# CHAPTER V

## Constituents of the Essential Oil of Ferula Jaeschkeana Vatke

# CONSTITUENTS OF THE ESSENTIAL OIL OF FERULA JAESCHKEANA VATKE

## PREVIOUS WORK

The essential oil of Ferula jaeschkeana has been studied by some previous workers. Bersutskii[1] has examined the essential oil of the fruits which consists of 91% d-$\alpha$-pinene, 1-3% cumaldehyde, 5% azulene, 0.03% sulfur compounds and an aldehyde, the semicarbazone of which had a m.p. 176-77°.

Goryaev et al.[2] studied the essential oil obtained by the steam distillation of the stems and leaves of the flowering plants and the following compounds were identified by gas chromatography: $\alpha$-pinene(by far the largest component), camphene, $\beta$-pinene, $\Delta^3$-carene, limonene, caryophyllene and calamenene.

Chaudhary and Handa[3] have studied the chemical composition of the essential oil of the roots. The authors report the occurrence of 1-d-pinene, 1-cadinene hydrocarbons and azulenes.

## PRESENT WORK

For the present investigation, the roots of Ferula jaeschkeana Vatke were percolated in cold with acetone. The acetone extracts on steam distillation gives a brown coloured essential oil, whose smell is reminiscent of the roots. The GLC of this material (Fig.1) indicated

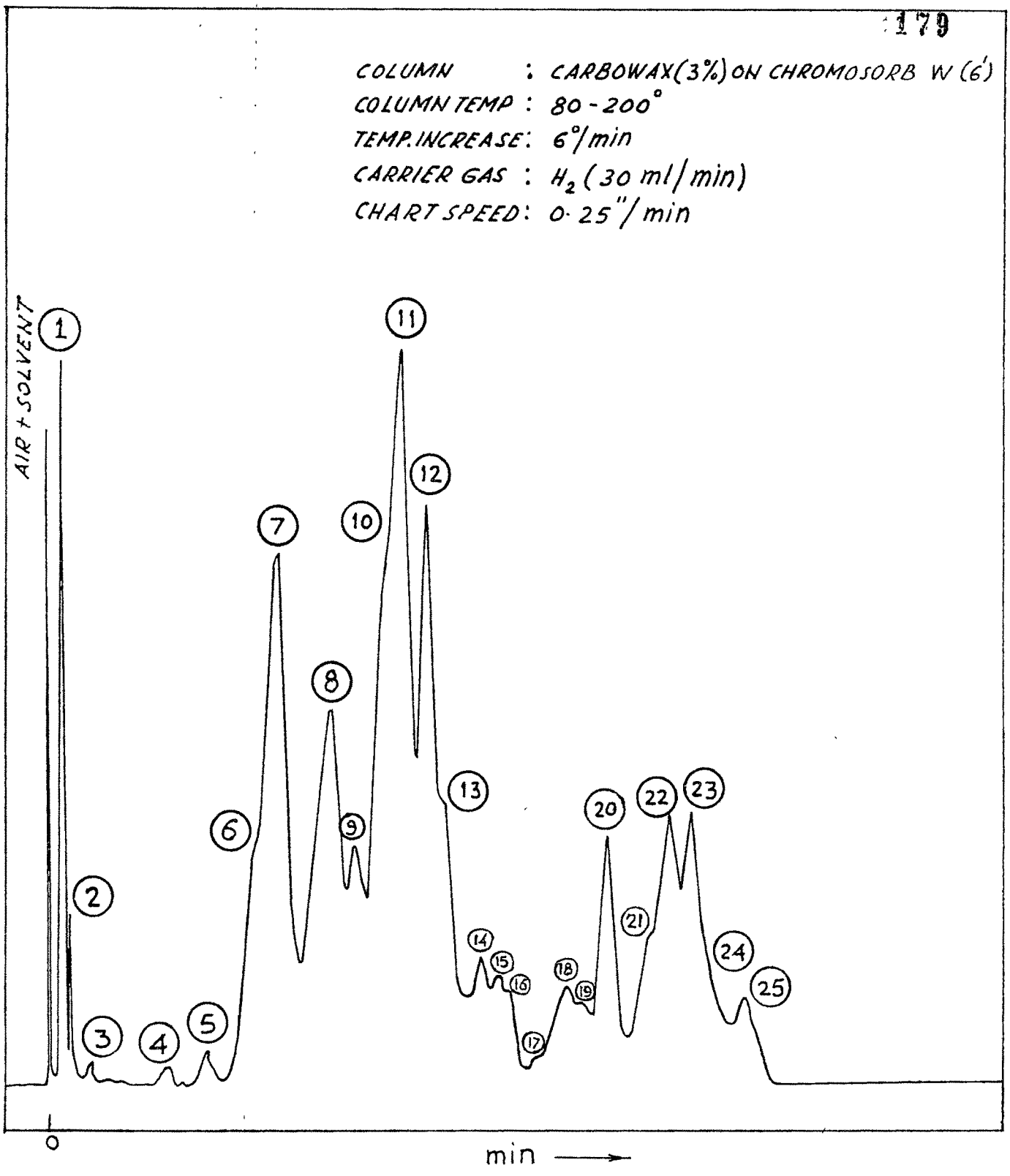



FIG. I. TEMP. PROGRAMMED GLC OF THE ESSENTIAL OIL OF FERULA JAESCHKEANA

it to be a mixture of atleast twenty five compounds.

A commercial sample of the essential oil of Ferula jaeshkeana oil is also available*. Since the GLC of both the commercial sample of the oil and the oil obtained from steam distillation of acetone extract of Ferula jaeshkeana was essentially identical, we utilised commercial sample of oil for further studies.

Isolation of various components

Since the GLC of the total oil showed it to be a complex blend of several compounds, it was thought worthwhile to carry out a broad cut separation of the total oil on alumina thereby reducing the complexity of the mixture. Thus the total oil was chromatographed on alumina (gr.II) and fractions eluted by petroleum ether, benzene, benzene-methanol and methanol were collected separately. Fractions having essentially identical TLC patterns were pooled and this way four groups were obtained. Based on the GLC of these groups(Fig.II-V) suitable fractions were selected for the isolation of the various components. The isolation was carried out using a judicous combination of preparative GLC and column chromatography (over $AgNO_3$-impregnated silica gel).

*We are grateful to Dr.C.K.Atal of the Regional Research Laboratory, Jammu for the supply.

