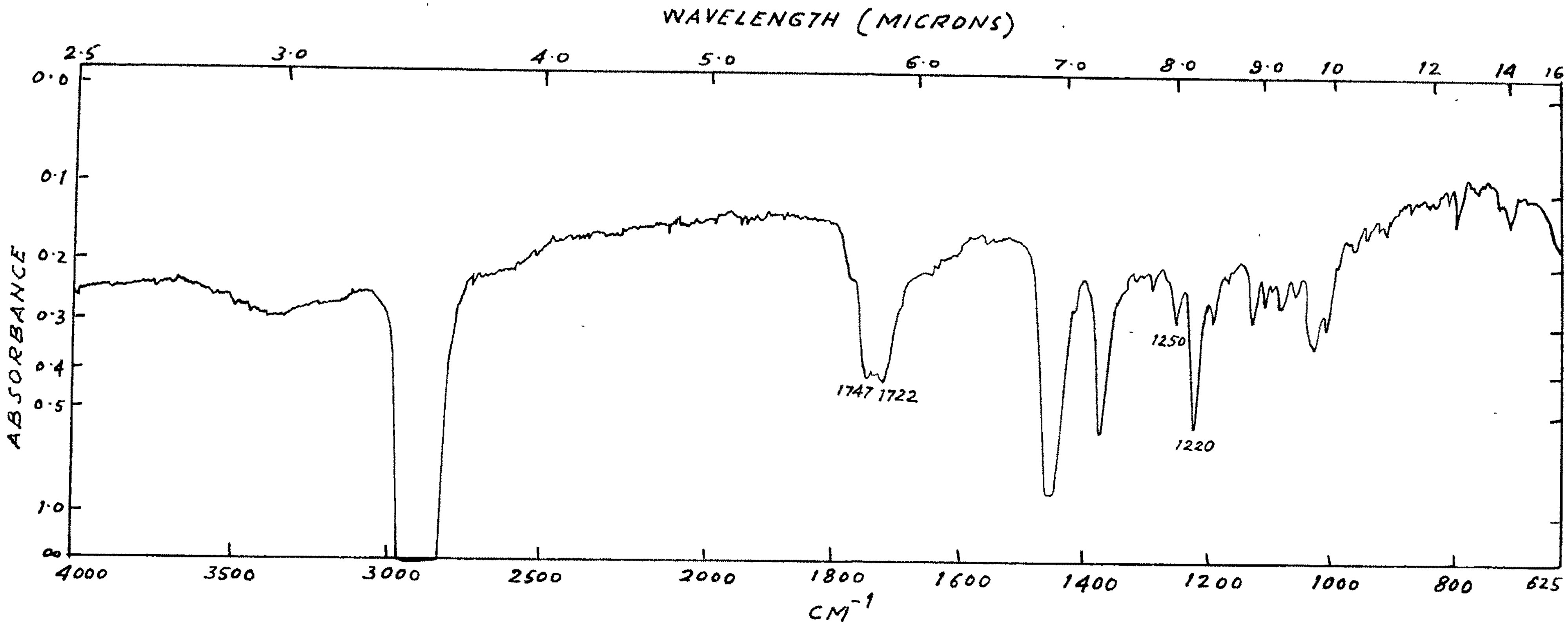


FIG. XVII. IR SPECTRUM OF ACETATE (12)

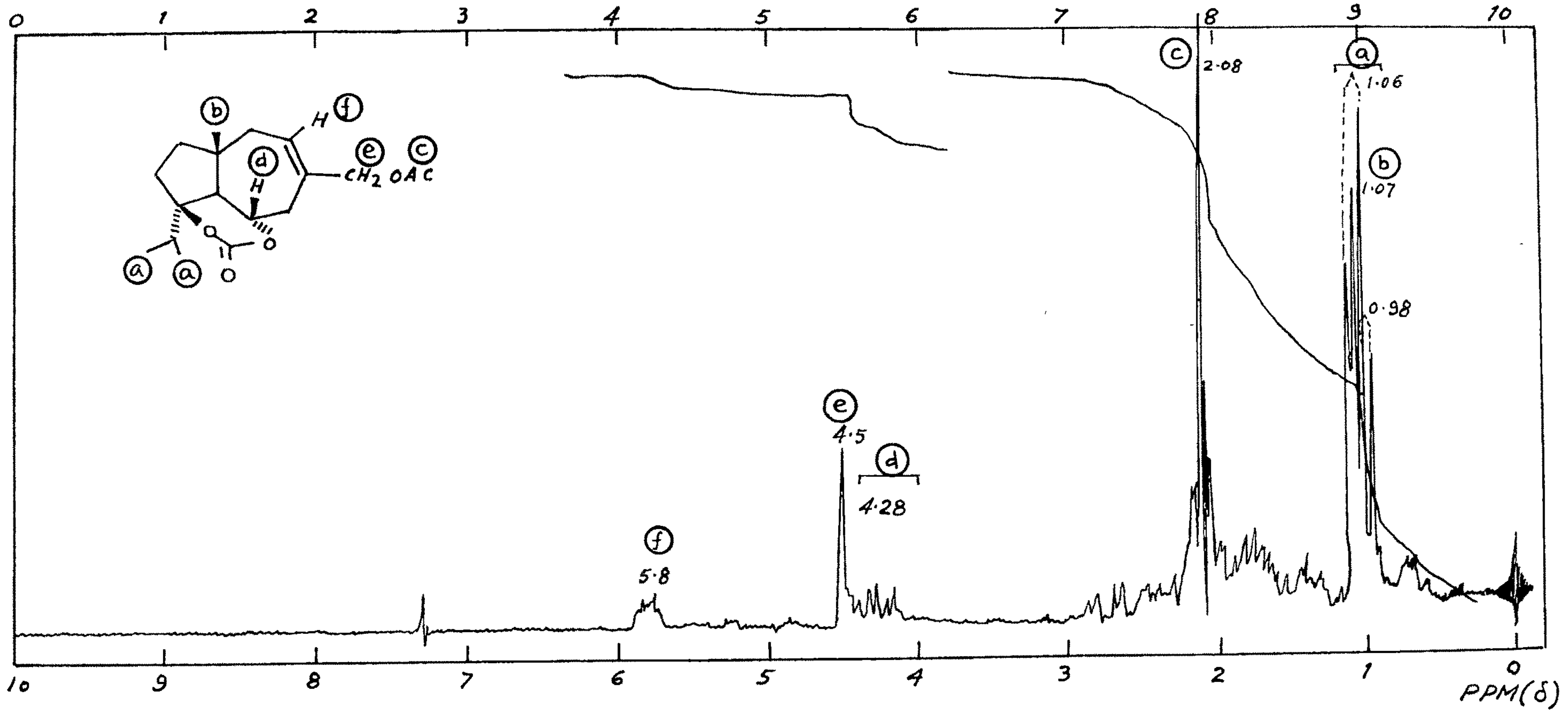


FIG. XVIII. PMR SPECTRUM OF ACETATE (12)

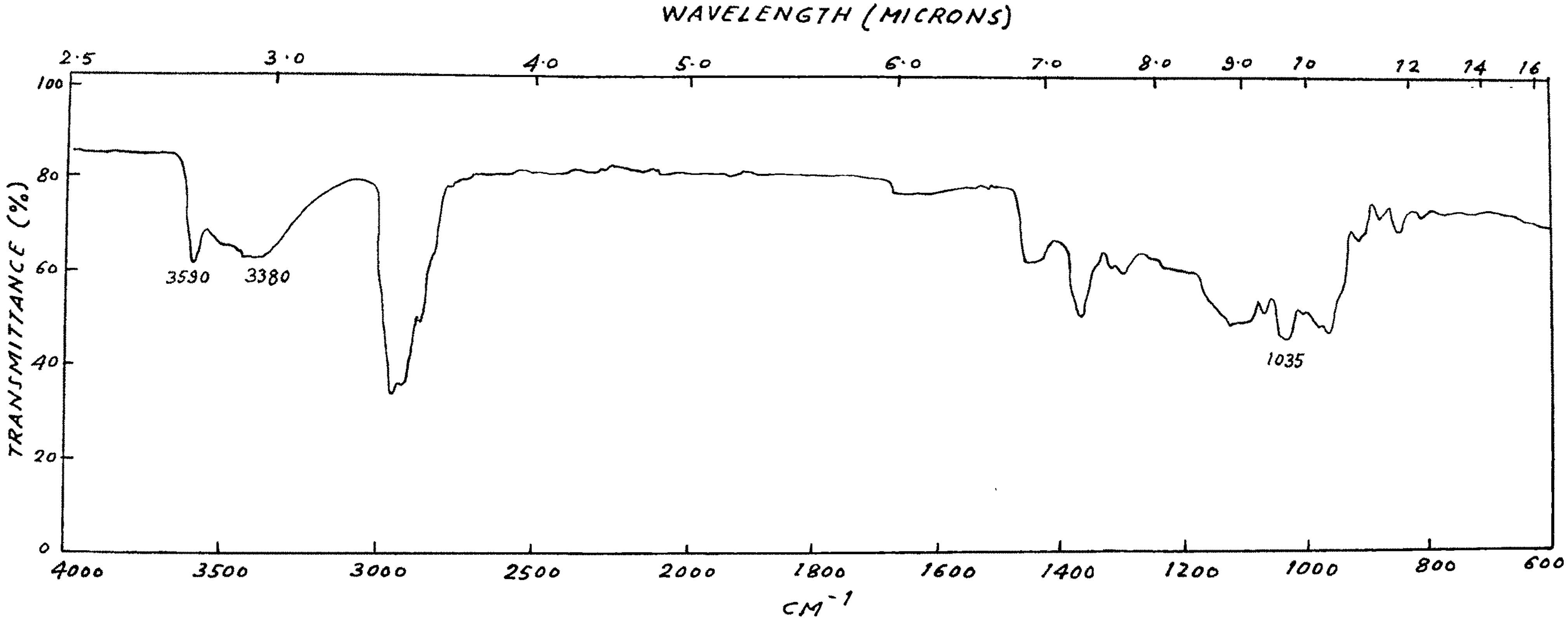


FIG. IXX. IR SPECTRUM OF TRIOL (13)

