C H A P T E R - III

PREPARATION AND PHOTOLYSIS OF Z-MONOCYCLOFARNESYL IODIDE

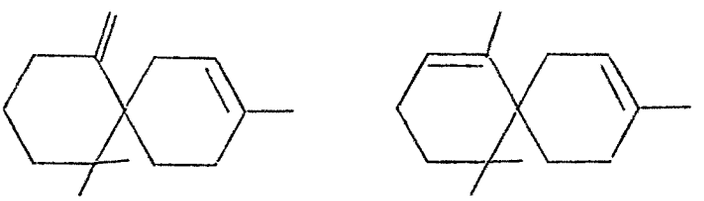
C O N T E N T S

ABSTRACT

This chapter describes the preparation of Z - monocyclofarnesyl iodide and its photolysis as an attempted synthetic route to the chamigrene skeleton.

A. INTRODUCTION

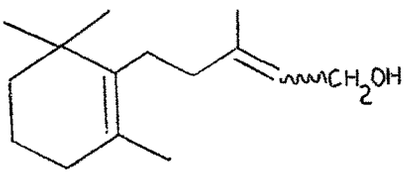
Chamigrene, a sesquiterpene hydrocarbon, was first isolated by Ito et al[1] from the neutral essential oil of the leaves of chamaecyparis taiwanensis Masam. This was later designated as β-chamigrene(1). The corresponding α-analogue(2) was isolated from the seed oil of Schizandra Chinesis Baillon[2].



1. 2.

Several syntheses of this novel carbon skeleton have been reported[2-4] many of which[3b,3d,4] belong to the 'biogenetic-type' category. One approach[4] tests the hypothesis that monocyclofarnesol(3) is a possible intermediate in the biogenesis of some kinds of sesquiterpenes. The acid catalyzed cyclization of Z - or E -(3) gives as one of the products α-chamigrene(2). The monocyclofarnesyl cation(4)

has been proposed as an intermediate.



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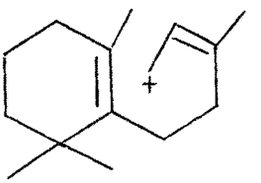
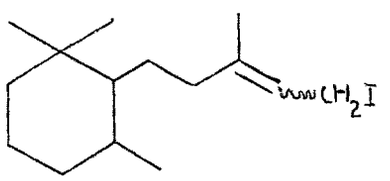


- 4.

B. A photochemical alternative

That photocyclization of suitably designed aliphatic iodides is a potential tool for the 'biogenetic-type' synthesis of a variety of terpene systems has amply been demonstrated[5]. It is thought that the cyclic products result from the hot carbocation generated on photolysis[5,6]. As a continuation of this study it was envisaged that a photoinduced intramolecular cyclization of monocyclofarnesyl iodide(5) could possibly lead to the chamigrene skeleton. Light induced homolysis of the C-I bond followed by electron-transfer[6] would give the cation(4) which could subsequently cyclize[4] to give(I) and/or(2). Of the two possible isomers of (5)

(Z - and E -), the Z-iodide(5a) seemed the more favourable substrate in view of the known propensity of Z- allylic iodides to yield a larger proportion of photocyclization in comparison with their E -analogues[5c]. Also Z-monocyclofarnesol gives a greater yield of α-chamigrene than the corresponding E - isomer[4].



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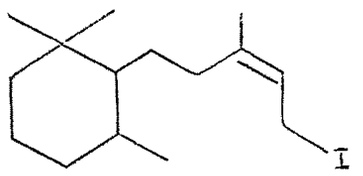


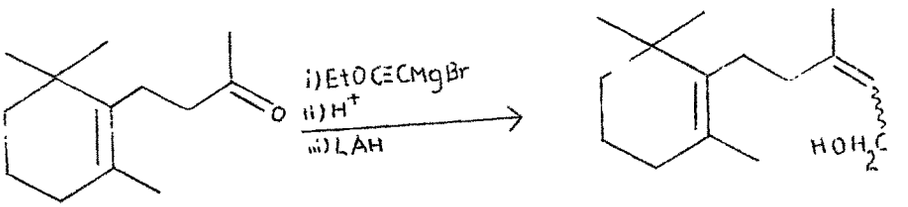
5a.

C. The Synthesis of Monocyclofarnesol(3)

(a) Known routes

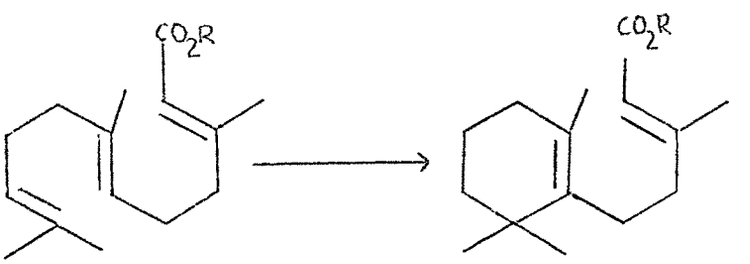
The known synthetic routes to monocyclofarnesol are as follows:-

(i) H.Schinz and co-workers[7] reported the conversion of dihydro-β-ionone(6) to monocyclofarnesic acid via a Grignard reaction(EtOC≡CMgBr). This could then be reduced to the alcohol.



6.

(ii) By the partial cyclization of farnesic acid:-
The cyclization of farnesic acid(7) with boron-trifluoride etherate in benzene solution yields monocyclofarnesic acid(8)[8]. This could easily be reduced to(3)



7. 8.

