CHAPTER II

Fragmentation of Homoallylic Alcohols : Synthesis and Fragmentation of 6 - Hydroxycamphene

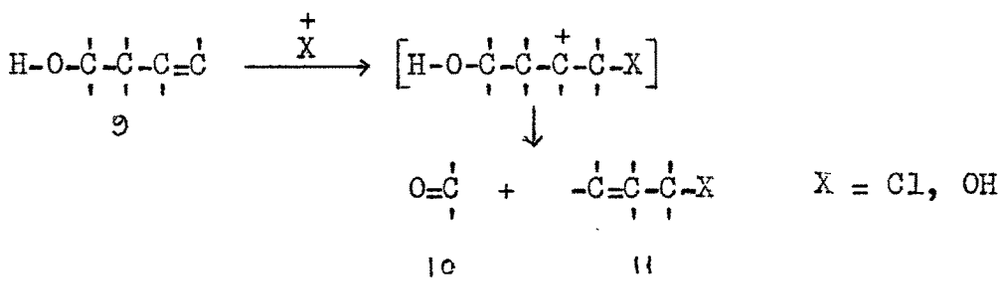
FRAGMENTATION OF HOMOALLYLIC ALCOHOLS: SYNTHESIS AND FRAGMENTATION OF 6-HYDROXYCAMPHENE

Abstract——An improved synthesis of 6-*exo* and *endo*-hydroxycamphenes is presented in this Chapter. The reaction of tricyclene with NBS is reinvestigated. Fragmentation reactions of the two homoallylic alcohols with a variety of electrophiles are described. The configuration of the hydroxyl group is inconsequential for this cleavage reaction.

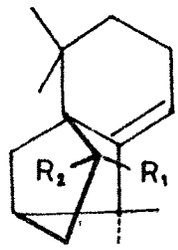
FRAGMENTATION OF HOMOALLYLIC ALCOHOLS: SYNTHESES AND FRAGMENTATION OF 6-HYDROXY CAMPHENE

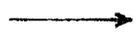
1. INTRODUCTION

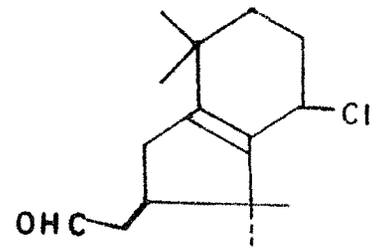
Fragmentation of Y-C-C-C-X systems, where X is a nucleofuge[1] which leaves as :X, and Y is a hetero atom with p-electrons, to -C=C- and Y⁺=C- moieties have been extensively studied[2] and frequently made use of in organic synthesis. Sukh Dev *etal*[3,4] discovered a related yet novel cleavage of homoallylic alcohols by reaction with electrophiles. Thus the alcohol 1, on treatment with chlorine, was reported to give an aldehyde 6. Similar fragmentation of alcohols 2,3 and 4 gave the corresponding aldehydes 6, 7 and 8 respectively. In generalized terms, this fragmentation can be depicted as follows (9→10+11)



This cleavage differs from Grob fragmentations[2] in producing allylic halides or alcohols, instead of olefins and, in







1 R_1=H ; R_2= OH

2 R_1=OH; R_2=H

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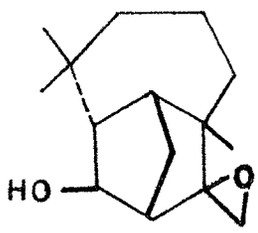

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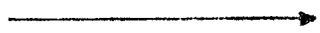

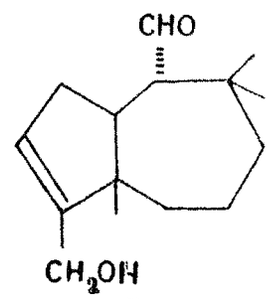

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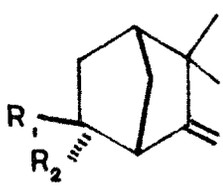
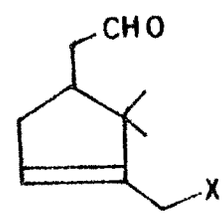




4 R_1OH, R_2 H

5 R_1 H; R_2 H

8 , X = Cl

appropriate cases, this can be of distinct value for synthetic operations.

With an aim to study the scope and generality of this fragmentation reaction, two homoallylic alcohols, namely, 6-exo-hydroxycamphene 4 and 6-endo-hydroxycamphene 5 were selected. The syntheses of these two homoallylic alcohols and their fragmentation with various electrophiles like bromine, bromine azide and mercuric acetate, form the subject matter of this Chapter.

2. SYNTHESIS OF HOMOALLYLIC ALCOHOLS (4 and 5)

2.1 6-exo-Hydroxycamphene (4)

The alcohol 4 , which was needed in comparatively large quantities was originally synthesised by Sukh Dev et al[5] in less than 40% yield from tricyclene 12 , by opening of the cyclopropane ring with N-bromosuccinimide(NBS) followed by solvolysis. Later, it was also isolated[6] from Chrysanthenum Japanese Makino and named as nojigiku alcohol. More recently Hershbach et.al[7] synthesised it in 18% yield starting from camphene. In order to synthesise the desired 4 in good yields, reaction of tricyclene 12 with NBS was reinvestigated and the conditions were optimised for the synthesis of 4 from tricyclene 12 via 6-bromocamphene 13.

The treatment of tricyclene 12 with NBS leads predominantly to the formation of 6-exo-bromocamphene 13. The reaction when carried out under different conditions viz in presence and absence of peroxide, with or without exposure to light and in different solvents like carbon-tetrachloride and chloroform gave different conversions. The best conversions were obtained when the reaction was carried out in dry $CHCl_3$ in absence of peroxide and without irradiation. Under these conditions tricyclene gave a product containing ~70% of 6-exo-bromocamphene 13 (GLC, PMR). Also present in the reaction mixture were unreacted tricyclene 12 (18-20%), camphene 14 (8-10%) and small quantities (2-4%) of another product identified as the dibromide 15 (vide infra). None of 10-bromotricyclene 16, which could have logically formed along with 13, was present in the reaction mixture as indicated by the absence of a signal due to CH_2Br in the region of 3.70-3.90 ppm in the PMR spectrum. Separation of different components by fractionation or column chromatography was found difficult. So the crude reaction mixture was solvolysed with lithium carbonate in aqueous dioxane (90-95°, 72 hr). The solvolysis product was a mixture of alcohols, in which tricyclenol 17 and 6-exo hydroxy camphene 4 were the predominant components in the ratio 3:2 (GLC and PMR).

Attempts to separate 17 and 4 on SiO_2-$AgNO_3$ column proved infructuous. None of the alcohol 17 could be eluted from the column, for it was transformed to 6-exo-hydroxycamphene 4. It was later discovered that tricyclenol 17 prepared by an alternative route (vide infra) largely (65-70%) rearranged to 6-exo-hydroxycamphene when adsorbed over 10% $AgNO_3$ on silica gel column for 72 hr. Also, the alcohol 4 partially fragmented to the aldehyde 19 which was eluted together with 6-exo-hydroxycamphene.

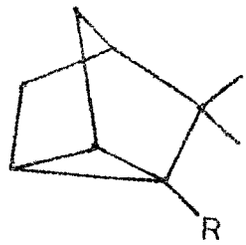
To avoid complication caused by $AgNO_3$ on silica gel, the chromatography of solvolysed mixture was next carried out on alumina when the following fractions were obtained:

i) unreacted tricyclene 12

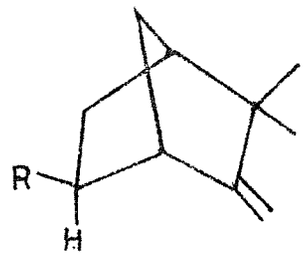
ii) a mixture of camphene 14 and dibromocamphene 15[7].

iii) A sample of pure 15 was obtained by carrying out a preparative GLC of this mixture on 5% carbowax, 20M supported on chromosorb W at 100°. The ratio between Z and E isomers as estimated from PMR(C=CHBr, s,5.65 and 5.89 ppm) was ~ 6:1.

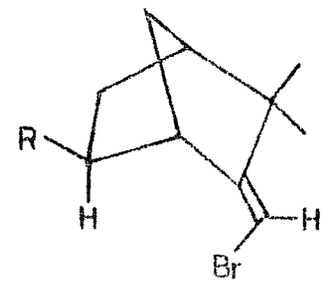
iii) A mixture of alcohols 4, 17 and 18 (designated as mixture A). Preparative GLC of this mixture on 5% carbowax, 20M supported on chromosorb W at 160° provided samples of pure 4 and 17. However, 18 was contaminated with 4.