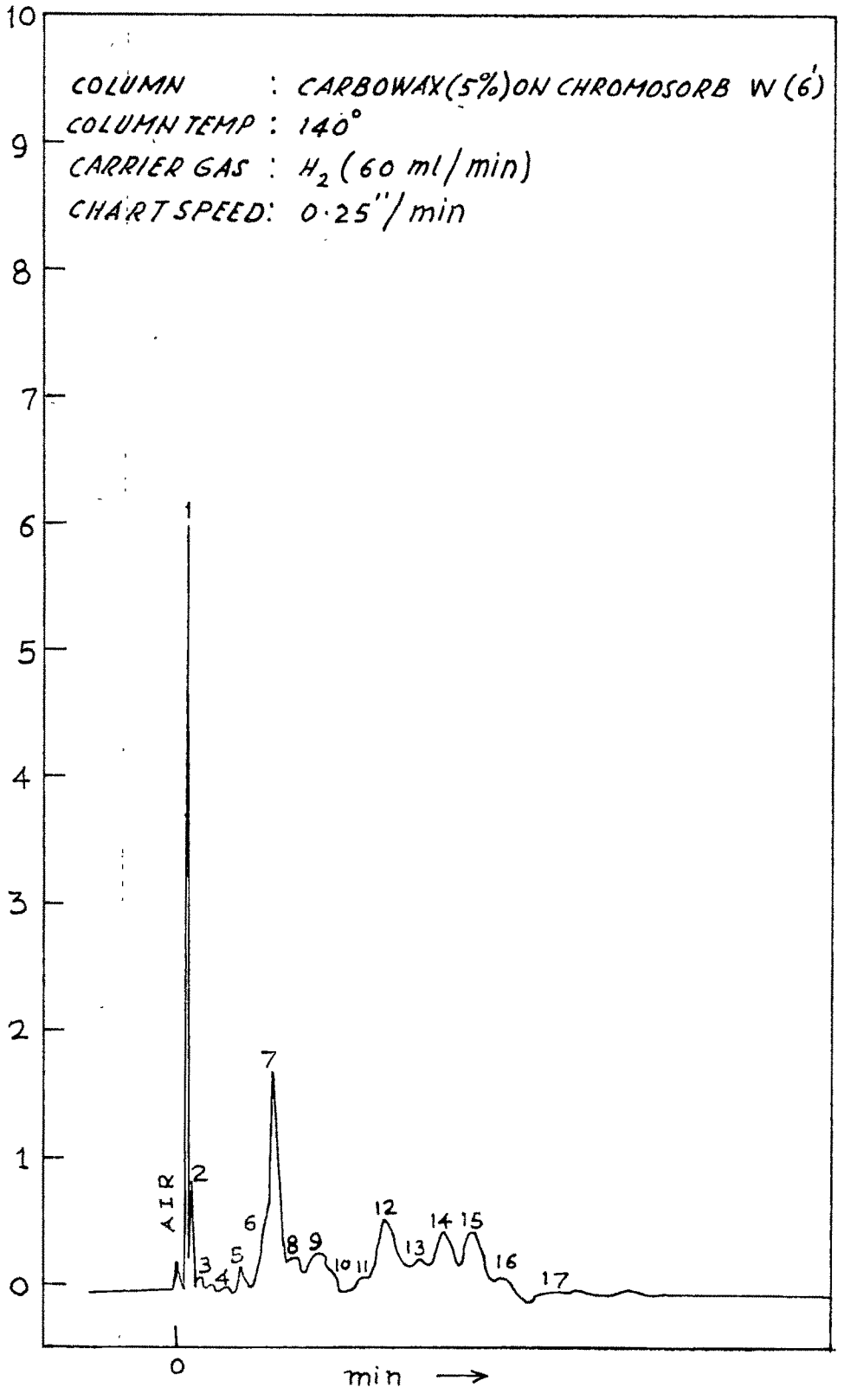



FIG. 11. GLC OF FRACTION 1 (BROAD CUT FROM $Al_2O_3$ CHROMAT) OF F. JAESCHKEANA OIL

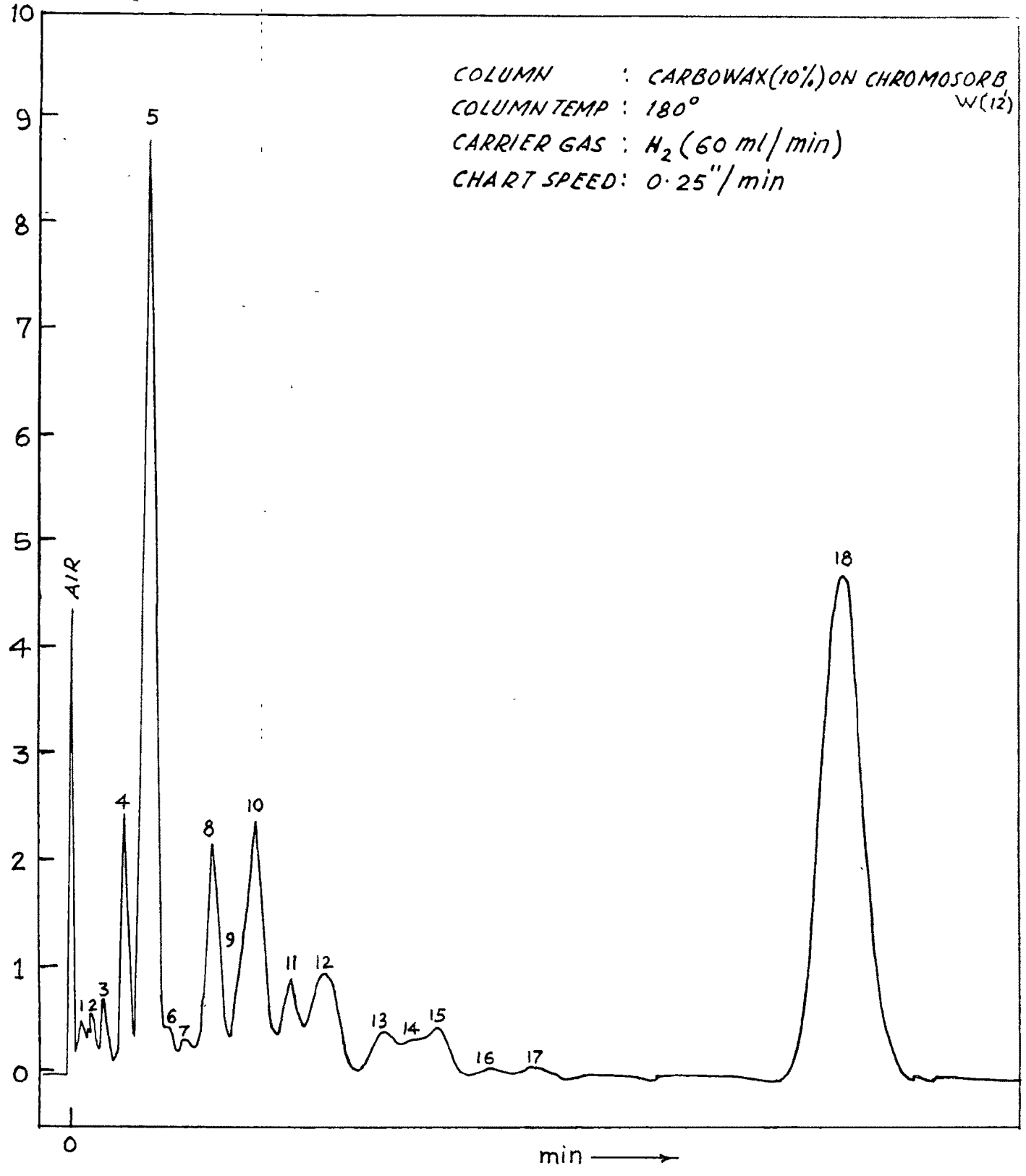



FIG. III. GLC OF FRACTION II (BROAD CUT FROM $Al_2O_3$ CHROMAT) OF F. JAESCHKEANA OIL

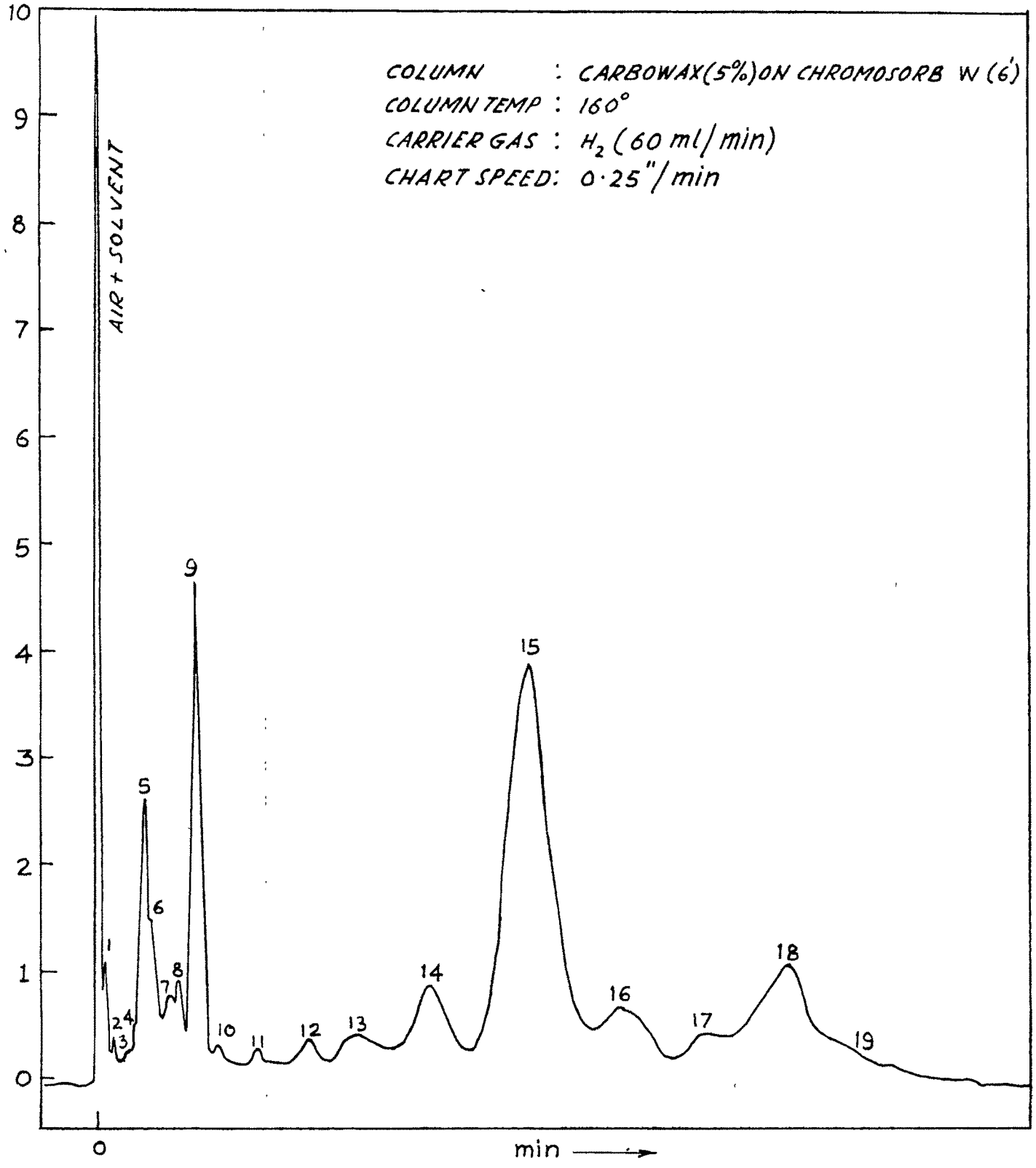



FIG. IV. GLC OF FRACTION III+IV
(BROAD CUT FROM $Al_2O_3$ CHROMAT) OF F. JAESCHKEANA OIL

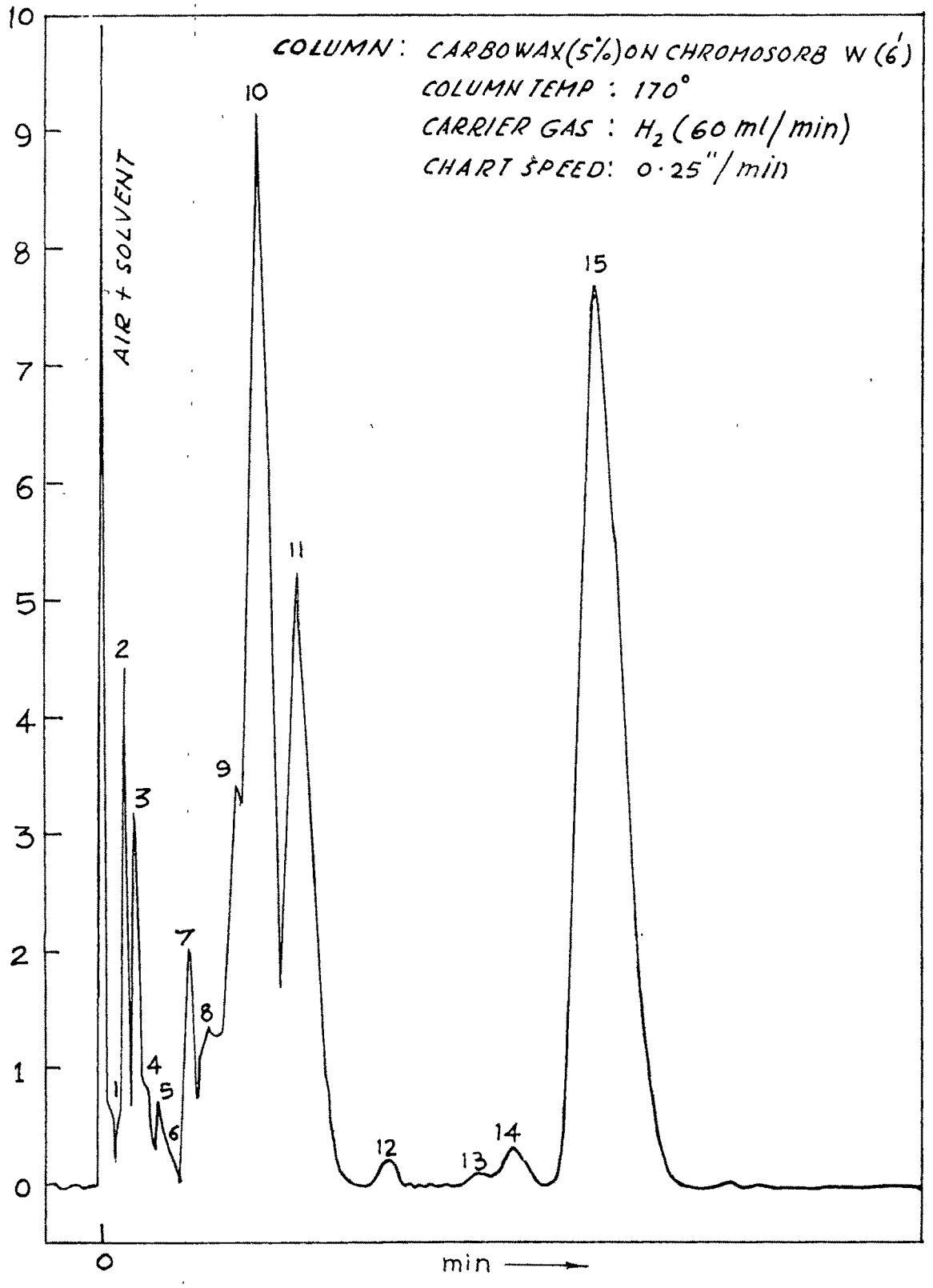



FIG. V. GLC OF FRACTION V
(BROAD CUT FROM $Al_2O_3$ CHROMAT) OF F. JAESCHKEANA OIL

The identification of the various constituents was carried out by a study of their spectral data. The mono and sesquiterpene hydrocarbons were not separated and were identified by coinjection with the authentic samples. Once the pure component had been obtained and characterised, their position in the GL chromatogram was finally settled by the peak-accenuation technique using pure isolated components in mixed chromatograms.

