C H A P T E R - 3

REARRANGEMENT OF (+)-α-LONGIPINENE EPOXIDE, REVISED STRUCTURE OF ISOCENTDAROL

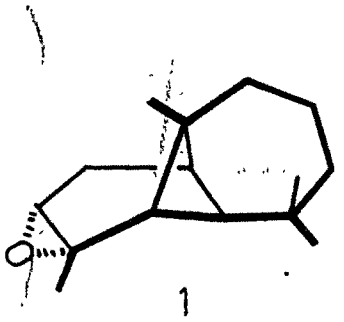
Abstract

This Chapter describes an extension of the work described in previous Chapter, acid catalyzed rearrangement of (+)-α-longipinene epoxide to several products. The major pathway involves a fragmentation reaction, either as such or after a Wagner Meerwein rearrangement. However, in view of the formation of the diol, identical with isocentdarol, it is proposed that the stereochemistry at carbon-7 of isocentdarol should be revised.

I N T R O D U C T I O N

In an extension of the work described in Chapter-2 of this Part, acid-catalysed rearrangement of (+)-α-longipinene epoxide (1) has been investigated. However, it would be relevant first to summarize the work known in the literature regarding acid-catalyzed rearrangement of α-pinene epoxide (3)[1-5] (Fig. 1).

α-Pinene epoxide (3) with BF_3-etherate in ether gives a complex mixture of p-cymene, aldehyde (5) and (6), pinocamphone (7), trans-carveol (8), the fluaro alcohol (9) and a minor compound which was not identified. A rationale was put forth by M.P. Hartsharn and co-workers[6] to explain the formation of the aldehydes (4) and (5) (Fig. 2). α-Pinene epoxide (3) when treated[3,7] with $MgBr_2$ gives exclusively the aldehyde (5). For maximum residual solvation of the developing C2-carbonium ion by departing O atom of the epoxide, the axial cleavage[8] mode of reaction would be followed to give carbonium ion (10) at full charge separation. Throughout this process of charge separation in the C2-O bond the C3-H bond would be maintained in the plane of the developing C2-carbonium ion, not a



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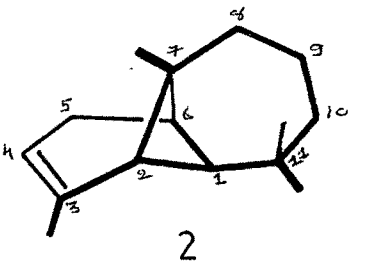

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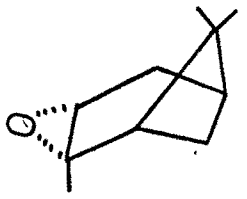

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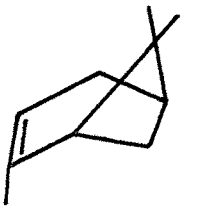

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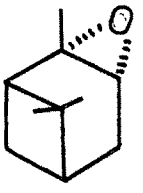
Fig. 1



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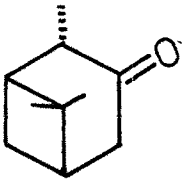

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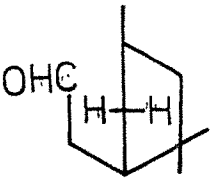

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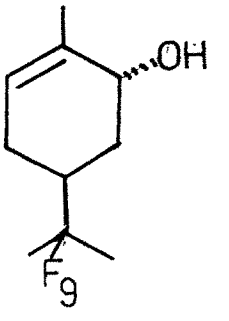

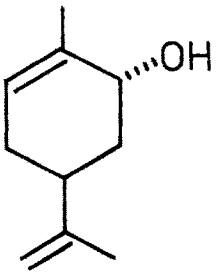

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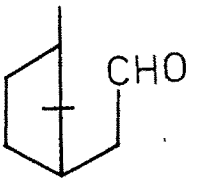

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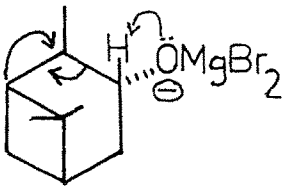

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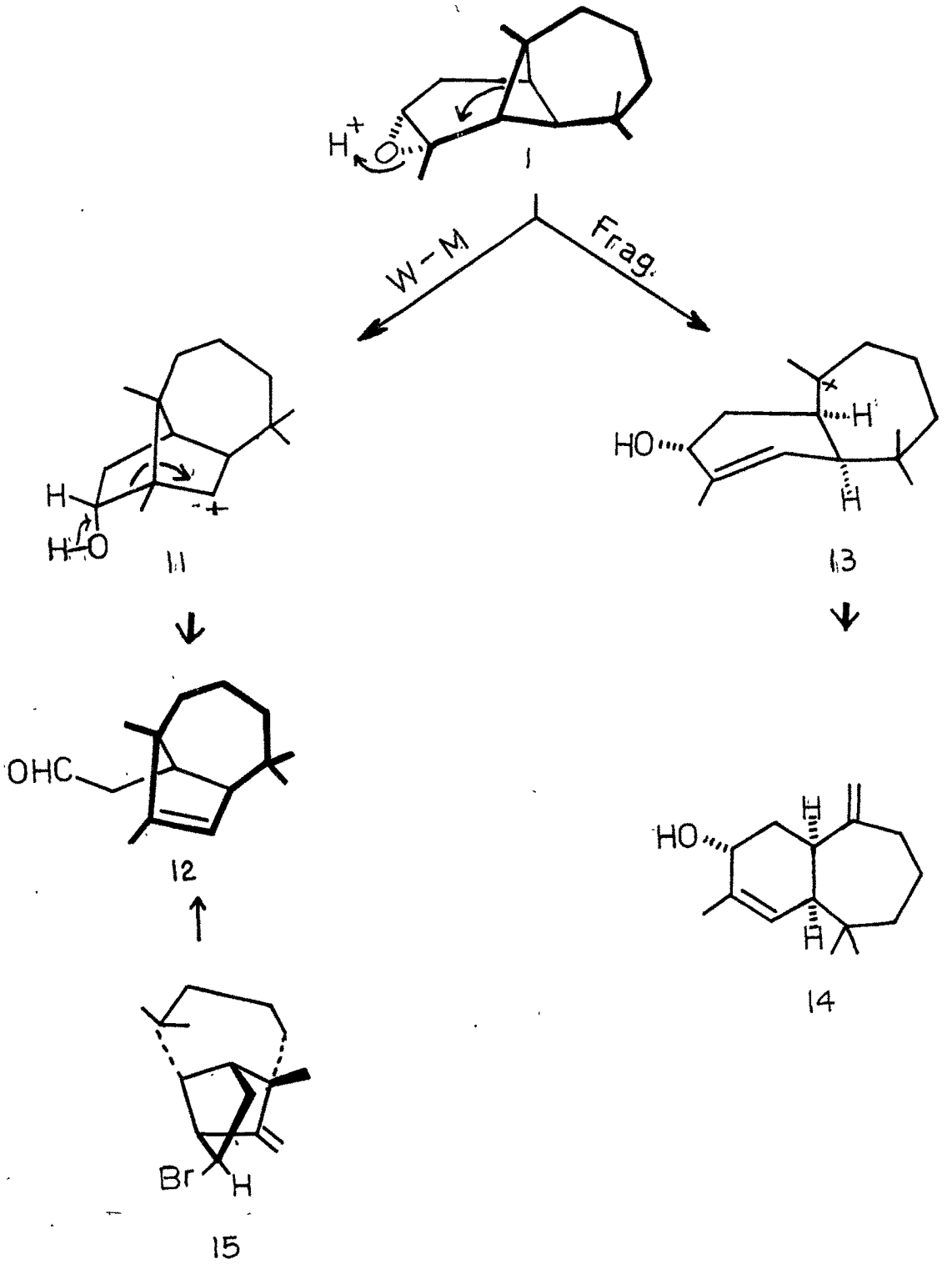
Fig. 2. Acid catalyzed rearrangement products of α-pinene epoxide.

favourable position for hydride migration by the 3β-H. The collapse of carbonium ion (10) to give aldehyde (5) is envisaged as an essentially concerted process.

PRESENT WORK

(±)-α-Longipinene epoxide (1) was prepared by adding peroxyacetic acid in chloroform under the similar conditions as described in Chapter 1 (Part 1). Peroxy acetic acid will attack preferentially on the "α" face of the double bond due to the steric hindrance to approach from the "β" face[9] to furnish stereochemistry depicted in (1).

(±)-α-Longipinene epoxide (1) when treated with perchloric acid in aq. dioxane gave rise to numerous products which were separated chromatographically. The major pathway involves a fragmentation reaction, either as such or after a Wagner-Meerwein rearrangement (Fig. 3). The result is the formation of an allylic alcohol (14), the aldehyde (12) and a diol (15, m.p. 179°). Allylic alcohol (14) and the aldehyde (12) constitutes some



1 11 12 13 14 15

Fig. 3. Acid catalyzed rearrangement of (+)-α-longipinene epoxide.

80-85% of the total product and were isolated in almost equal quantities (30-35%), along with the formation of three diols. The product composition is given in Fig. 4.

The aldehyde (12) is a product of Wagner-Meerwein rearrangement of (+)-α-longipinene epoxide (1) *via* the carbonium ion (11). The formation of only one aldehyde (12) can be explained when one considers the intermediate carbonium ion (11). The ion (11) being very prone to rearrangement *via* Crob fragmentation gives the aldehyde (12). Also the aldehyde (12) formation from 4-bromo-xy-longifolene (15) by fragmentation has been reported[10] (Fig. 3).

Allylic alcohol (14) results from fragmentation of (+)-α-longipinene epoxide (1) *via* the carbonium ion (13) (Fig. 3).

The attack of the loan pair of electrons from a water molecule at C-7 of 1 led to the opening of epoxide with simultaneous fragmentation of the molecule to give the diol (16), which is formed to the extent of

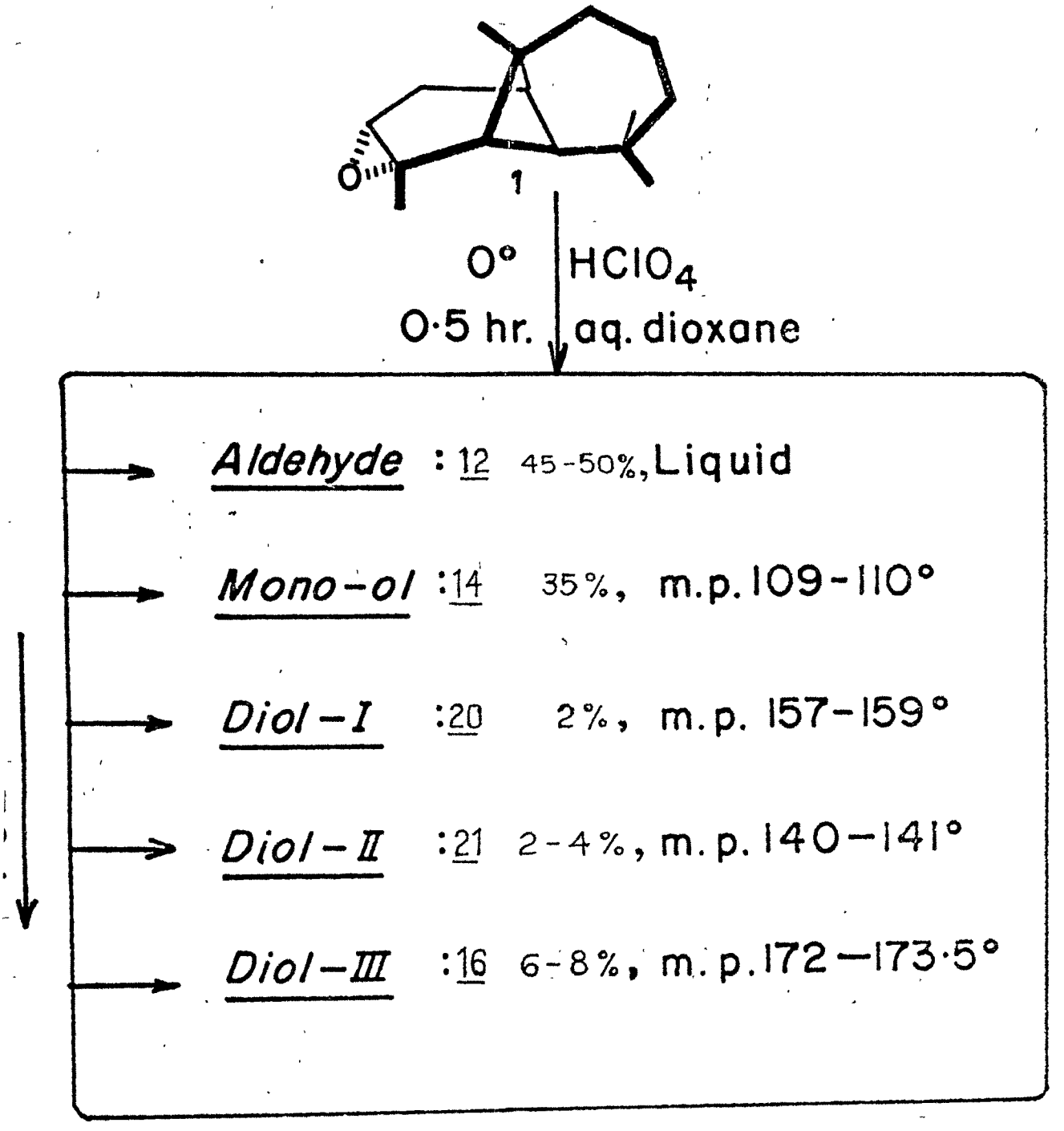


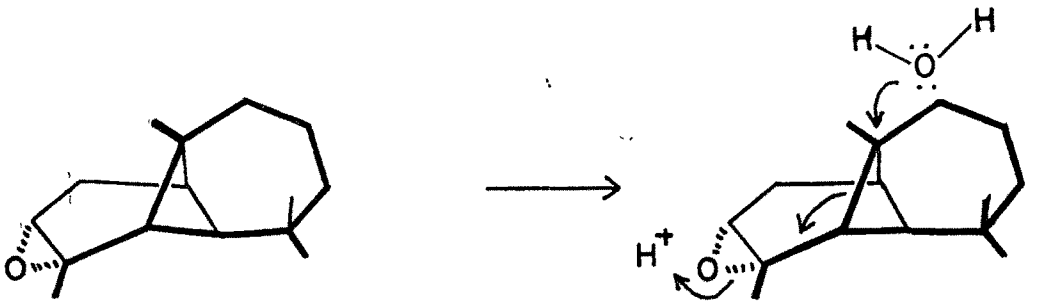
Fig. 4. Products obtained by acid catalyzed cleavage of (+)-α-longipinene epoxide.

6-8% and has been found identical with isocentdarol (17), isolated earlier by Kulshreshtha and Rastogi[11] from the essential oil of Cedrus deodara. The dehydration product of the diol (16) is the same allylic alcohol (14).

However, in view of the diol (16) formation from 1, it is proposed that the stereochemistry at C-7 of isocentdarol (17) should be revised (Fig. 5). Since (+)-α-longipinene (2) being a rigid molecule, the lone pair of electrons from a water molecule will attack C-7 from the less hindered α-face to give 16 giving an α-hydroxy at C-7. This is further supported as the structure of nimachalol (19) now revised to 18 in which configuration at C-7 is reversed on the basis of X-ray analysis[12, 13].

The identity of diol (16) to that of naturally occurring isocentdarol (17) was confirmed by TLC and spectral data (^{1}H-NMR, IR[13]) of their acetate[11], by comparison.