The yields of (8) however were very low(~25 percent)

(iii) The Reformatsky reaction has also been used[9] though here again the yields are low.

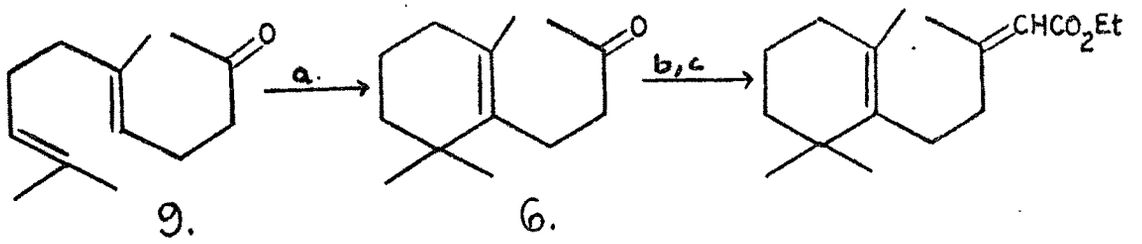
$$(\underline{6}) \xrightarrow[BrCH_2COOR/Zn]{} (\underline{8}) \longrightarrow (\underline{3})$$

(iv) The Wittig-Horner reaction on dihydro-β-ionone($\underline{6}$) followed by LAH reduction of the resulting ester gives the desired alcohol($\underline{3}$)[4]

$$(\underline{6}) \xrightarrow[(ii)(EtO)_2\overset{O}{\overset{\|}{P}}CH_2CO_2Et]{(i)NaH} (\underline{8}) \xrightarrow{LAH} (\underline{3})$$

(v) More recently Yamomoto and his group[10] have developed a method for the synthesis of($\underline{3}$) from geranylacetone($\underline{9}$) with dihydro-β-ionone as an intermediate. It involves the monocyclization of ($\underline{9}$) to dihydro-β-ionone followed by its conversion to an α,β-unsaturated ester and its subsequent reduction to($\underline{3}$) (Scheme-I).

(vi) The most recent method has been reported by Negishi et al[11] (Scheme-2). This method gives exclusively the E-alcohol(stereoisomeric purity of 98 percent).



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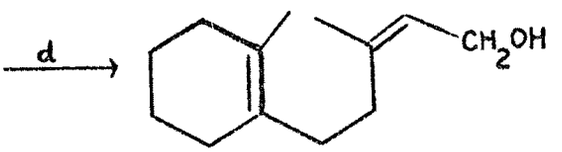
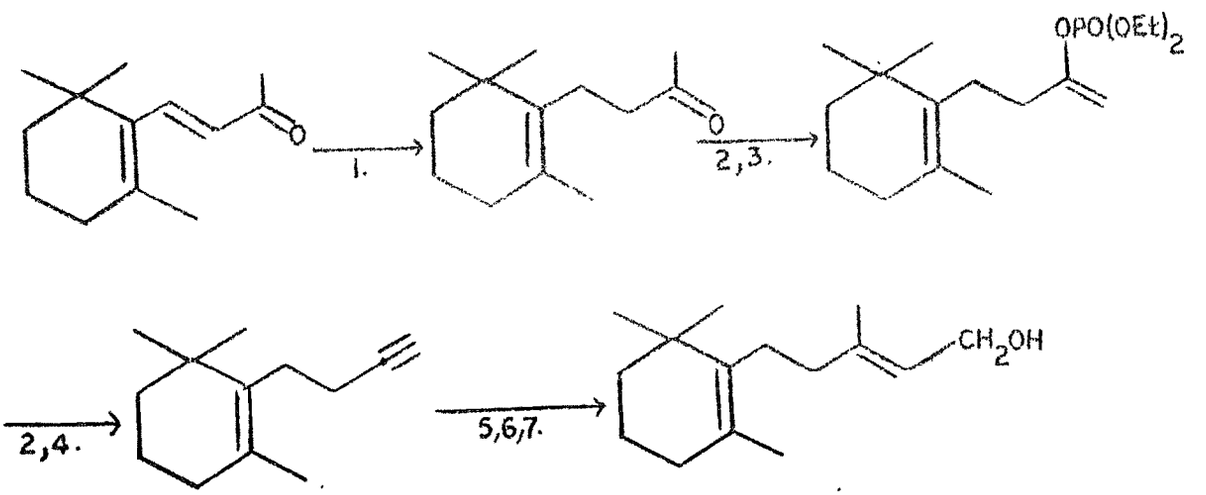


3.

a) HCOOH
b) $Me_3SiCHLiCO_2Et$
c) E,Z Separation
d) AlH_3

SCHEME–1

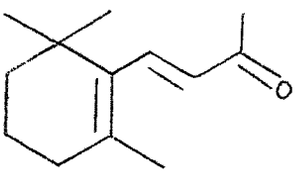


1) LAH/ CuI
2) LDA
3) $ClPO(OEt)_2$
4) HCl
5) Me_3Al, Cl_2ZrCp_2
6) n-BuLi
7) $(CH_2O)_n$

SCHEME–2

b) The present approach

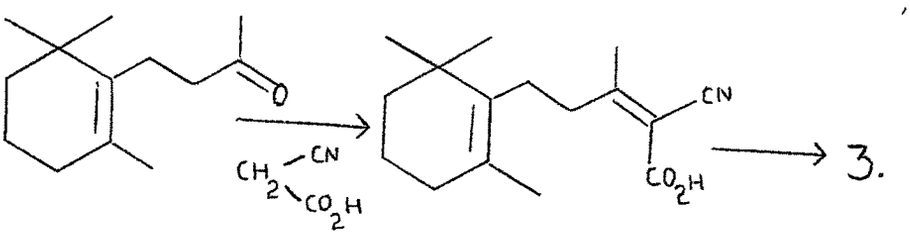
The starting compound chosen was dihydro-β-ionone(6) which could be obtained by the partial hydrogenation of β-ionone(10) in ethanol using Raney-Nickel as a catalyst[12].