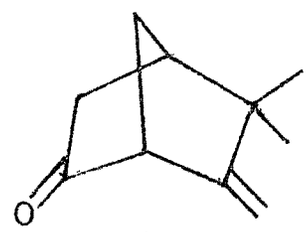
12 R = CH_3
16 R = CH_2Br
17 R = CH_2OH
20 R = COOH
22 R = CH_2OCrO_3H



13 R = Br
14 R = H



15 R = Br
18 R = OH



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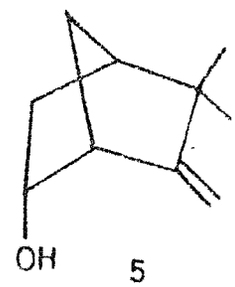

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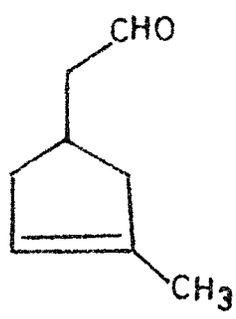

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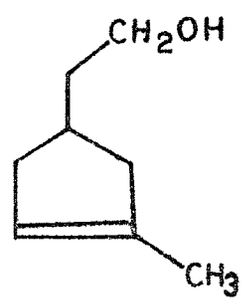

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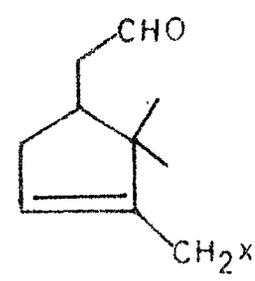

23 X = Br
25 X = Hg (OAc)

The formation of tricyclenol 17 appears to be kinetically favoured as it underwent easy equillibration to 4 under acidic conditions.

The most convenient way to prepare 6-exo-hydroxycamphene 4 in yields better than those reported earlier was to treat the alcohol mixture A with perchloric acid (0.35%) in aqueous dioxane (90%), when tricyclenol 17 was almost completely transformed into 4. The impurities of 18 could be removed by sublimation and ~60% yield of 4 was obtained.

The same alcohol mixture A could be used for preparing tricylenol 17 in good yields. On oxidation with Jones reagent, the mixture A yielded tricyclinic acid 20 in 68% yield. Clearly 6-exo-hydroxycamphene(4) present in mixture A was also isomerised to tricyclenol 17 when the latter was oxidised to 21. Preponderance in the formation of 20 over 6-keto camphene (21, derivable from 4) is suggestive of a large rate difference in oxidation of 4 and 17. This may be a result of more severe nonbonded interaction[8] of chromate ester grouping with the gem-dimethyl group in the intermediate 22 from 4. LAH reduction of 21 gave a quantitative yield of tricyclenol 17.

2.2. 6-endo-Hydroxycamphene(5):

The alcohol 4, on oxidation with pyridine-chromic acid, yielded the 6-ketocamphene 21[5], which on reduction with tri-

tert-butoxylithium aluminium hydride gave the epimeric alcohol 5 in quantitative yield.

3. FRAGMENTATION OF HOMOALLYLIC ALCOHOLS

The fragmentation of homoallylic alcohols 4 and 5 was studied using various electrophiles as described below:

3.1. With Bromine: Treatment of alcohol 4 in carbon tetrachloride with molar equivalent of bromine in presence of sodium carbonate gave a product in almost quantitative yield, which was unstable even at room temperature and its properties had to be studied only in solution, as attempts at purification through distillation or chromatography (SiO_2-gel or Al_2O_3) led to decomposition. Colour test (yellow colour with tetranitro methane) and spectroscopic data [IR,(CCl_4): C<u>H</u>O, 2770, 1720 cm^{-1} and C=C, 1650 cm^{-1}; PMR (CCl_4): C=C<u>H</u>$_2$, 5.76 ppm, C<u>H</u>O, 9.73 ppm] indicated the presence of an olefinic aldehyde. Based on mechanistic consideration and above data, the product was be assigned structure 22. Further, this assignment was confirmed by direct correlation with the known α-campholenic alcohol 24[9], by reduction with LAH in dry ether. Fragmentation of homoallylic alcohol 5 with bromine gave the same product.

3.2. With Bromine Azide: Alcohols 4 and 5, when treated with a solution of molar equivalent of bromine azide in dichloromethane gave the same fragmentation product 23 in quantitative yield.

3.3. With Mercury(II)Acetate: The fragmentation of alchols 4 and 5 was also studied with mercury(II)acetate. When the homoallylic alcohols were treated with $Hg(OAc)_2$, the fragmentation took place to give the organomercurial 25 (PMR: C<u>H</u>O , 9.73 ppm; C=C<u>H</u> 5.8 ppm), which on demercuration with $NaBH_4$/NaOH gave α-campholenic alcohol in quantitative yield.

Irrespective of whether the addition of halogens and pseudohalogens to 6-exo-hydroxycamphene takes place via a free radical or ionic mechanism, no normal addition products have been obtained. The additions of halogens to 6-hydroxycamphene were all carried out in presence of air so that contribution from the radical pathway can be expected to be minimal. The ionic addition of the electrophiles to 6-hydroxycamphene can give rise to an acyclic carbonium ion 26 which is amenable to fragmentation or to a cyclic halonium ion 27, which may change to acyclic carbocation 26 or may directly fragment in a synchronous manner, without forming the intermediate carbocation. Whatever may be the nature of

transition state, it is found that alcohols 4 and 5 fragment easily with a variety of electrophiles. Finally the configuration of hydroxyl group is inconsequential as the epimeric alcohols 1 and 5 fragment with equal ease to give the same product.

4. EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum ether and petroleum ether refer to the fractions b.p. 40-60° and 60-80° respectively. All solvent extracts were finally washed with brine and dried over anhydrous sodium sulphate.

The following instruments were used for spectral/analytical data: Perkin-Elmer Infra red Spectrophotometer, model 267; Perkin-Elmer P-32 (90 MHz) NMR Spectrometer; Varian Mat CH-7 Mass Spectrometer(70 eV,direct inlet system); Hewlett-Packard 5712A and 7624A Gas Chromatographs (Al.columns, 180 cm x 0.06 cm; support, 60-80 mesh chromosorb W; carrier gas, H_2). All PMR spectra were recorded with 15-20% solution in CCl_4(unless otherwise stated) with TMS as internal reference; signals are reported in ppm(δ); while citing PMR data the following abbreviations have been used: s, singlet; d,doublet; m,multiplet; bs,broad signal. While summarising mass spectral data, besides the molecular ion, ten most abundant ions(m/e) are reported with their relative intensities.

Silica gel for column chromatography (100-200 mesh) was washed with hot water till sulphate-free, dried, activated at 125-30° for 6-8 hr and standardised. TLC was carried out on SiO_2-gel layers(0.25 mm) containing 15% gypsum and activated at 110-115° (2 hr).

Action of N-Bromosuccinimide on Tricyclene (12)

A mixture of tricyclene (12) (13.6 g, 0.1 mol) and NBS (17.6 g, 0.1 mol) in alcohol free, purified chloroform (50 ml) was refluxed on water bath for 24 hr under nitrogen. After NBS was consumed (24 hr, tested with KI solution), the reaction mixture was cooled to room temperature, washed free of succinimide with water (20 ml x 3) and dried. Removal of solvent gave a yellow coloured liquid (20.5 g) which contained the required 6-exo-bromocamphene (~70%)(GLC) as the major product. PMR (CCl_4):-C-Me's (3H, s, 1.0 and 1.05 ppm); CHBr(1H, dd, 3.9 ppm; J_1=3Hz, J_2=6Hz); C=CH_2(2H, s, 4.80 and 4.95 ppm).

Action of aq. Li_2CO_3 on Bromide mixture

The above mixture of bromides (20.5 g) and Li_2CO_3 (10.5 g) in 50% aq. dioxane (60 ml) was plunged in an oil bath at 95±2° and stirred at same temperature for 48 hr. The reaction mixture was cooled to room temperature, diluted with 2% aq. acetic acid(50 ml) and extracted with ether (30 ml x 3). The organic extracts were washed with water (20 ml x 2) and dried (Na_2SO_4). Removal of solvent offered a gummy residue (15.5 g). A portion(2.1 g) of this residue ~~which~~ was chromatographed over alumina (IIB, 75 g, 24 x 2 cm) with tlc monitoring (SiO_2, solvent 5% EtOAc in C_6H_6)

Frac. 1	Pet ether	20ml x 2	0.305 g	Tricyclene.
Frac. 2	Pet ether	20ml x 3	0.350 g	a mixture of bromides and hydrocarbon.
Frac. 3	Benzene	20ml x 3	1.450 g	a mixture of alcohols 17 & 18 (Mixture A).

Frac. 2 was further separated by preparative GLC (5% carbowax, 20 M supported on chromosorb W at 100°).

GLC component 1 (dibromocamphene 15). PMR(CCl_4): $-\overset{|}{\underset{|}{C}}$-Me's (6H, s, 1.22 ppm); $CH_2=\overset{|}{C}-C\underline{H}$(1H, bs, 3.22 ppm) $C\underline{H}Br$(1H, m, 4.41 ppm); $C=C\underline{H}Br$(1H, s, 5.66 ppm).

GLC component 2(Camphene, 14); m.p. 48-49°.

Frac. 3 was also separated by preparative GLC(5% carbowax, 20 M supported on chromosorb W at 160°)

GLC component 1(tricyclene alcohol , 17); m.p. 101°. IR(CCl_4) (FIG 1): OH 3600, 3380 and 1010 cm^{-1}. PMR(CCl_4)(FIG 2); $-\overset{|}{\underset{|}{C}}$-Me's (6H, s, 0.95 ppm); $C\underline{H}_2OH$(2H, s, 3.69 ppm).

GLC component 2 (6-exo-hydroxycamphene 4); m.p. 43° (lit[5]. 41-43°). IR(CCl_4)(FIG 3): OH 3600, 3440 and 1050 cm^{-1}; C=C 3060, 1650 and 885 cm^{-1}. PMR(CCl_4)(FIG 4): $-\overset{|}{\underset{|}{C}}$-Me's (3H, s, 0.96 and 1.05 ppm); $CH_2=\overset{|}{C}-C\underline{H}$ (1H, s, 2.60 ppm); $O\underline{H}$(1H, bs, 3.04 ppm); $C\underline{H}OH$(1H, dd, 3.75 ppm, J_1=3Hz, J_2=6Hz); $C=C\underline{H}_2$ (1H, s, 4.65 and 4.80 ppm).