Besides these products, two other diols, diol-I (20, m.p. 153-54°C) and diol-II (21, m.p. 148-148.5°C) were isolated in minor amounts (2-3%). These compounds have been assigned structures (20) and (21). Diol-I (20) is the product obtained by the attack of the lone pair of



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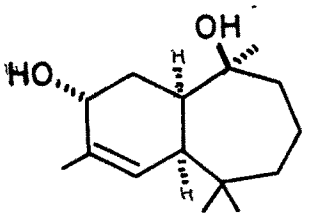

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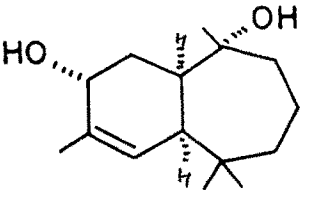
ISOCENTDAROL

(KULSHRESHTHA & RASTOGI 1976)



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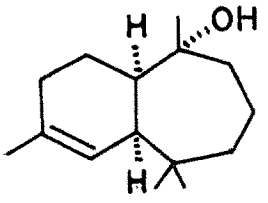

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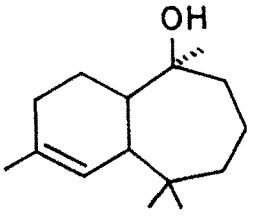

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Fig. 5. Revised structure of isocentderol and himachallol

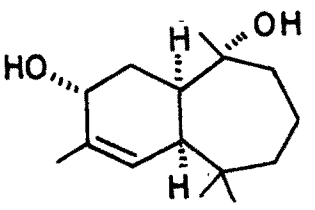
electrons from a water molecule to the carbonium ion (11) before it undergoes fragmentation to the aldehyde (12) (Fig. 6).

Diol-II (21) may evidently arise from the carbonium ion (11) by a trans-annular attack by the nucleophile on C-9 with simultaneous migration of the α-hydrogen (hydride ion) at C-9 to the electronc defficient centre as described for the formation of longibornane-9-ol (22)[14].

Thus both diol-I (20) and diol-II (21) arise from the same species (11).

Structure of Diol-I

Longibornane (25) type of carbon skeleton of the diol-I (20) was confirmed by converting it into a hydrocarbon (25) which in turn is compared with the hydrocarbon obtained from the known compound longibornon-9-ol[14]. The ketone (23) derived from this was reduced to hydrocarbon (25)



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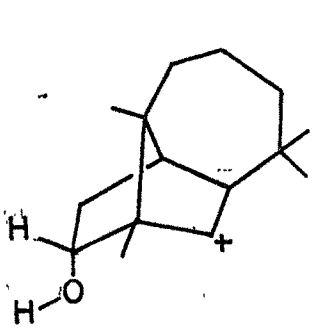

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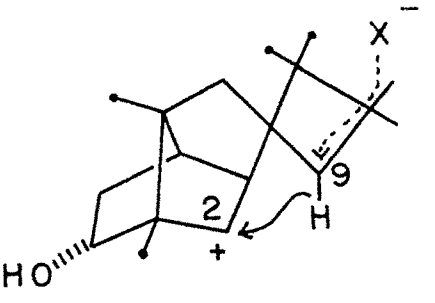

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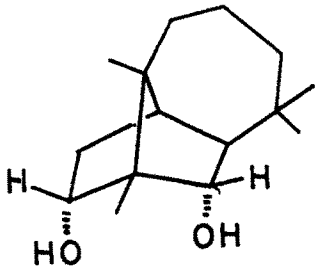

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Diol-I

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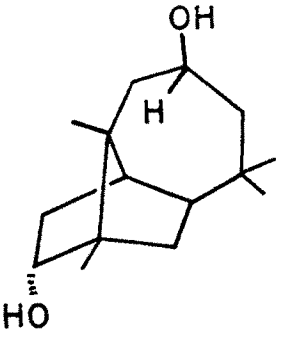

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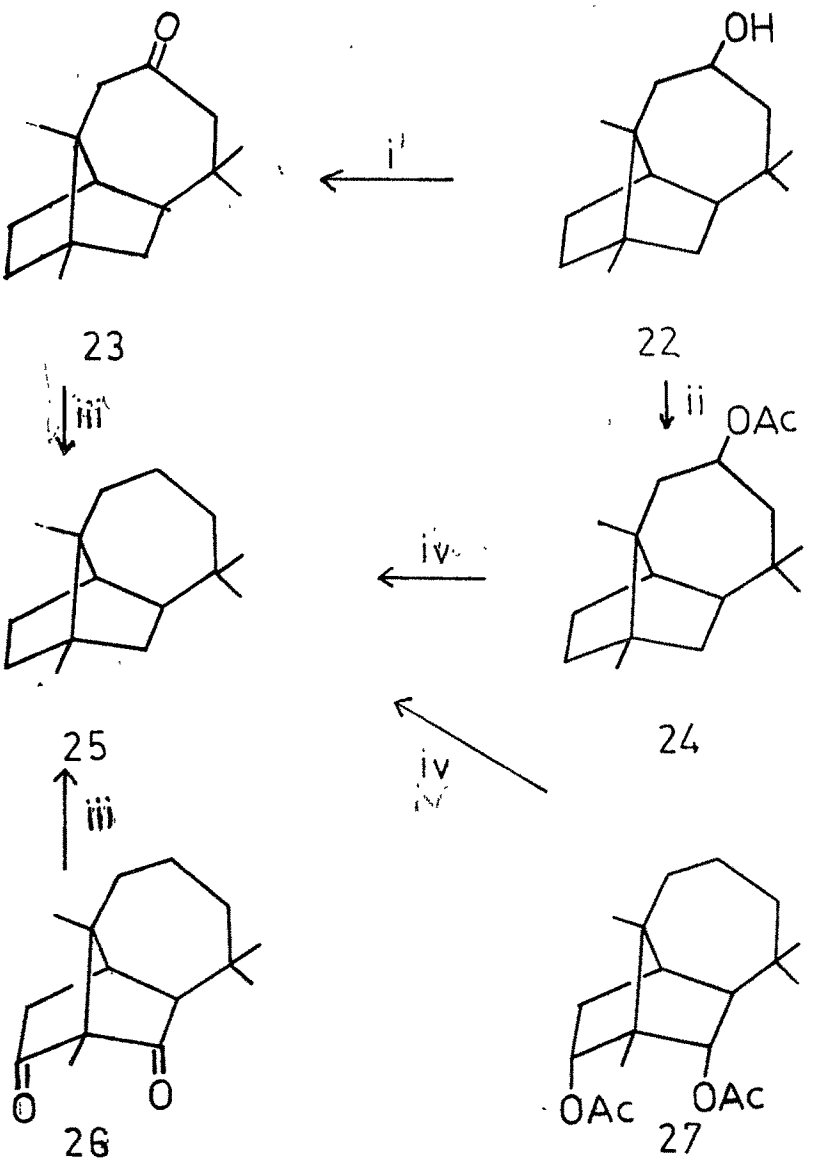
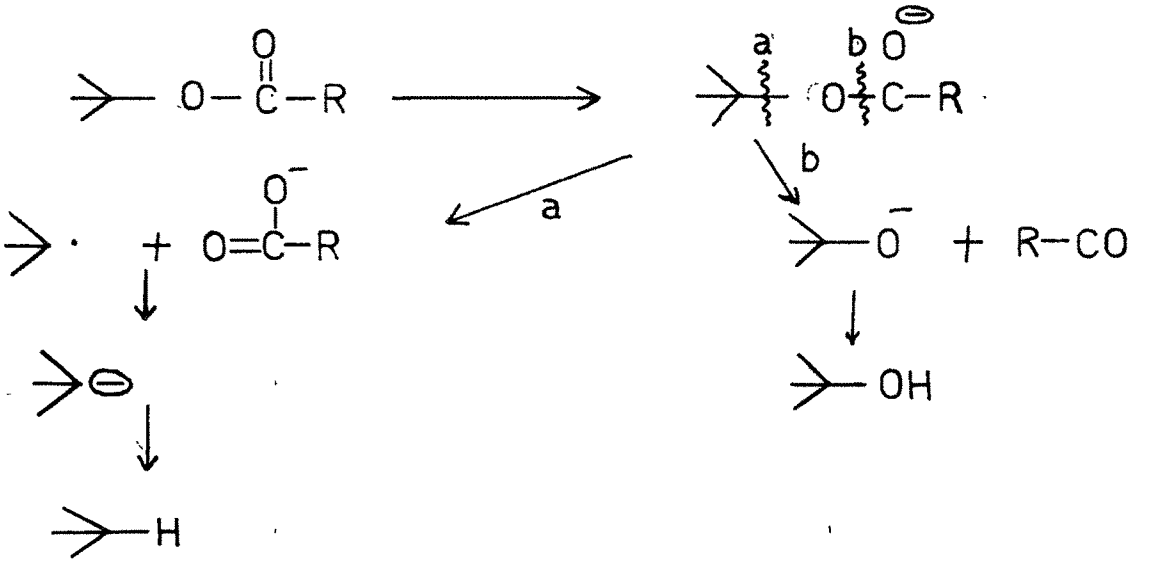
Diol-II

Fig. 6. Formation of diol-I and Diol-II

by Wolf-Kishner reduction[14,16]. Similarly, the diketone (26) of diol-I (20) obtained by oxidation with pyridinium chlorochromate[17], on Wolf-Kishner reduction gave a hydrocarbon (25) which had the same retention time on GLC to that of hydrocarbon obtained from longibornane-9-one (23) (Fig. 7).

Selective replacement of a hydroxyl group by hydrogen is a synthetic transformation of considerable importance.[18] It has been reported[19] that sterically hindered alcohols can be conveniently and efficiently converted into the corresponding alkanes by metal-amine reduction of the derived esters. The only side reaction is the generation of the starting alcohol. Mechanism (Fig. 7) involves radical fragmentation of the initially formed radical anion (28). Mode (a), and thence deoxygenation, evidently becomes the favoured process when cleavage of this C-O bond is attended by a sufficient release of unfavourable steric interactions. Otherwise mode (b) is preferred when the alcohol is regenerated (Fig. 7). Acetate (24) and diacetate of diol-I (27) were reduced by metal-amine reduction to the hydrocarbons which were found to be identical (retention time and R_f value).





Scheme 1. Reduction of derivatives of diol-I to saturated hydrocarbons
Reagents: i) Pyridinium chlorochromate
ii) acetic anhydride-pyr., iii) Wolf-Kishner reduction
iv) Li-ethylenediamine

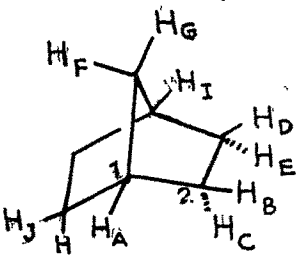
Scheme 2. Metalamine reduction mechanism.

Fig. 7

Diol-I (20) with acetic anhydride-pyridine at room temperature gave the diacetate. This indicates hydroxyl group at C-8 should also be endo. Because an exo-8-hydroxyl group in such type of molecule would be strongly hindered by the double bridge system on the top side of the molecule as well as by the 2- and 9-methyl groups.[22]

Extensive nmr studies on nor-bornyl derivatives (28, Fig. 8) have shown that, in general, the following coupling constant can be assigned J_{AC} 0, J_{CD} = 2.4-6.0 and J_{CE} = 5.9-8.4 Hz when the substituent at C-2 is exo and J_{AB} = 3.8-5.6, J_{BD} = 7.5-11.5 and J_{BE} = 2.2-5.2 Hz when the substituent is endo[20]. In some instances coupling (J_{BI}, J_{BJ}, and J_{CF} = 1-2.1 Hz) through four sigma bonds has been observed[21] (Fig. 8).

Comparing the spectral data of culmorin (29) and its derivatives (diketone and diacetate) with that of dio-I (20, and its diketone and diacetate) revealed similarities, but the only difference is the position of the hydroxyl group at C-10 in case of diol-I (20) instead at C-11 in culmerin (29, Fig. 8)[22]. The C-8 proton, C<u>H</u>OH of culmorin (29) comes at δ 3.86 as a doublet, J = 5 Hz and the same proton comes at δ 5.3



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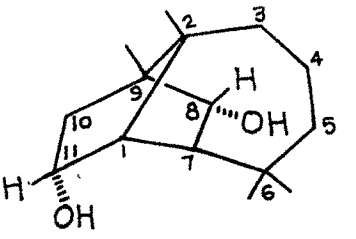

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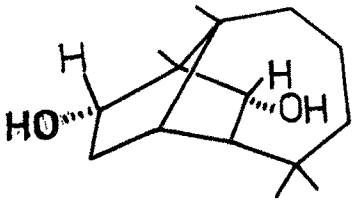

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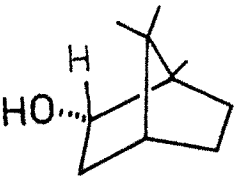

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Fig. 8. Structure of diol-I

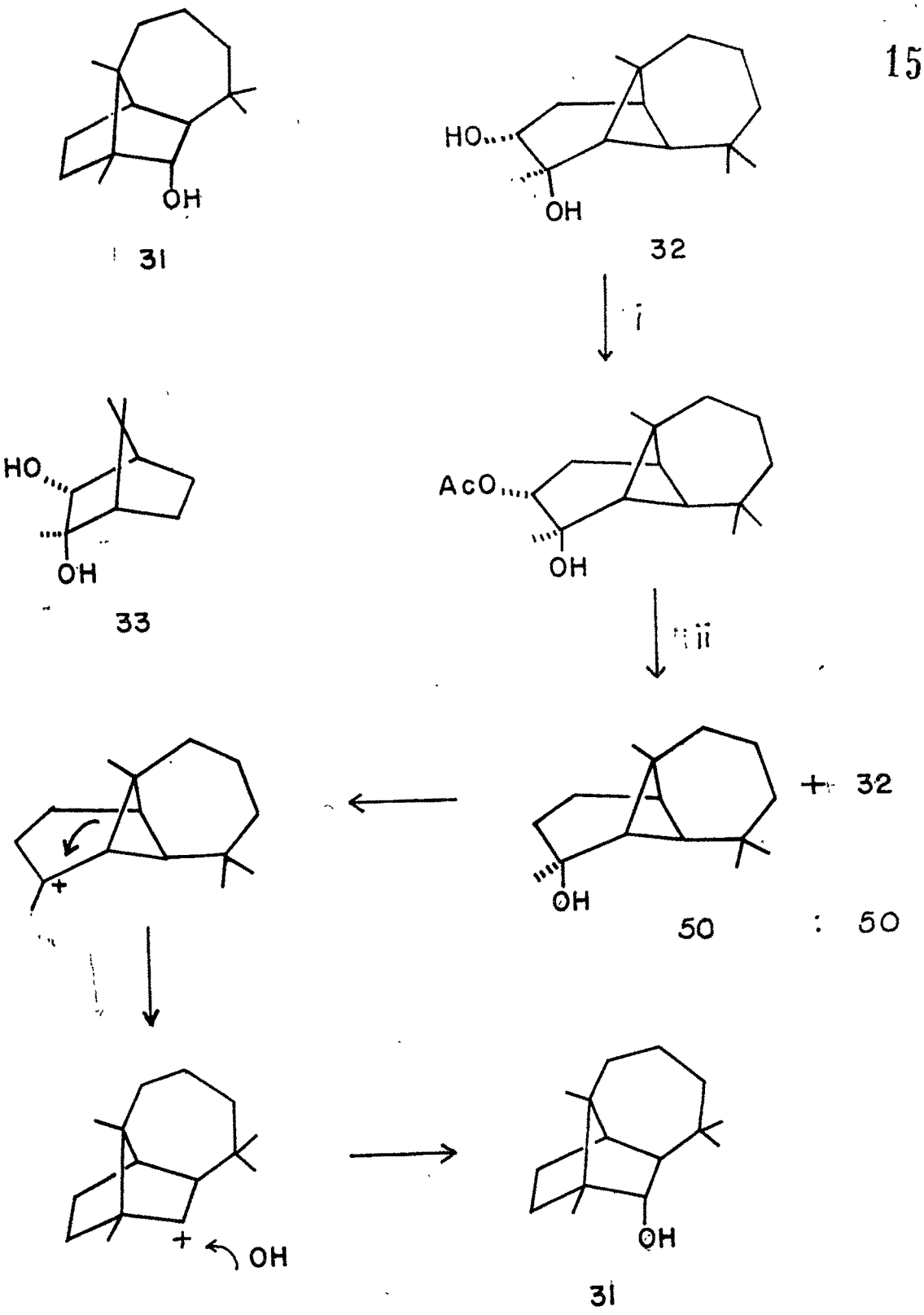
as a dd, J = 6 and 1 Hz in its acetate derivative[22]. Similarly, in diol-I (20), C-8 proton, CHOH comes at δ3.87 as a broad singlet (unresolved doublet) which resolves in its acetate derivative at δ5.34 as a dd, J = 5 and 1.5 Hz. The predicted J values for 8-H are 5 and 1.5 C/sec.[22] Also the C-11 proton of culmarin (29) comes at δ4.52 as a sextet with J = 9.5 and 4 Hz. The same proton in its acetate derivative comes at 5.05 as an octet with J = 9.5 and 4 Hz. This indicates the coupling of C-11 proton giving $J_{10,11}$; $J_{1,11}$, and $J_{10,11}$ which are 9.5 and 4 Hz. Similarly, in diol-I (20), C-10 proton couples only with C-11 protons giving partially resolved dt, J = 1.5 and 10 Hz at δ4.1. Similar pattern was observed for the CHOH proton of borneol (30)[23] The same proton of diol-I in its acetate derivative comes at δ4.97 as a dt resolved properly with J = 10 and 2 Hz, well accord with the predicted values. The values are in well accord with the given structure of diol-I (20) also.