10.

Conversion to the semicarbazone derivative and repeated crystallization(three times) from ethanol and subsequent hydrolysis afforded pure(6) (95 percent pure, Mp. of semicarbazone 160-161°). With this as starting material three different routes were attempted.

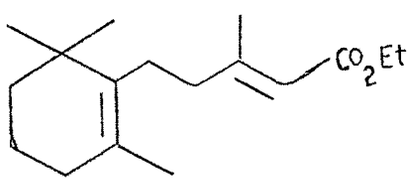
i) The scheme visualized was



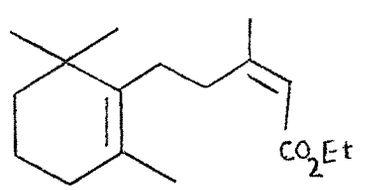
This approach was however given up as the Knovenagel condensation of (6) with cyanoacetic acid in the presence of ammonium acetate and acetamide[13] yielded a complex mixture of eight compounds(GLC).

ii) The Wittig-Horner reaction route[4] mentioned earlier was also attempted.

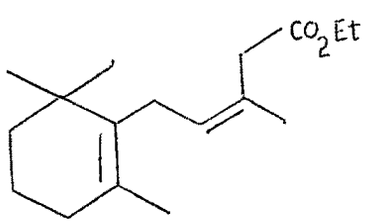
The first step involves the Wittig-Horner reaction between dihydro-β-ionone(6) and the yield generated from $(EtO)_2P(O)CH_2CO_2Et$ using sodium hydride as base. Either benzene or THF(dry) could be used a solvent and the reaction temperature reported was 0^o. Further it was reported that when benzene was used as solvent in addition to the two required isomers(11a and 11b) two more isomers(11c and 11d) were obtained in the product mixture.



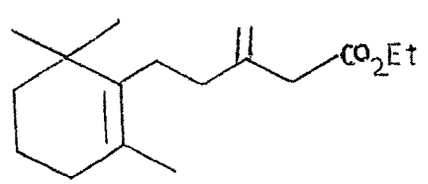
11a.



11b.



11c.



11d.

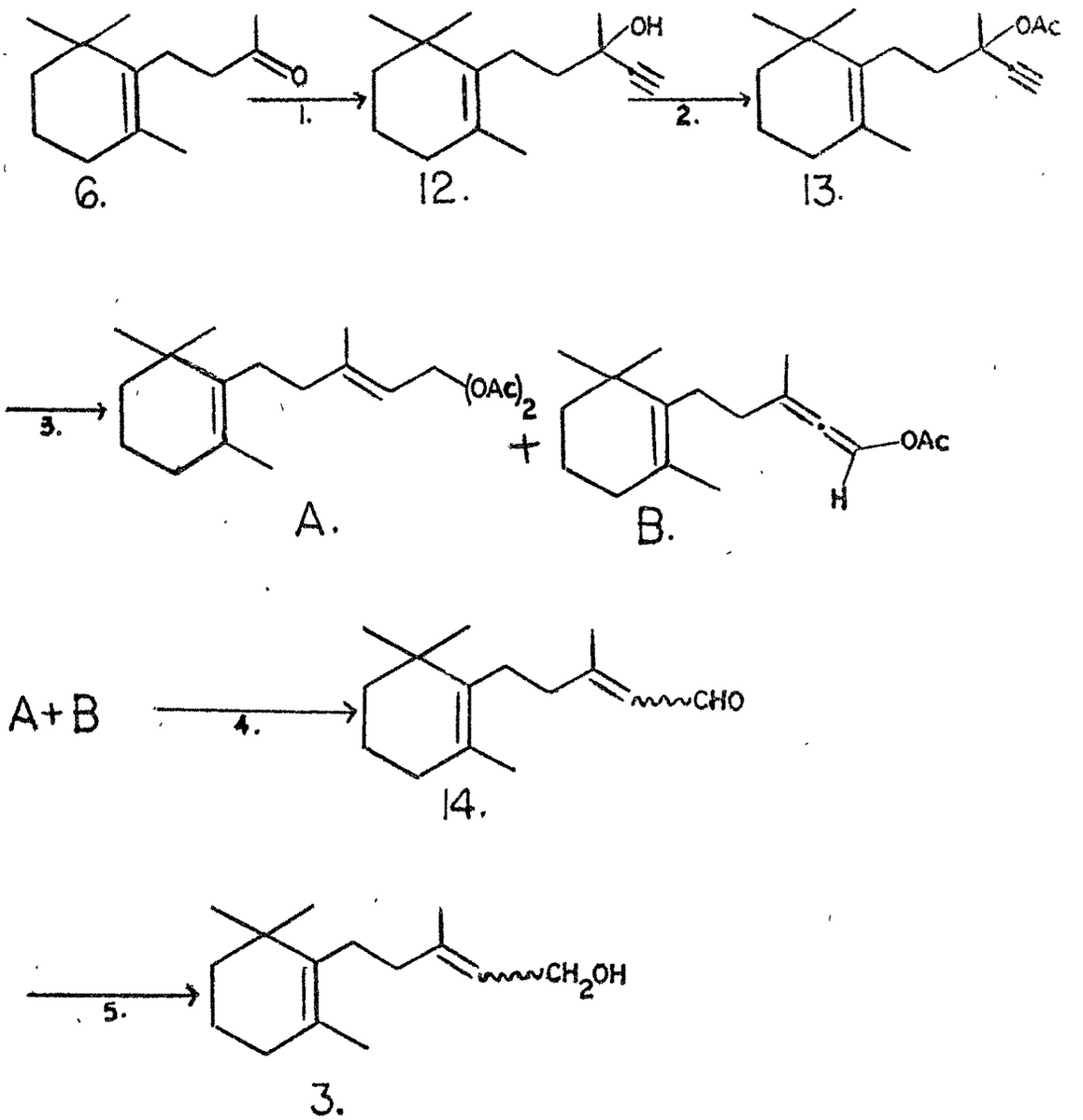
In our hands however the reaction failed under the prescribed conditions(temp.-0°) and all of the starting material was recovered. We found that the reaction proceeds very smoothly at 50° giving almost quantitative yields of the esters. Furthermore, the product ratio obtained was 65 percent of the trans- ester(11a), 28 percent of the cis- ester(11b) and only 7 percent of the unwanted isomers (11c) and (11d). Studies also showed that the product ratio obtained is sensitive to the amount of reagents used. A slight excess of triethyl phosphonoacetate gave(11a) almost exclusively(~90 percent) and (11c) and (11d) in less than three percent. The required Z- and E- esters (11b and 11a) were separated by column chromatography(10 percent $AgNO_3$ on SiO_2-gel) and characterized by their PMR spectra.