Action of aq $HClO_4$ on Tricyclenol (17)

To a mixture of alcohols 4, 17 and 18 (6.0 g) obtained from the solvolysis of bromides was introduced to a 0.35% solution of $HClO_4$ in aq. dioxane (5.0 ml) and kept at $45\pm1^{\circ}$ for 80 hours under N_2 atmosphere. At the end of 80 hours, the reaction mixture was cooled to room temperature and quenched with 5% $NaHCO_3$ (20 ml) and extracted with ether (30 ml x 3). The extracts were washed till neutral with water (20 ml x 3) and dried (Na_2SO_4). Removal of solvent offered a gummy residue (6 g). Pure 18 was obtained by the sublimation of the residue at $80^{\circ}/20$ mm; m.p. 101°. IR($CHCl_3$)(FIG 5): OH 3610,3450 and 1060 cm^{-1}; C=C 3080, 1650 and 895 cm^{-1}. PMR($CDCl_3$)(FIG 6); $-\overset{|}{\underset{|}{C}}-Me$'s(3H, s, 1.02 and 1.10 ppm); $CH_2=\overset{|}{C}-C\underline{H}$ (1H, s, 3.02 ppm); $C\underline{H}Br$ (1H, bs, 3.70 ppm); $C=C\underline{H}Br$(1H, s, 5.72 ppm).

Residue after sublimation was crystallised (pet ether) to give alcohol 4 as white needles (m.p.43-44°, 4 g, 66%).

6-Ketocamphene(21)

To a complex prepared by adding chromic acid (6.4 g, 0.064 mol), to pyridine (64 ml) was added a solution of 6-exo-hydroxycamphene 4 (2.4 g 0.016 mol) in pyridine (16 ml).

The resulting mixture was stirred for 23 hours. At the end of this time water (100 ml) was added and the solution extracted with ether (30 ml x 3). The ether extracts were washed with water (10 ml x 2), 5% hydrochloric acid (10 ml x 2), 5% sodium hydroxide (10 ml x 2), and water (10 ml x 2) and dried. Removal of solvent furnished a white solid which was crystallised from light petroleum to give 21 (2.1 g, 89%); m.p. 75-76° (Lit[5] 75°). IR(CCl_4)(FIG 7): C=O 1750 cm^{-1}; C=C 3070, 1650 and 890 cm^{-1}. PMR(CCl_4)(FIG 8): -C-Me's (3H, s, 1.00 and 1.09 ppm); -C=CH_2 (2H, s, 4.80 and 5.01 ppm); CH_2=C-CH (1H, bs, 3.00 ppm).

6-endo-Hydroxycamphene (5)

A solution of ketone 21 (0.450 g, 3 m mol) in dry THF (15 ml) was added to a stirred solution of tri-tertiary butoxy lithium aluminium hydride (1.2 g, 6 m mol) in dry THF (20 ml) at 5° over a period of 30 minutes. The reaction mixture was stirred for an additional 8 hr at room temperature. At the end of this time water (25 ml) was added and the reaction mixture was extracted with ether (30 ml x 3). The ether extracts were washed with water (10 ml x 3) and dried. The solvent was removed by careful distillation to offer a crystalline solid, alcohol 5 (0.405 g, 80%); m.p. 101° (Lit[5].m.p.101°). IR(CCl_4)(FIG 9): OH 3600,

3340 and 1050 cm^{-1}; C=C 3060, 1650 and 885 cm^{-1}). PMR (CCl_4) (FIG 10):-C-Me's(6H,s,1.10 ppm); CH_2=C-CH(1H,d, 2.7 ppm; J=5 Hz); CHOH(1H, bs, 4.05 ppm); C=CH_2(2H,s, 4.94 ppm).

Jone s oxidation of alcohol mixture A:

To a solution of alcohol mixture A (1.1g) in acetone (20 ml) at 0° Jone s reagent was added and reaction mixture was stirred for 3 hrs at room temperature. At the end of this time water(25 ml) was added and extracted with ether (20 ml x3). Ether extracts were washed with 10% sodium bicarbonate (10 mlx3), water (10 ml) and dried. Removal of solvent furnished 6-keto-camphene 21.

Aqueous layer was acidified with dil HCl and again extracted with ether (30 ml x 3). The combined ether extracts were washed with water (10 ml x 2) and dried. Removal of solvent furnished the crystalline acid 20 (0.8 g, 66%); m.p. 150°(Lit[9] m.p. 151°). IR(Nujol):C=O 1670 cm^{-1}. PMR(CCl_4):-C-Me's (6H, s, 1.07 ppm).

Tricyclene alcohol 17

A solution of 20 (0.166 g, 1 m mol) in dry ether (30 ml) was added dropwise to a stirred suspension of LAH (100 mg) in dry ether (10 ml) kept below 20° by external cooling.

After addition, the mixture was stirred for 2.5 hr at room temperature and for 30 min. under reflux. At the end of this period, excess LAH was destroyed by cautious addition of water. The ethereal solution was separated and the aqueous layer was extracted with ether (20ml x 2). The combined ether extracts were washed with water (10mlx3), brine (10 ml x 1) and dried. Removal of solvent furnished a white solid which was crystallised from acetonitrile to give 17 (150 mg, ~100%).

Fragmentation of 6-hydroxycamphene (4)

(i) With Bromine:

To a cooled solution (-5 ± 2°) of homoallylic alcohol (4)(152 mg, 1 m mol) in carbontetrachloride (10 ml) containing Li_2CO_3(203 mg, 3 m mol) was introduced a cold solution of bromine (5 ml, 160 mg of Br_2; 1 m mol) during 5 min, keeping the temperature -5 ± 3°. The yellow colour of bromine was discharged immediately as the addition of bromine was over. Then Li_2CO_3 was filtered off and washed with CCl_4 (2 ml x 2). The solvent was evaporated at 10 ± 2° under reduced pressure to get a residue of bromoaldehyde 23 (230 mg, ~100%). IR(CCl_4)(FIG 11):CHO 2710 and 1725 cm^{-1}; C=C 1650 cm^{-1}. PMR(CCl_4)(FIG 12):-$\dot{C}$-Me's (3H,s, and 1.05 ppm); $\underline{CH_2}$Br(2H, bs, 3.92 ppm); C=C$\underline{H}$ (1H, bs, 5.59 ppm, Wh=6Hz); C$\underline{H}$O (1H, t, 9.75 ppm, J = 1.5 Hz).

The above bromoaldehyde (23)(230 mg, 1 m mol) in ether (10 ml) was added dropwise to a stirred slurry of LAH (250 mg) in ether (10 ml) and stirred at room temperature (30 ± 1°) for 24 hr. Under N_2. Excess of LAH was destroyed by cautious addition of water and extracted with ether (15 ml x 3). The combined ether extracts were washed (water and brine) and dried. Removal of solvent furnished α-campholenic alcohol 24 (150 mg, ~100%), b.p. 110-115^{o}(bath)/2.5 mm. IR(CCl_4)(FIG 13): OH 3340 and 1050 cm^{-1}; C=C 1645 and 800 cm^{-1}. PMR(CCl_4) (FIG 14):-C-Me's(3H, s, 0.76 and 0.97 ppm); CH=C-Me(3H,s,1.61 ppm); CH_2OH(2H, m, 3.59 ppm); =CH (1H, bs, 5.20 ppm). These spectral values are consistent with the data reported by Sukh Dev *et al*[10].

Similarly, fragmentation of 6-*endo*-hydroxycamphene 5 with bromine gave the same bromoaldehyde 23 (IR and PMR).

(ii) With Bromine Azide:

BrN_3 (122 mg, 1 m mol) in CH_2Cl_2(20 ml) was introduced into a cooled (0°) solution of 6-*exo*-hydroxycamphene 4 (152 mg, 1 m mol) in CH_2Cl_2 (5 ml) in presence of Na_2CO_3 (203 mg, 3 m mol) during 20 min. and stirred for 15 min. The inorganic salt was filtered off and washed with CH_2Cl_2 (5 ml x 2). The solvent was removed under reduced pressure to give bromoaldehyde 23 (230 mg, ~100%).

Similar reaction of the epimeric alcohol 5 with BrN_3 gave the same aldehyde 23.

(iii) With Mercury(II)Acetate:

To mercury(II) acetate (318 mg, 1 m mol) in water (5 ml) and THF (2.5 ml) was added a solution of 6-exo-hydroxycamphene 4(152 mg, 1 m mol) in THF(2.5 ml). The reaction mixture was stirred at room temperature for 1 hr. The organomercurial acetate was reduced in situ by stirring with 3N NaOH (5 ml) and 0.5M $NaBH_4$ in 3M NaOH(5 ml). The reaction mixture was extracted with solvent ether (20 ml x 3). The combined ether extracts were washed with brine (5 ml), dried and concentrated. The residue was distilled to give α-campholenic alcohol 24 (150 mg, ~100%).

Similar reaction of the endo-alcohol 5 also gave campholenic alcohol 24.