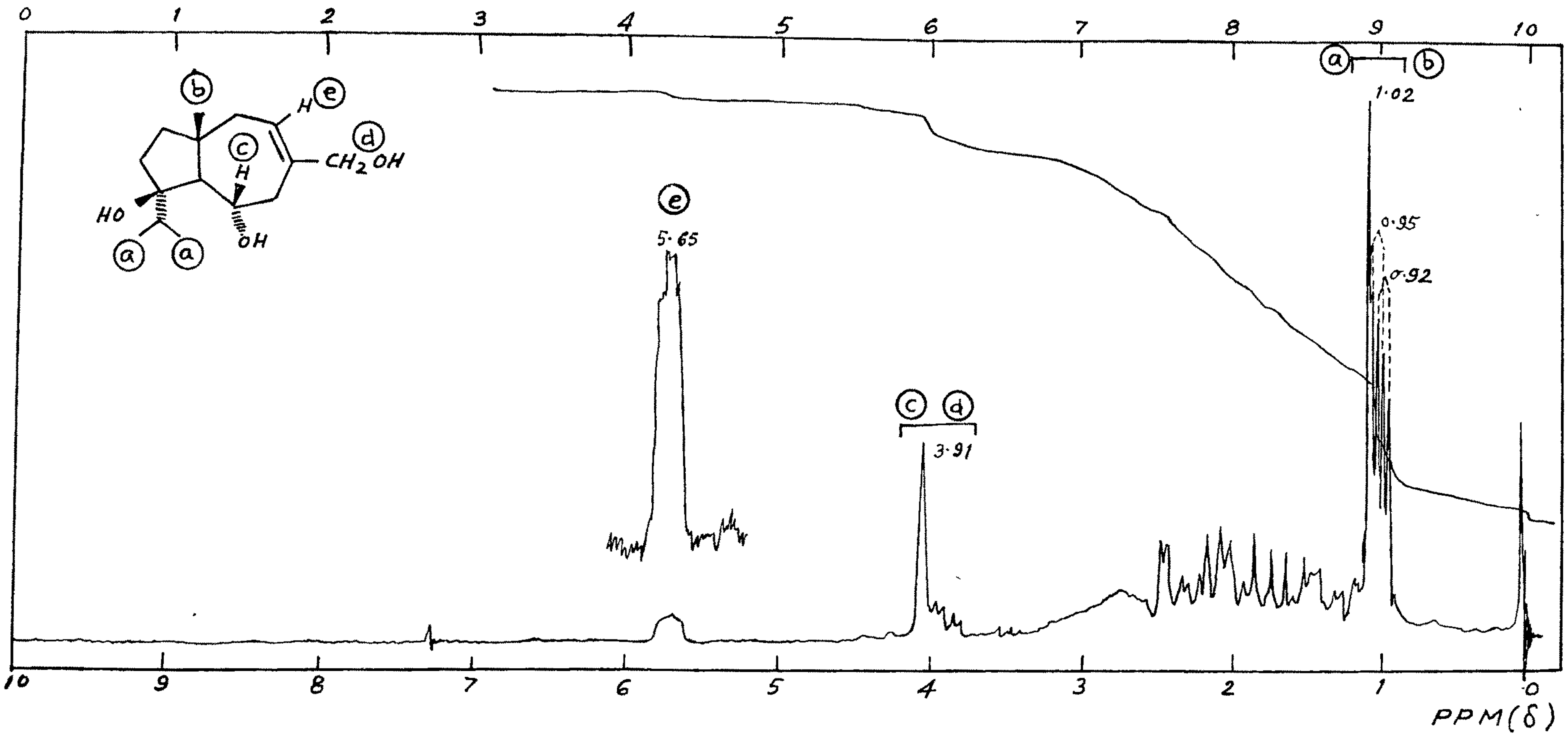


FIG. XX. PMR SPECTRUM OF TRIOL (13)

using DDQ[13] giving allylic aldehyde (14). UV: λmax 240 nm (ϵ 11340); IR(Fig.XXI): OH, 3520, 1040 cm^{-1}; C=O 1675 cm^{-1} and $-C=C\underline{H}$ 1635, 850 cm^{-1}; PMR (Fig.XXII):$-C\underline{H}OH$(IH,m,3.84 ppm), $-C\underline{H} = C-C=O$ (1H, m, 6.71 ppm) and $\underline{H}-C=O$ (1H , s,924 ppm). The hydroxy-aldehyde (14) was next converted into the corresponding mesylate (15). IR(Fig. XXIII): OH 3520 cm^{-1}; C=O 1689 cm^{-1}; C=CH 1645 and $-O-SO_2-C$ 1175 cm^{-1}; PMR (Fig.XXIV): $-SO_2-\underline{Me}$(3H, s, 3.14 ppm) and $-C-\underline{H}-CO-SO_2-CH_3$ (1H, triplet of doublets at 4.85 ppm, $J_1=J_3=3$Hz and $J_2=10$Hz). The mesylate was found to be extremely unstable and was used up immediately for the subsequent reduction. Reduction of the mesylate proceeded smoothly at -5° giving mainly three products as revealed by TLC(solvent: 50% EtOAc in benzene).

These compounds were separated by chromatography over SiO_2 gel. The compound corresponding to Rf 0.42 b.p. 175-85°(decomp)(bath)/0.5 mm analysed for $C_{15}H_{24}O_2$ (M^+ at m/e 236). UV: λmax 246.5 nm(ϵ,4483); IR(Fig.XXV): OH 3590, 3440 cm^{-1}. PMR (Fig. XXVI):$-C-\underline{Me}$ (3H,s,0.96 ppm),$-CH\underline{Me}_2$(6H,2d,0.91 and 0.95 ppm,J = 7Hz each),$-C\underline{H}_2OH$ (2H, s,4.08 ppm), $C=C\underline{H}$ (1H, m, 5.73 ppm) and $-CH=CH-$(2H, s,5.91 ppm). Based on these data structure (16) is assigned to this compound.

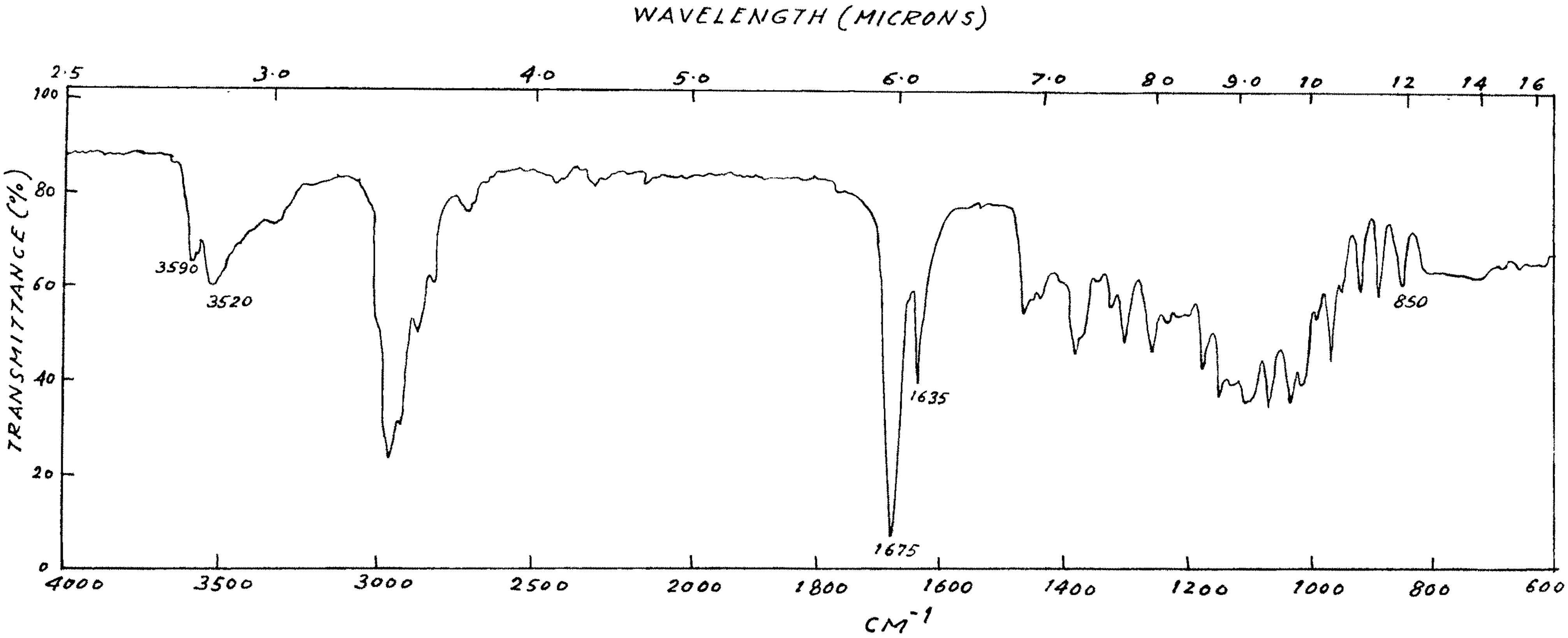


FIG. XXI. IR SPECTRUM OF ALLYLIC ALDEHYDE (14)