The LAH reduction the esters(11b) and (11a) was reported at room temperature and supposedly gave 95 percent yield of the alcohol(3) after a two hour reaction period. Our observation was that this reduction was not so facile; longer reaction times were necessary. There were also signs of the formation of a side-product which probably is the α,β-saturated alcohol(a broad peak at 3.61 in the PMR spectrum possibly for the α- to hydroxyl protons). This

impediment was overcome by first stirring at 0° for 2 hrs, then gradually allowing the reaction mixture to attain room temp. and further stirring for 2 hrs.

iii) The third approach attempted consists of the sequence of reactions shown in Scheme-3

This Scheme parallels that reported by Isler and coworkers[14] which was later subjected to some modifications[5c] in the conversion of geranylacetone to farnesol. This sequence has not been reported on dihydro-β-ionone so far thus presenting a new approach to the synthesis of (3). Thus dihydro-β-ionone(6) on acetylenation yielded the tertiary alcohol(12) which was acetylated with Ac_2O/H_3PO_4 to furnish the monoacetate(13). The acetate on treatment with acetic acid and catalytic amounts of Ag_2CO_3 rearranges to a mixture of the allenic acetate and diacetate(A and B). It has been reported[5c] that the conditions described by Isler for the basic hydrolysis of the mixture(A and B) ie with Na_2CO_3 proved unsatisfactory in the case of farnesol. Sodium methoxide in methanol was used. In the present case however, treatment of the mixture



1) $HC\equiv CH, K^{+}\ ^{-}OC(CH_3)_2C_2H_5$
2) Ac_2O/H_3PO_4
3) $AcOH, Ag_2CO_3$
4) Na_2CO_3
5) LAH

SCHEME—3

(A) + (B) with sodium methoxide gave the aldehyde(14) which immediately underwent a Retro-Aldol reaction resulting in the starting dihydro-β-ionone(as shown by PMR). Reverting back to Isler's conditions gave the desired aldehyde(14) which was easily reduced(LAH) to give monocyclofarnesol(3). The alcohol thus obtained was a mixture of 60 percent E - and 40 percent Z-isomers (as per NMR). No 1,2-dihydro alcohol could be detected in the LAH reduction product. The Z - and E - monocyclofarnesols were separated by column chromatography (5 percent $AgNO_3$ on SiO_2-gel).

D. Preparation of Z-Monocyclofarnesyl Iodide(5a)

Of all the methods available[15,16] for the conversion of alcohols to the corresponding iodides, the use of trimethyl silyl halides seems to be the one of choice by virtue of the low reaction temperatures needed(room temp.), the neutral conditions employed, short reaction times and the purity of products obtained. Jung[16] was the first to report the use of iodo trimethyl silanes in the conversion of alcohols to iodides. Treatment with alcohols with iodotrimethyl silane in a chlorinated hydrocarbon solvent at 25° under a nitrogen atmosphere gave the corresponding iodide. More recently[17] iodotrimethyl silane has been used for converting esters(RCOOR)to iodides(RI).

A convenient modification of Jung's procedure has been recently published[18] which employs the more easily available chlorotrimethyl silane. Here a solution of the alcohol and sodium iodide (dry) in acetonitrile is treated with chlorotrimethyl silane under a nitrogen atmosphere at 25° to give the corresponding iodide in high purity and yields. This method was reported to have wide applicability and was therefore adopted for the conversion of Z - monocyclofarnesol into its iodide(5a). The reaction was very smooth giving good (90 percent) yields of the pure iodide (as per NMR).

E. Photolysis of Z-Monocyclofarnesyl iodide

Due to its extreme instability the Z-monocyclofarnesyl iodide had to be immediately taken up for photolysis. A 1 percent solution of (5a) in dry THF containing a molar equivalent of triethylamine was irradiated[5b] at 50° for 2.5 hr when the photostationary state was reached(TLC). An analysis (GLC) of the product mixture obtained showed a complex composition of atleast fifteen compounds. No trace of either α- or β- chamigrene could be detected on comparison of the NMR of the product mixture with authentic spectra[19] and consequently no further analysis of the products was attempted.