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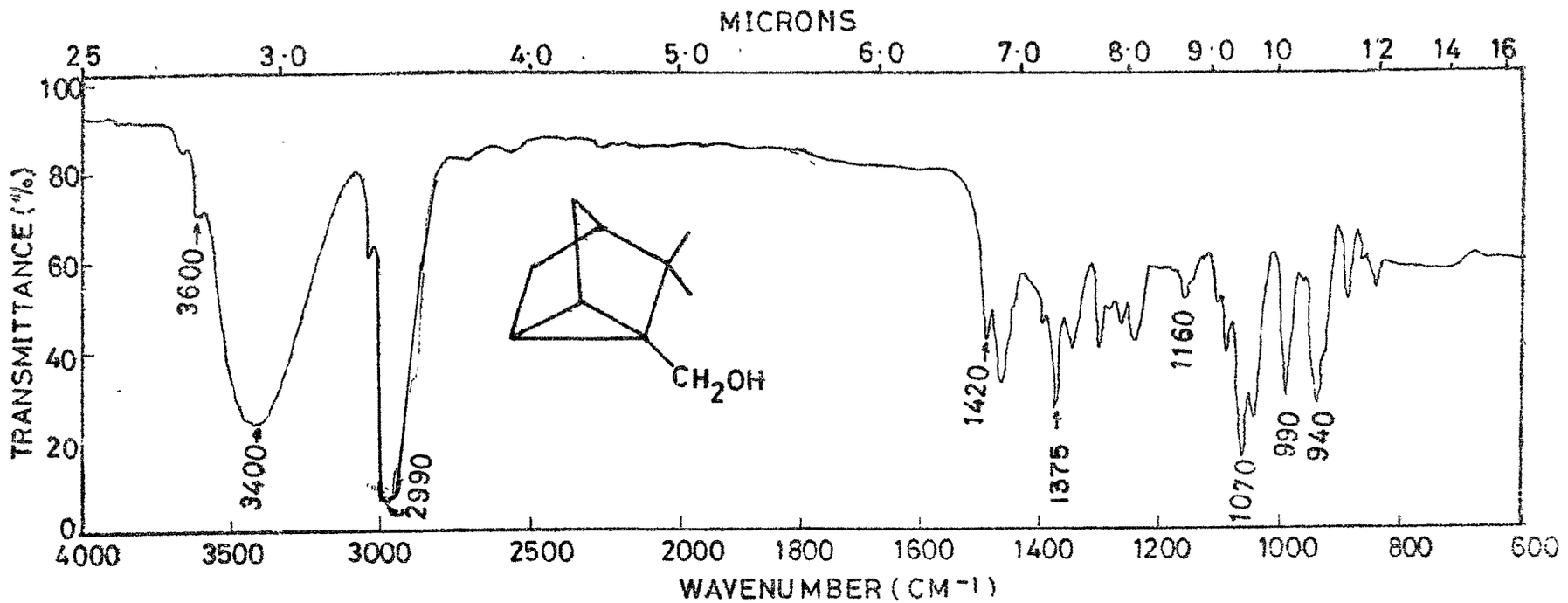

FIG. 1: IR SPECTRUM OF TRICYCLENE ALCOHOL (17)

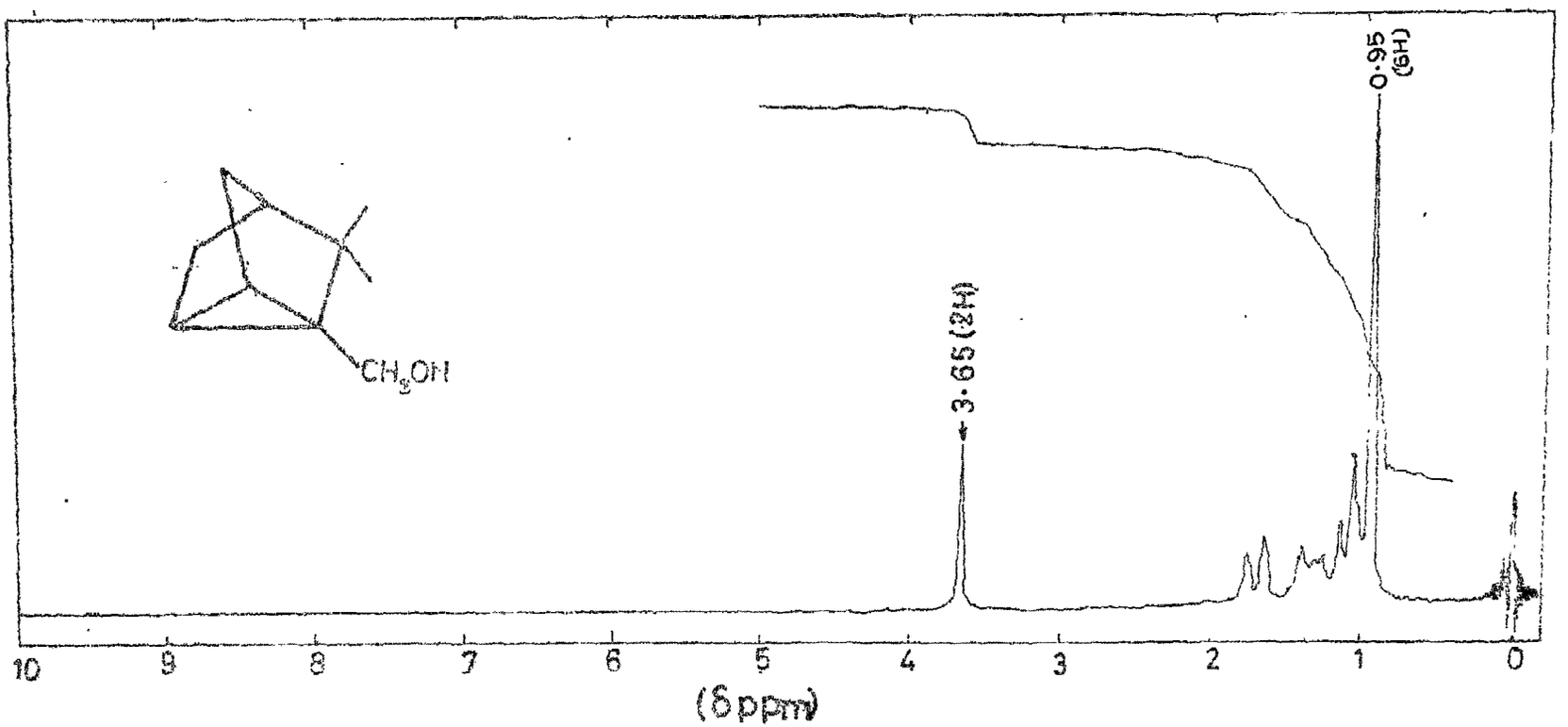

FIG2: PMR SPECTRUM OF TRICYCLENE ALCOHOL (17)

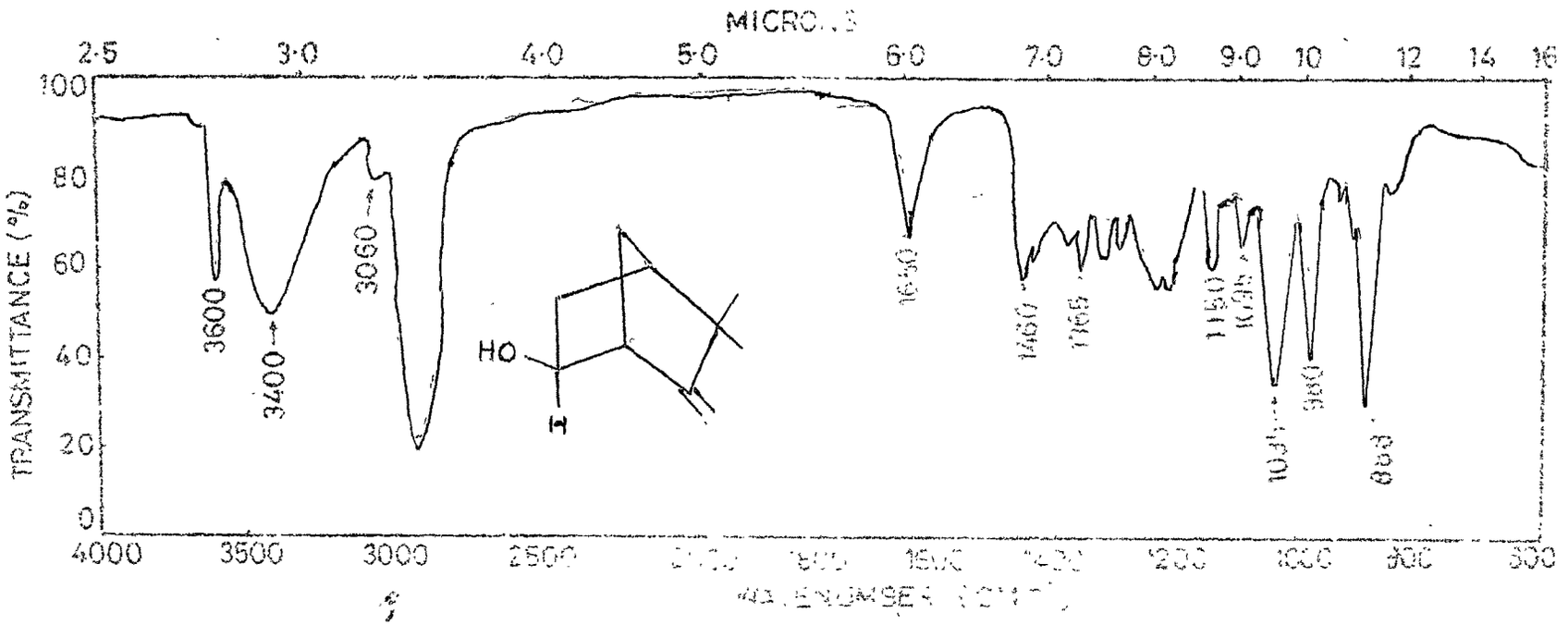

FIG. 3: IR SPECTRUM OF 5-EXO-HYDROXYCAMPHENE (4)