Table I gives the percentage composition of the oil. Thus in this study, presence of $\alpha$-pinene, $\beta$-pinene, limonene, caryophyllene and humulene was established. In addition verbenone, myristicin, elemicin, neojaeshkeanadiol (Chapter III) and two new sesquiterpene alcohols have been isolated. These two alcohols have been designated as sesquiterpene alcohols I and II.

Sesquiterpene alcohol-I

This compound, b.p. 135-45°(bath temp)/0.7 mm, $[\alpha]_D$+13.88° (c,2.16) analyses for $C_{15}H_{26}O$($M^+$ at m/e 222). Its IR spectrum (Fig.VI) exhibits a strong OH absorption (3450,1040 $cm^{-1}$). Its PMR spectrum (Fig.VII) indicates the following structural feauters: one-C-Me (3H,s,0.75 ppm)$\underline{Me}_2$-C-OH(6H,s,1.13 ppm)-C=C$\underline{Me}$(3H,s, 1.62 ppm) and -C=C$\underline{H}$(1H,m,5.26 ppm). By D-exchange (PMR) presence of one hydroxyl is inferred. A strong

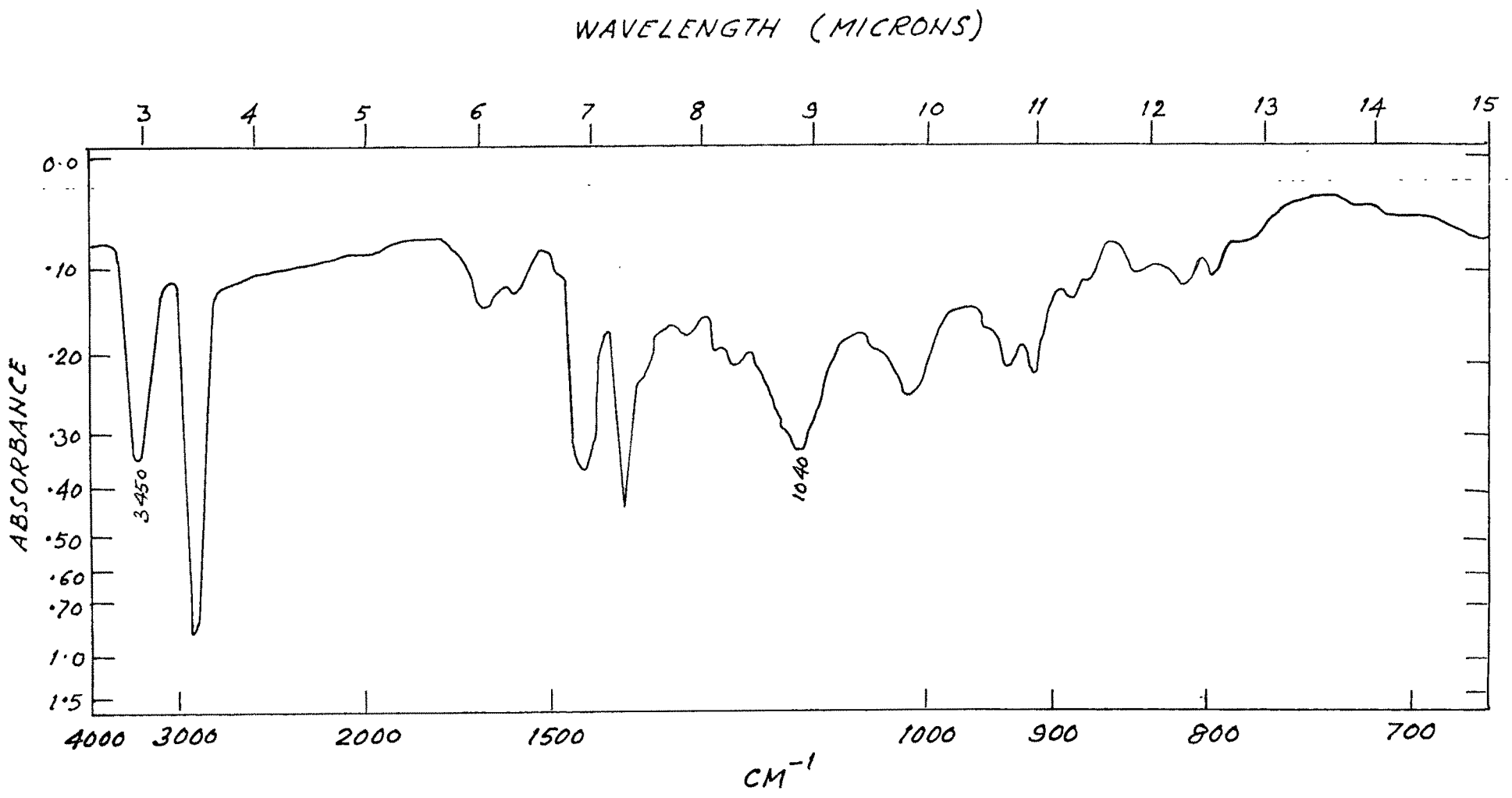



FIG. VI. IR SPECTRUM OF SESQUITERPENE ALCOHOL - I

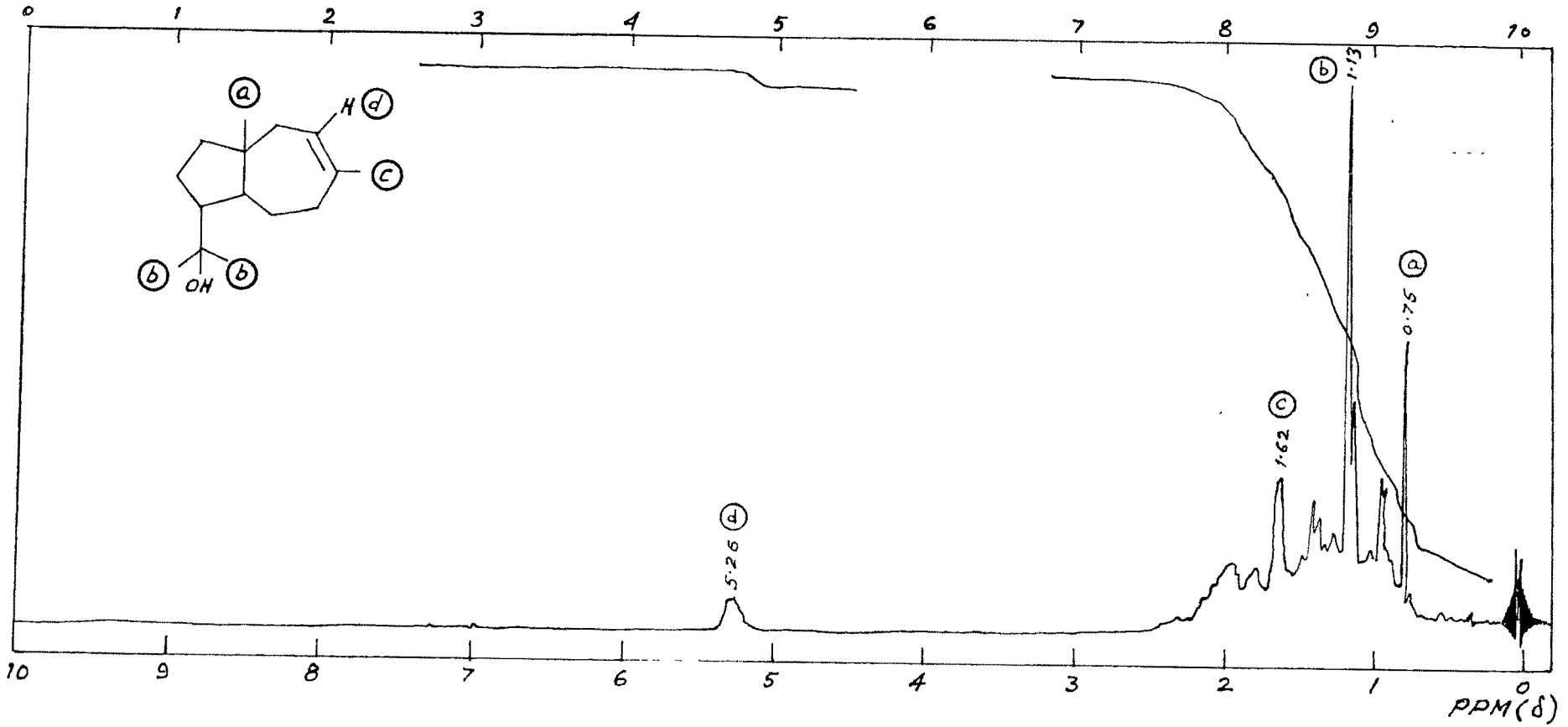



FIG. VII. PMR SPECTRUM OF SESQITERPENE ALCOHOL - I

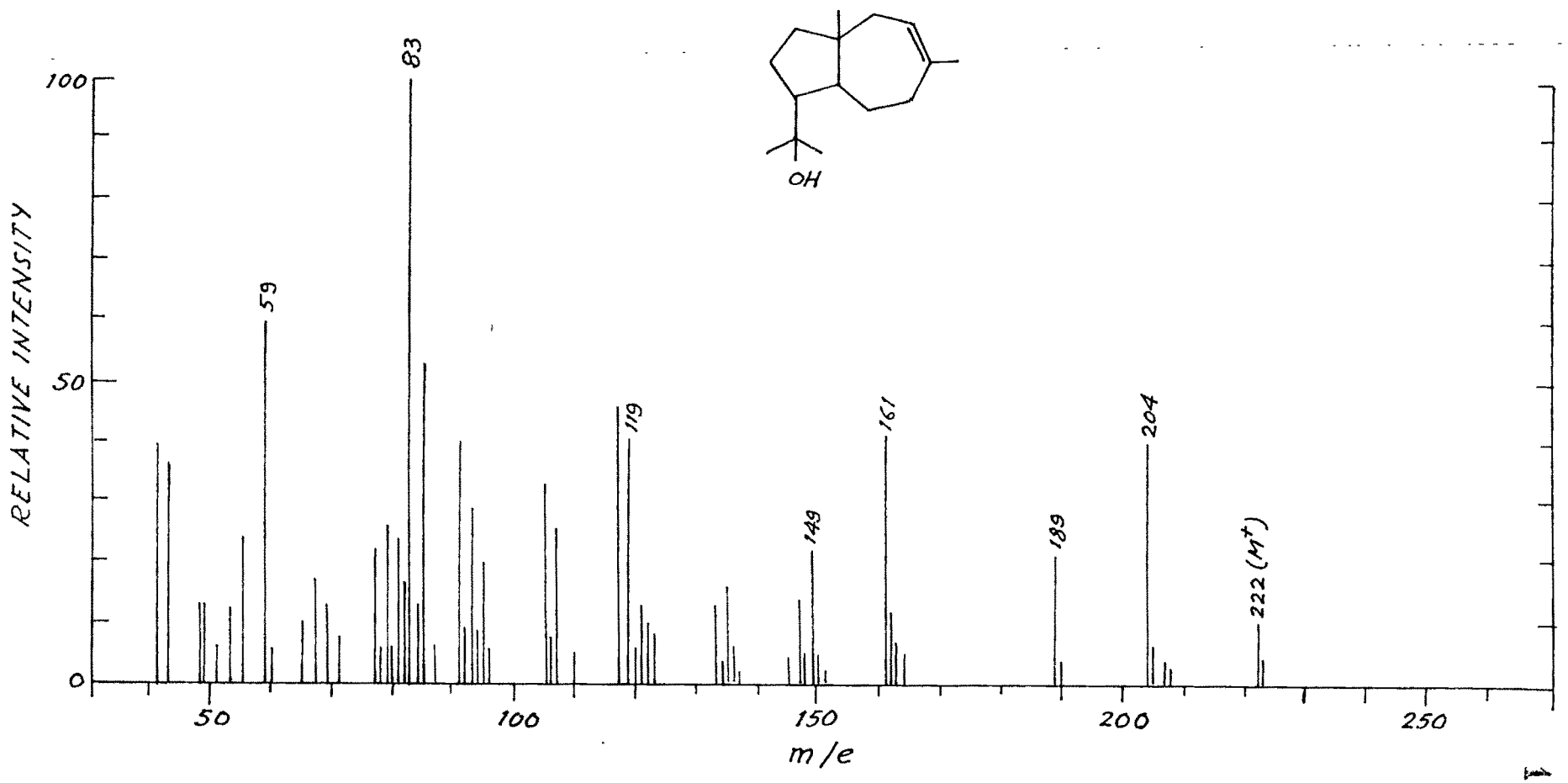
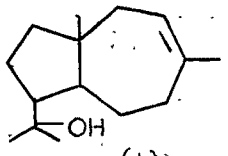