F. Concluding remarks

Obviously our initial objective of achieving a synthesis of the 'spiro' chamigrene skeleton via a photoinduced intramolecular cyclization of Z - monocyclofarnesyl iodide has not been realized. Though our mode of detection does not preclude the presence of trace amounts of either α- or β-chamigrene this approach can have no synthetic utility.

EXPERIMENTAL

All mp's and bp's are uncorrected. For general remarks see Chapter-I, Section-II(Experimental).

1) Knovenagel condensation on dihydro-β-ionone(6)

Purified dihydro-β-ionone(1.74 g, 0.01 mole), cyanoacetic acid(0.9 g, 0.01 mole), acetamide(0.04 g) ammonium acetate (0.04 g) and α-tocopherol(0.5 g, antioxidant) in dry benzene (3 ml) was boiled under nitrogen atmosphere in the absence of water at 110-130°. After the water has boiled off, 0.3 ml acetic acid was added dropwise and refluxing was continued for 50 to 60 hrs. Later the mixture was cooled and poured into water (5 ml) and 2.5 ml ether, the aqueous layer extracted with ether(5 ml x 3) and the combined ethereal extracts washed with water and then aq. sodium hydroxide solution (10 percent, 5 ml x 2). The H_2O and NaOH washings were combined and shaken with ether and all the ether fractions combined and dried(Na_2SO_4). Removal of the solvent gave a residue(1.2 g). Analysis by GLC(5 percent carbowax, 200°) showed it to be a mixture of eight compounds.

2) Wittig-Horner reaction on dihydro-β-ionone(6)

Sodium hydride(2 g, 50 percent,0.042 mole) was placed in 1cc dry benzene and the slurry cooled to 20°. Triethyl-phosphonoacetate(1.12 g, 0.005 mole) was added dropwise

under stirring. After completion of the addition stirring was continued at room temp. for 1 hr. At the end of this period, dihydro-β-ionone(0.500 g, 0.0025 mole) was added dropwise during which some evolution of heat was observed. The solution was stirred at 50° for 1 hr. during which time a gummy precipitate develops. The reaction mixture was then cooled and taken up in a large excess of water (20 ml) and extracted with ether(5 ml x 3). The combined ethereal extract was dried(Na_2SO_4) and evaporated to give the crude mixture of esters(0.68 g, ~100 percent yield).

(i) Separation of Z - and E esters (11b and 11a)

GLC of the mixture showed a composition of 58 percent (11a), 35 per cent (11b) and 7.1 percent of (11c) and (11d). The required isomers (11a) and (11b) were separated by column chromatography(10 percent $AgNO_3$-SiO_2-gel, grade-IIB).

CHROMATOGRAM - I

Column dimensions = 0.6 cm x 38 cms

Amt. of silica gel = 2.0 g

Wt. of compd. loaded = 0.5 g

Fraction Nos.	Solvent	Vol. of eluate.	Wt. (mg)	Remarks.
1 to 11	Pet.ether	2 ml x 11	-	-
12 to 18	Pet.ether	3 ml x 7	150	(11b)
19 to 23	Pet.ether	3 ml x 5	40	(11b) + (11a)
24 to 40	Pet.ether + 0.5% THF	3 ml x 17	180	(11a)
41 and 42	Pet.ether + 1% THF	3 ml x 2	20	(11a)
43 to 46	- do -	3 ml x 4	-	-
46 onwards	- do -			Impurities.

The Z-isomer(11b) was obtained in 100 percent purity while the E - isomer(11a) was 96 percent pure(GLC). Their PMR spectra agreed with the reported values[4]

PMR:

(i) (11a): gem di Me's(6H,s,1.0 ppm); C=CH-CO_2Et(1H, m, 5.55 ppm); two CH_3C=C(6H; 3H singlets at 1.67 and 1.93 ppm);

(ii) (11b): gem di Me's(6H, s, 1.0 ppm); C=CHCO_2Et(1H, m, 5.55 ppm); two CH_3C=C(6H;3H singlets at 1.60 and 2.14 ppm).

ii) Reduction of the esters to the alcohol(3)

A suspension of 200 mg lithium aluminium hydride in dry ether(2 ml) was cooled to 0^{o} and to it was added a solution of the ester(cis + trans) (1 g; 0.0038 mole) in dry ether(1 ml) in a dropwise manner, under stirring, over a period of about fifteen munutes. After completion of addition the stirring was continued for two hrs. Then the reaction mixture was allowed to gradually attain room temp. and the stirring continued for a further period of 2 hrs. The reaction mixture was then decomposed with cold water, 5 percent HCl and extracted with ether(10ml x 3). The

combined extract washed with water, dried(Na_2SO_4) and evaporated to yield 0.97 g of the alcohol(3)(97 percent yield). Purification was by column chromatography (vide infra).