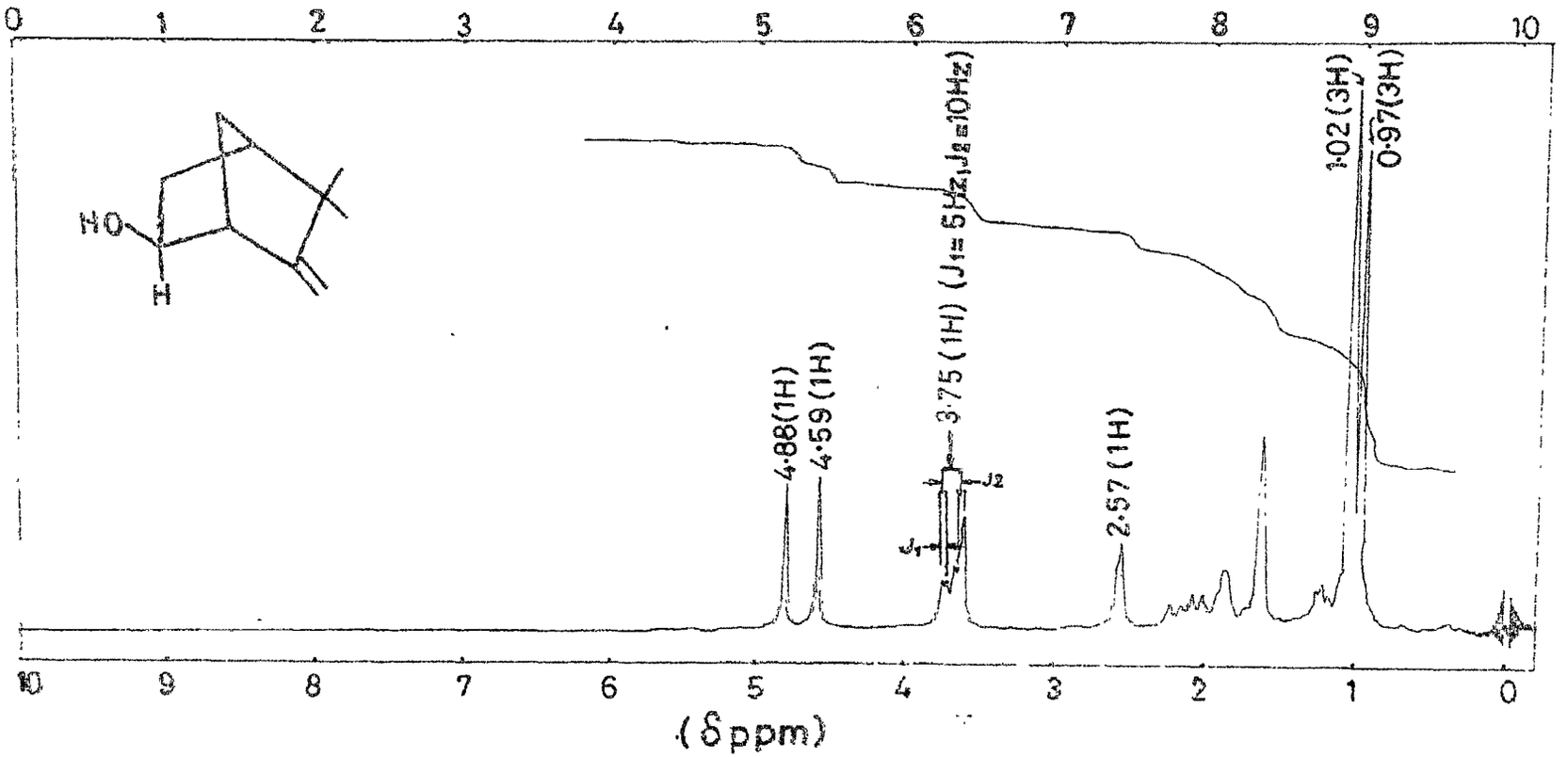

FIG: 4: PMR SPECTRUM OF 6-EXO-HYDROXYCAMPHENE (4)

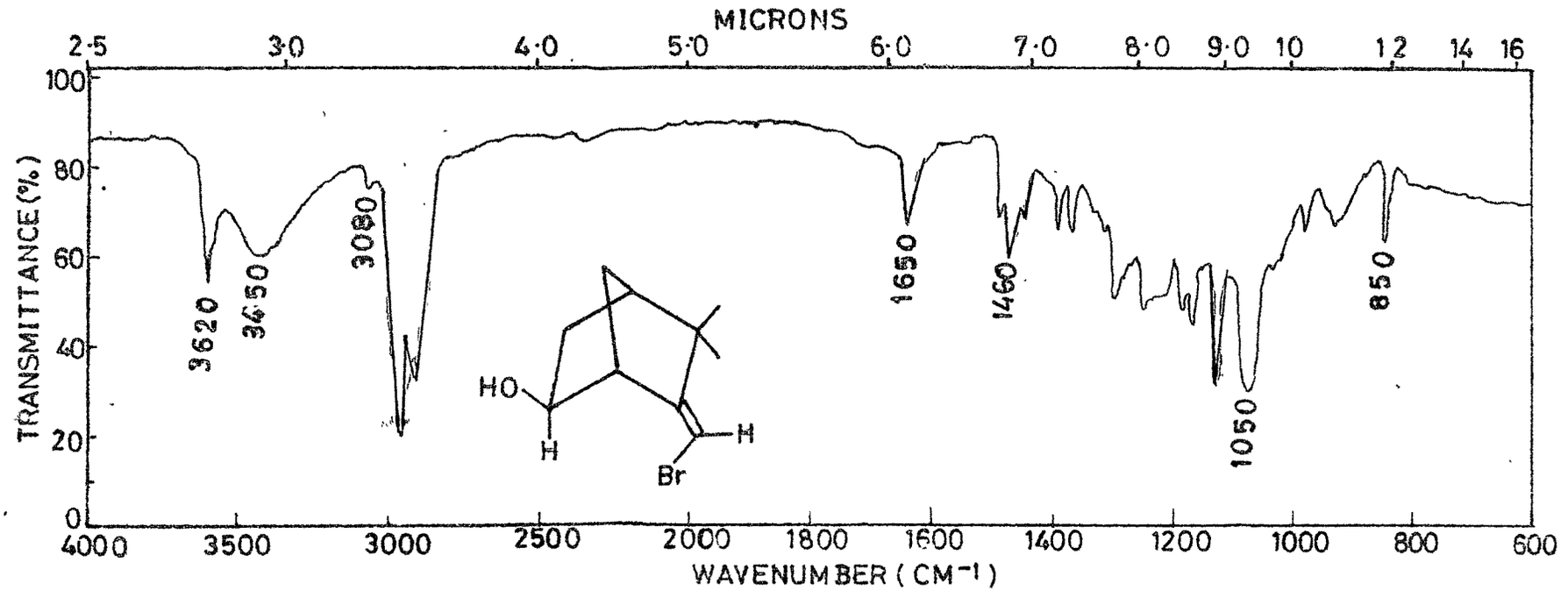

FIG. 5. IR SPECTRUM OF (E)-6-EXO-HYDROXY-10-BROMOCAMPHENE (18)