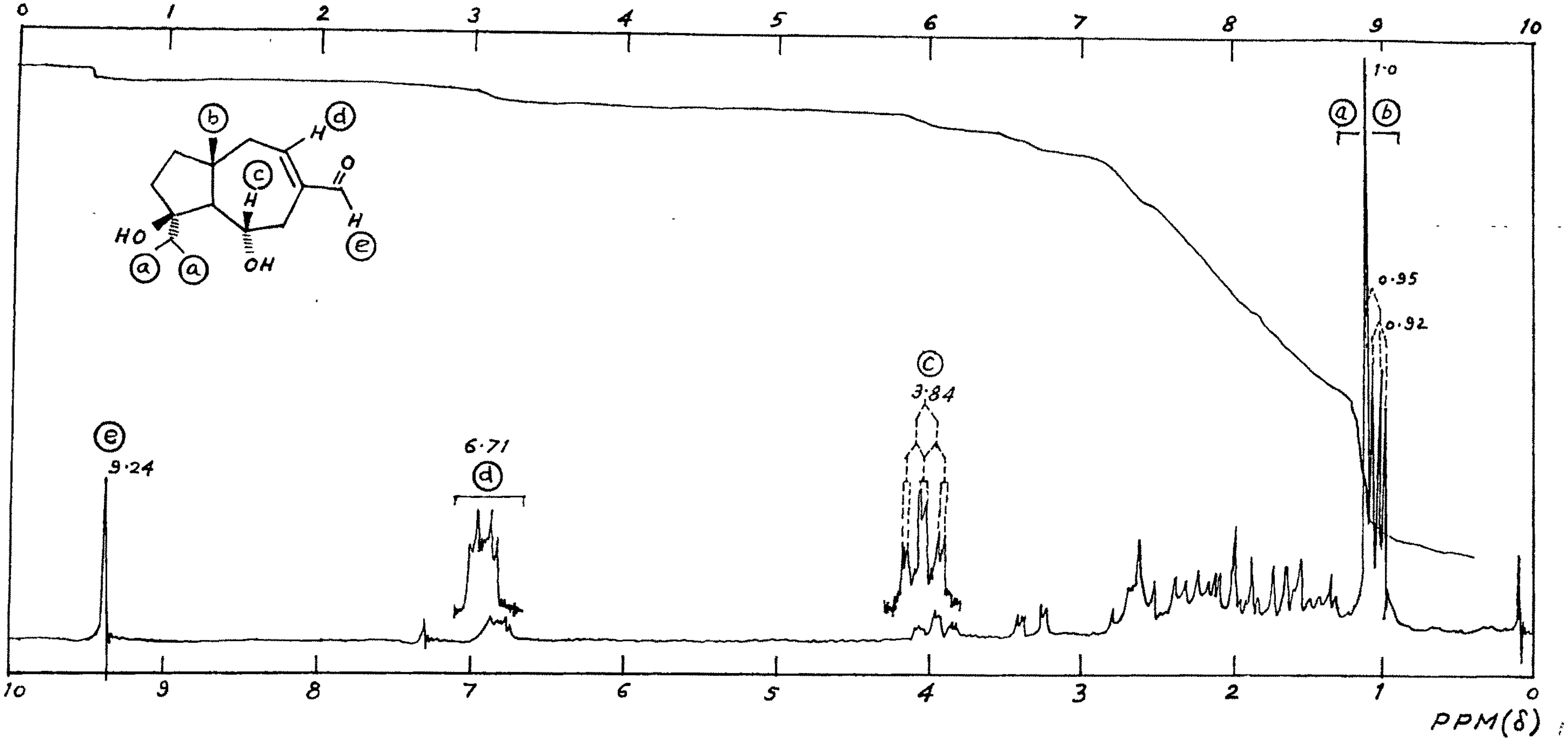


FIG. XXII. PMR SPECTRUM OF ALLYLIC ALDEHYDE (14)

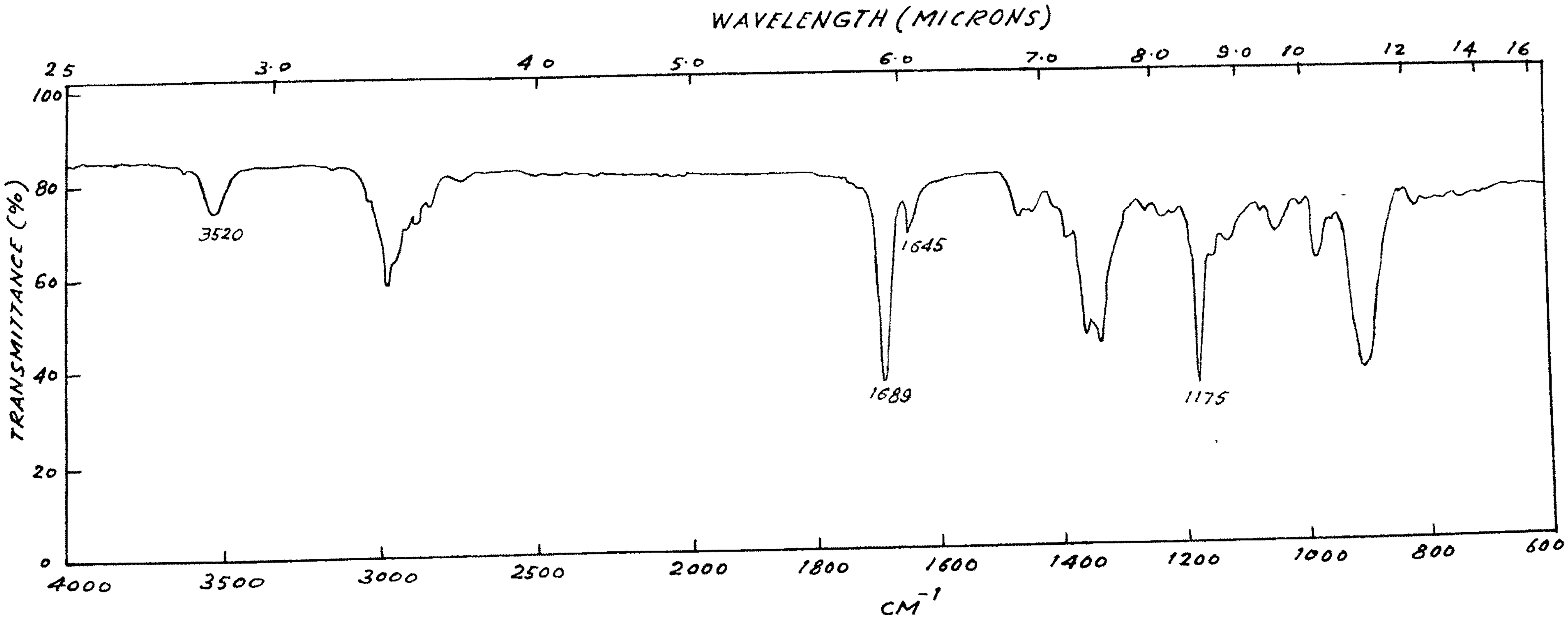


FIG. XXIII. IR SPECTRUM OF MESYLATE (15)

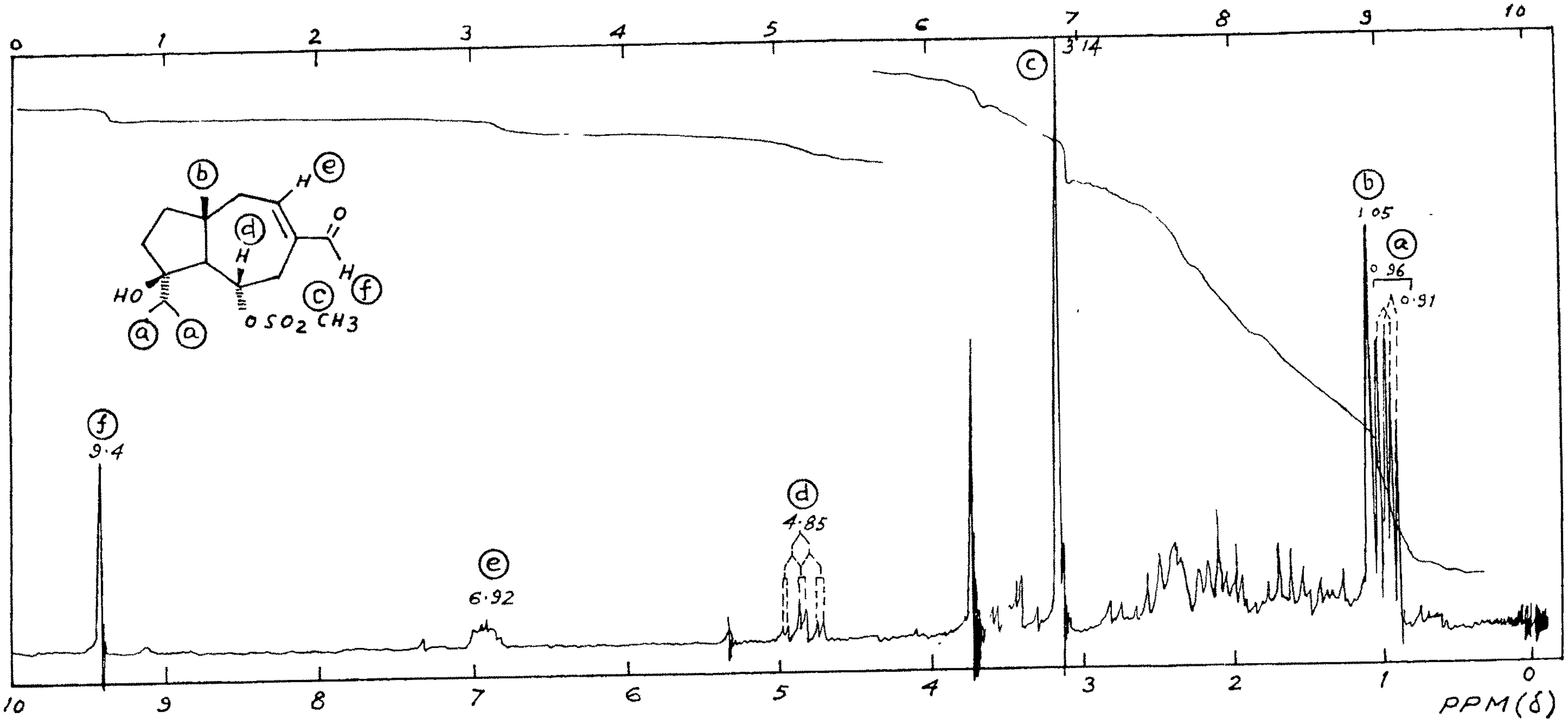


FIG. XXIV. PMR SPECTRUM OF MESYLATE (15)

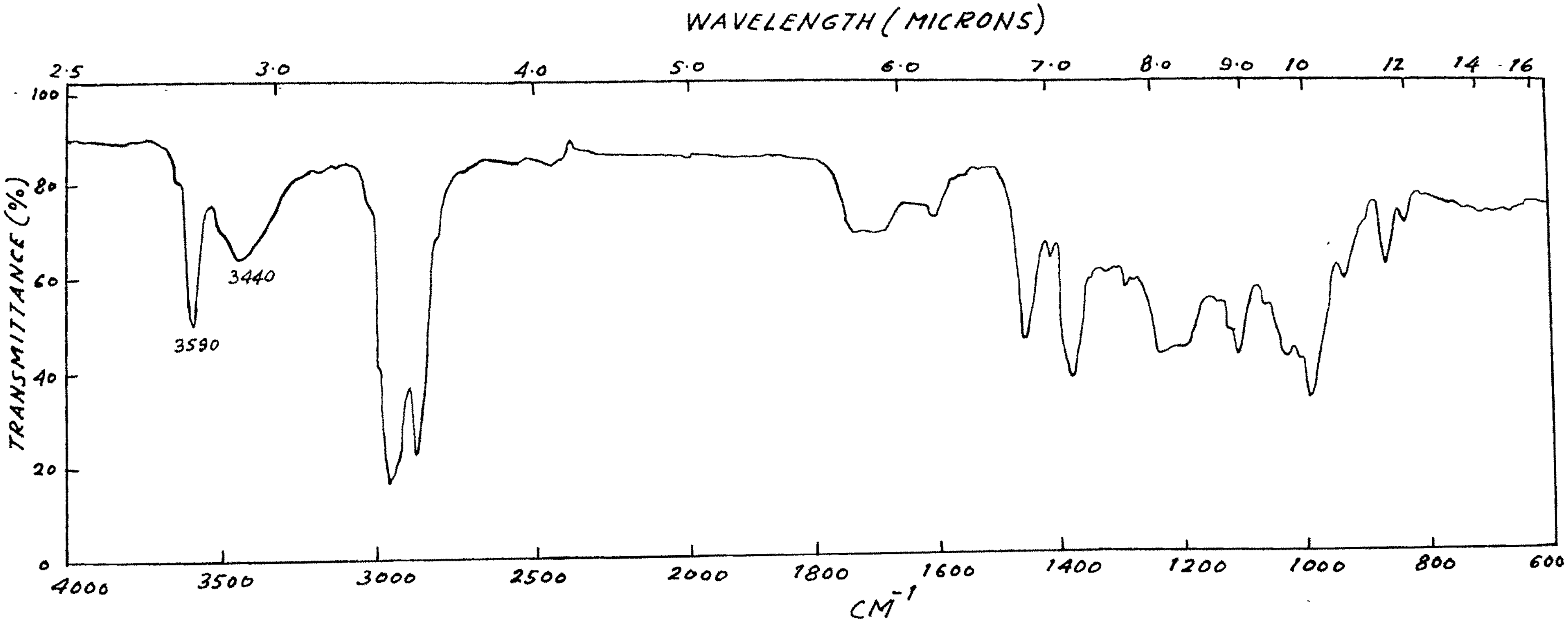


FIG. XXV. IR SPECTRUM OF COMPOUND (16)