3) The Acetylene-addition route(Scheme-3)

(i) Acetylene addition on(6):

Anhydrous ether(18 ml) was cooled to -15° and saturated with dry purified acetylene gas for 1 hr. Under mechanical stirring with the acetylene flow at a rate of 15 lit/hr. A solution of dihydro-β-ionone(6) (15 g, 0.086 moles) in dry ether(17 ml) and a solution of potassium(5 g) dissolved in anhydrous(refluxed and distilled over Na) t-amyl alcohol(63 ml) were added separately to the ether solution of acetylene under vigorous mechanical stirring over a period of 2 hrs. The acetylene flow rate was raised to 32-35 lit/hr during this addition and the reaction mix. kept at -10 to -15°. After complete addition the reaction mixture was further stirred for 4 hr. at 0° with the acetylene gas flow rate reduced to 15 lit/hr. when by tlc(10 percent pet.ether, 5 percent EtOAc in benzene) it was revealed that the reaction was complete. The reaction mixture

was further stirred for 4 hr. at 0° with the acetylene gas flow rate reduced to 15 lit/hr. when by tlc(10 percent pet.ether, 5 percent EtOAc in benzene) it was revealed that the reaction was complete. The reaction mixture was decomposed by cold water, the product taken up in ether(30 ml x 3), washed with 5 percent NH_4Cl(20 ml x 2) followed by water till the aqueous layer was neutral. Drying(Na_2SO_4) of the ether extract followed by removal of solvent furnishes the crude tertiary alcohol(12). Distillation yields the pure material(bp.102-4°/0.9mm) in good yield (15.5 g, 90 percent yield).

IR(Neat): O-H 3400 cm^{-1}, C≡C-H 3305 cm^{-1}

PMR: gem di-Me's(6H, s, 1.01 ppm); CH_3C-OH(3H,s, 1.50 ppm); CH_3C=C(3H, s, 1.62 ppm), C≡C<u>H</u>(1H, s, 2.41 ppm).

MS : m/e 220(M^+,10%), 149(60%), 123(70%),121(93%), 96(70%), 93(70%), 91(50%), 81(100%), 79(67%), 69(83%).

Anal: Found, C, 81.58; H,10.70. $C_{15}H_{24}O$ requires C,81.83; H, 10.91.

(ii) Tertiary alcohol to acetate(13):

In a 100 ml 3-necked flask equipped with a thermometer, reflux condenser and dropping funnel was taken 10g(0.046 mole) of (12). A mixture of acetic anhydride(8.028 g, 0.078 mole) and H_3PO_4(0.115 g) was added during one hour with stirring whereby the temp. rises to ~50°. After complete addition it was kept overnight at room temp. when it shows complete conversion(tlc). The reaction mixture was poured over cold water and extracted with ether (70 ml x 3). The combined extract washed with cold water and dried(Na_2SO_4). Evaporation of solvent gives the acetate(12 g, quantitative). A small portion of the acetate was distilled for its spectral data (bp. 135-140°(bath)/3.5 mm).

IR(Neat) : C≡C-H 3300 cm^{-1}; C=O 1745 cm^{-1}; C-O 1245 cm^{-1}.

PMR : gem di Me's (6H, s, 1.0 ppm); CH_3-C-O(3H, s, 1.59 ppm); CH_3C=C(3H, s, 1.66 ppm); C≡C-H(1H, s, 2.39 ppm)

MS: m/e 262(M^+,7%), 220(50%), 187(79%), 159(61%), 131(73%), 121(100%), 95(82%), 93(81%), 81(80%)

Anal: Found C, 77.99; H, 10.23, $C_{17}H_{26}O_2$ requires C,77.85; H,9.92.

(iii) Acetate to allenic acetate + diacetate(A+B):

The above acetate(10 g, 0.038 mole) was rearranged by treatment with glacial acetic acid(20 g, 0.33 mole) and silver carbonate (0.05 g) and warming to 90° under a nitrogen atmosphere for 1.5 hr whereby due to heat of reaction the inner temp. after 1 hr reached 110°C. The reaction mixture was then cooled, poured into water and extracted with Et_2O(30 ml x 3). The combined ether extracts was washed with water and dried (Na_2SO_4). Evaporation of ether gives the allenic acetate + diacetate mixture as a pale yellow oil (12 g) which without further purification was put for hydrolysis.

(iv) Hydrolysis with sodium methoxide:

1 g of the above mixture was added to a solution of sodium methoxide(0.1 g Na dissolved in 30 ml methanol) and the mixture kept at room temp. for 1 hr. The reaction mixture was poured into water(20ml), saturated with brine and extracted with ether(30 ml x 3). Drying(Na_2SO_4) followed by solvent removal from the combined extract gave a residue (0.6 g). It's PMR was identical to that of authentic dihydro-β-ionone.

PMR: gem di Me's (6H, s, 0.98 ppm); $\underline{CH_3}C=C$(3H,s,1.55 ppm); $\underline{CH_3}-C=O$(3H, s, 2.04 ppm).

(v) Hydrolysis with sodium carbonate:

The above mixture of acetates(12 g) in 50 ml methanol was stirred with a solution of 2.5 g(0.024 mole) sodium carbonate in water(10 ml) under a nitrogen atmosphere at 60° for 1.5 hr. The mixture was then poured into water and extracted with pet.ether(bp.60-80°, 30 ml x 3). Drying(Na_2SO_4) followed by solvent removal gave the aldehyde (14, Z+E) which was purified by passing through a short column of silica gel(6.7 g, overall yield of steps(iii) and (v) is 80 percent).

IR(CCl_4): C=O, 1680 cm^{-1}

PMR: HC=O(1H, m, 9.9 ppm).

(vi) Aldehyde to alcohol(3):

To a cooled(0°) well dispersed suspension of LAH(0.6 g, 80 percent active) in dry ether is added under stirring a solution of 3 g(14) in dry ether (3 ml) over a period of 15 min. After completion of addition, stirring is continued at 0° for 1 hr at the end of which the reaction mixture was decomposed with cold water and extracted with ether(5ml x3). The ether extract was dried(Na_2SO_4) and then evaporated to give the crude mixture of Z - and E - monocyclofarnesol(3) (3.0 g).