FIG. VIII. MASS SPECTRUM OF SESQUITERPENE ALCOHOL - I

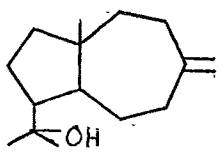
peak at m/e 59 ($\overset{+}{=}\overset{4}{OH}$, 60%) in its mass spectrum (Fig.VIII) confirms the presence of a $Me_2$-C-OH group. On the basis of the above spectral data and consideration of the biogenetic pattern, coupled with its co-occurrence with jaeshkeanadiol, sesquiterpene alcohol-I is assigned structure (I)




(1)

Sesquiterpene alcohol-II

This $C_{15}H_{26}O$ sesquiterpenoid, b.p. 140-45°(bath temp)/0.7 mm, $[\alpha]_D$+32.37° has absorptions at 3400, 1650 and 890 $cm^{-1}$ in its IR spectrum (Fig. IX) indicating the presence of OH and exo-methylene functions. Its PMR (Fig.X) shows signals assignable to $Me_2$-C-OH(6H,s, 1.14 ppm),-C-Me(3H,s,0.69 ppm) and -C=$CH_2$(2H,d,centered at 4.55 ppm, J=24 Hz). As expected its mass spectrum (Fig.XI) shows a strong peak at m/e 59 ($\overset{+}{=}$OH , 100%) and the absence of (M-43) peak lends an additional support for placing the hydroxyl as in sesquiterpene alcohol-I. Thus from the above data it is likely that the compound is the double bon isomer of alcohol-I and is assigned structure(2)




(2)