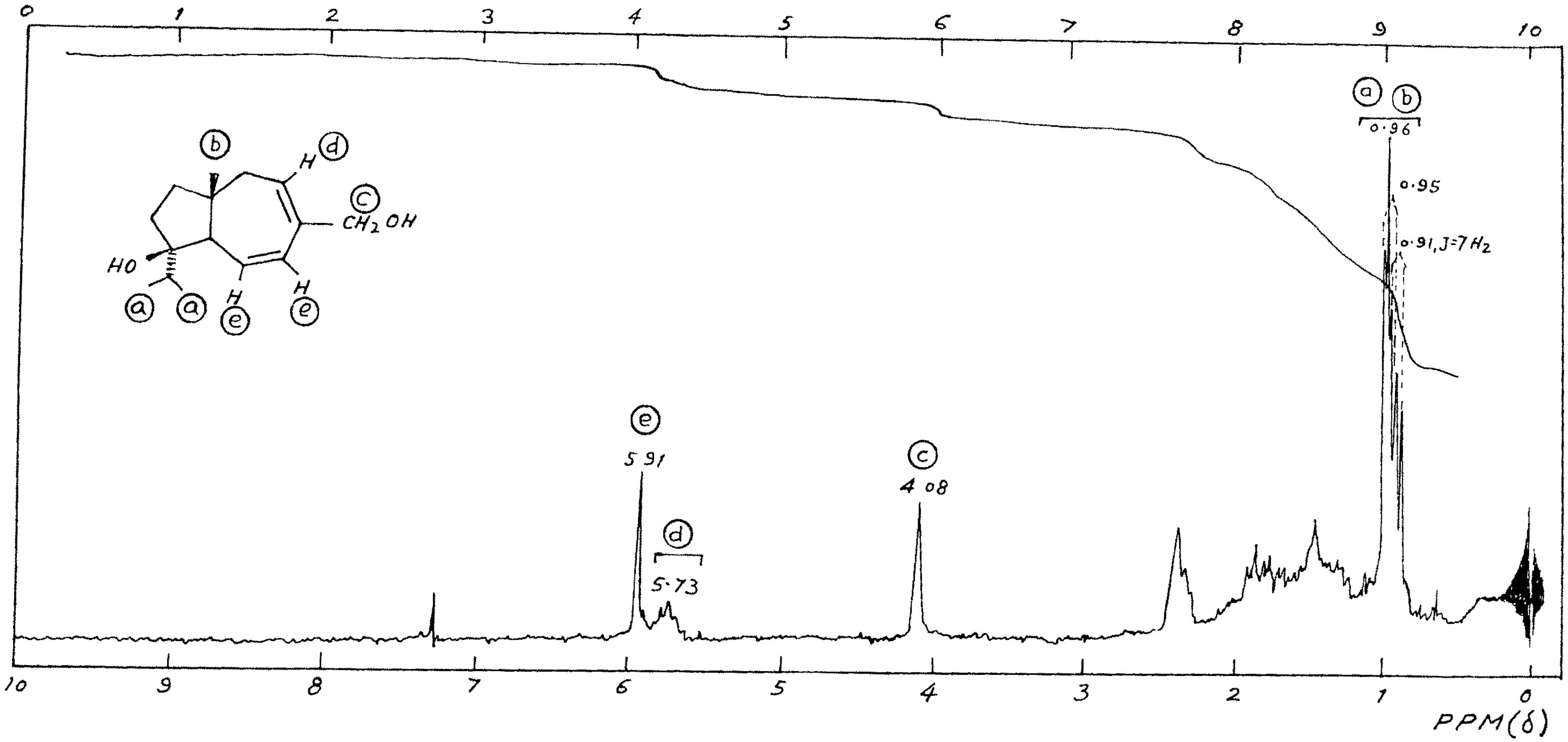
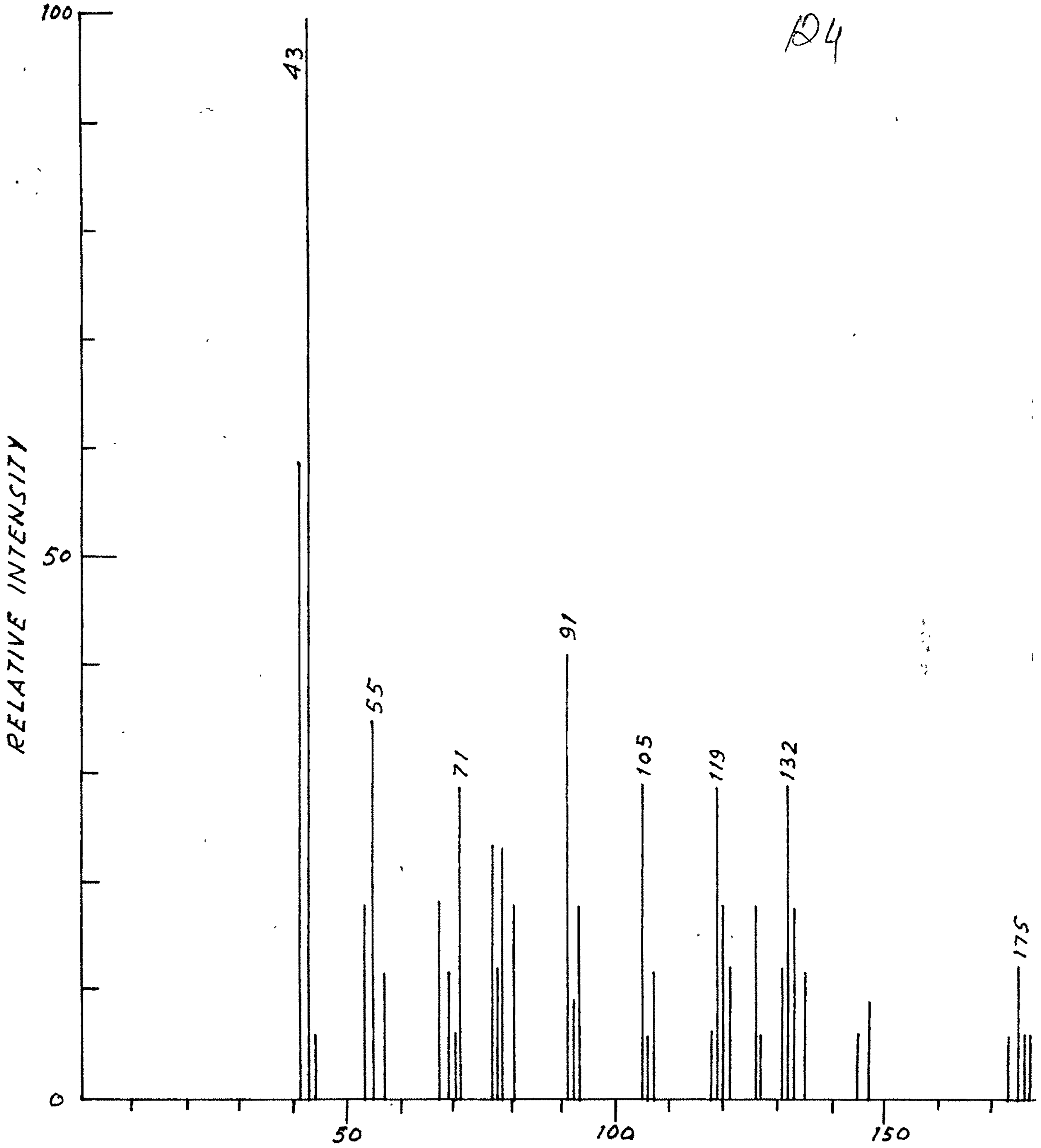


FIG. XXVI PMR SPECTRUM OF COMPOUND (16)