Structure of Diol-II

Similarly, pyridinium chlorochromate oxidation[17] of diol-II (21) gave hydroxy ketone instead of diketone,

which on Wolf-Kishner reduction gave a comolex mixture of products. Similarly, acetylation at room temperature furnished a monoacetate instead of diacetate which on metal-amine reduction gave diol-II (21) as the major product along with traces of mono-ol which display a doublet, 1H, at δ4.16 with J = 5Hz. The structure suggested for mono-ol was 31. The formation of hydroxyketone and hydroxyacetate derivative indicates one of the hydroxyl group to be tertiary. So only possibility left is, it should be a product of trans-diaxial opening of (+)-α-longipinene epoxide (1) in which nucleophile will attack from the opposite side of the oxirane. So structure for diol-II (21) is now proposed as 32, which is derived from α-epoxide (1). The formation of mono-ol (31) can be explained now considering structure of diol-II as 32 as shown in Fig. 9. Comparing the spectral data of 32 with similar type of trans-diol (33)[24] of pinane series, they are matching except for the extended methylene bridge protons and a quaternary methyl group in case of diol-II (32).

The trans-diol (34) with the opposite stereochemistry of both the hydroxyl groups was also prepared by applying the conditions as in the case of (+)-α-pinene[24]. cis-Hydroxylation of (+)-α-longipinene (2) gave cis-diol (35) and a hydroxy ketone as the major products along with other cleaved products



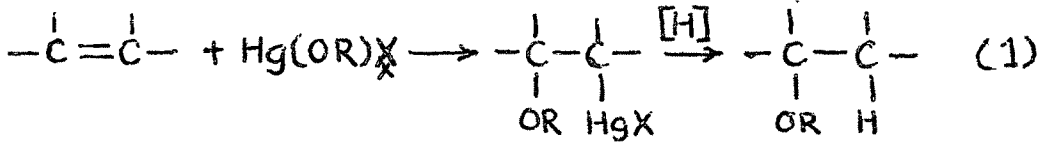
Reagents: i) Acetic anhydride-Pyr.
ii) Li-ethylene diamine

Fig. 9: Mono-ol formation from diol-II

(not further identified). The selective reduction of hydroxy-ketone (36) using sodium borohydride in dry methanol furnished major trans-diol (34) along with the formation of other diol having same R_f value to that of cis-diol (35). The so- obtained trans-diol (34) and trans-diol (32) obtained by trans-diaxial opening of (1), both of them show different IR and ^{1}H-NMR. This supports that the diol-II (32) is derived from α-epoxide (Fig. 10).

Finally it was proved by its (32) synthesis from marsupellol[25] by oxymercuration-demercuration, which is equally mild procedure as hydroboration-oxidation, without evident rearrangement, for achieving the anti-Markovnikov hydration of carbon-carbon double bond[26,27], (Fig. 10).

Stoichiometrically the oxymercuration-demercuration reaction consists in the addition of a mercuric salt or of the elements of a mixed mercuric salt, Hg(OR)X, to an olefinic double bond. Reduction of the carbon-mercury bond (demercuration) gives the corresponding alcohol, ether or ester.[28]



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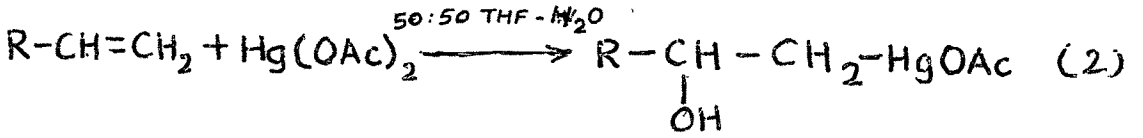

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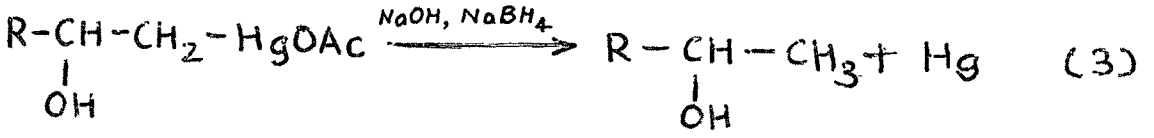

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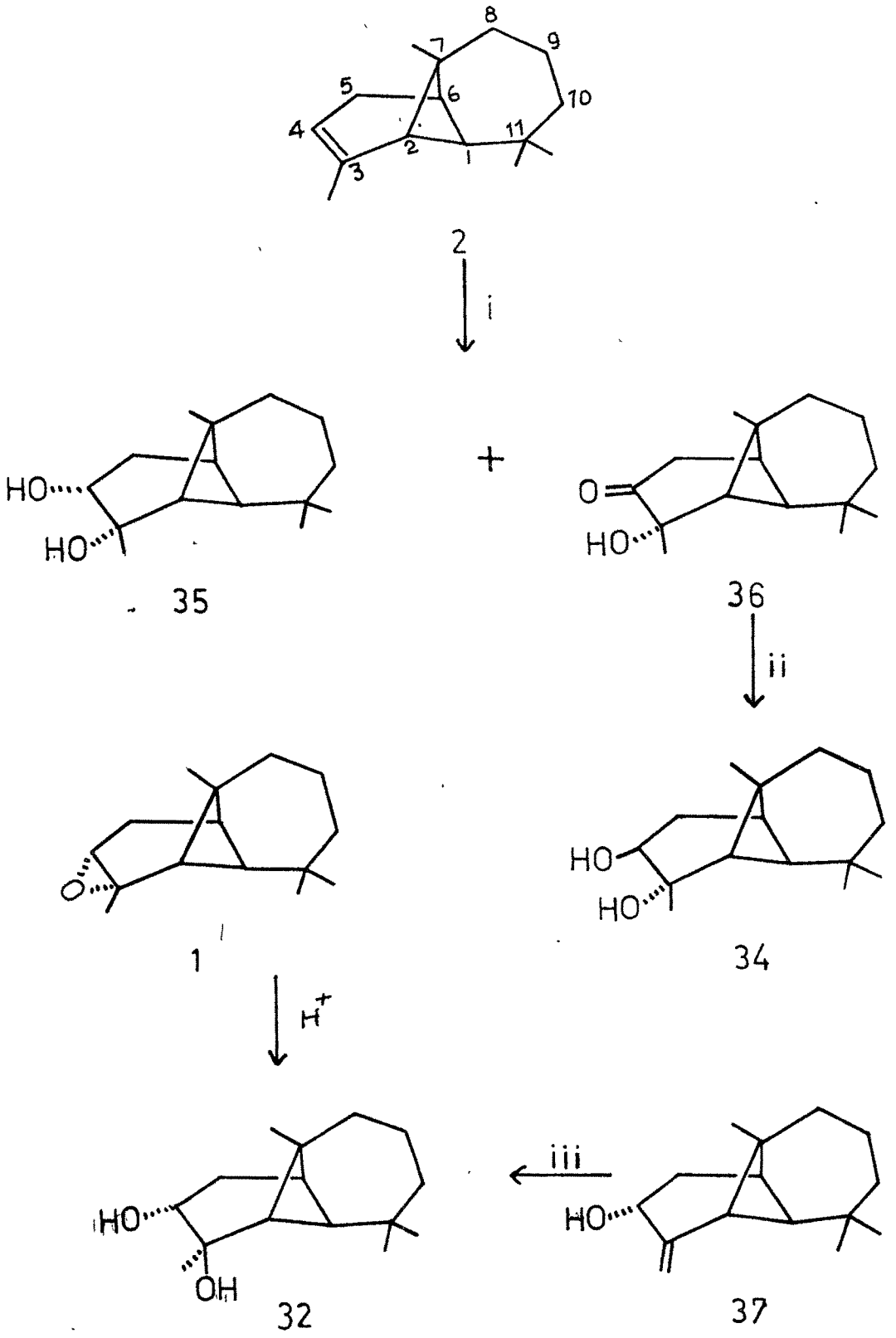


Reagents: i) Potassium permanganate
ii) $NaOH_4$-dry MeOH
iii) $Hg(OAc)_2$-$NaBH_4$

Fig. 10. Synthesis of isomeric diols of (+)-α-longipinene

Oxymercuration-demercuration of marsupellol (37) furnished a trans-diol along with some other unidentified products. The trans-diol obtained by OMDM show superimoosable IR as well as ^{1}H-NMR to that of diol-II (32), which was obtained from epoxide rearrangement.

E X P E R I M E N T A L

For general remarks see page 71

(+)-α-Longipinene epoxide (1)

It was essentially prepared as mentioned in Chapter 1 (Part-I). (+)-α-Longipinene (2, 52 g, 0.382 mole) and sodium bicarbonate (41.9 g, 0.4875 mole) were taken in Chloroform (156 ml). To the stirred solution, 30% peroxy-acetic acid (azeotropic, 100 ml, 0.4 mole) was then added slowly at low temperature (-5 to -3°C, 3 hr). The contents were stirred for an additional hour at the same temperature. The crude product (56.9 g, 97.9% yield) obtained after usual work-up, was precisely fractionated on a spinning-band column (45 theoritical plates) to furnish pure (+)-α-longi-pinene epoxide (1, 44 g, 75.74% yield), which had the following characteristics.

n_D^{25} 1.4936

$[\alpha]_D$ + 69.6 ($CHCl_3$, c 4.6%).

R_f 00.67 (solvent: 25% Ethyl acetate in toluene)

IR: (liq.) (Fig. 11): 2960, 2868, 1715, 1465, 1450, 1430, 1376, 1350, 1208, 913, 828 cm^{-1}.

^{1}H-NMR (Fig. 12): Me-C (9H, s, 0.94, 0.86, 0.90 ppm)

Me-C-C (3H, s, 1.31 ppm).

-C-C-H (1H, s, 2.91 ppm).

Mass : m/z 220 (M^+, 8.01%), 204 (24.7%), 161 (23.7%), 105 (100%).

Perchloric acid opening of (+)-α-longipinene epoxide (1)

To the stirred solution of (+)-α-longipinene epoxide (1, 7.0 g, 0.0343 mole) in dioxane-water (21-5 ml) was added perchloric acid (0.20 ml, 60%) dropwise maintaining a reaction temperature of 0-2°C (1.5 hr), when TLC (Fig. 13, solvent: 25% EtOAc in toluene) indicated essentially complete conversion. The product was taken up in ether (75 ml) and washed with water (10 ml x 3). Aqueous layer was back extracted with ether (15 ml x 2). The combined ether layers were washed with water (10 ml x 2), 10% sodium bicarbonate (10 ml x 1, alkaline), water (10 ml x 1), brine (10 ml x 2, neutral), dried and evaporated to furnish the crude product (7.04 g). The crude product after acetylation (pyridine/Ac_2O, room-temp., 16 hr) was analyzed on GLC (Fig. 14, 10% SE-30, 6', 200°, H_2 as carrier gas) revealed the presence of atleast six components. The above product (7.0 g) was chromatographed over Al_2O_3/II (column dimentions: 65 x 2.2 cms) with TLC monitoring of fractions obtained with light petroleum and light petroleum containing increasing quantities of ethyl acetate and finally with

methanol. Different fractions were further processed as follows:

Hydrocarbons (R_f. 0.7). The material (0.3583 g) eluted with light petroleum (100 ml x 6) was essentially a mixture of hydrocarbons consisting of longifolene in major amounts.

Aldehyde (12, R_f 0.675). The product (2.1 g) eluted with 2-3% ethyl acetate in light pet. (100 ml x 8) was purified by distillation (b.p. 130-2°/2 mm) to give pure aldehyde having following physical and spectral characteristics

b.p. 130-2°/2 mm

R_f. 0.675 (solv. 25% EtOAc in toluene)

n_D^{25} 1.4985

$[\alpha]_D$ + 15.54 ($CHCl_3$, c 3.8%).

IR (liq.) (Fig. 15): 3040, 2961, 2871, 1725, 1462, 1362, 832 cm^{-1}.

^{1}H-NMR (Fig. 16): Me-C 3H, s, 0.877 and 6H, s, 0.944 ppm).
Me-C=CH (3H, s, 1.54 ppm)
Me-C=CH (1H, s, 5.4 pom)
CHO (1H, dd, 9.655 ppm) J = 2 x 3 Hz).

Mass : m/z 220(M^+, 48%), 205 (17.3%), 105 (100%).

Mono-ol (14, R_f 0.525). The material (2.1 g) eluted with 5% ethyl acetate in light pet. (100 ml x 8) was purified by crystalization in acetonitrile. Pure sample showed the following characteristics:

m.p. 109°C

R_f. 0.525 (solv. 25% EtOAc in toluene)

$[\alpha]_D$ -117.65 ($CHCl_3$, c 1.3%).

IR (KBr) (Fig. 17): 3260, 3075, 2930, 2825, 1630, 1452, 1065, 1021, 889 cm^{-1}.

^{1}H-NMR (Fig. 18): Me-C (3H, singlets at 0.95 and 1.00 ppm).
C=CH_2 (2H, s, 4.76 opm)
Me-C=CH (3H, bs, 1.76 opm)
Me-C=CH (1H, bs, 5.48 opm)
CHOH (1H, bs, 3.94 ppm).

Mass : m/z 220 (M^+, 43%), 205 (34%), 149 (37%), 109 (100%).

(Found C, 81.82; H, 10.91. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%).

Mixture of diols. The material (0.80 g) eluted with 6-50%

ethyl acetate in light pet. (100 ml x 15) was essentially a mixture of three components. It was rechromatographed over SiO_2 gel/IIA (2.5 x 34 cms) as before and the fractions eluted with

i) 10% EtOAc-light pet. (35 ml x 10) gave pure diol-I (20, 0.08 g)

ii) 12% EtOAc-light pet. (35 ml x 16) gave pure diol-II (21, 0.08g)

and iii) EtOAc (35 ml x 4) gave pure diol-III (16, 0.500 g).

They were further purified by crystallization in acetonitrile. Pure samples have the following characteristics:

DIOL-I (20).

m.p. 153-154°C

R_f . 0.225 (solv. 25% EtOAc in toluene)

$[\alpha]_D$ - (EtOH, c 2.16%).