(vii) Separation of Z - and E - monocyclofarnesols:

On the basis of PMR the mixture appeared to contain the isomers in the proportion [cis] : [trans], 40:60. Separation was affected by column chromatography over 5 percent $AgNO_3$-SiO_2-gel (grade, II B).

CHROMATOGRAM -II

Column dimensions = 1.7 cm x 105 cm

Amt. of silica gel = 120 g.

Wt. of compd.loaded= 3.5 g.

Fraction Nos.	Solvent	Vol.of eluate	wt. (g)	Remarks.
1 to 10	Pet.ether	5ml x 10	-	-
11 to 20	Pet.ether + 1 percent EtOAc	5ml x 10	-	-
21 to 25	Pet.ether + 5 percent EtOAc	5ml x 5	-	-
26 to 30	-do-	5ml x 5	0.02	Impurities
31 to 34	-do-	5ml x 4	-	-
35 to 41	-do-	5ml x 7	0.9	cis-(3)
42 to 49	-do-	5ml x 8	1.0	cis+trans-(3)
50 to 60	-do-	5ml x 11	1.1	trans-(3)

Pure Z - and E - monocyclofarnesols were obtained by this procedure and they were characterised from their PMR and IR spectra. The PMR values coincide with those reported[4] for these compounds.

(i) Z - (3)

IR(CCl_4): O-H 3390 cm^{-1}; C=C 1670 cm^{-1}

PMR: gem di Me's(6H, s, 1.02 ppm); CH_3-C=C (3H,s, 1.63 ppm); CH_3-C=CCH_2OH(3H, s, 1.79 ppm); CH_2OH(2H, d, 4.04 ppm, J=7 Hz) CH=C(1H, t, 5.36 ppm,J= 7Hz).

(ii) E -(3)

IR(CCl_4): O-H 3400 cm^{-1}; C=C 1670 cm^{-1}

PMR: gem di Me's (6H, s, 1.0 ppm); CH_3-C=C(3H,s,1.60 ppm); CH_3-C=CCH_2OH(3H, s, 1.70 ppm); CH_2OH(2H, d, 4.02 ppm, J=6.5Hz) CH=C(1H,t,5.36 ppm,J=6.5Hz).

4) Preparation of Z -monocyclofarnesyl iodide(5a)

To a solution of 2 g(0.02 mole) cis-monocyclofarnesol(3) in 10 ml purified acetonitrile was added 1.5 g NaI(dry; 0.02 mole) and stirred for five minutes under a nitrogen(dry) atmosphere. To this was added with continued stirring, gradually, 2.16 g(0.02 mole) of chlorotrimethyl silane.

After addition the stirring was continued for half an hour at the end of which the reaction mixture was taken up in ether(5 ml x 3) and the combined extract washed successively with water, aq. $Na_2S_2O_3$(10 percent, 10ml x 2) and dried (Na_2SO_4). Evaporation of the ether at room temp. in vacuo affords the pure iodide(2.7 g, 90 percent yield). Due to extreme instability it had to be immediately taken up for photolysis.