D4
RELATIVE INTENSITY
100
50
0
43
55
71
91
105
119
132
175
50
100
150

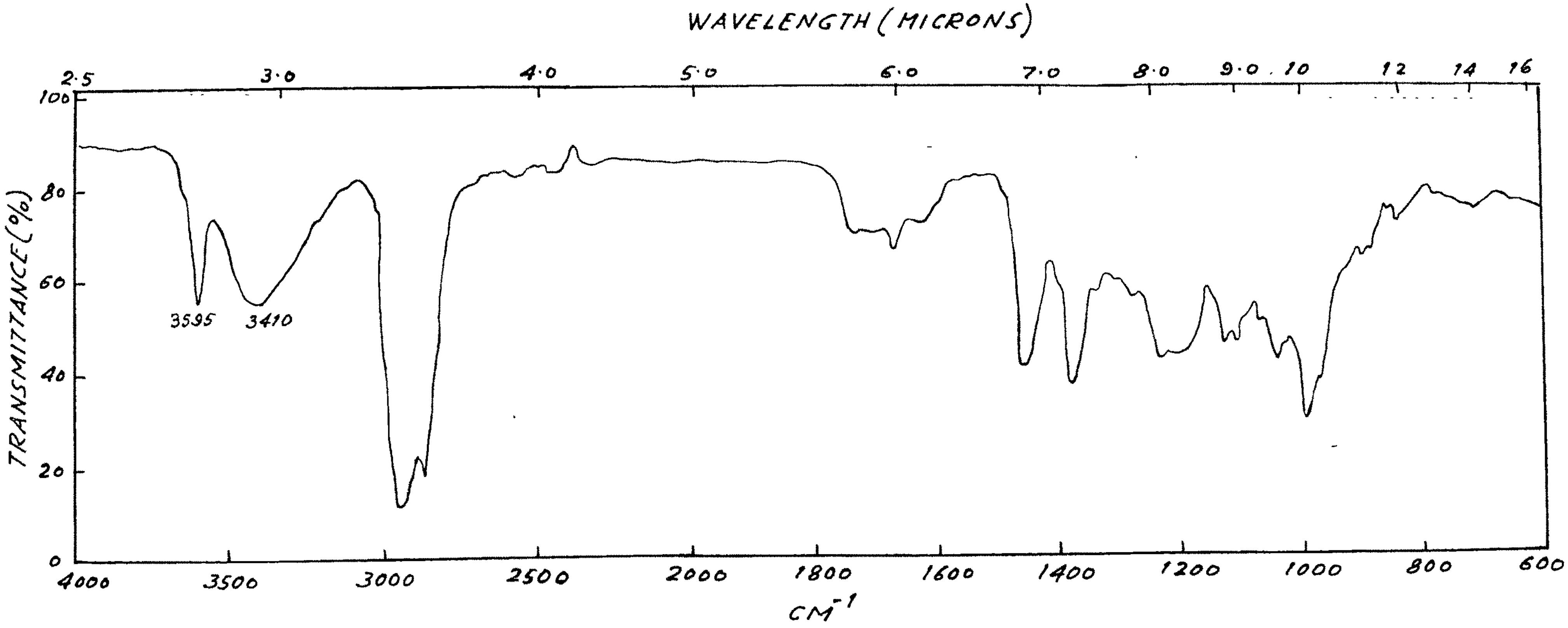


FIG. XXVIII. IR SPECTRUM OF COMPOUND (17)

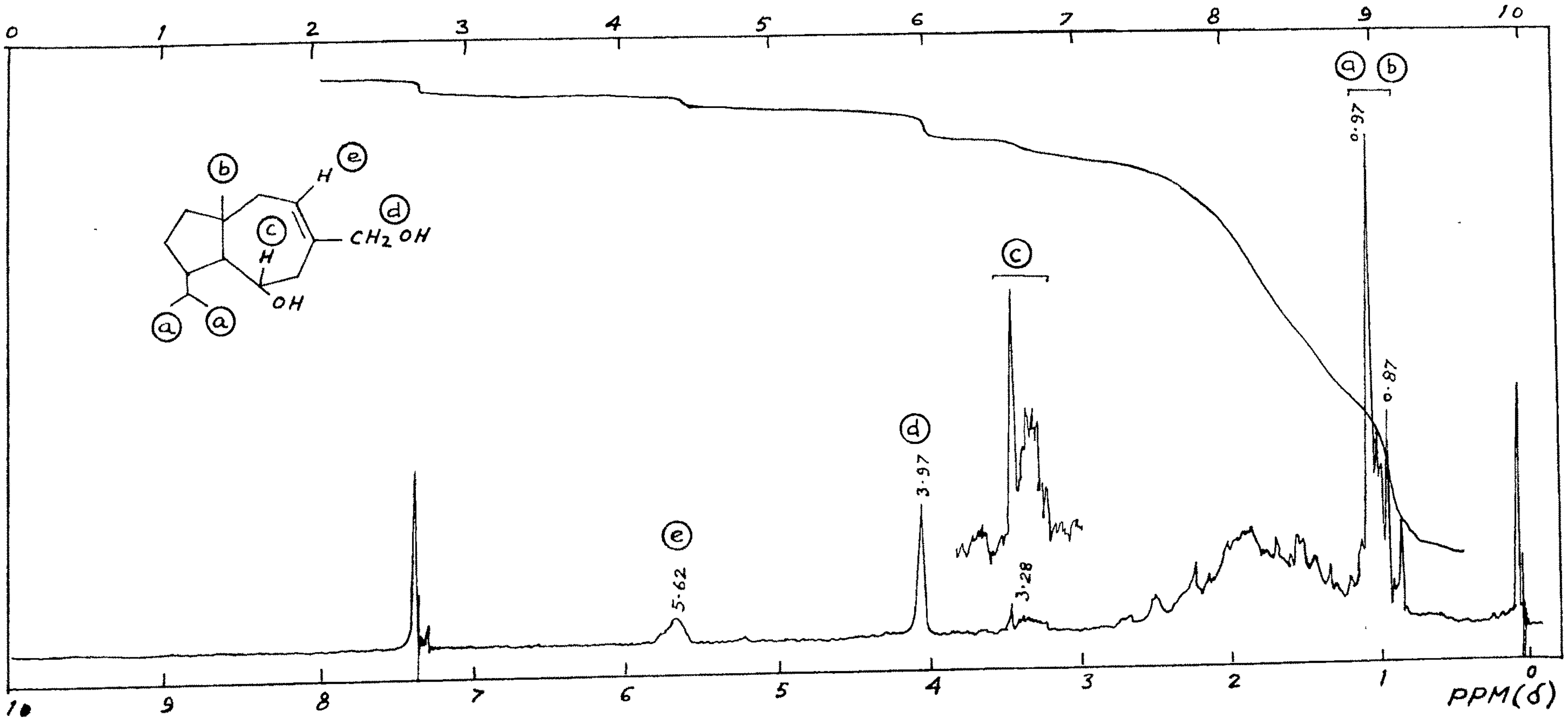
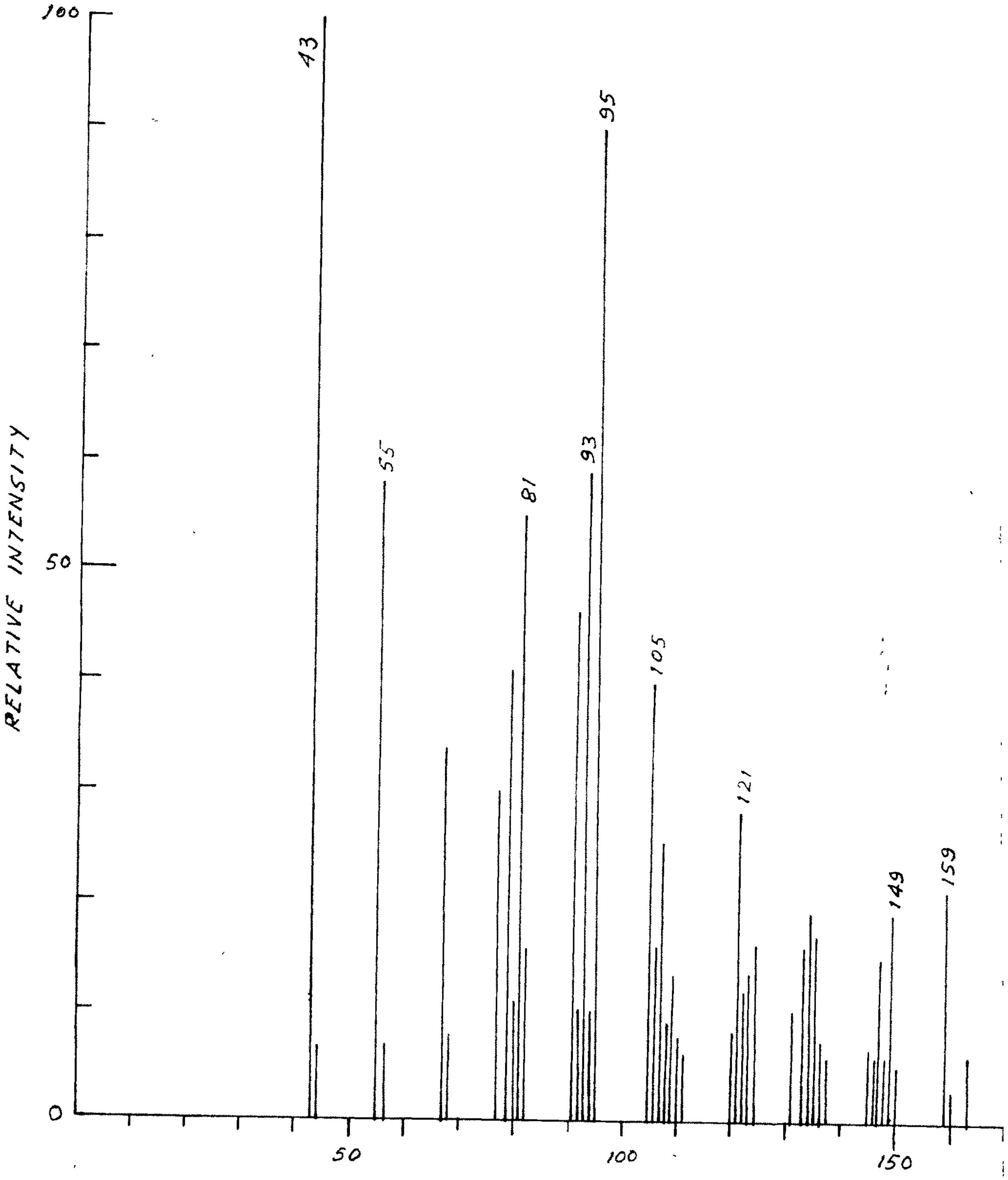
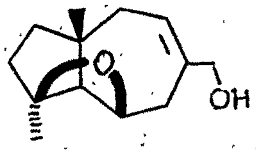


FIG. XXIX. PMR SPECTRUM OF COMPOUND (17)

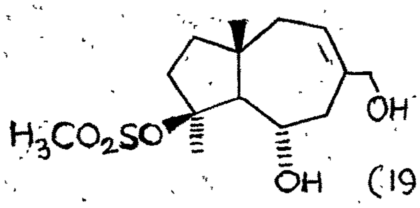
127


100
50
0
RELATIVE INTENSITY
43
55
81
93
95
105
121
149
159
50
100
150

The compound corresponding to Rf 0.31 b.p. 175-185° (decomp)(bath)/0.4 mm analysed for $C_{15}H_{26}O_2$(M^+, m/e 238). IR(Fig. XXVIII):OH 3595 and 3410 cm^{-1}), PMR (Fig.XXIX):-C-$\underline{Me}$ and -CH$\underline{Me}_2$(9H, m, between 0.87 and 0.97 ppm),-C$\underline{H}$OH(1H, m, 3.28 ppm) -C$\underline{H}_2$OH(2H, s, 3.97 ppm) and -C=C$\underline{H}$(1H, m, 5.62 ppm). On the basis of these data this compound is assigned structure (17). This compound might be arising through the intermediacy of oxetane (18) or mesylate (19), which might have formed by the intramolecular transfer of mesylate group (see Fig.X).