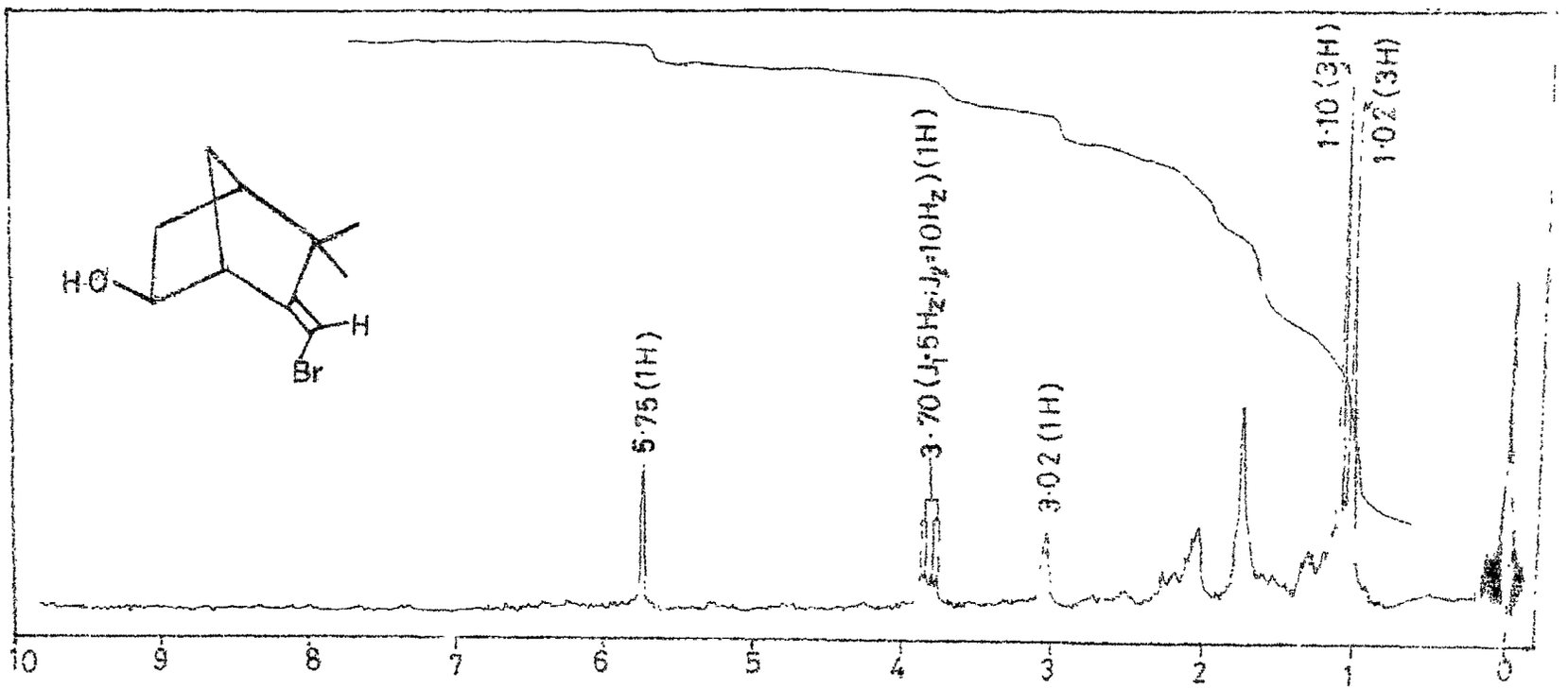

FIG 6 : PMR SPECTRUM OF (E) 6-EXO-HYDROXY-10-BROMOCAMPHENE (18)

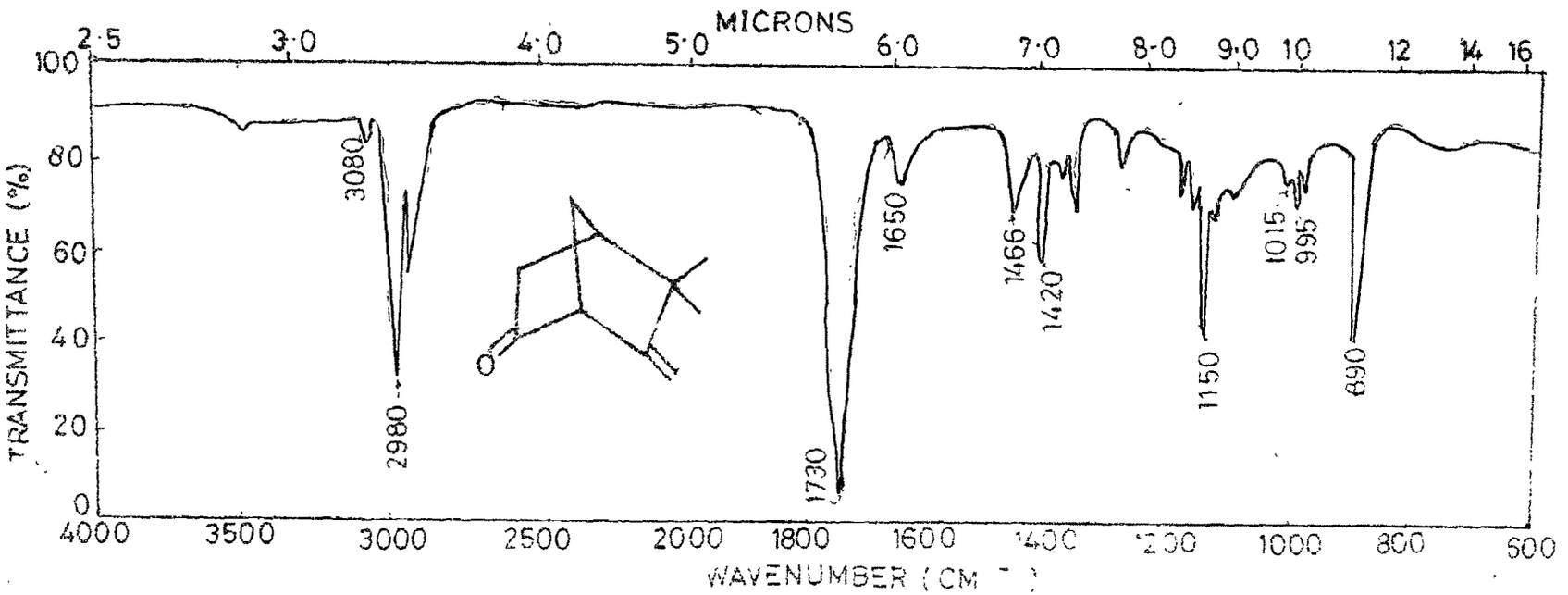

FIG. 7: IR SPECTRUM OF 6-KETOCAMPHENE (21)

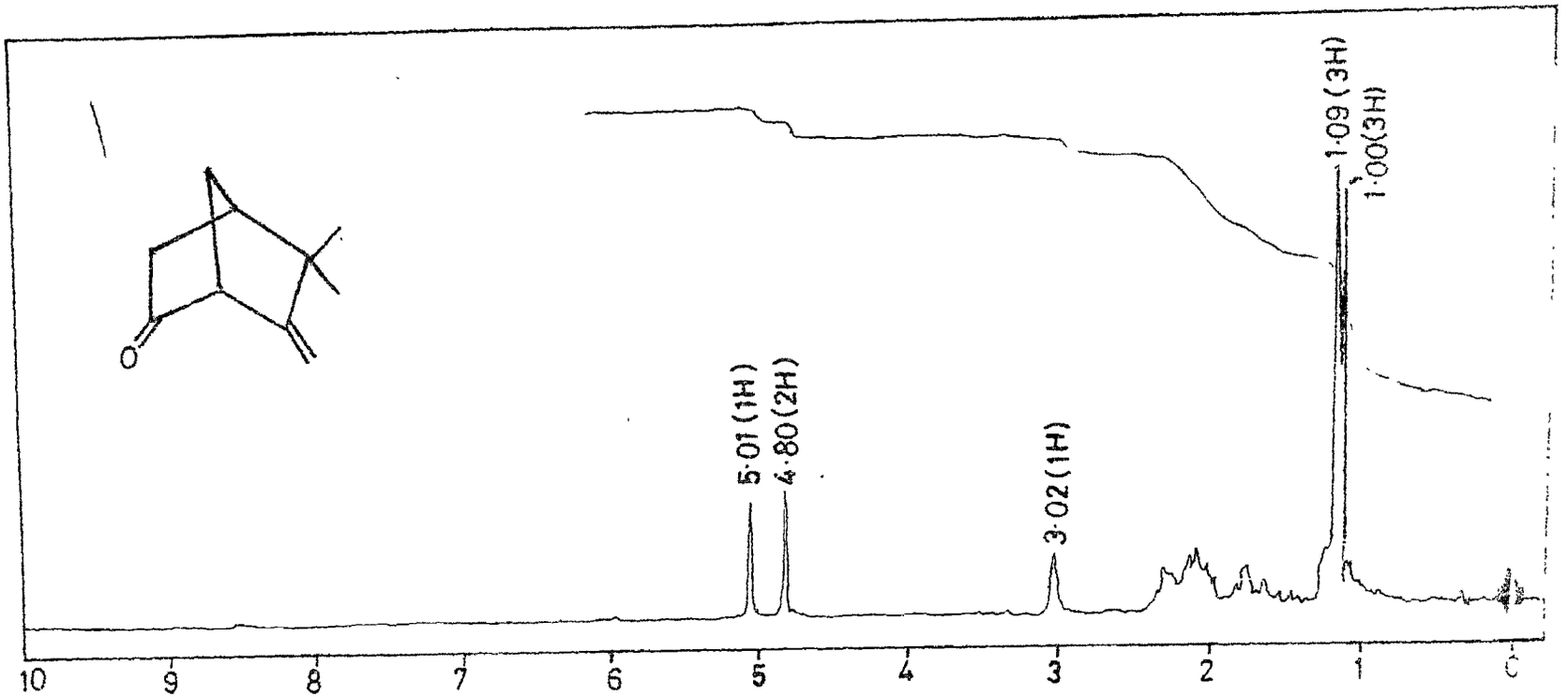

FIG 8: PMR SPECTRUM OF 6-KETOCAMPHENE(21)