IR (KBr) (Fig. 19): 3240, 2950, 1448, 1362, 1280, 1117, 1049 cm^{-1}

^1H-NMR (Fig. 20): Me-C (3H singlets at 0.8, 0.98 and 1.02 ppm)

Me-C-CHOH (3H, s, 1.02 ppm)

CHOH (1H, bs, 3.37 ppm)

CHOH (1H, dd not resolved properly, 4.1 ppm)

Mass : m/z (220 (M^+-H_2O, 68%), 191 (31%), 133 (50%), 107 (100%).

(Found: C, 75.54; H, 11.26. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.98%).

Diol-II (32)

m.p. 148-148.5°C

R_f 0.1437 (solv. 25% EtOAc in toluene).

$[\alpha]_D$ - 33.33 ($CHCl_3$, c 1.8%).

IR (KBr) (Fig. 21): 3320, 3380, 2918, 2842, 1453, 1361, 1205, 1100, 1022, cm^{-1}

^1H-NMR ($CDCl_3$) (Fig. 22): Me-C (6H, s, 0.901 and 3H, s, 1.03 ppm)

Me-C-OH (3H, s, 1.33)

CHOH (1H, dd, 4.28 ppm, J = 4 & 10 Hz).

Mass: m/z 220 (M^+-H_2O, 16%), 177 (40%), 136 (30%), 135 (33%), 123 (54%), 109 (83%), 95 (100%).

(Found C, 75.51; H, 11.05. $C_{15}H_{26}O_2$ requires C, 75.58; H, 10.98%).

Diol-III (16)

m.p. 174-180°C (Lit.[11] m.p. 165°C)

R_f. 0.05 (solv. 15% EtOAc in toluene)

$[\alpha]_D$ + 94 (EtOH, c 1.7%) (Lit.[11] $[\alpha]_D$ + 5 (EtOH, c, 1%)

IR (KBr) (Fig. 23): 3410, 2960, 1630, 1282, 1044
1020, 908 cm^{-1}.

^1H-NMR (DMSO-d_6)(Fig. 24): Me-C (3H, singlets at
0.82 and 1.01 opm)
Me-C-OH (3H, s, 1.28 pom).
Me-C=CH (3H, d, 1.67, J = 1.5 Hz)
Me-C=CH (1H, dd, 5.75, J = 1.5 & 5 Hz)
CHOH (1H, bs, 4.05)

Mass : m/z 220 ($M^+ - H_2O$, 11%), 133 (86%),
135 (77%), 109 (100%).

(Found C, 75.45; H, 11.10. $C_{15}H_{26}O_2$ requires C, 75.58;
H, 10.98%).

General procedure for pyridinium chlorochromate oxidation of diols

To the stirred solution of diol (0.0001 mole) in

dry CH_2Cl_2 (3 ml) was added pyridinium chlorochromate (0.0093 mole). The contents were stirred at room temp. (30 ± 1°C, 5 hr) when TLC (solv. 15% EtOAc in toluene) indicated essentially complete oxidation. The reaction mixture was passed through a column (SiO_2 gel, 3 x 1.7 cms) and eluted with dry ether (50 ml). Evaporation of solvent furnished the crude product which was further purified by preparative TLC (solv. 15% EtOAc in toluene). Pure samples had the following characteristics.

Diol-I-diketone (26)

m.p. 105.5-106.5°C (crystallized in CH_3CN).

$[\alpha]_D$ -240 ($CHCl_3$, c, 0.25%).

IR(KBr) : 2920, 1740, 1708, 1446, 999 and 941 cm^{-1}

^{1}H-NMR ($CDCl_3$) : Me-C (3H, singlets at 0.922, 0.944, 1.666, 1.177 ppm)

Mass : m/z 234 (M^+, 100%), 121 (96%), 123(90%), 110(75%).

(Found C, 76.23; H, 9.41. $C_{15}H_{22}O_2$ requires C, 76.92; H, 9.4%).

Diol-II-hydroxy ketone

m.p. 139.5-141°C

IR (KBr) : 3450, 2916, 2855, 1709, 1445, 1106, 1083 and 915 cm^{-1}.

^{1}H-NMR : Me-C (3H singlets at 0.92, 0.944 and 0.944 ppm)

Me-C-OH (3H, s, 1.22 ppm).

Mass : m/z 236 (M^+, 12%), 208 (82%), 123 (82%), 109 (85%), 81 (100%).

(Found C, 76 ; H, 9.9 . $C_{15}H_{24}O_2$ requires C, 76.27; H, 10.16%).

General procedure for acetylation of diols

To the solution of diol (0.001 mole) in dry pyridine (1 ml) was added acetic anhydride (0.8-1 ml) and the reaction mixture was kept at room temperature for 16 hrs. Acetic anhydride and pyridine were removed on water bath (60-70°C) under reduced pressure (35 mm). The residue was taken up in chloroform (10 ml). The organic layer was washed with water (2 ml x 3), N/2 hydrochloric acid (2 ml x 2), water (2 ml x 1), 10% sodium bicarbonate (2 ml x 1) and

finally with water (2 ml x 1) and brine (2 ml x 2), dried and solvent evaporated to furnish the crude product of high purity. Pure samples had the following characteristics:

Diol-I-diacetate (27)

Colour - colourless viscous liq.

$[\alpha]_D$ - 45.68 ($CHCl_3$, c 3.94%).

IR (liq.) : 2940, 1708, 1355, 1250, 1025 and 910 cm^{-1}

^1H-NMR : Me-C (3H singlets at 0.778, 0.878, 0.945 and 0.955 ppm .

Me-CO (6H, s, 1.97 ppm)

CHOAc (1H, dt, 4.97 ppm, J = 10 and 2.5 Hz)

CHOAc (1H, dd, 5.34 ppm, J = 5 and 1.5 Hz)

Mass : m/z 322 (M^+, 4.4%), 262 (99%), 220 (99%), 242 (99%), 176 (82%), 161 (99%), 91 (100%).

(Found C, 70.41; H, 9.24. $C_{19}H_{30}O_4$ requires C, 70.8; H, 9.3%).

Diol-II-hydroxy acetate (32-OAC)

Colour : colourless viscous liquid
solid at low temperature

$[\alpha]_D$ + 65.59 ($CHCl_3$, c, 0.93%).

IR (KBr) : 3467, 2910, 2846, 1710, 1362, 1228, 1010, 950 and 915 cm^{-1}.

^1H-NMR : Me-C (3H, singlets at 0.89, 0.9, 1.4 and 1.8 ppm)
CHOAc (1H, dd, 5.45 ppm, J = 10 & 4 Hz)
Me-CO (3H, s, 2.06 ppm).

Mass : m/z 280 (M^+, 4.4%), 220 (100%), 177 (7%), 121 (75%), 109 (80%).

(Found C, 72.53; H, 10.00. $C_{17}H_{28}O_3$ requires C, 72.85; H, 10.00%).

General procedure for Wolf-Kishner reduction of ketone

The ketone (0.001 mole) dissolved in dry diethylene glyclol (0.9 ml) was added to diethylene glycol (0.9 ml) in which sodium (0.012 g) and anhy. hydrazine (0.018 g) had

been earlier dissolved. The reaction mixture was first heated at 170° (10 hr) and then at 220° (24 hr). The product was cooled, diluted with water (5 ml) and acidified with aq. HCl to congo red. This was extracted with ether (10 mlx 4), the extract washed with brine and dried. Solvent was flushed off and residue taken up in light petroleum and filtered through Al_2O_3/I (1 g), the column being washed with petroleum. The solvent was removed and the residue distilled (Bath 125-135°/ 4 mm) to give colourless distillate which was analyzed on GLC (Fig. 25).

The hydrocarbons obtained by Wolf-Kishner reduction of diol-I-diketone was having same RRT to that of hydrocarbons obtained from longibornan-9-one (23). (GLC, Fig. 25).

General procedure for deacetylation of acetate

The acetate (0.4 mmol) was refluxed with lithium (28 mmol) and ethylenediamine (20 ml) under N_2 atmosphere for 10 hr. The reaction mixture was added to chilled water and extracted with ethyl acetate (15 ml x 3) after saturating aq. phase with sodium chloride. The usual work-up gave the crude product, chromatographed over SiO_2CG/II-A (18" x 0.9 cms),

light petroleum eluted hydrocarbon (40%) and finally ethyl acetate eluted regerated alcohol (50-60%).

cis-hydroxylation of (+)-α-longipinene (2)

To a cold (ice bath) solution (0-5°C) of 4.08 g (0.02 mole) of (+)-α-longipinene (2) in 45 g 90% aqueous acetone was added with stirring 6.32 g (0.04 mole) of pulverized potassium permanganate over a period of 8 hr. The reaction mixture was stirred at 0-5°C for an additional 24 hr, filtered, evaporated to 12 ml, and extracted with ethyl acetate (20 ml x 3). The combined organic layers were washed with brine (10 ml x 2), dried and evaporated to give 4.2056 g of the crude product. The part of it (3.8 g) was chromotographed over SiO_2 gel (65 g, 2.7 x 51 cms) where eluent 4-5% ethyl acetate in light petroleum (100 ml x 4) eluted 0.58 g of hydroxy ketone (36) and - the eluent 9-14% ethylacetate in light pet. (100 ml x 12) eluted 0.55 g of tne cis-diol (35)

Pure samples had the following characteristics:

Hydroxy-ketone (36)

m.p. 157-159°C

$[\alpha]_D$ -11.42 ($CHCl_3$, c 3.59%).

IR (KBr) : 3460, 3010, 2939, 2862, 1710, 1375, 1250, 1065, 916 and 890 cm^{-1}

^1H-NMR : Me-C (3H, s, 0.844 ppm and 6H, s, 0.933 ppm). Me-COH (3H, s, 1.38 ppm).

Mass : m/z 236 (M^+, 7.3%), 208 (41%), 207 (41%), 109 (84%), 81 (58%), 43 (100%).

(Found C, 76.49; H, 10.43. $C_{15}H_{24}O_2$ requires C, 76.27; H, 10.16%).

Cis-diol (35)

m.p. : 134.5-135.25°C

$[\alpha]_D$: + 38.194 ($CHCl_3$, c, 2.98%).

IR(KBr)(Fig. 26): 3260, 2924, 1451, 1375, 1058, 1040, 956, 872 cm^{-1}

^1H-NMR ($CDCl_3$) (Fig. 27): Me-C (3H, s, 0.8 and 6H, s, 0.87 ppm)

Me-C-OH (3H, s, 1.3 ppm).

CHOH (1H, dd, 3.96 ppm, J = 4 & 9 Hz)

Mass : m/z 238 (M^+, 5%), 220 (15%), 123 (25%) 95 (41%), 85 (40%), 41 (100%).

(Found C, 75.41; H, 10.99. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.00%)

Reduction of hydroxy ketone (36)

A cold (0°C) solution of 00.38 g (0.0016 mole) of ketol (36) and 0.15 g (0.004 mole) of sodium borohydride in 8 ml of dry methanol was stirred under nitrogen at 0°(2 hr). The methanol was removed under reduced oressure and the residue oortioned between water and ethyl acetate. The usual work-uo and evaooration of solvent gave 0.38 g (99%) of tne crude oroduct which was chromatogranhed over SiO_2-gel (13 g, 1.7 x 14 cms) where the eluent 10-20% ethyl acetate in light pet. (100 ml x 4) gave 0.171 g (45%) of trans-diol (34) which showed following physical and soectral characteristics:

trans-Diol (34)

m.o. 109.5-110.5°C

IR (KBr) (Fig. 28): 3362, 2921, 2963, 1376, 1078, 1042, 1019, 1001 and 886 cm^{-1}

^{1}H-NMR (Fig. 29) : Me-C (9H, s, 0.9 ppm).
Me-C-OH (3H, s, 1.31 ppm)
CHOH (1H, dd, 4.08 ppm, J = 5 & 11 Hz)

(Found C, 75.67; H, 11.17. $C_{15}H_{26}O_2$ requires C, 75.58, H,11.00%)

Oxymercuration-demercuration of marsupellol (37)

In a 50 ml flask, fitted with a magnetic stirrer, was placed 0.638 g (0.02 mole) of mercuric acetate. To this was added 3.0 ml of water (in which the salt dissolves), followed by 3.0 ml of THF. Then 0.44 g (0.02 mole) of marsupellol (37) was added. The reaction mixture was stirred for 6 hr to complete the oxymeruration stage. Then 3.0 ml of 3.0 M sodium hydroxide was added, followed by 3.0 ml of a solution of 0.50 M sodium borohydride in 3.0 M sodium hydroxide. The mercury was allowed to settle. Sodium chloride was added to saturate the water layer. The upper layer of THF was separated, dried and evaporated to furnish 0.44 g (95-6%) of the crude product which was chromatographed over SiO_2-gel (13 g, 1.2 x 20 cms) where the eluent 6-15% ethyl acetate in light pet. (50 ml x 6) gave 0.123 g (28%) of pure t-diol (32), having superimposable IR and ^{1}H-NMR to that of diol-II (32) obtained by acid catalyzed cleavage of (+)-α-longipinene epoxide (1).

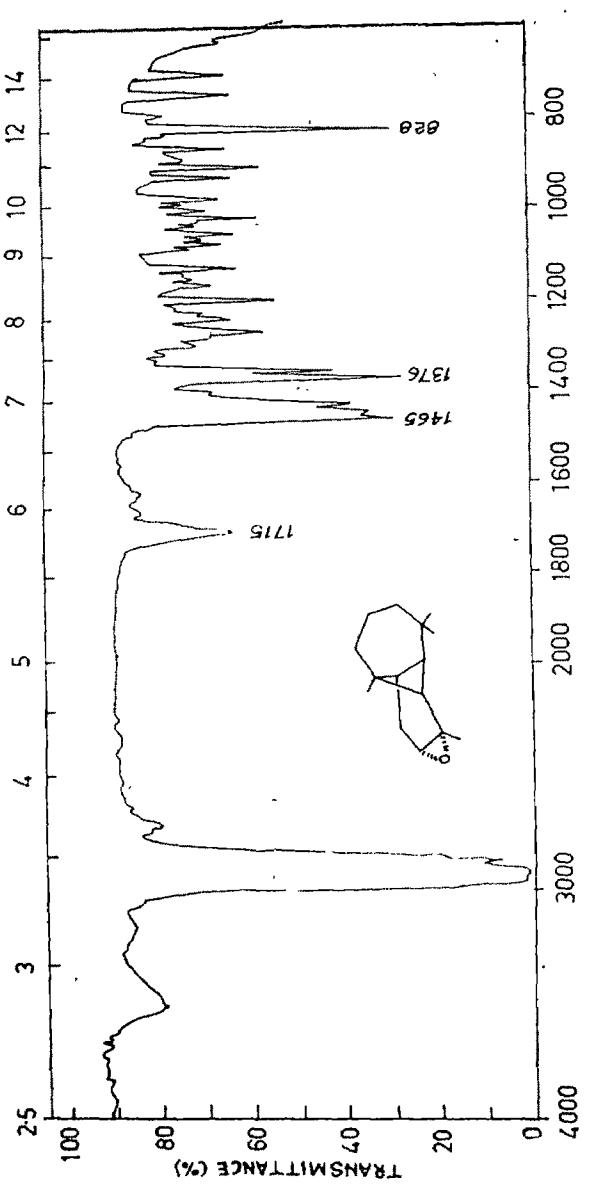


FIG.11 : IR SPECTRUM OF (+)-α-LONGIPINENE EPOXIDE(1)