(18)



(19)

As discussed in the case of LAH reduction of jaeschkeanadiol monomesylate (3), in this case too, the possibility of oxetane formation seems less likely on steric grounds.

The compound having Rf 0.17 was found to be triol(13) on the basis of its spectral data (IR, PMR).

Thus, even this alternative approach to convert jaeschkeanadiol to neojaeschkeanadiol was rendered unsuccessful due to the failure of reduction of mesylate (15) to provide the desired neojaeschkeanadiol. This is surprising in view of the fact that jaeschkeanadiol monomesylate(3) on reduction with LAH gives alchol (5) as the major product. Unfortunately the reduction of mesylate (15) took an abnormal course.

EXPERIMENTAL

Acetylation of epoxyjaeschkeanadiol

Epoxyjaeschkeanadiol (0.1 g), pyridine (1 ml), acetic anhydride (1 ml) were left at room temperature overnight. The solvents were flashed off and the residue was diluted with water, extracted with ether (3 x 25 ml) and the ether solution was washed with 10% HCl aq (2x10ml), $NaHCO_3$ aq (10%, 2x10ml), brine and dried. Solvent removal afforded the acetate which was crystallised from light petroleum, m.p. 136-37°, $[\alpha]_D$ +25.24°(c, 1.5%)(Found: C, 68.76; H, 10.24. $C_{17}H_{28}O_4$ requires: C, 68.89; H 9.52%). Mass: major ions at m/e 253(M-43, 64%), 236(M-60, 25%), 193(100%), 175(77%), 165(71%), 151(69%), 123(72%), 109(67.5%), 95(62%), 55(51%) and 43(62%).

Cyclic carbonate of epoxyjaeschkeanadiol

Epoxyjaeschkeanadiol(0.05g) was dissolved in chloroform (alcohol free, 10 ml) containing pyridine (0.5 ml) and the solution was cooled to 0°C in an ice-salt mixture. A solution of phosgene in toluene (20%, 1 ml) was added and the mixture was stirred for 75 min.(ice-water). It was then left at 0° overnight (14 hr). Ice cold water was added to decompose excess of phosgene and the solution was extracted with ether (3x 25 ml). The ether solution was further washed with 2N HCl aq (2 x 10 ml), Na_2CO_3 aq (5%, 2 x 10ml), water(3 x 10ml), brine and dried. Solvent removal gave compound (0.06 g) which was crystallised from ether-petroleum ether (40-60°), mp.203-204°. IR:-O-CO-O 1750, 1230 cm^{-1}; PMR:-C-Me(3H,s,1.16 ppm), -CHMe$_2$(6H, 2d at 0.93 and 1.03 ppm, J=7Hz each) -O-C-Me(3H,s,1.42 ppm) and H-C-O-CO-O-(1H,t,4.28 ppm)(Found:C,68.10; H, 8.15 $C_{16}H_{24}O_4$ requires: C, 68.57; H, 8.57%).

Epoxidation of jaeshkeanadiol

(A) Using Perbenzoic acid in benzene

Jaeshkeanadiol (0.1g) was dissolved in benzene (5 ml) and the solution was cooled thoroughly with ice-salt mixture. A solution of perbenzoic acid in benzene (0.5120 N, 1.8 ml) was added to it and the mixture was left at 15° for 15-16 hr. After dilution with ice cold water, the aqueous solution was extracted with ether (3 x 20ml) and the ether extract was washed with satd. solution of Na_2SO_3 aq (2x10 ml),satd.Na_2CO_3 aq (4 x 10 ml), water (4 x 10 ml) and finally with brine. Solvent removal from the dried extract furnished compound (0.105 g) which was crystallised from ether-light petroleum, m.p. 102-103°, $[\alpha]_D$+34.44°(c, 1.14). IR: OH 3400, 1040 cm^{-1}; PMR:-C-Me(3H,s,1.15 ppm, -CHMe$_2$(6H, 2d at 0.87 and 0.94 ppm, J=7Hz each), -C-O-C-Me(3H,s,1.4 ppm) and HC-OH (1H,t,4.08 ppm).

(B) Using perbenzoic acid in chloroform

In this case epoxidation was carried out as above with the only difference that PBA in chloroform was used for epoxidation. Thus a mixture of jaeshkeanadiol (1 g), PBA(0.65N, 10.4 ml) in chloroform(12ml) was left at 15° for 20 hr. The usual work up then gave compound (1.2 g) which was found to be complex mixture on TLC (solvent: C_6H_6-30% EtOAc). It was chromatographed on silica gel (IIB, 40 g, 1.8 x 33 cm)

Fr.1	C_6H_6	4 x 50 ml	Nil
Fr.2	C_6H_6-5% EtOAc	4 x 50 ml	0.102 g
Fr.3	-do-	6 x 50 ml	0.09 g complex mixture
Fr.4	-do-	6 x 50 ml	0.036 g Liquid
Fr.5	-do-	5 x 50 ml	0.1457 Complex mixture.
Fr.6	-do-	20 x 50 ml	0.464 g
Fr.7	C_6H_6-10% EtOAc	10 x 50 ml	0.1 g Mixture
Fr.8	C_6H_6-50% EtOAc	5 x 50 ml	0.1902g Solid

Fraction-2 was crystallised from light petroleum, m.p. 91-2°. It was found to be jaeshkeanadiol on the basis of its spectral data (PMR).

Fraction-4 was distilled, b.p. 200-210°(bath)/0.8 mm. IR(CCl_4): OH 3600,3460,1015 cm^{-1}, C=O 1706 cm^{-1} and C=C 1650 cm^{-1}; PMR:-C-Me(3H,s,1.26 ppm),-$CH\underline{Me}_2$(3H each at 0.88 and 0.95 ppm),-C=C-$\underline{Me}$(3H,m,between 1.68 and 1.81 ppm)

-C$\underline{H}$OH(1H, m, 4.28 ppm),-C=C$\underline{H}$(1H each at 4.84 and 5.02 ppm) and $\underline{H}$-C=O(1H,d,9.96 ppm, J=2Hz). Structure (1B) is assigned to this compound on the basis of spin-decoupling studies(PMR) as well as consideration of mechanistic aspects.

Fraction-6 was crystallised from ether-light petroleum m.p. 102-103°. It was found to be the required epoxy jaeschkeanadiol from its spectral data (PMR) and mixed m.p. with an authentic sample of epoxyjaeschkeanadiol.

Fraction-8 was crystallised from benzene, m.p. 96-8°

IR : OH 3380 cm^{-1} and -C=C 1635 cm^{-1}

PMR: -C-$\underline{Me}$(3H, s, 1.06 ppm),-CH$\underline{Me}_2$(6H, 2d centered at 0.88 and 0.93 ppm, J=7Hz), two C$\underline{H}$OH(2H,bm,4.14 ppm) and -C=C$\underline{H}_2$(2H, d, at 5.15 ppm, J=16Hz)(Found :C,70.7; H,10.12 $C_{15}H_{26}O_3$ requires: C, 70.87; H, 10.23%)

Structure (1A) is assigned to this compound on the basis of its spectral data. This compound was identical in all respects (m.p., mixed m.p. IR, PMR) with the one obtained from isomerisation of epoxyjaeschkeanadiol over alumina (vide infra).

(C) Using tert. butylhydroperoxide

Jaeschkeanadiol (0.1 g) was dissolved in benzene (10ml) and to this was added molybdenum acetylacetonate (1.25 mg). The mixture was refluxed and to this refluxing solution was added tert.butylhydroperoxide (80%, 0.03834 g) in benzene (1.5 ml). The solution was then refluxed for 17 hr. The TLC(solvent: C_6H_6-30% EtOAc) of the reaction mixture indicated that reaction had not gone to completion. Heating was discontinued at this stage and after cooling the reaction mixture was decomposed with ice-water and extracted with ether (3 x 20ml). The ether extract was washed with a satd. solution of Na_2SO_3 aq (2x15 ml), water (3x10ml) and brine. The dried extract on evaporation of solvent gave the product (0.1 g). It was chromatographed over silica gel (IIB, 20 x 0.90 cm)

Fr. 1	C_6H_6	5x10ml	0.067g	Mixture rich in jaeschkeanadiol
Fr. 2	C_6H_6-2% EtOAc	4x15ml	nil	
Fr. 3	C_6H_6-5% EtOAc	8x15ml	0.03g	Epoxyjaeschkeanadiol
Fr. 4	C_6H_6-10% EtOAc	12x15ml	0.004g	Not investigated

Fraction-3 crystallised from ether-light petroleum, m.p. 102-103°. It was found to be the desired epoxyjaeschkeanadiol on the basis of its spectral data and mixed m.p. with an authentic sample.

Jaeshkeanadiol monomesylate (3)

Jaeshkeanadiol (0.125 g) was dissolved in methylene chloride (1 ml) containing triethylamine (0.14 ml). The solution was cooled thoroughly (ice-salt) and to this cooled solution was added methanesulfonyl chloride (0.08 ml) under stirring. The reaction mixture was stirred for an additional 2 hr (ice-water), after that it was decomposed with ice-water and extracted with methylene chloride (2 x 15 ml). The organic layer was washed with 2N HCl aq (2 x 10 ml), satd. $NaHCO_3$ aq (2 x 10 ml), water (3 x 10 ml), brine and dried. On evaporation of the solvent in vacuo, the oily mesylate obtained (0.145 g) was crystallised from petroleum-ether (40-60), m.p. 72-73° (yield 0.086 g)

IR : OH 3510, 1020 cm^{-1}; $-O-SO_2-C$ 1150, 1430 cm^{-1}.

PMR: -C-Me(3H, s, 1.03),-$CH\underline{Me}_2$(6H,2d, 0.88 and 0.94 ppm, J= 7Hz each), $-C{=}C\underline{Me}$(3H, s, 1.83 ppm), $\underline{Me}-SO_2-C$(3H, s, 3.05 ppm),$-C\underline{H}-O-SO_2Me$(1H,m,4.92 ppm)$-C{=}\underline{CH}$ (1H, m,5.58 ppm).