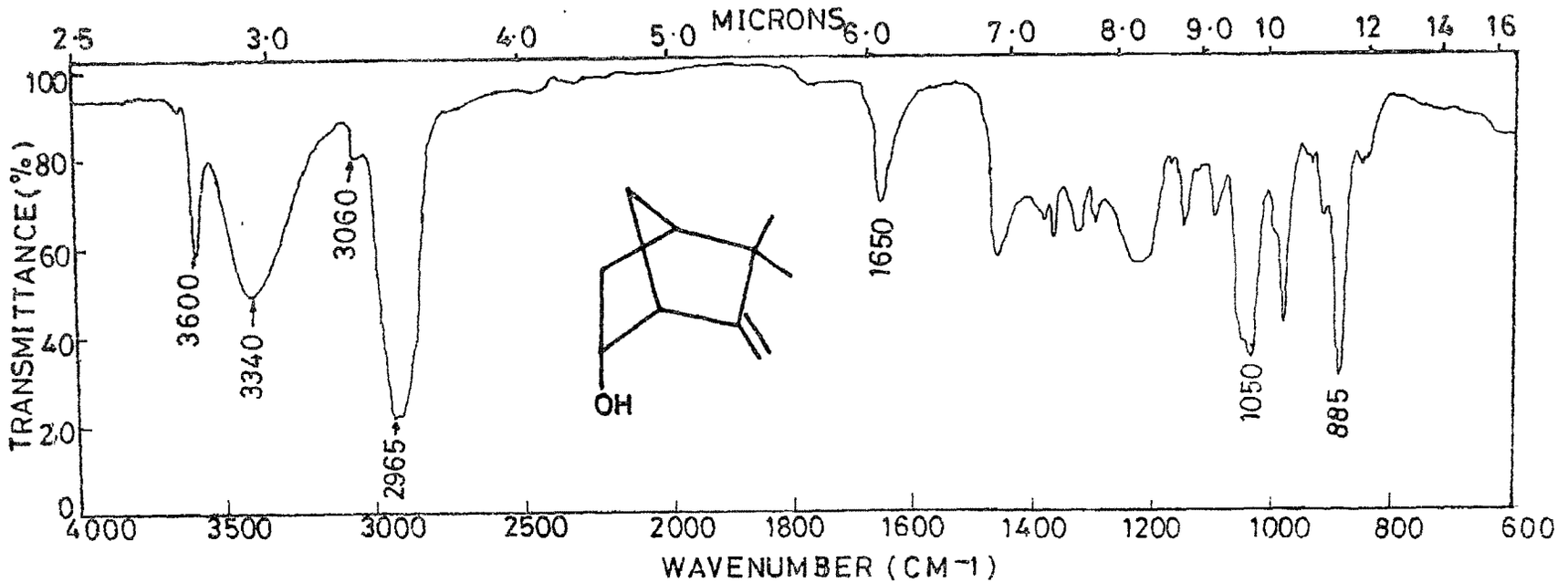

FIG.9: IR SPECTRUM OF 6-ENDO -HYDROXYCAMPHENE(5)

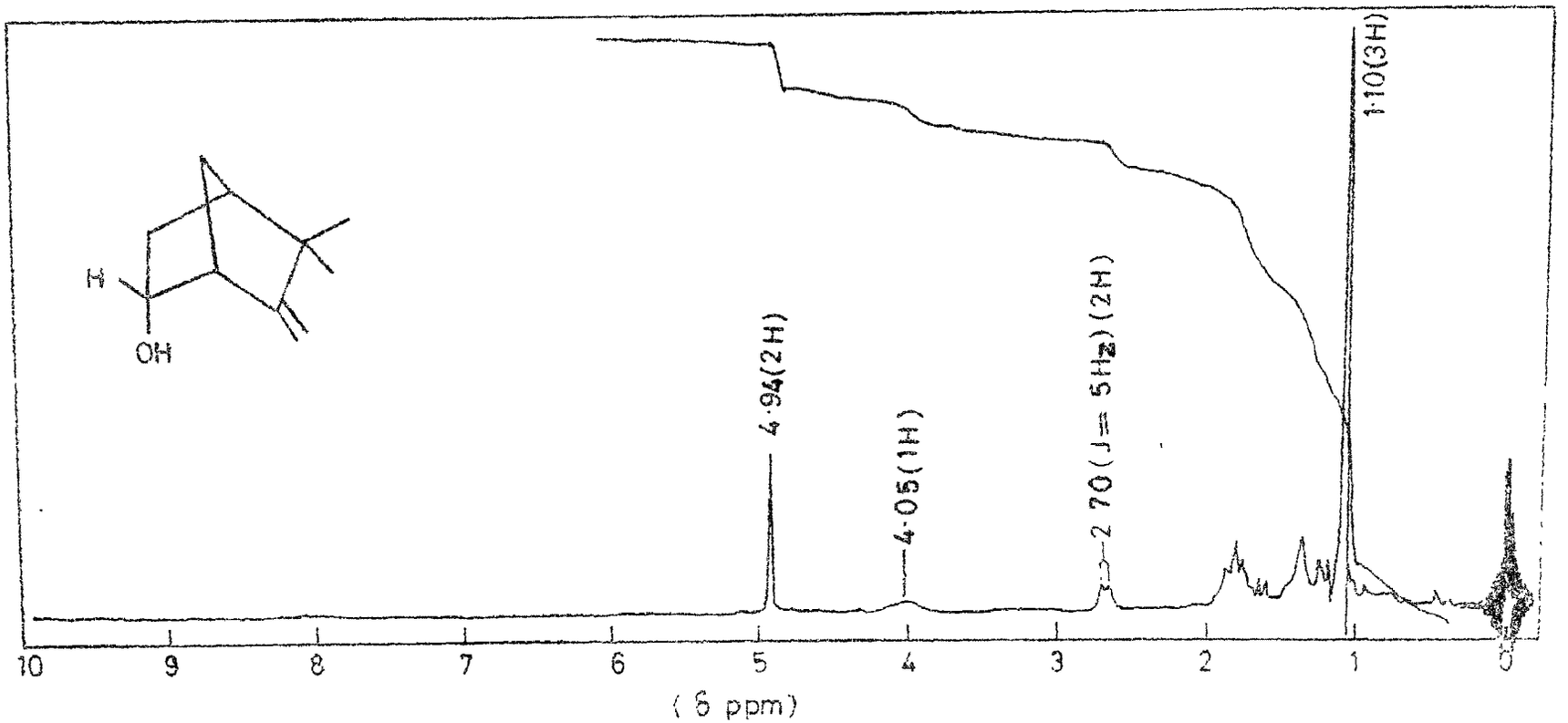

FIG.10: PMR SPECTRUM OF 6-ENDO-HYDROXYCAMPHENE (5)

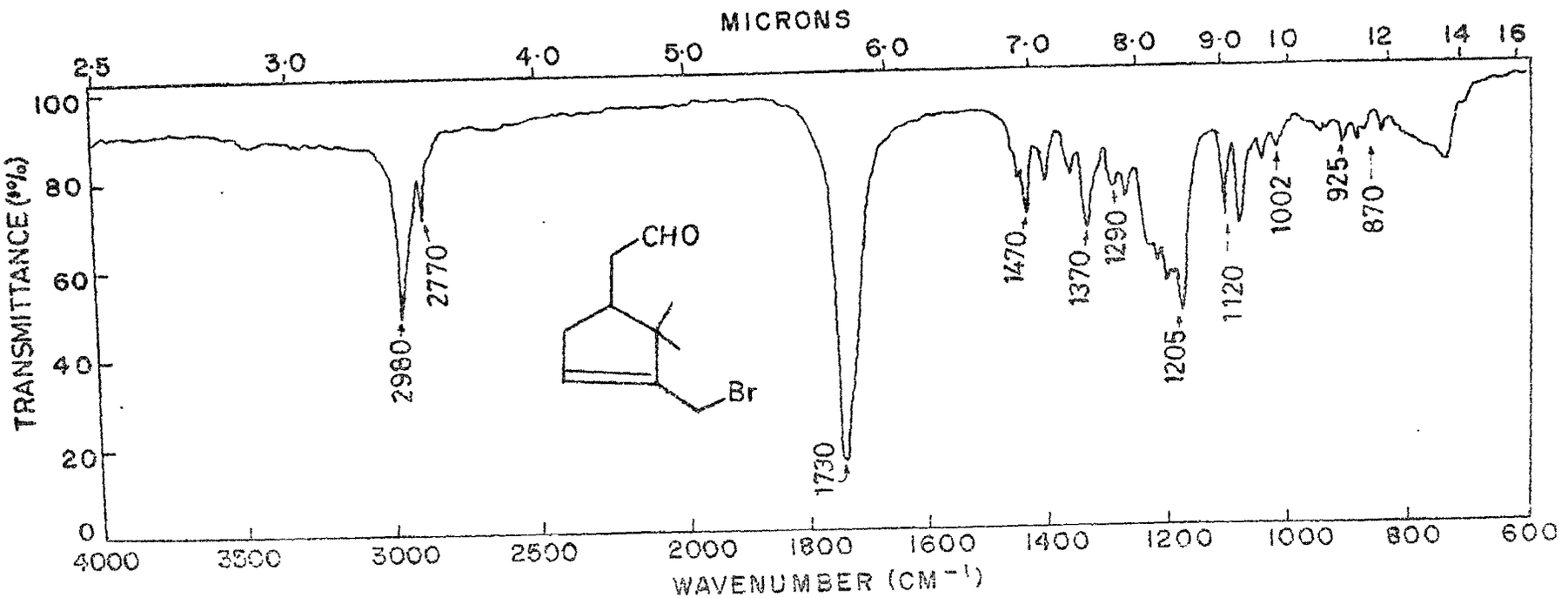

FIG.11: IR SPECTRUM OF 2/2,2-DIMETHYL-3-BROMOMETHYL CYCLOPENT-3-EN-1-YL ACETALDEHYDE (23)