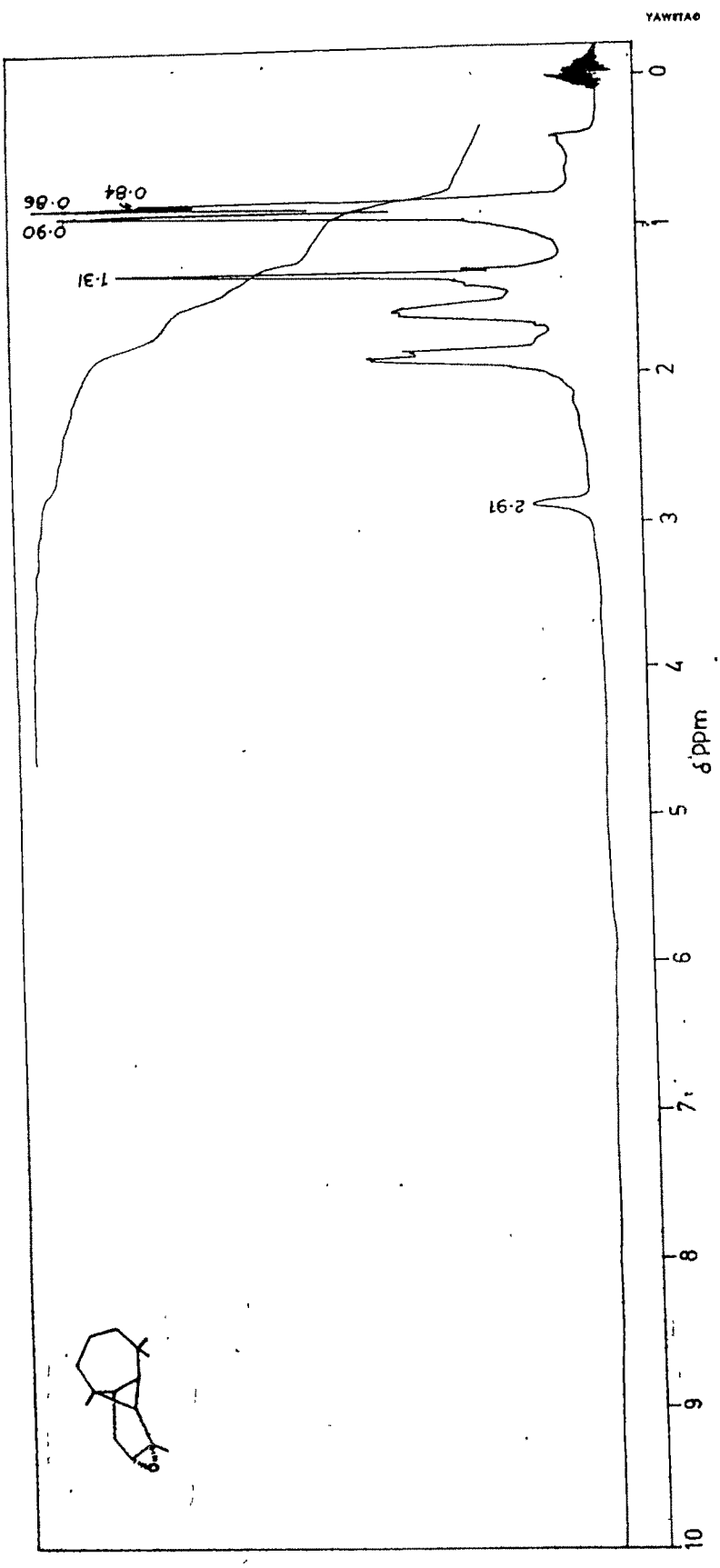
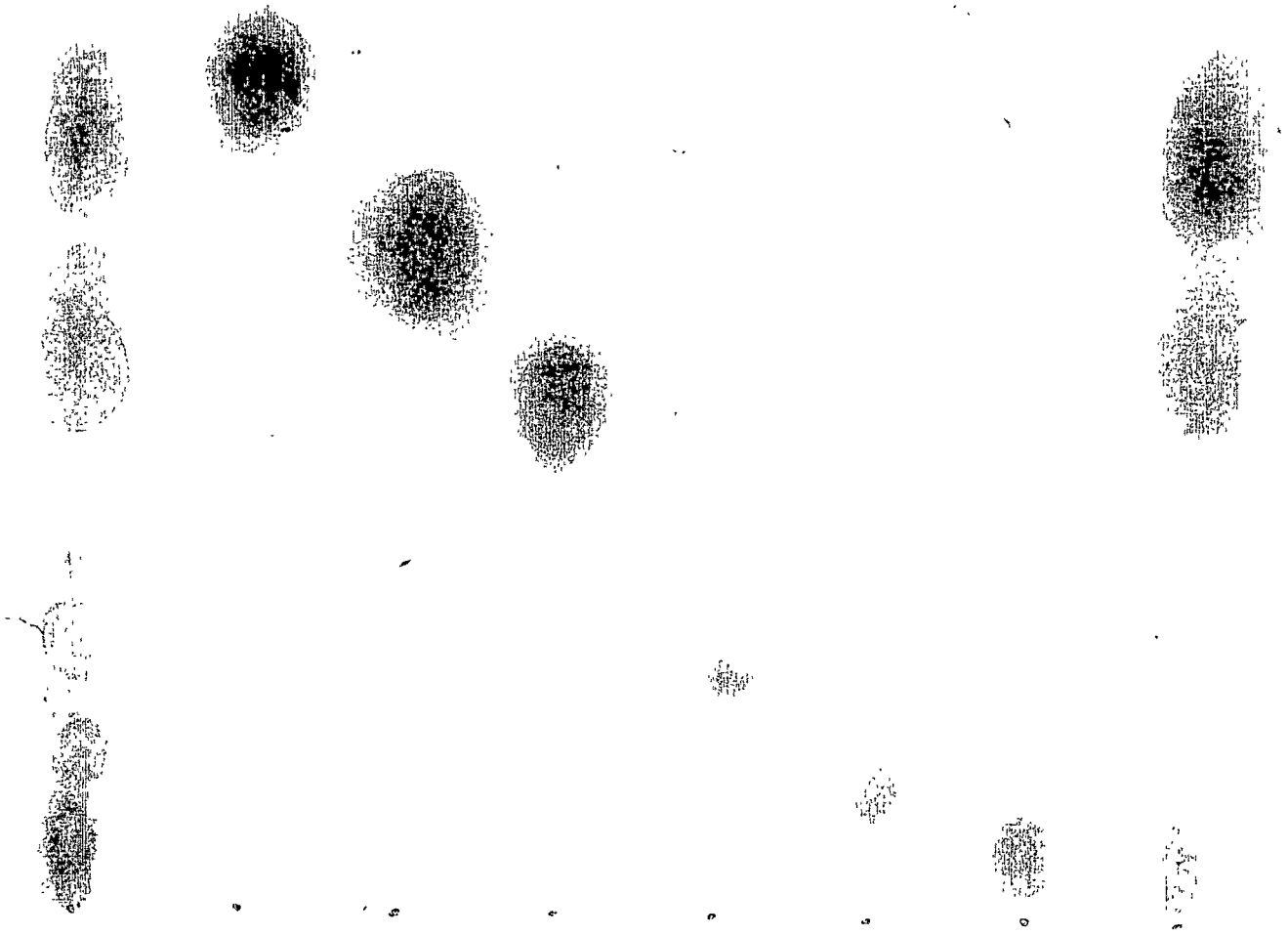


FIG.12 : ^1H-NMR SPECTRUM OF (+)-α-LONGIPINENE EPOXIDE(1)



Solvent system : 25% ethyl acetate toluene
Spots (colour): 1. crude products, 2. Hydrocarbons (pink)
3) Aldehyde (Blue),4) Monol (Blue)
5) Diol-I (pink), 6. Diol-II (pink)
7) Diol (16) (Blue), 8. Crude products

Fig. 13. TLC OF CRUDE AND ISOLATED PRODUCTS

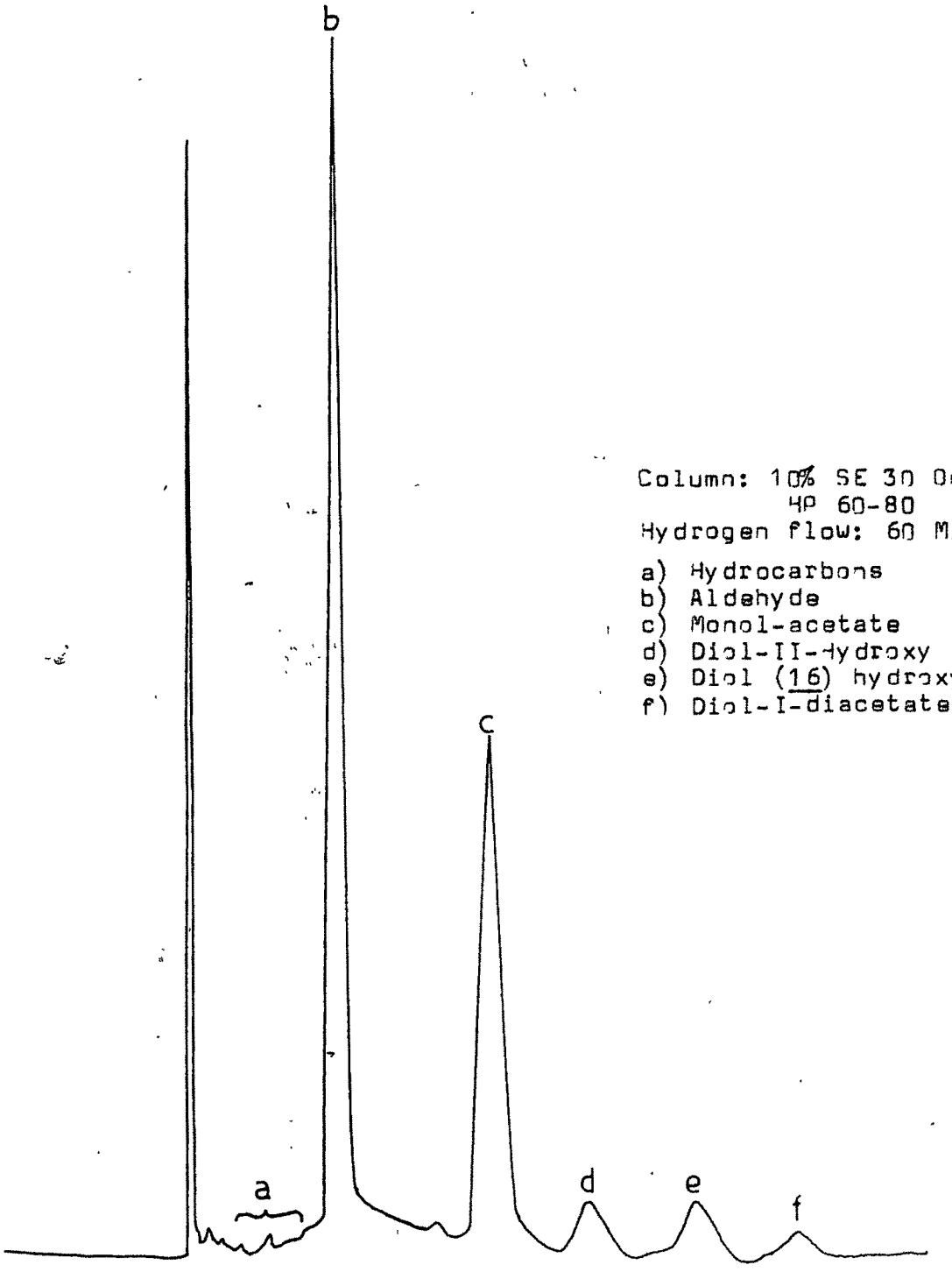


Fig. 14: GLC OF CRUDE PRODUCT OF EPOXIDE OPENING AFTER ACETYLATION

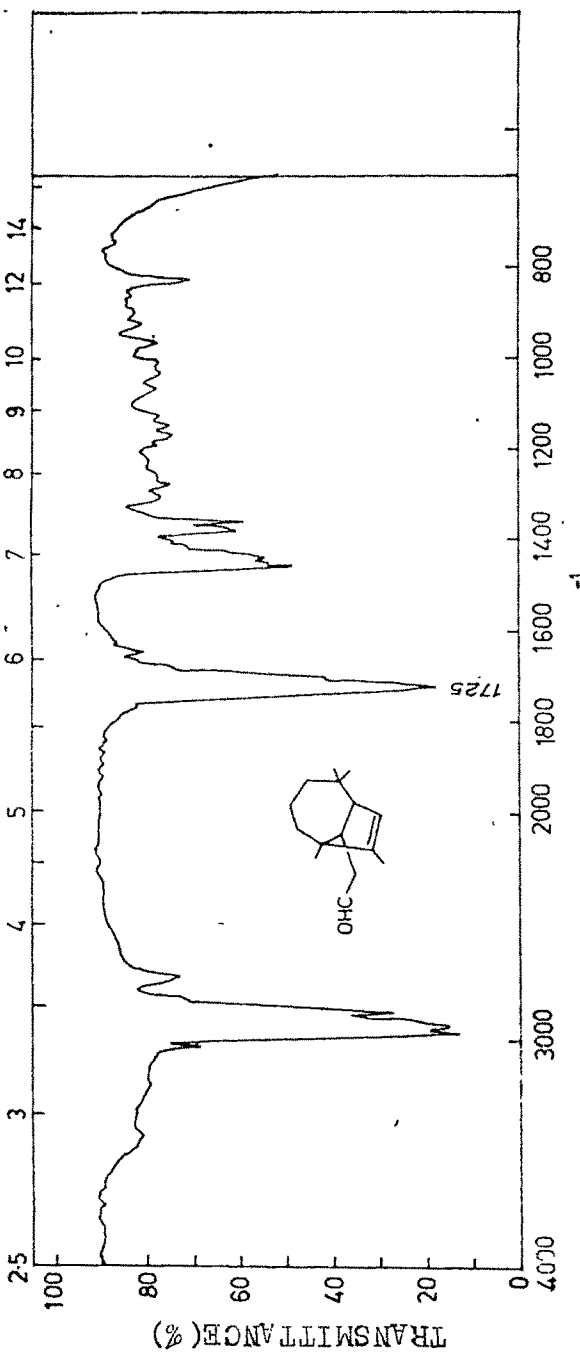


FIG. 15 : IR SPECTRUM OF ALDEHYDE(12)