Reduction of mesylate (3)

A solution of the above mesylate (0.3 g) in THF(4 ml) was added to a stirred suspension of LAH (0.28g) in THF (6 ml) at 0 to 5°. After the addition, the strring was continued for an additional 2 hr during which time the temperature of the mixture was allowed to rise to room temp. Excess of hydride was decomposed by careful addition of water (0.5 ml), 15% NaOH aq(0.5 ml) followed by water (1.5 ml). The white grannular solid was filtered off and washed with ether (20 ml). Removal of the solvent furnished compound (0.222 g) which was found to be a mixture of at least three compounds on TLC (15% EtOAc in C_6H_6). It was chromatographed on SiO_2(IIB, 5 g, 18 x 0.9 cm).

Fr. 1. C_6H_6	5x15 ml	Nil	
Fr. 2. C_6H_6-5% EtOAc	10x15 ml	0.14 g	Liquid Rf 0.64
Fr.3. -do-	2x15 ml	0.01 g	Rejected
Fr. 4. C_6H_6 -10% EtOAc	5x15 ml	0.03 g	J.diol

Fraction 2 was distilled, b.p. 150-60°(bath)/2.5 mm It appeared as an elongated spot on TLC (15% EtOAc in C_6H_6). All attempts to resolve this spot were unsuccessful. However its GLC* (190°, flow rate 120ml/min) showed it to be a mixture of atleast six compounds. Two compounds were separated by preparative GLC*(190°, flow rate 120ml/min, batch size: 20 µl). The major component (RT 8.4) was distilled, b.p.110-20° (bath)/0.1 mm.

IR($CHCl_3$): OH 3580, 1360, 1115 cm^{-1}

PMR:-C-Me (3H,s,0.96 ppm),-CHMe$_2$(6H,2d, 0.88 and 0.95 ppm, J=7 Hz each)-C=CMe(3H,s,1.77 ppm)-C=CH (1H,m,5.42 ppm)

Mass: m/e 222 (M^+,4%),204(4%),179(97%),161(47%),123(46%), 107(53%),95(39%),81(63%),71(54%),55(49%),43(100%)

(Found: C,80.87; H, 11.72 $C_{15}H_{26}O$ requires: C, 81.08;H 11.71%

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*Hewlett Packard 7624-A, Column:3/8" x 12', 20% silicone SE-30 on Chromosorb W(45-60 mesh)

The minor compound (RT 7) was distilled, b.p. 150-60° (bath)/2.5 mm.

IR($CHCl_3$): OH 3590, 1040 cm^{-1}
PMR:-C-$\underline{Me}$ and -CH$\underline{Me}_2$(9H, m, between 0.88 and 1.01 ppm), -C=C$\underline{Me}$(3H,s,1.65 ppm), -C$\underline{H}$OH(1H,m,3.28 ppm) and -C=C-$\underline{H}$ (1H,m,5.34 ppm)
Mass: m/e 222(M^+,4%),204(29%),179(73%),161(58%),119(45%), 108(99%),107(92%),105(66%),93(61%),82(84%),81(99%),43(100%)
(Found :C,80.79;H,12.21 $C_{15}H_{26}O$ requires: C, 81.08;H,11.71%)
Based on this data structure(6) is assigned to this compound.

SeO_2 oxidation of (5)

The major component from the above reduction was oxidised using SeO_2

(A) A solution of freshly sublimed selenium dioxide (0.02g) in dioxane (5ml) containing water (1ml) was added to a solution of alcohol (5)(0.075 g) in dioxane (4 ml). The solution was warmed on water bath (80-90°) for about 3 hr and then left at room temperature for 1 hr during which time the solution rapidly yellowed and the colour intensified to orange and then red as selenium precipitated. The solution was then filtered and the filtrate was diluted with water and extracted with ether (3 x 10 ml). The ether extract was repeatedly washed with satd $NaHCO_3$ aq (5x5ml), water and brine. Solvent removal from the dried extract gave a product, which was found to be a complex mixture on TLC(15% acetone in C_6H_6). The presence of desired neojaeshkeanadiol was not revealed by TLC. It was not further investigated.

(B) The above mentioned oxidation reaction was repeated again, but this time employing DMSO as a solvent. Thus to a solution of SeO_2(0.058 g) in DMSO(4 ml) containing water (1.5 ml) was added a solution of alcohol (5)(0.2 g) in DMSO (1 ml). After warming the mixture on water bath for about 10 min. it was left at room temp for 4 hr during which time red selenium separated. The solution was filtered and worked up as above to get an identical complex mixture (TLC) as mentioned earlier. The study was not pursued further.

Reaction of epoxyjaeshkeanadiol with lithium diethylamide

Lithium diethylamide was made by adding a solution of n.butyllithium[14] in light petroleum (0.869 N, 102 ml) to ice-cold solution of diethylamine (9.09 ml) in ether (50ml). After 15 min a solution of epoxide (1.1 g) in ether (30 ml) was added (the solution immediately became turbid) and the mixture was refluxed for 7 hr, cooled and poured into water (50 ml). The aqueous layer was extracted with ether (3x30ml) and the organic layer was washed with 2N HCl aq (3x10 ml), satd $NaHCO_3$ aq(3x10ml), water, brine and dried. Evaporation of the solvent gave compound (1.0g) which was found to be a mixture of atleast 6-7 compounds on TLC(50% EtOAc in C_6H_6). It was chromatographed over SiO_2(IIB, 1.5 x 30 cm).

Fr.1	C_6H_6	6 x 40ml	0.2 g	Mixture
	C_6H_6-5% EtOAc	2 x 40ml		
	C_6H_6-10% EtOAc	2 x 40ml		
Fr.2	C_6H_6-10% EtOAc	2 x 40ml	0.05g	Rejected
Fr.3	C_6H_6-10% EtOAc	2 x 40ml	0.18g	Epoxyjaeshkeanadiol
	C_6H_6-15% EtOAc	3 x 40ml		
Fr.4	C_6H_6-20% EtOAc	2 x 40ml	0.05g	Mixture
Fr.5	C_6H_6-30% EtOAc	7 x 40ml	0.2 g	Allylic alcohol

Fraction-3 was crystallised from ether-light petroleum, m.p. 102-103°. It was found to be starting epoxyjaeshkeanadiol from its PMR spectrum (m.p. mixed m.p.)

Fraction-5 was crystallised from benzene, m.p.96-8°. IR: OH 3380, 1045 cm^{-1}; C=CH 1635,900 cm^{-1}; PMR:-C-$\underline{Me}$(3H,s,1.08 ppm), -CH$\underline{Me}_2$(6H,2d at 0.9 and 0.95 ppm, J=7Hz each),-C$\underline{H}$OH (2H,bm, centered at 4.17 ppm)-C=C$\underline{H}_2$(2H, d, at 5.16 ppm, J = 16 Hz)(Found:C,70.7; H,10.12. $C_{15}H_{26}O_3$ requires:C,70.87; H, 10.23%), These data fit well for the allylic alcohol(8).

Action of Al_2O_3 on epoxyjaeshkeanadiol

(A) Neutral Al_2O_3

Epoxyjaeshkeanadiol (4 g) was added to a thick slurry of alumina (neutral, activity I,280 g) in a 1:1 mixture of light petroleum-benzene (330 ml) in a one litre round bottomed flask. The flask was flushed with N_2 and shaken mechanically for 10 hr and then kept aside for 24 hr. The solvent was filtered and the Al_2O_3 washed with 30% MeOH in ether (2.5 l) in several portions. The combined filtrate was carefully stripped off solvent to get a residue (3.742 g) which was found to be a mixture of atleast four compounds on TLC(50% EtOAc in C_6H_6). It was chromatographed over SiO_2(IIB, 164 g, 3 x 40 cm).

Fr. 1	C_6H_6	2x100 ml	0.113 g	Mixture
Fr. 2	C_6H_6-5% EtOAc	4x100 ml		
Fr. 3	C_6H_6-10% EtOAc	7x100 ml	0.780 g	Complex mixture rich in epoxy-jaeshkea-nadiol.
Fr. 4	C_6H_6-15% EtOAc	6x100 ml		
Fr. 5	C_6H_6-15% EtOAc	4x100ml	2.371 g	Allylic alcohol
Fr. 6	C_6H_6-20% EtOAc	15x100 ml		

Fraction 5 and 6 were mixed and crystallised from benzene m.p. 96-8°. It was found to be the desired allylic alcohol(8) from its spectral data (PMR).

(B) Al_2O_3 doped with NaOH

NaOH doped Al_2O_3 was prepared according to Joshi and Sukh Dev[9]. Thus neutral Al_2O_3(50g) was covered with NaOH aq (100 ml containing 1.5 g of the hydroxide). After 48 hr at ∽ 25°, the excess soln. was drained off, Al_2O_3 dried at 120° in air for 16 hr and then calcined at 450° for 1 hr under N_2.

Epoxyjaeshkeanadiol (1 g) was added to a slurry of modified Al_2O_3 (100g) in 1:1 mixture of light petroleum and benzene (120 ml) in a 500 ml R.B.Flask. The flask was flushed with N_2 and mechanically shaken for 6 hr and left aside for 20 hr. Usual work up afforded a residue (0.891 g) which was found to be a mixture of atleast five compounds (TLC, 50% EtOAc in C_6H_6). The required allylic alcohol(8) was obtained (0.31 g, 30%) by chromatography over SiO_2-gel.

Treatment of allylic alcohol(8) with phosgene

The allylic alcohol (1g) was dissolved in chloroform (alcohol free, 30 ml) containing pyridine (7.6 ml) and the mixture was cooled to 0°(ice-salt). A solution of phosgene in toluene(20%, 18 ml) was added dropwise into cooled mixture and the mixture was stirred for 1 hr and left at 15° for 12 hr. Excess of phosgene was carefully destroyed by gradual addition of ice cold water. After extraction with ether (3 x 25 ml), the ether soln was successively washed with 2N HCl aq(2x10ml), 5% Na_2CO_3 aq(2x10ml), water (3x10 ml) and brine. Solvent removal from the dried extract gave compound (1.06g) which was crystallised from CH_2Cl_2-light petroleum, m.p.120-22°. IR:O-CO-O 1750, 1250 cm^{-1}, no OH absorption. PMR:$-C-\underline{Me}$(3H, s, 1.08 ppm)$-CH\underline{Me}_2$(6H, 2d, 1.0 and 1.07 ppm, J=7 Hz each), $-\underline{CH}-O-CO-O$(1H, triplet of doublets, 4.33 ppm, $J_1=J_3=5Hz, J_2=11$ Hz), $-C\underline{H}_2Cl$(2H,s,4.08 ppm),$-C=C\underline{H}$(1H, m, 5.92 ppm). Mass:m/e 298 (M^+,1%) 220(18%),211(55%),169(29%),175(99%),151(58%),133(59%), 119(50%),105(66%),91(37%),55(72%),43(100%).(Found: C,64.0; H,7.42. $C_{16}H_{23}O_3Cl$ requires: C,64.33; H,7.7%)

Treatment of chloride (10) with ethanolic KOH

To a solution of the above chloride (0.05 g) in ethanol (2.5 ml) was rapidly added KOH (0.181 g) in water (0.15 ml) under N_2. After stirring for 4 hr, the solution was filtered to remove the precipitated salt. The filtrate was concentrated under vacuo, diluted with water and extracted with ether (3x10ml). The ether extract was washed with water till neutral, brine and dried. Sovent evaporation furnished compound (0.046 g) which was found to be a mixture of atleast three compounds (TLC). The PMR of the crude compound indicated it to be a mixture rich in ether (11). No attempt was made to separate individual component.