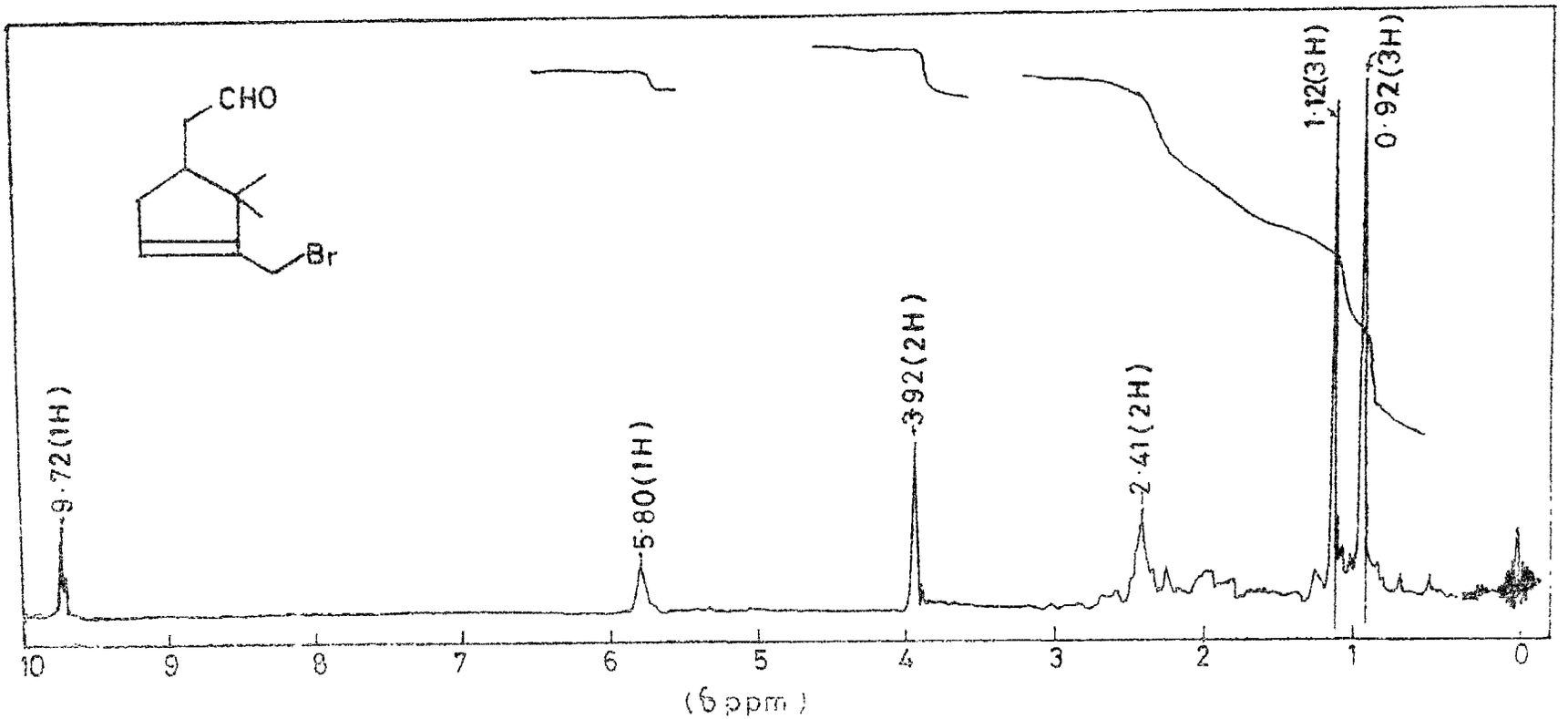

FIG. 19: PMR SPECTRUM OF 2[3-BROMOMETHYL-2,2-DIMETHYL-3-CYCLOPENTENYL]-ETHALDEHYDE

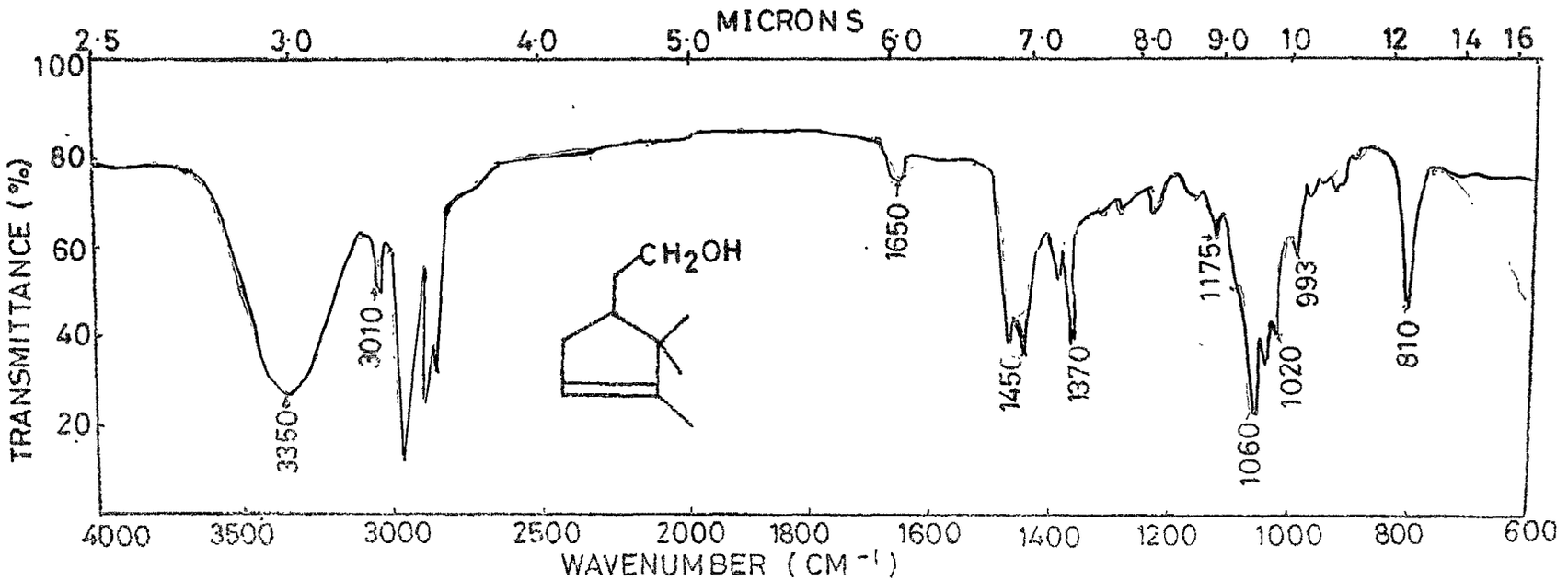

FIG 12 : IR SPECTRUM OF α-CAMPHOLENIC ALCOHOL (24)

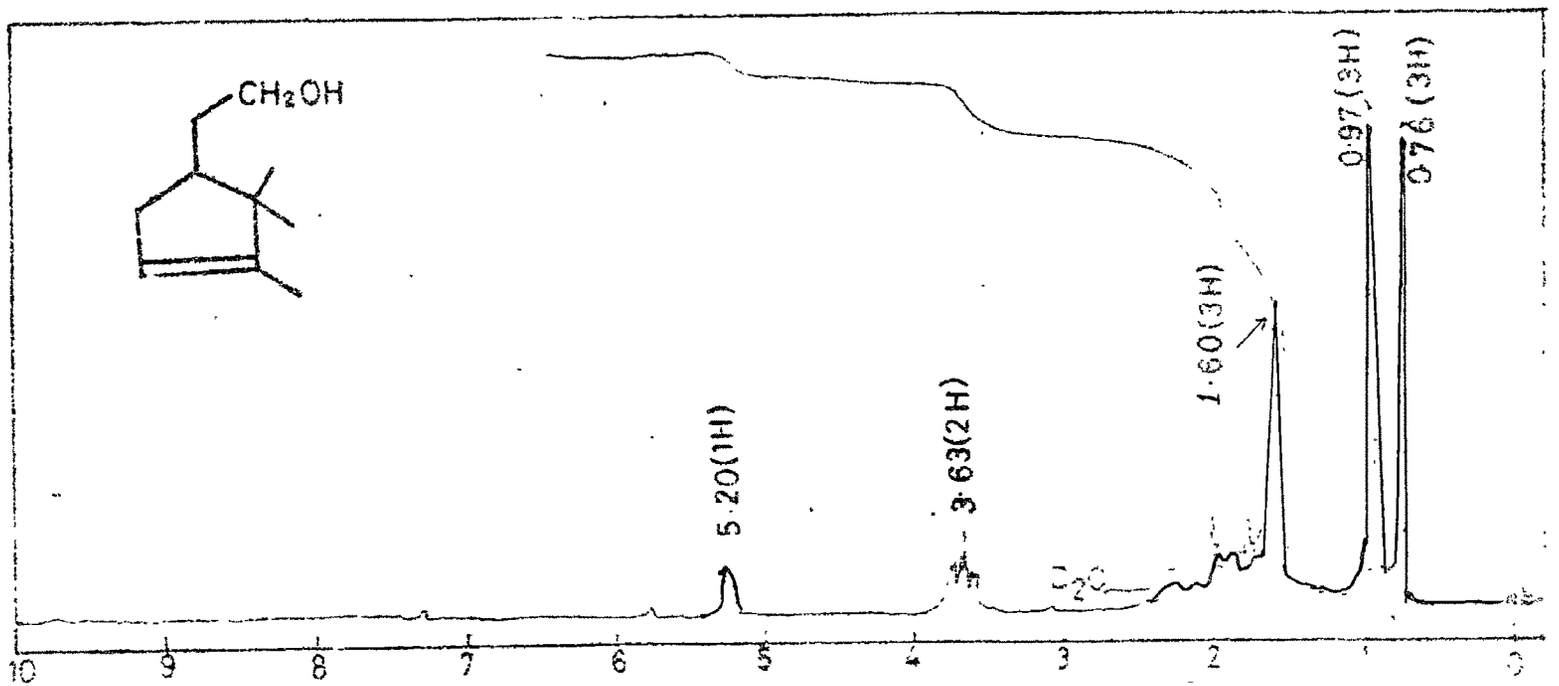

FIG 14 PMR OF SPECTRUM OF α-CAMPHOLENICALCOHOL (24)