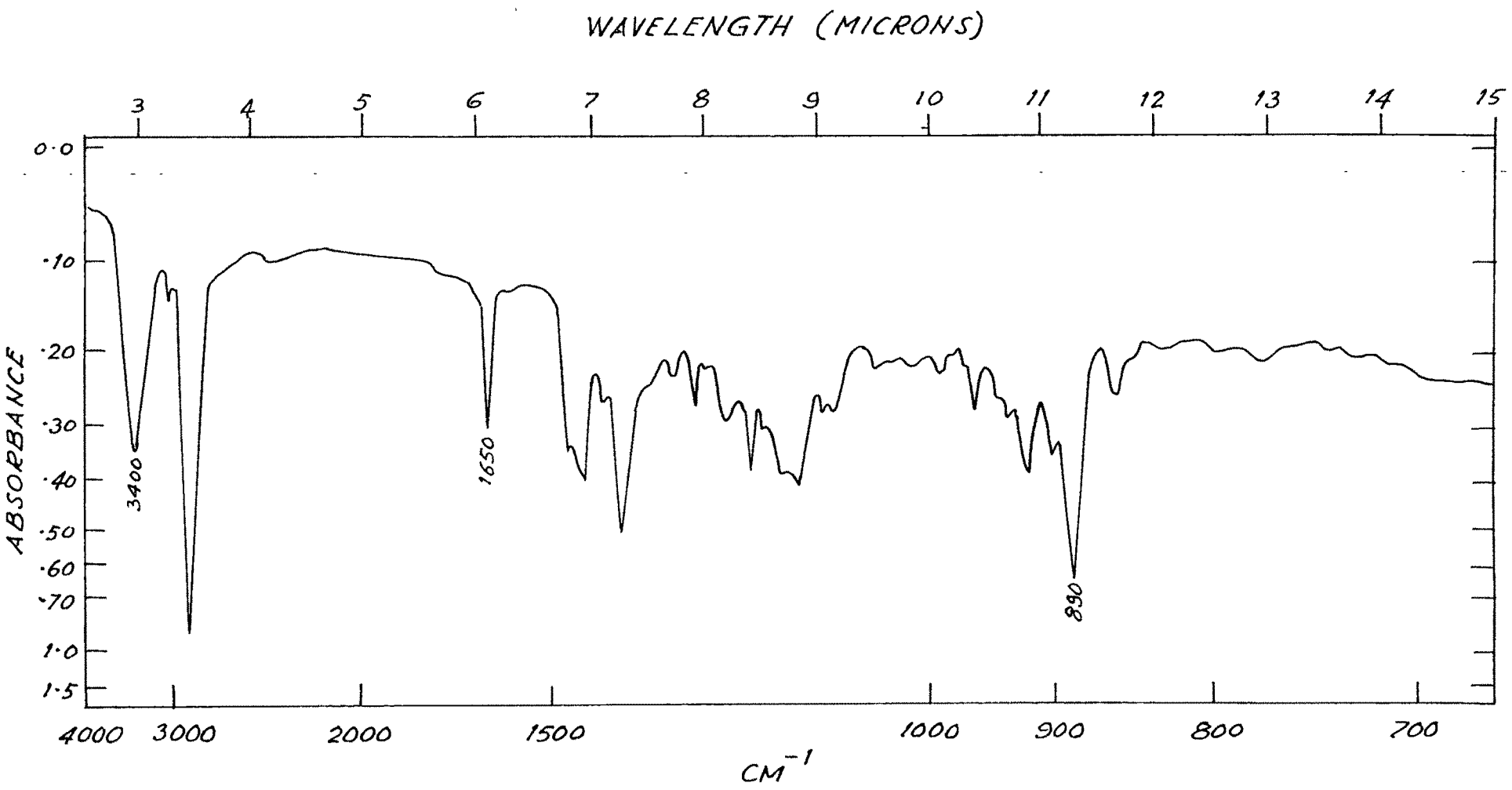



FIG. IX. IR SPECTRUM OF SESQUITERPENE ALCOHOL - II

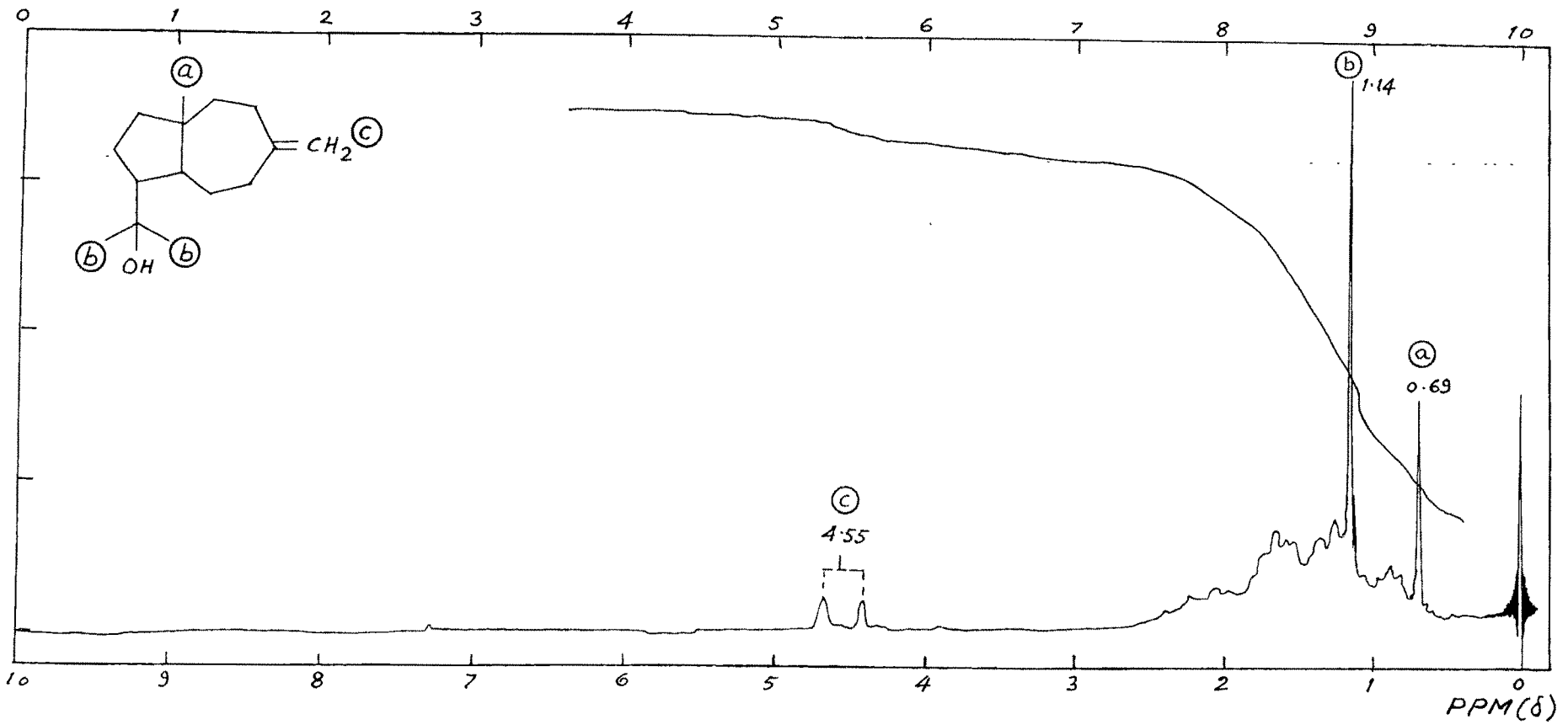



FIG. X. PMR SPECTRUM OF SESQUITERPENE ALCOHOL - II

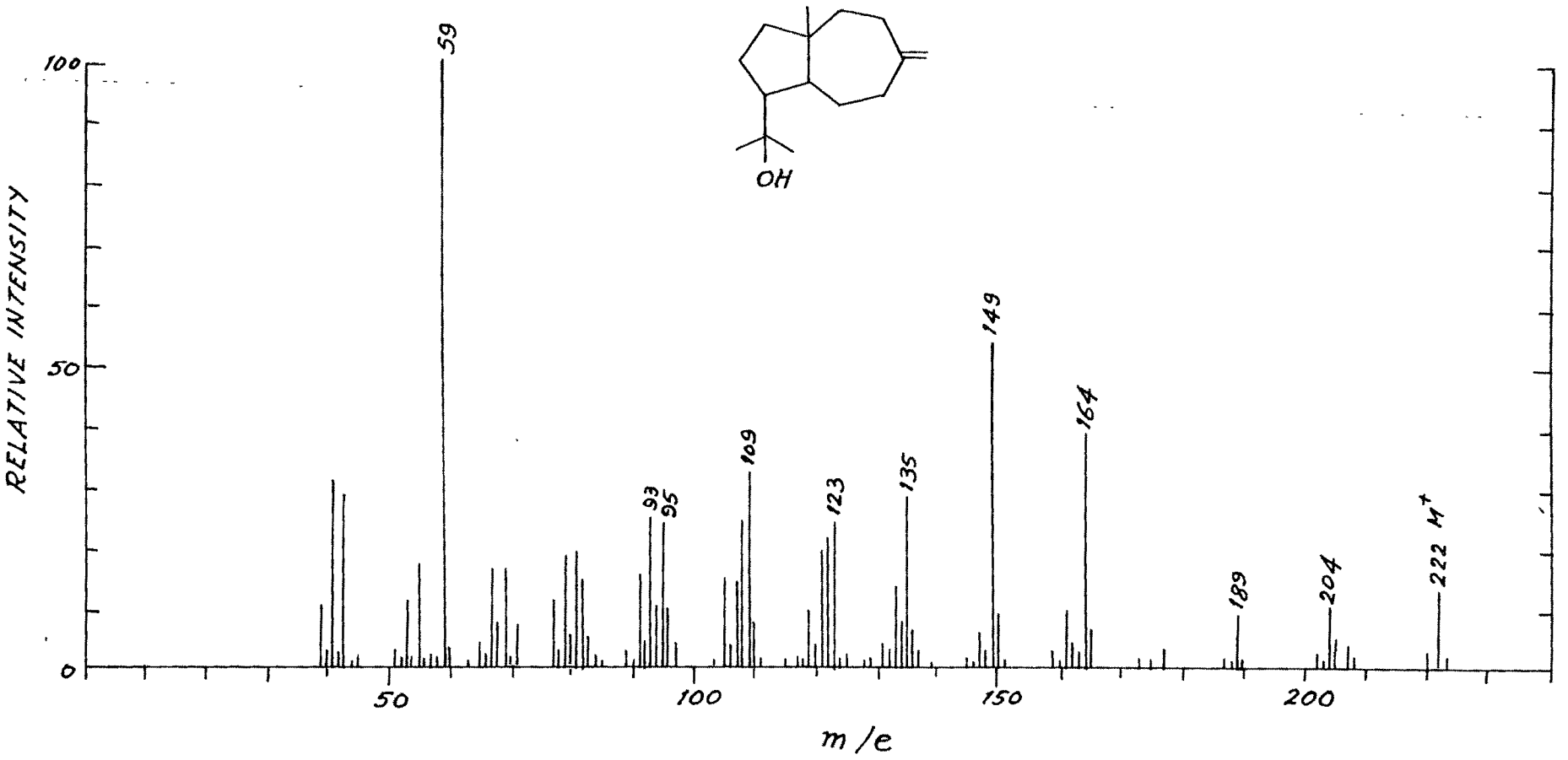
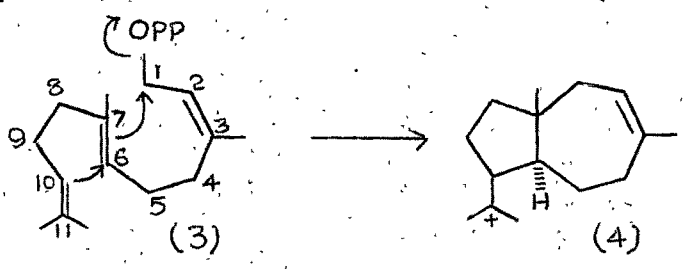



FIG. XI. MASS SPECTRUM OF SESQUITERPENE ALCOHOL - II

Biogenetic considerations

Biogenesis of sesquiterpenes of daucane class is considered[5] to involve a concerted trans-antiparallel cyclization of a suitably folded cis-farnesyl pyrophosphate chain(3) to the ion (4) which, in principle, can be considered as the immediate precursor of the daucane-based sesquiterpenoids



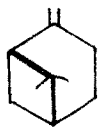

(3) (4)

Ion (4) on $OH^-$ take up can give sesquiterpene alcohol-I

TABLE 1. COMPOSITION OF ESSENTIAL OIL OF FERULA JAESHKEANA

| GLC peak | Compound | Structure (Fig.XII) | % |
|---|---|---|---|
| 1 | -pinene | 1 | 2.57 |
| 2 | -pinene | 2 | 0.66 |
| 3 | limonene | 3 | 0.29 |
| 4 | Unidentified | | 0.22 |
| 5 | -do- | | 0.36 |
| 6 | -do- | | 1.39 |
| 7 | -do- | | 13.10 |
| 8 | Caryophyllene | 4 | 10.56 |
| 9 | Unidentified | | 0.17 |
| 10 | Verbenone-Humulene | 5,6 | 22.70 |