IR(Crude): OH 3650,3580,3500 cm^{-1};$-C-O-C$ 1080 cm^{-1}

PMR(Crude):$-C-\underline{Me}$(3H,s,1.01 ppm)$-CH\underline{Me}_2$(6H, 2d, 0.9 and 0.93 ppm, J=7 Hz each),$-OCH_2\underline{CH_3}$(3H,t,1.18 ppm, J=7 Hz),$-O\underline{CH_2}CH_3$ (2H,q,3.43 ppm, J=7 Hz)$-\underline{CH_2}OC_2H_5$ and $-C\underline{H}OH$ (3H,m, 3.84 ppm),$-C=C\underline{H}$(1H,m,5.68 ppm).

Reaction of chloride (10) with NaOAc

Allyl chloride (1.0 g) was dissolved in AcOH (20 ml) and to this was added freshly fused NaOAc (2.86 g) and cuprous chloride (0.1 g). The reaction mixture was heated at 90-100°(bath) for a period of 7.5 hr, cooled, diluted with water and extracted with ether (3 x 30 ml). The organic layer was washed free of acid with 5% Na_2CO_3 aq (4x15 ml), water (4x10ml), brine and dried. The residue (0.994 g) obtained on concentration of the dried extract was found to be a mixture on TLC (30% EtOAc in C_6H_6) from which the major compound was obtained pure by chromatography over SiO_2(IIB, 22g, 1.5 x 28.5 cm)

Fr.1	C_6H_6	4 x 30 ml	Nil	-
Fr.2	C_6H_6-20% EtOAc	2 x 30 ml	0.756	Allylacetate
Fr.3	C_6H_6-5% EtOAc	7 x 30 ml		
Fr.4	C_6H_6-30% EtOAc	4 x 30 ml	0.1g	Polar compounds

Fraction 2 was crystallised from CH_2Cl_2-light petroleum, m.p.113-115°,

IR:-O-CO-O 1747,1220 cm^{-1};OAc 1722,1250 cm^{-1}; PMR:-C-Me(3H, s,1.07 ppm)-CHMe$_2$(6H, 2d, 0.98 and 1.06 ppm, J=7 Hz each),OAc (3H,s,2.08 ppm),-CH-O-CO-O(1H,m,4.28 ppm),-CH$_2$OAc(2H,s,4.5 ppm) and -C=CH(1H,m,5.8 ppm). (Found:C,66.99; H, 7.91, $C_{18}H_{26}O_5$ requires:C, 67.05; H,8.07%).

Treatment of allyl acetate (12) with ethanolic KOH

The above acetate (0.75 g) in ethanol (25 ml) was treated with KOH (1.165 g) in water (1.2 ml) under N_2. After stirring for 2 hr it was worked up in the usual manner to get a gummy compound (0.589 g), which was TLC pure (50% EtOAc in C_6H_6).

IR($CHCl_3$): OH 3590,3390, 1035 cm^{-1}; no C=O absorption.
PMR:$-C-\underline{Me}$(3H,s,1.02 ppm),$-CH\underline{Me}_2$(6H,2d,0.92 and 0.95 ppm, J=7 Hz each),$-C\underline{H}OH$ and $C\underline{H}_2OH$ (3H,m,at 3.91 ppm),$-C=C\underline{H}$(1H,m, 5.65 ppm).
Mass:m/e 254(M^+,1%), 236(9%),211(57%),193(48%),175(100%), 151(53%),147(37%),133(42%),123(41%),55(39%),43(80%).

Oxidation of triol (13) with DDQ

To a solution of triol (0.52 g) in dioxane (25 ml) was added DDQ(0.354 g) and the soln was heated at 50-60°(bath) for 16 hr. The yellow ppt of 2,3-dichloro,5-6-dicyanohydroquinone was filtered off and washed with ether. The filtrate was diluted with water and extracted with ether (3x25ml). The ether soln was washed with 10% NaOH aq(5x10ml), water (5x10ml), brine and dried. Solvent removal gave residue (0.505 g) from which the desired aldehyde was obtained pure by passing through a column of SiO_2-gel(IIB-eluent benzene -10% EtOAc). It was crystallised from CH_2Cl_2-petroleum ether (40-60°), m.p. 107-109°.
UV: λmax 240 mm(ϵ,11340). IR: OH 3590, 3520, 1040 cm^{-1}; C=O 1675 cm^{-1} and C=CH 1635, 850 cm^{-1}; PMR:$-C-\underline{Me}$(3H,s,1.0 ppm), $-CH\underline{Me}_2$(6H,2d,0.92 and 0.95 ppm, J=7 Hz each),$-C\underline{H}OH$(1H,m,3.84 ppm),

-C$\underline{H}$=C-C=O(1H,m,6.71 ppm) and $\underline{H}$-C=O (1H,s,9.24 ppm). Mass:m/e 234(M^+-18,5%). 209(100%),191(75%),149(22%), 145(53%),119(19%),107(22%),91(22%),71(21%),55(29%),43(55%) Found: C,70.96; H,9.64. $C_{15}H_{24}O_3$ requires: C; 71.44;H, 9.52%).

Mesylate of hydroxyaldehyde(15)

Methanesulfonylchloride (0.17 ml) was added to a stirred soln of aldehyde (14)(0.45g) in CH_2CL_2(10 ml) containing Et_3N(0.37 ml) at-5°. After stirring for additional 2.5 hr (ice-water), the reaction mixture was diluted with water and worked up in the usual manner to get on oily residue (0.5 g). The compound was highly unstable (decomposes at room temp giving tarry product) and was used up immediately for subsequent reduction. IR:($CHCl_3$):OH 3520 cm^{-1}, C=O 1689 cm^{-1}, C=CH 1645 cm^{-1} and O-SO_2-C 1175 cm^{-1}. PMR:-C-$\underline{Me}$(3H,s,1.05 ppm),-CH$\underline{Me}_2$(6H,2d, 0.91 and 0.96 ppm, J = 7Hz each),-SO_2-$\underline{Me}$(3H,s,3.14 ppm)-H-CO SO_2Me(1H,triplet of doublets, at 4.85 ppm, J_1=J_3=3 Hz and J_2= 10Hz),-C$\underline{H}$=C-C=O(1H,m,6.92 ppm) and -H-C=O(1H,s,9.4 ppm).

Reduction of mesylate (15)

To a suspension of LAH (0.44 g) in THF (10 ml) was added at -5° a soln of mesylate (15)(0.56 g) in THF (10 ml) and the reaction mixture was stirred for 2 hr (ice-water). Excess of hydride was destroyed by addition of water (2 ml), 15% NaOH aq (2 ml) followed by water (6 ml). The white granular ppt was filtered and washed with more ether (20 ml). The combined filtrate on concentration under vacuo afforded compound (0.431 g), which was a mixture of atleast 3 compds as revealed by TLC (50% EtOAc in C_6H_6). It was chromatographed over silica gel (IIB, 1.5 x 25 cm).

Fr. 1	C_6H_6	5 x 10 ml	Nil	-
Fr. 2	C_6H_6-5% EtOAc	5 x 10 ml	-do-	-
Fr. 3	C_6H_6-10% EtOAc	4 x 10 ml	0.077g	Liquid Rf 0.42
Fr. 4	C_6H_6-10% EtOAc	5 x 10 ml	0.082g	Mixture
Fr. 5	C_6H_6-15% EtOAc	10 x 10 ml		
Fr. 6	C_6H_6-20% EtOAc	10 x 10 ml	0.052g	Liquid Rf 0.31
Fr. 7	C_6H_6-25% EtOAc	5 x 10 ml	0.02 g	Rejected
Fr. 8	EtOAc	5 x 10 ml	0.064g	Gum Rf 0.17

Fraction 3 was distilled, b.p. 175-85° (decomp)(bath)/0.5mm UV: λmax 246.5 mm(ε, 4483). IR ($CHCl_3$):OH 3590, 3440 cm^{-1}; PMR:-C-$\underline{M}$e(3H, s, 0.96 ppm), -CH$\underline{M}e_2$(6H, 2d, 0.91 and 0.95 ppm J=7Hz each),-C$\underline{H}_2$OH(2H,s,4.08 ppm)-C=C$\underline{H}$(1H,m,5.73 ppm)and -C$\underline{H}$=C$\underline{H}$(2H, s,5.91 ppm); Mass:m/e 236(M^+,6%),218(6%),193(6%),175(12%), 132(29%),119(29%),105(29%),91(41%),71(29%),55(35%),43(100%)

(Found : C,76.75; H, 9.69. $C_{15}H_{24}O_2$ requires:C,76.28;H,10.17%) On the basis of this spectral data, structure (16) is suggested for this compound.

Fraction-6 was distilled, b.p.175-185°(decomp)(bath)/0.4 mm IR($CHCl_3$): OH 3595, 3410 cm^{-1}; PMR:$-C-\underline{M}e$ and $-CH\underline{M}e_2$(9H, m, between 0.87 and 0.97 ppm),$-C\underline{H}OH$(1H,m,3.28 ppm),$-C\underline{H}_2OH$(2H, s,3.97 ppm) and $-C{=}C\underline{H}$ (1H,m,5.62 ppm); Mass:m/e 238(M^+,5%), 220(40%),195(52%),177(31%),159(21%),149(19%),121(27%),105(38%), 93(59%),43(100%). (Found:C,75.22;H,11.21 $C_{15}H_{26}O_2$ requires: C,75.51; H,11.0%). These data fit well for the structure(17) suggested for this compound.

Fraction-8 was found to be triol (13) on the basis of its spectral data (PMR, IR).

SUMMARY

The two minor constituents isolated from the roots of Ferula jaeschkeana viz. epoxyjaeschkeanadiol and neojaeschkeanadiol are shown to possess structures (1) and (2) respectively. Structure (1) has been confirmed by a correlation with jaeschkeanadiol, whereas structure (2) is assigned based on spectral data alone.

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