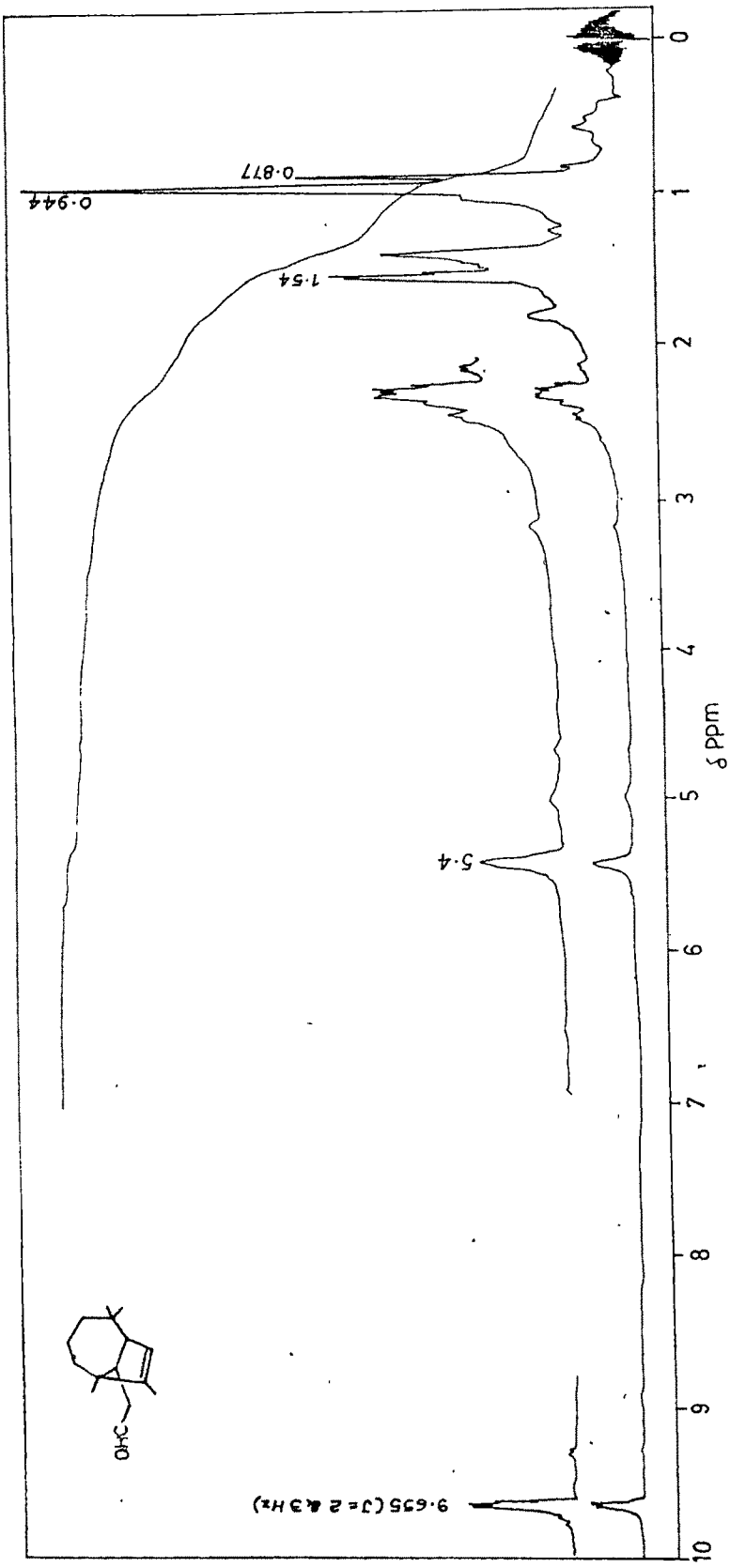


FIG.16 : ^{1}H-NMR SPECTRUM OF ALDEHYDE(12)

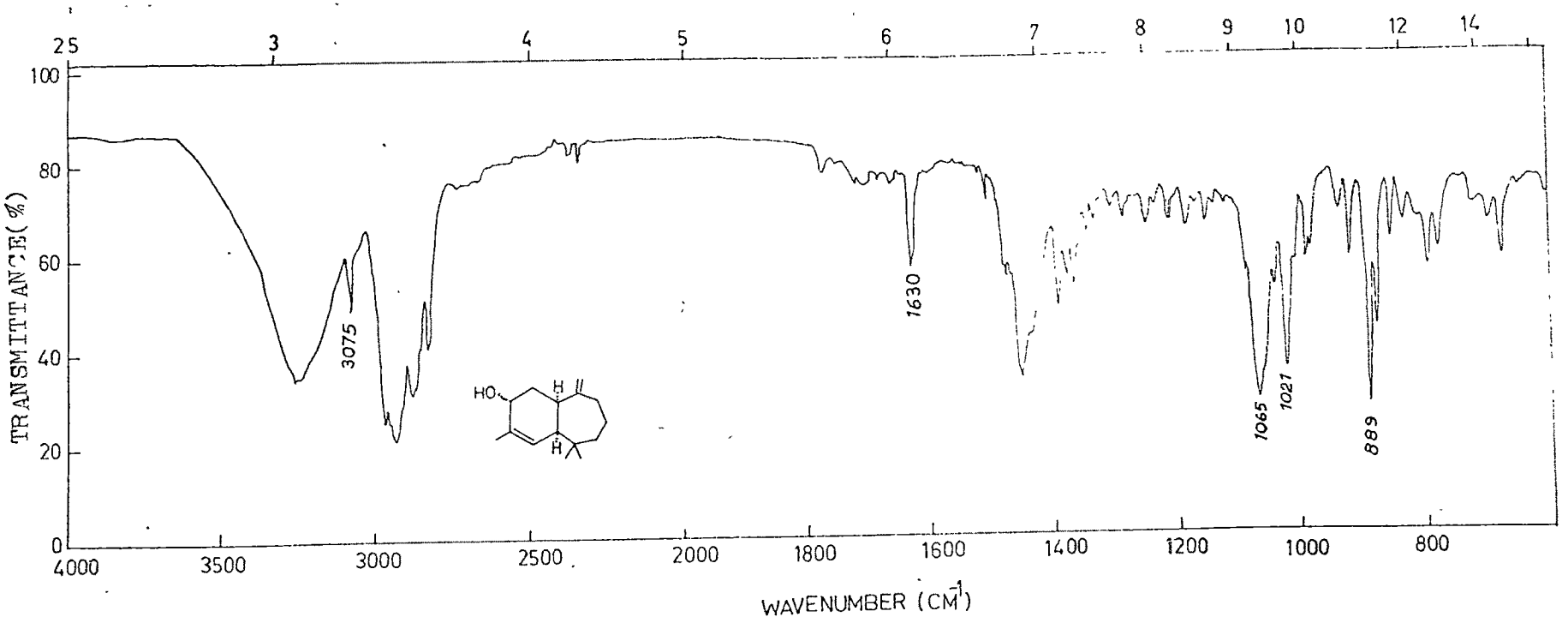


FIG.17 : IR SPECTRUM OF MONO-OL(14)

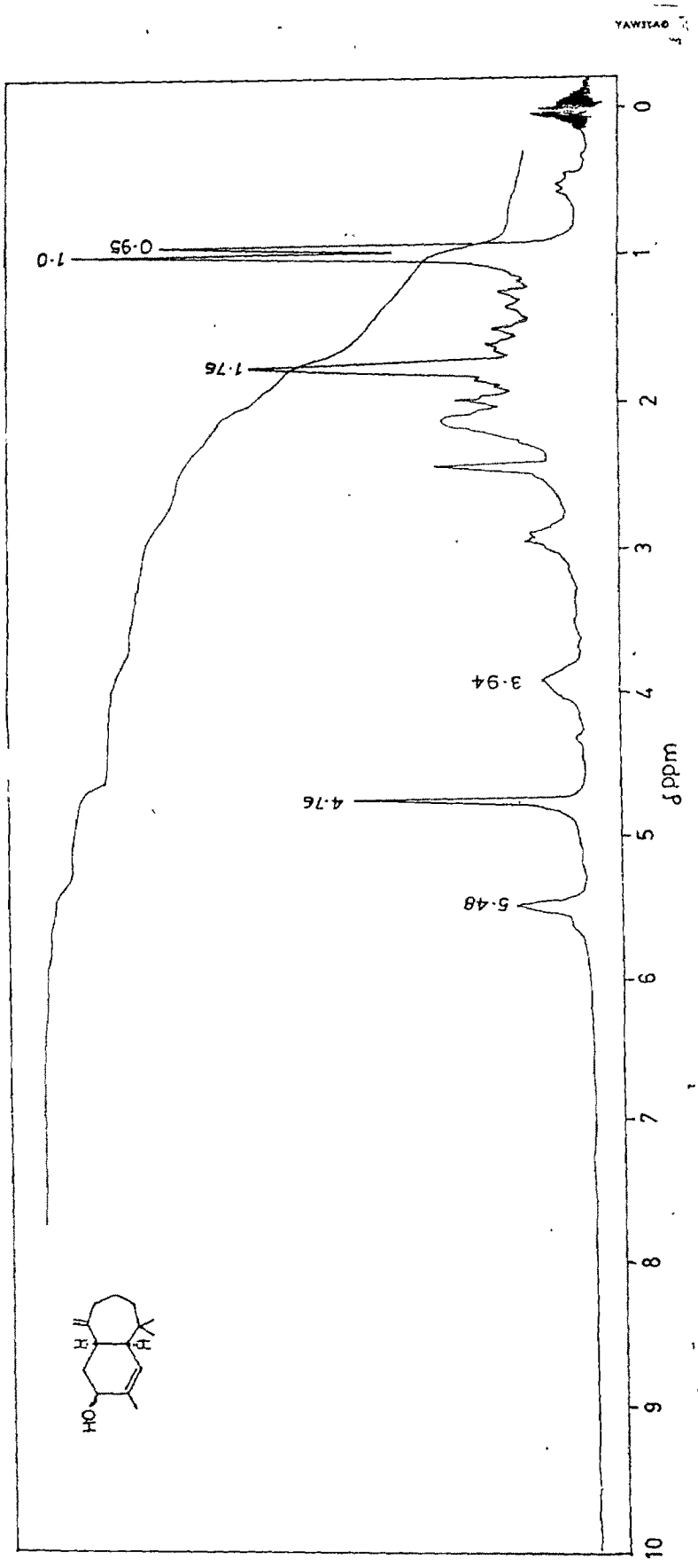


FIG.18 : ^{1}H-NMR SPECTRUM OF MONO-OL(14)

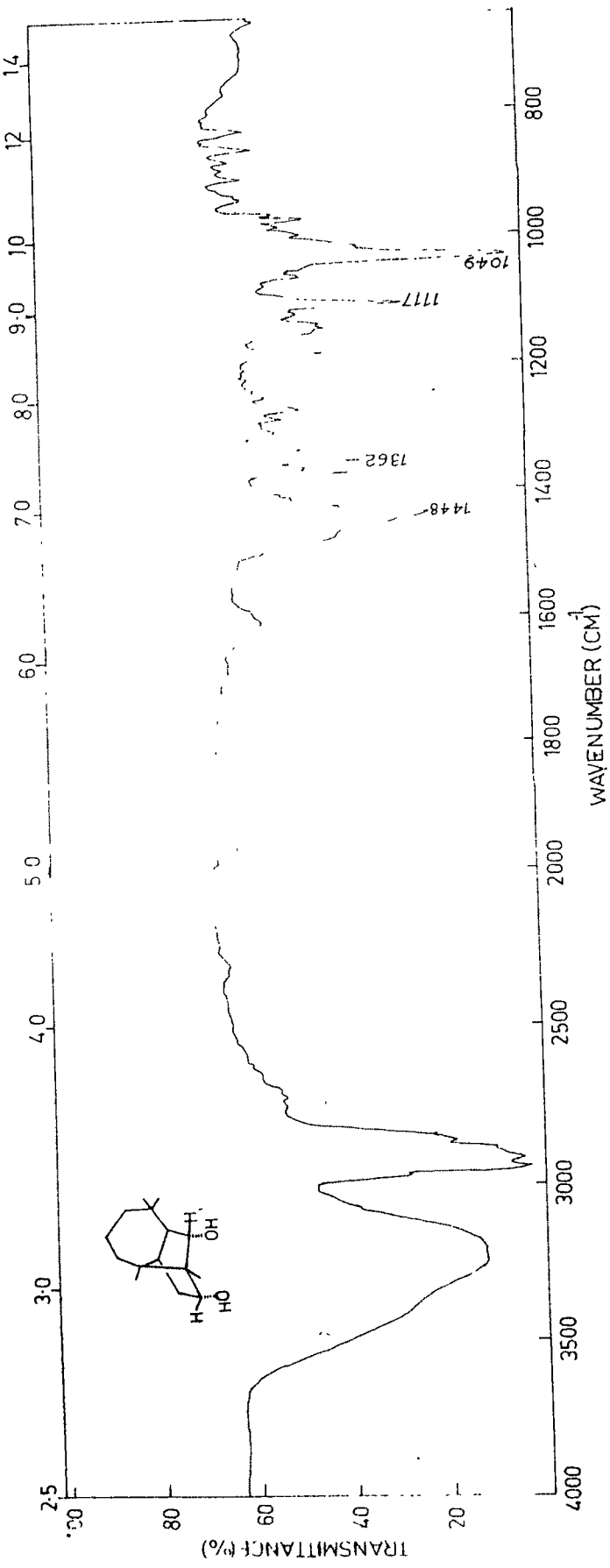


FIG.19 : IR SPECTRUM OF DIOL-I(20)

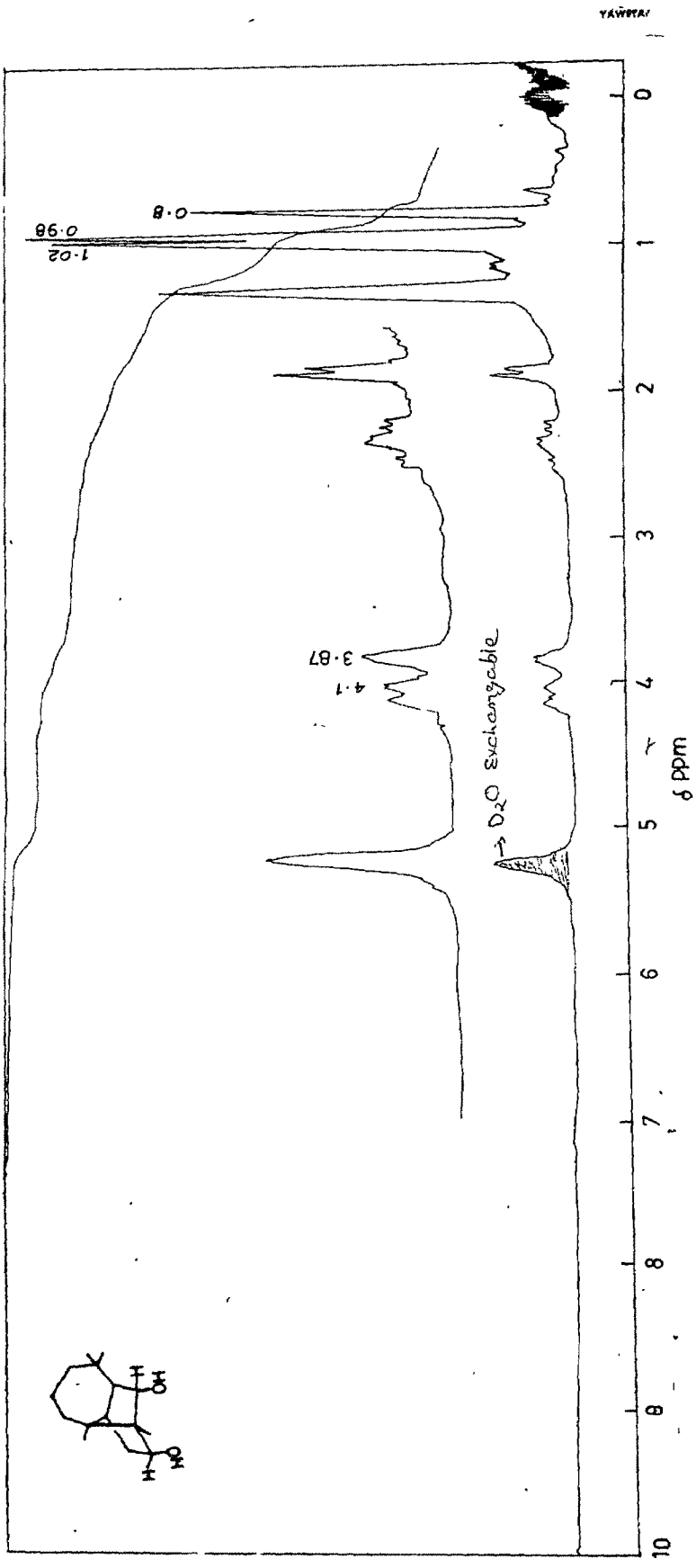


FIG.20 : ^{1}H-NMR SPECTRUM OF DIOL-I(20)