| 11 | | | |
| 12 | Unidentified | | |
| 13 | -do- | | 14.22 |
| 14 | -do- | | |
| 15 | -do- | | 5.22 |
| 16 | -do- | | |
| 17 | -do- | | |
| 18 | -do- | | 4.52 |
| 19 | -do- | | |
| 20 | -do- | | 4.78 |
| 21 | Myristicin, Elemicin | | |
| 22 | Sesquiterpene alcohol | 7-11 | 15.61 |
| 23 | I and II, Neojaeshkeana- | | |
| 24 | diol, and unidentified | | |
| 25 | Unidentified | | 1.54 |

(1)



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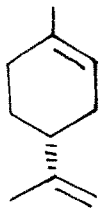
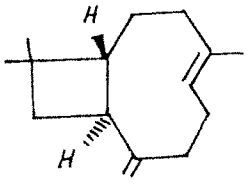
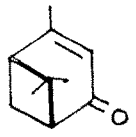


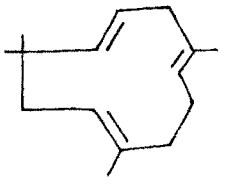
(3)



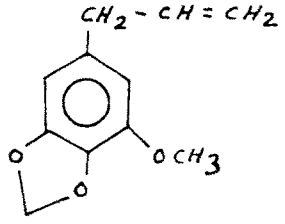

(4)



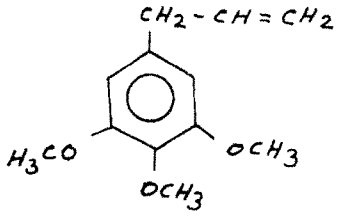

(5)



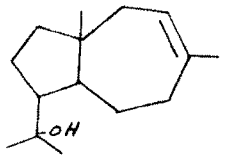
(6)




(7)




(8)

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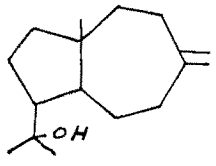


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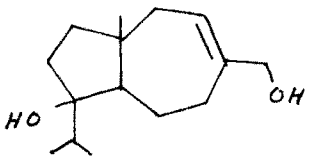


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FIG. XII. CONSTITUENTS OF ESSENTIAL OIL OF FERULA JAESCHKEANA VATKE

## EXPERIMENTAL

For general remarks, see Chapter II.