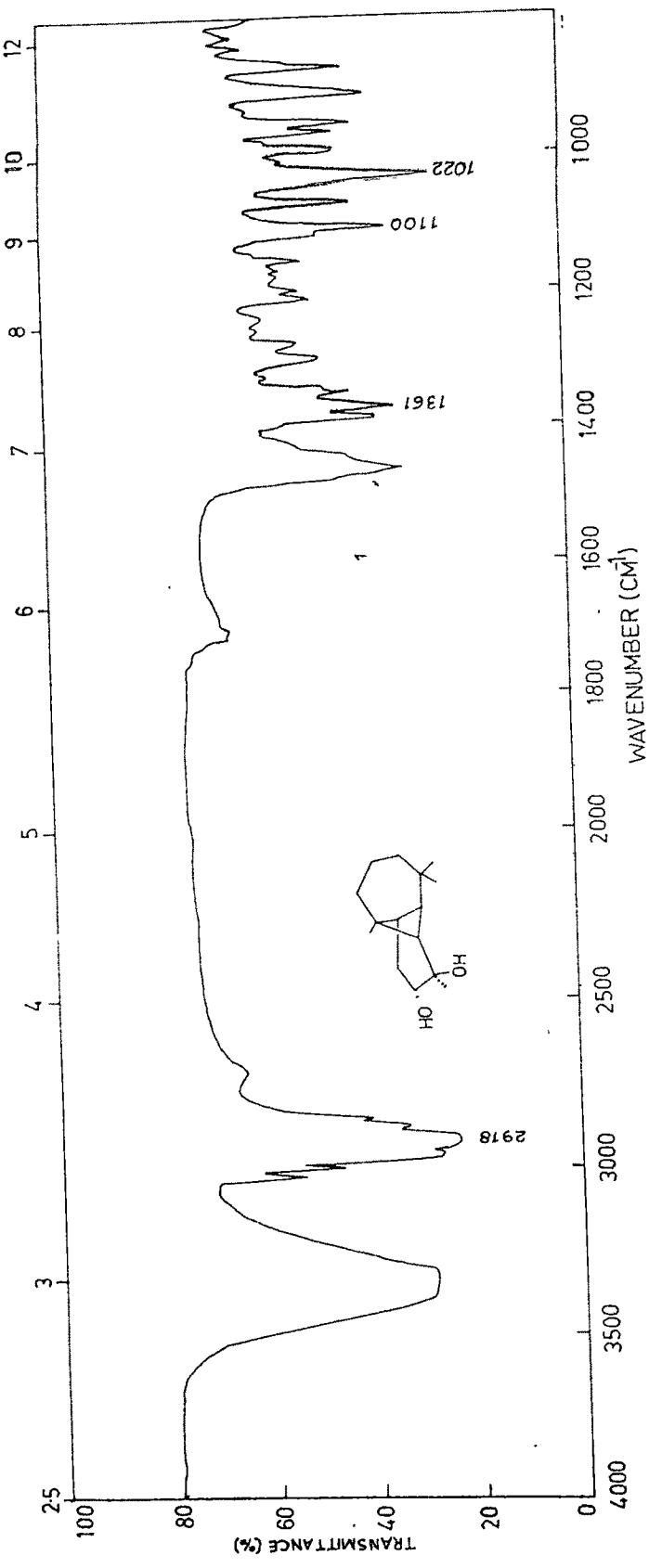


FIG.21 : IR SPECTRUM OF DIOL-II(32)

(LONGIPINANE-3β,4α-DIOL)

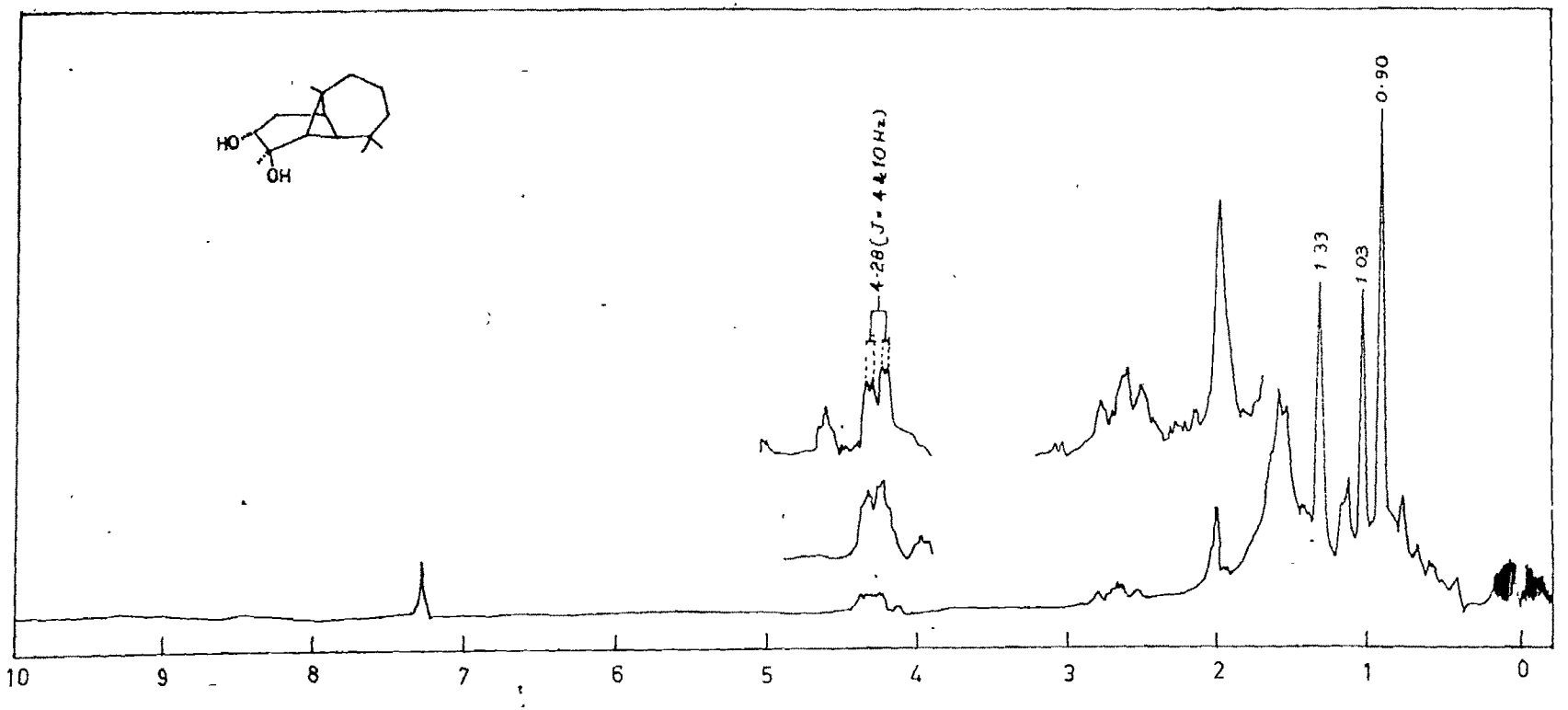


FIG.22 : ^{1}H-NMR SPECTRUM OF DIOL-II(32) ($CDCl_3$) (LONGIPINANE3β,4α-DIOL)

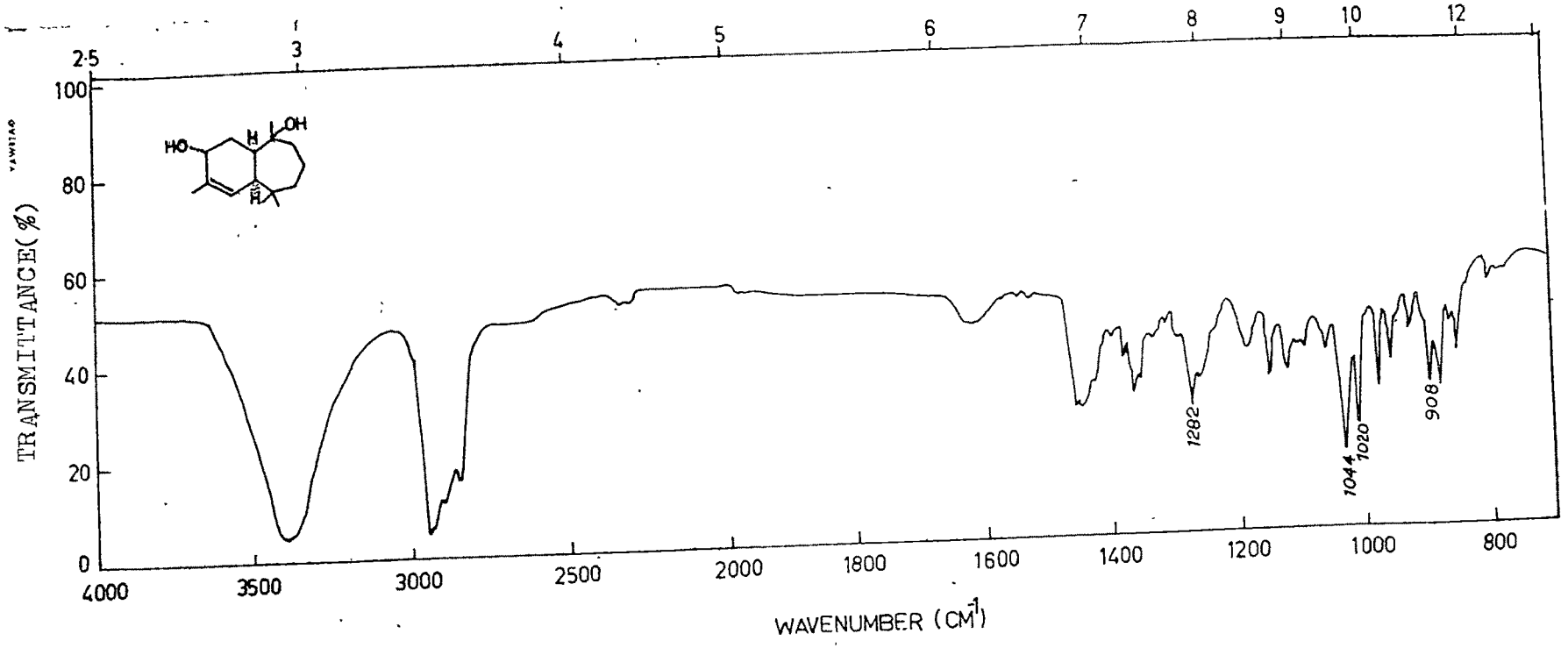


FIG.23 : IR SPECTRUM OF DIOL(16) (AND ISOCENTDAROL)

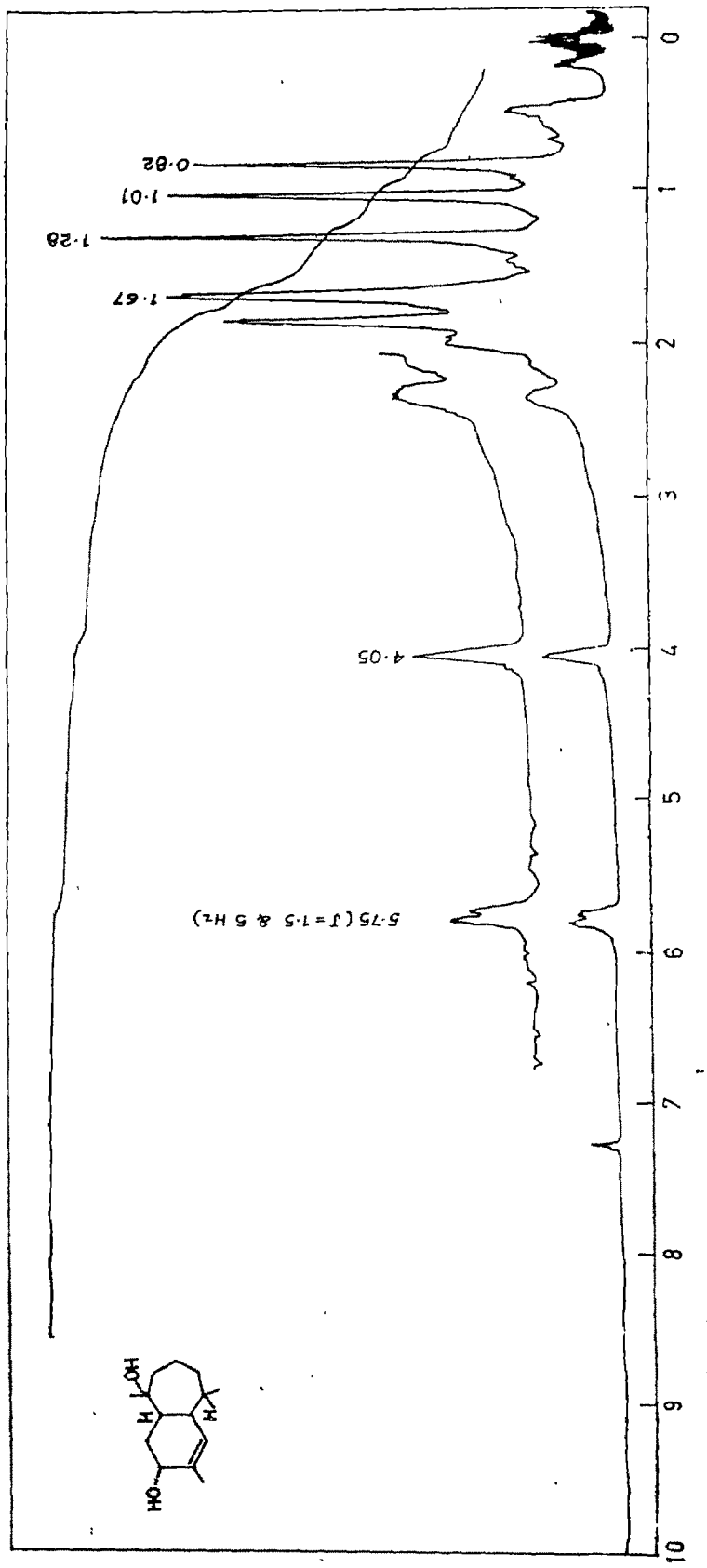
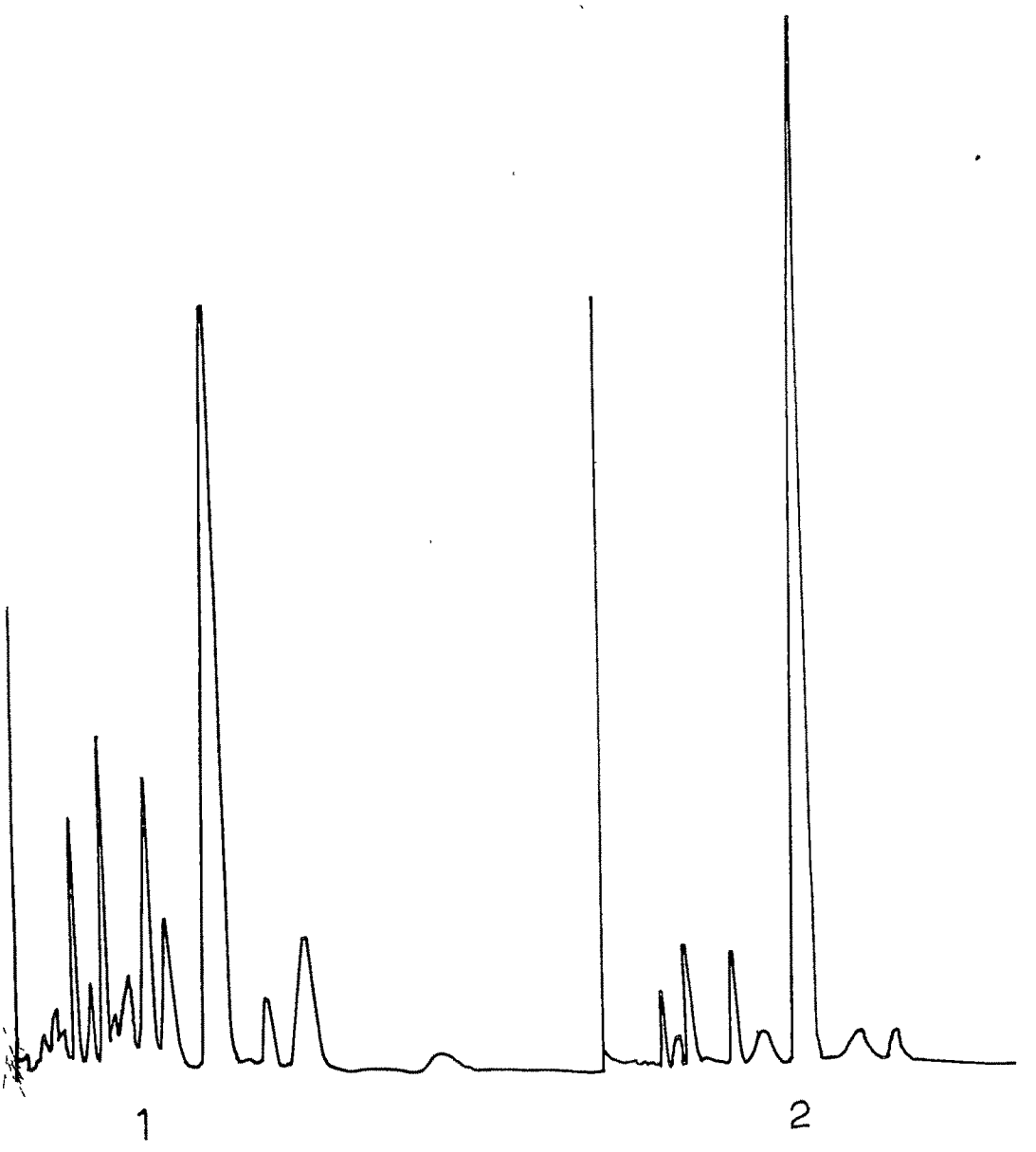


FIG.24 : ^{1}H-NMR SPECTRUM OF DIOL(16) (AND ISOCENTDAROL)



Column: 10% CW 20M (360 cm x 0.6 cm, Al-column)
Hydrogen flow : 60 Ml/min
Temp. 170°

1) **Hydrocarbons obtained from derivatives of Diol-I**

2) Hydrocarbons obtained from derivatives of longibornan-9-ol

Fig. 25. GLC OF REDUCTION PRODUCTS

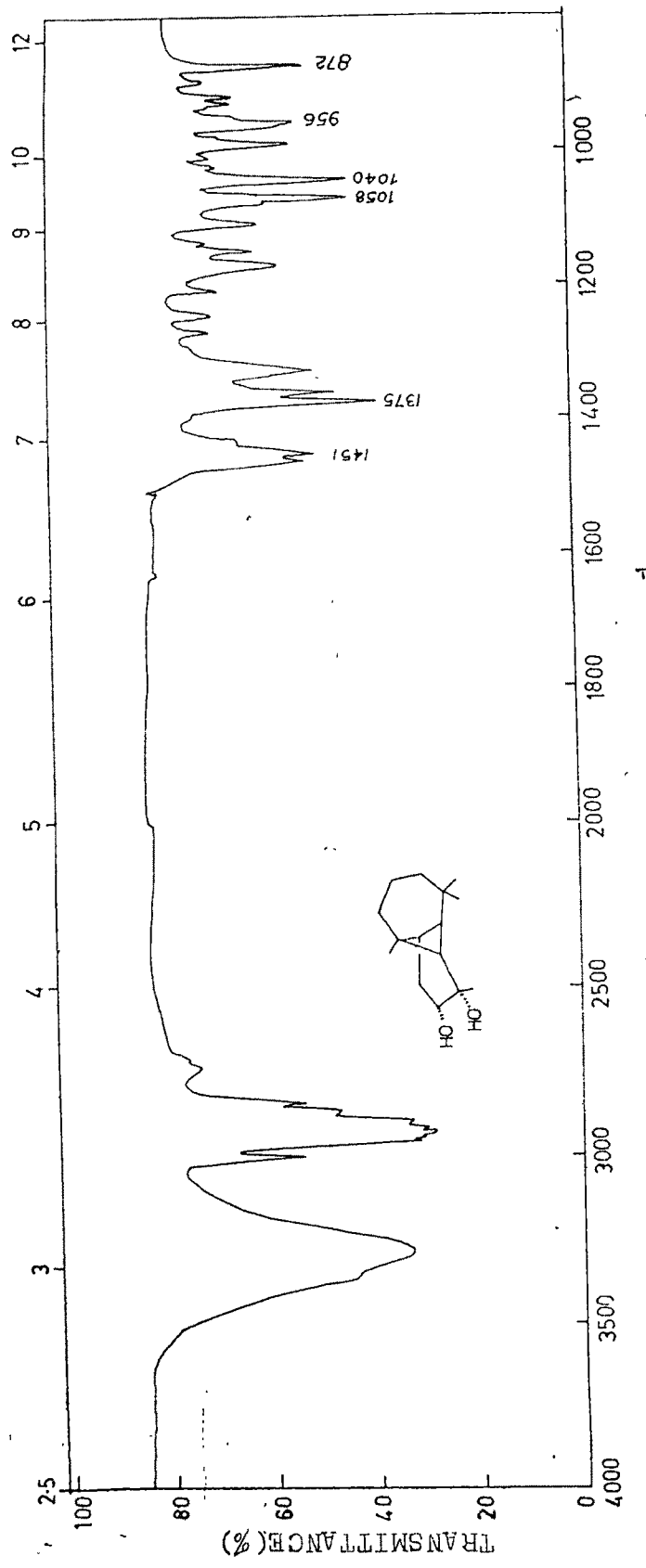


FIG.26 : IR SPECTRUM OF LONGIPINANE-3α,4α-DIOL(35)

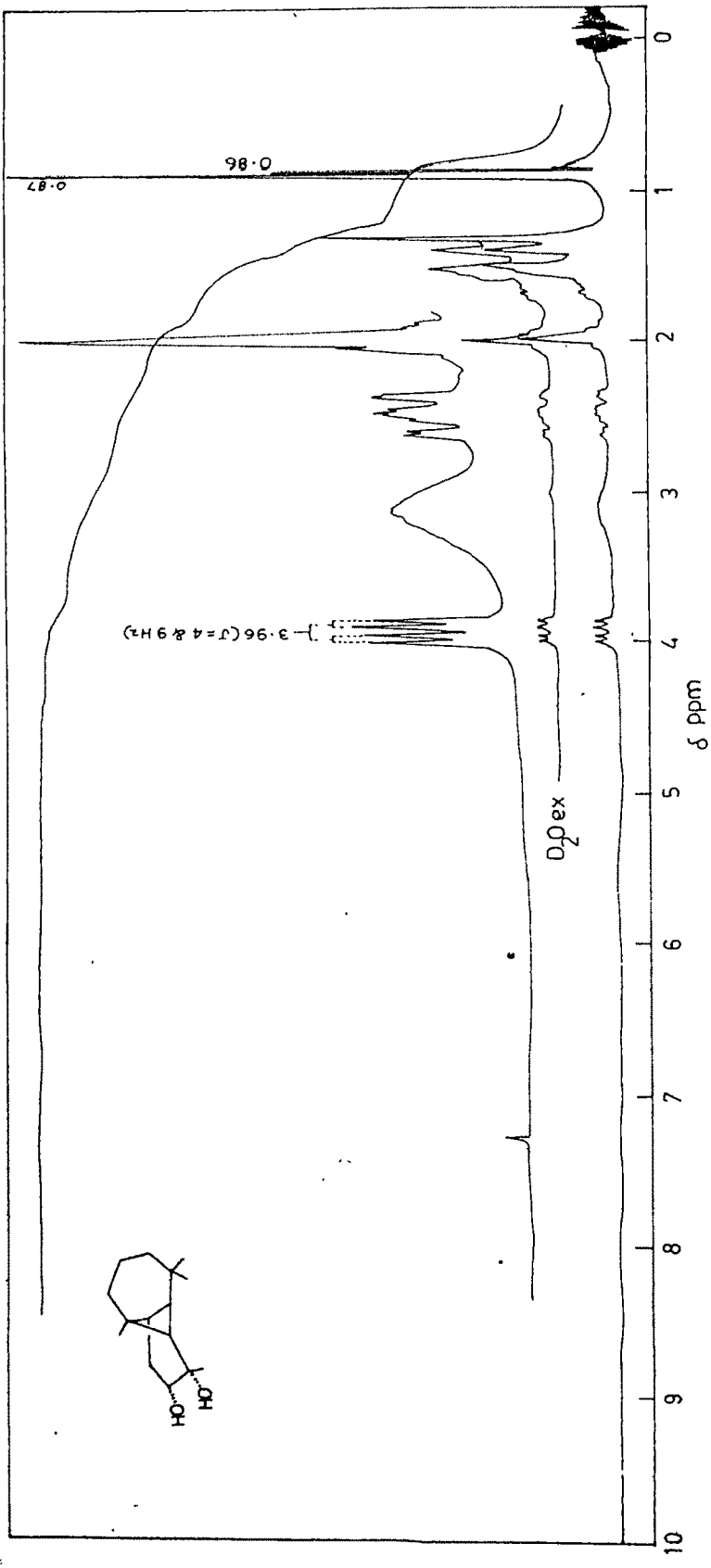


FIG.27 : ^{1}H-NMR SPECTRUM OF LONGIPINANE-3α,4α-DIOL(35)

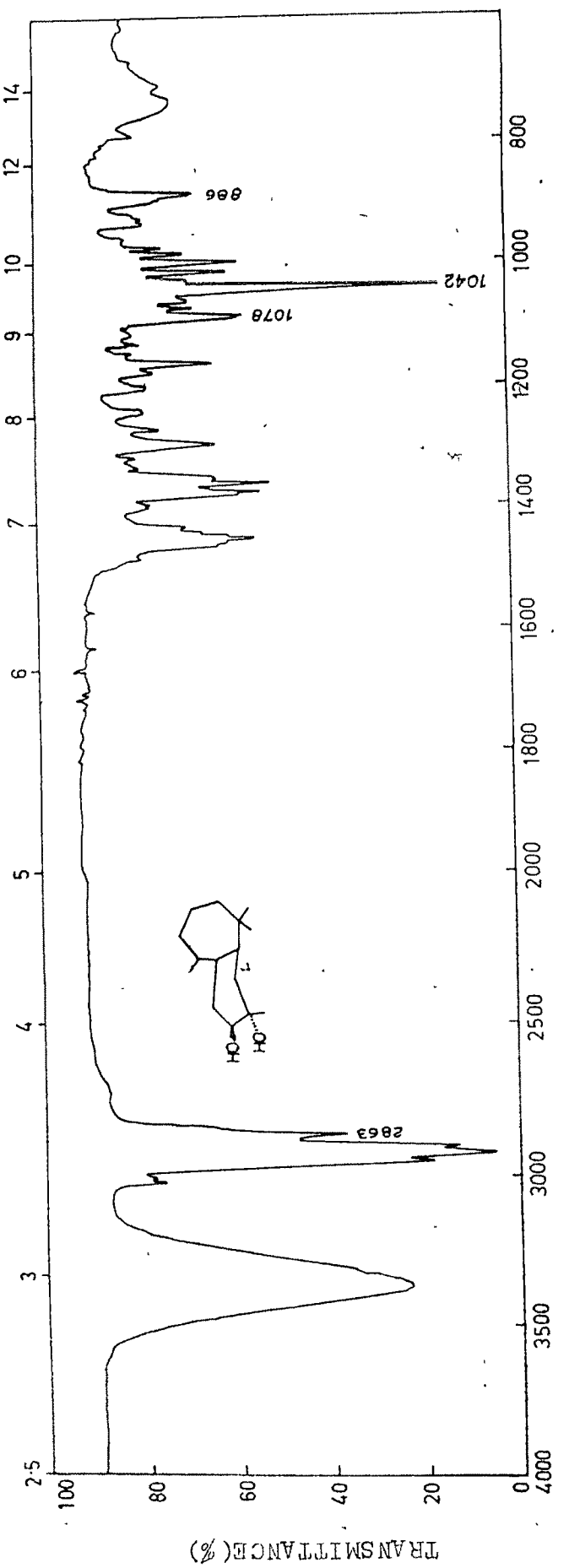


FIG.28 : IR SPECTRUM OF LONGIPINANE-3α,4β-DIOL(34)

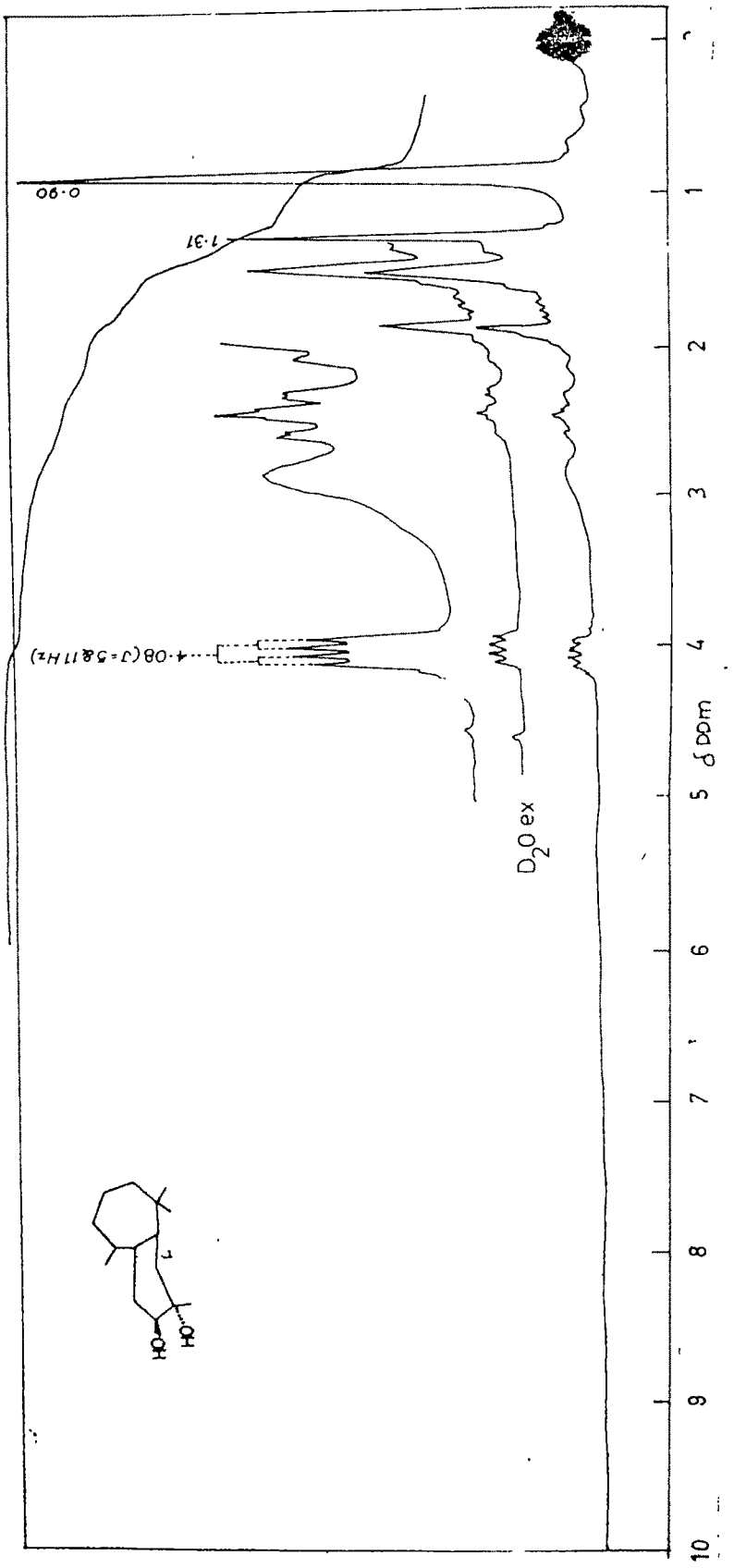


FIG.29 : ^{1}H-NMR SPECTRUM OF LONGIPINANE-3α,4β-DIOL(34)

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