The commercial sample of the essential oil of Ferula jaeshkeana had the following properties

Colour : Brown

Odour : Generally agreeable, with a faint asafoetida top note, and a predominantly sweet, liquorice aroma

$n_D^{25}$ : 1.4858

IR : 3440(OH), 1740(C=O), 890( $>C=CH_2$ ) $cm^{-1}$

The total oil (50 g) was chromatographed on alumina (act.II, 1 kg, column dimensions 47.5 cm x 6 cm).

| | | | | |
|---|---|---|---|---|
| Fr.1 | Light pet | 6x500 ml | 32.4 g | Hydrocarbons |
| Fr.2 | $C_6H_6$ | 5x500ml | 2.946g | Mixture |
| Fr.3 | $C_6H_6$ | 5x500 ml | 2.336g | Mixture |
| Fr.4 | $C_6H_6$-10% MeOH | 3x500 ml | | |
| Fr.5 | $C_6H_6$-10% MeOH | 2x500 ml | 6.403 g | Mixture |
| Fr.6 | MeOH | 2x500 ml | 0.189g | Polar Compounds. |

Frac.1 was a mixture of mono and sesquiterpene hydrocarbons. Its GLC (Fig.II)(Column: 1/4"x6'; 5% Carbowax on Chromosorb W (60-80 mesh); temp 140°; $H_2$:60ml/min , showed it to be a mixture of atleast seventeen compounds. The presence of $\alpha$-pinene, $\beta$-pinene, limonene, caryophyllene and humulene in this fraction was confirmed by the mixed GLC with authentic samples.

Frac.2 was found to be a mixture of atleast eighteen compounds (Fig.III) GLC: Column:¼"x12'; 12% Carbowax on Chromosorb W(60-80 mesh); temp 180°;$H_2$:60ml/min . From this fraction (2.5 g) the compound having RT 21.6 (41:26%)(peak 18, Fig.III) was separated by preparative GLC [Column:3/8"x6'. 20% Carbowax on Chromosorb W(45-60 mesh;temp 220°; $H_2$:120 ml/min; batch size: 20 µl]. This compound (0.342 g) b.p.90-100° (bath)/0:1 $mm^6$ was found to be myristicin.

IR: C=C 1635 $cm^{-1}$; $-O\diagdown\diagup O-CH_2$ 915 $cm^{-1}$; PMR: Ar-C<u>H</u>$_2$(2H,d, centered at 3.24 ppm, J=7Hz),Ar-O<u>CH</u>$_3$ (3H,s,3.86 ppm), -C=C<u>H</u>$_2$(2H, m, between 4.95 and 5.11 ppm) $-O\diagdown\diagup O-CH_2$(2H,s,5.87 ppm) and Ar-<u>H</u>(2H,d,at 6.25 ppm, J=2Hz)(Found: C,68.33; H,6.0 Calculated for $C_{11}H_{12}O_3$:C, 68.76; H, 6.25%)

Frac.3 and 4 were combined. It showed presence of atleast nineteen compounds on GLC (Fig.IV) [Column:¼"x6'; 5% Carbowax on Chromosorb W (60-80 mesh);temp 160°; $H_2$:60ml/min]. From this fraction (2.0 g) two components having RT 2.8(8.4%) and 19.2(13%)(peak 9 and 18 resp.,Fig.IV) were separated pure by preparative GLC [Column:3/8"x12'; 5% Carbowax on Chromosorb W (45-60 mesh); temp. 190°; $H_2$: 120 ml/min; batch size 20µl].

Compound RT 2.8 (0.059 g), b.p. 115-25° (bath)/5mm was established to be verbenone[7] on the basis of its spectral data. UV: λ max 253 nm(ε,6700); IR($CHCl_3$):C=O 1670 $cm^{-1}$ and C=C 1610 $cm^{-1}$; PMR: two -C-<u>Me</u>(3H each,s,

at 1.0 and 1.5 ppm) -C=C<u>Me</u>(3H,d, 2.0 ppm, J=2Hz) and -C=C<u>H</u>-C=O(1H,m, 5.63 ppm)(Found:C, 79.63; H,9.1 calculated for $C_{15}H_{14}O$:C,80.0; H,9.33%).

The other component RT 19.2 (0.084 g), b.p.155-65° (bath)/10 mm was identified as elemicin[8].
IR:C=C 3020 and 1590 $cm^{-1}$; PMR:Ar-C<u>H</u>$_2$(2H, d,3.2 ppm, J=6 Hz), Ar-OC<u>H</u>$_3$(6H,2s, at 3.71 and 3.72 ppm),-C=C<u>H</u>$_2$ (2H, m, between 4.97 and 5.12 ppm) and Ar-<u>H</u>(2H,s,6.28 ppm) Found :C, 68.81; H 7.33. Calculated for $C_{12}H_{16}O_3$:C,69.23; H, 7.69%)

<u>Frac.5</u> was found to be a mixture of atleast fifteen compounds (Fig.V) GLC: Column :¼"x6'; 5% Carbowax on Chromosorb W (60-80 mesh); temp 170°; $H_2$:60 ml/Min .
On attempting to separate the major component RT 12.4 (40.75%)(peak 15 in Fig.V) by preparative GLC [Column: 3/8"x12'; 5% carbowax on Chromosorb W (45-60 mesh); temp 200°; $H_2$:120 ml/min; batch size 30µl], it was observed that this component further resolved into two components. They were collected separately.
Of these, the major component RT 10(0.164 g) showed on TLC ($AgNO_3$-$SiO_2$ gel; $C_6H_6$-10% EtOAc) the presence of atleast four compounds. On attempting their separation (0.13g) by chromatography over $SiO_2$-gel impregnated with 10% $AgNO_3$, two compounds were obtained pure ($SiO_2$-$AgNO_3$, 0.9 cm x 34 cm)

| | | | | |
|---|---|---|---|---|
| Fr.1 | $C_6H_6$ | 8x15 ml | 0.004 g | Rejected |
| Fr.2 | $C_6H_6$-2% EtOAc | 3x20 ml | 0.018 g | Single |
| Fr.3 | $C_6H_6$-4% EtOAc | 4x20 ml | 0.03 g | Mixture |
| Fr.4 | $C_6H_6$-6% EtOAc | 4x20 ml | 0.026 g | Single |
| Fr.5 | EtOAc | - | 0.023 g | Polar Compounds. |

Frac.2 was distilled, b.p. 135-40° (bath temp)/0.7 mm, to give sesquiterpene alcohol-I, $[\alpha]_D$+13.88°(C,2.16)(Found: C,81.55; H, 11.82, $C_{15}H_{26}O$ requires: C, 81.09: H, 11.79%) IR:OH 3450, 1040 $cm^{-1}$; PMR:-C-Me (3H,s,0.75 ppm), $Me_2$-C-OH (6H,s,1.13 ppm),-C=CMe(3H,s,1.62 ppm) and -C=CH(1H, m,5.26 ppm) Based on these spectral data structure (1) is assigned to this alcohol.

Frac.4 was distilled, b.p. 140-45°(bath)/0.7 mm $[\alpha]_D$ +32.37° to give sesquiterpene alcohol-II. (Found:C, 81.19: H, 11.22. $C_{15}H_{26}O$ requires: C, 81.09:H, 11.79%). IR:OH 3400, 1650 $cm^{-1}$; C = $CH_2$ 890 $cm^{-1}$; PMR:-C-Me(3H, s, 0.69 ppm), -$Me_2$-C-OH (6H,s,1.14 ppm) and -C=$CH_2$(2H, d, centered at 4.55 ppm, J=24Hz). Structure (2) is consistent with these spectral data.

The minor component RT 15 (0.076 g) from the above mentioned preparative GLC of Frac. 5 was obtained only in 59% purity. The PMR of the crude mixture

indicated the presence of neojaeshkeanadiol in predominant amount. Further purification of the fraction was not attempted.

## SUMMARY

The essential oil of Ferula jaeschkeana has been studied and the presence of α-pinene, β-pinene, limonene, humulene and caryophyllene has been established. In addition, verbenone, elemicin, myristicin, neojaeschkeanadiol and two new sesquiterpene alcohols have been isolated. From a study of their spectral data and from biogenetic considerations, the new alcohols are assigned structures(1) and (2).

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