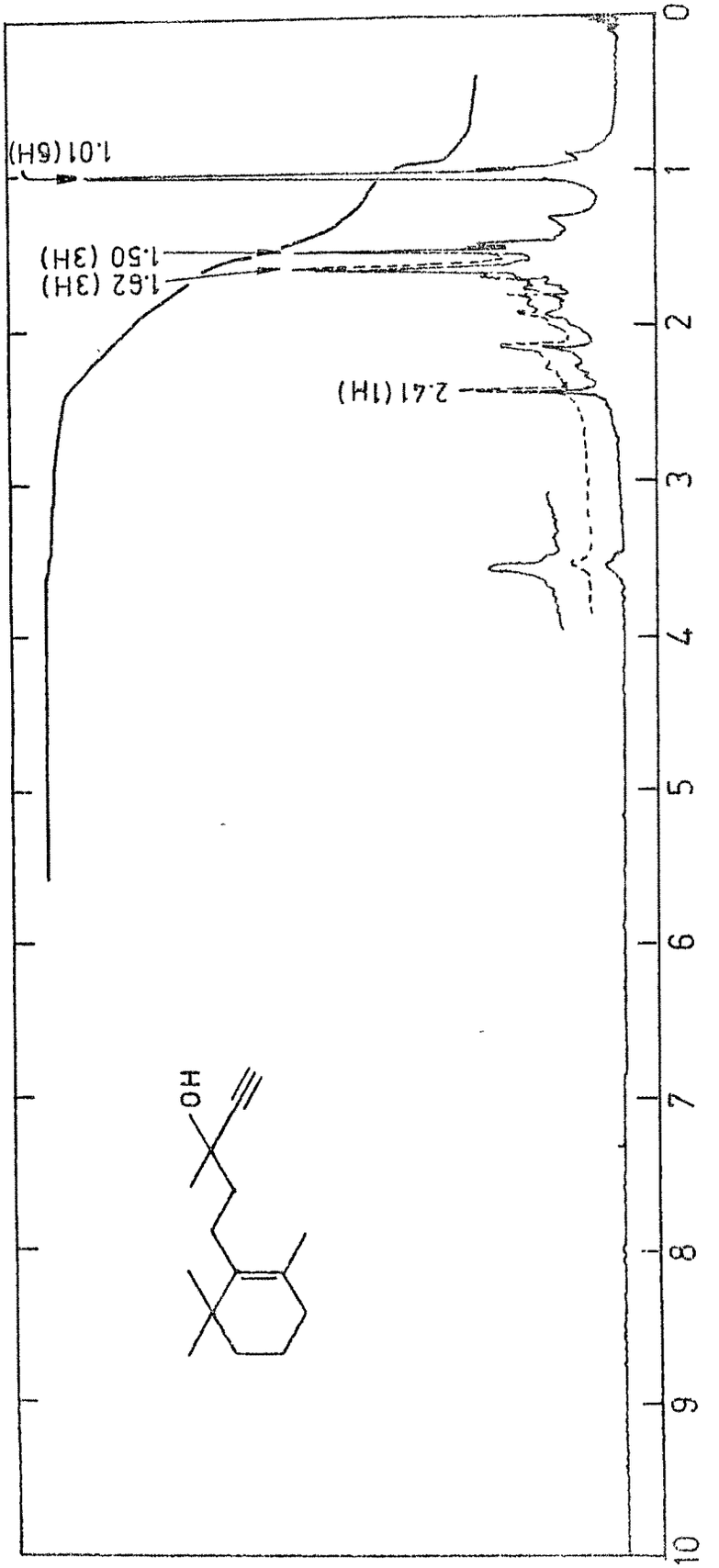
IR(CCl_4) : C=C 1648 cm^{-1}

PMR: gem di Me's (6H, s, 1.0 ppm); CH_3C=C(3H, s, 1.60 ppm); CH_3-C=CCH_2OH(3H, s, 1.70 ppm); CH_2I(2H, d, 3.88 ppm, J=8.5Hz); HC=CΣlH, t, 5.56 ppm, J=9Hz).

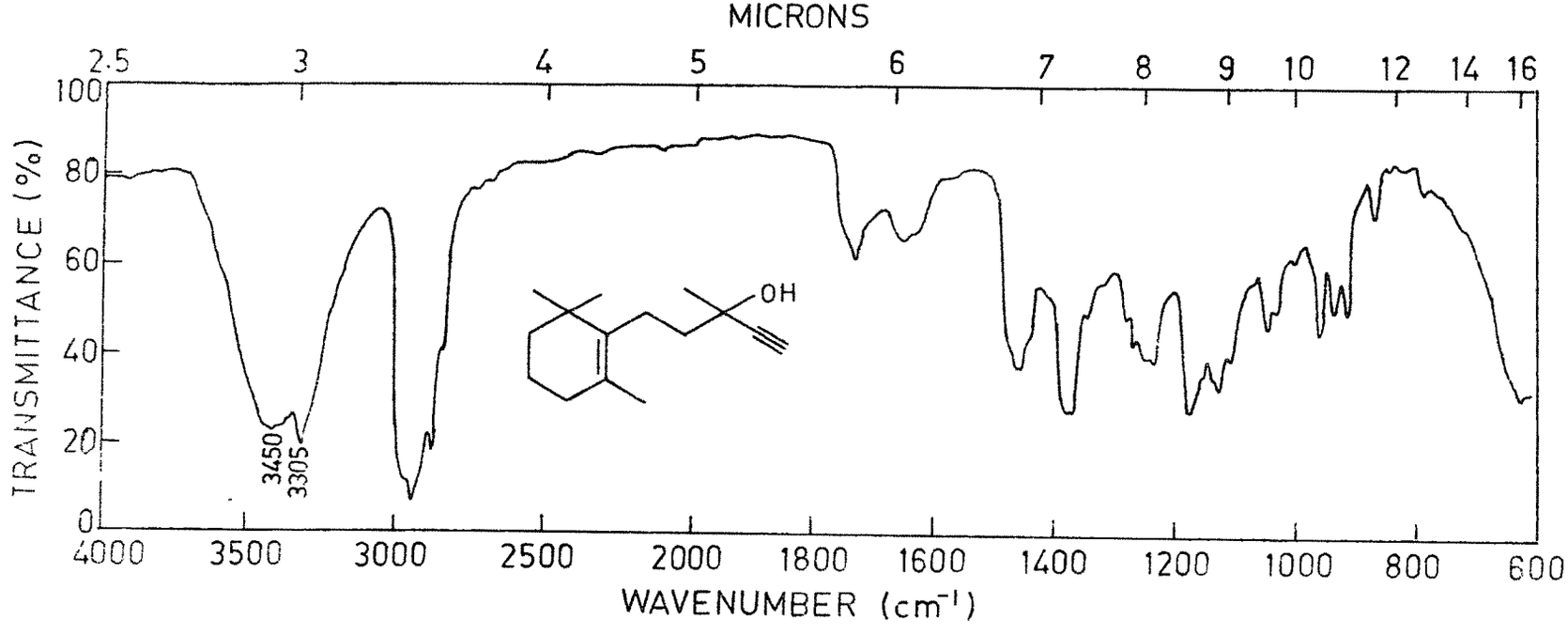
5) Photolysis of Z -monocyclofarnesyl iodide(5a)

A solution of 2.5 g(0.01 mole) cis-monocyclofarnesyl iodide(5a) and 1.0 g(0.01 mole) Et_3N in 250 ml dry, peroxide free THF was irradiated with a 400 W, medium pressure mercury vapour lamp at 50° under a blanket of nitrogen for 2.5 hr when the photostationary state was reached(TLC, pet.ether). The solvent was carefully stripped off, the residue dissolved in a minimum amount of pet.ether and eluted through a short column of silica gel(1.5 x 40 cm,IIA).

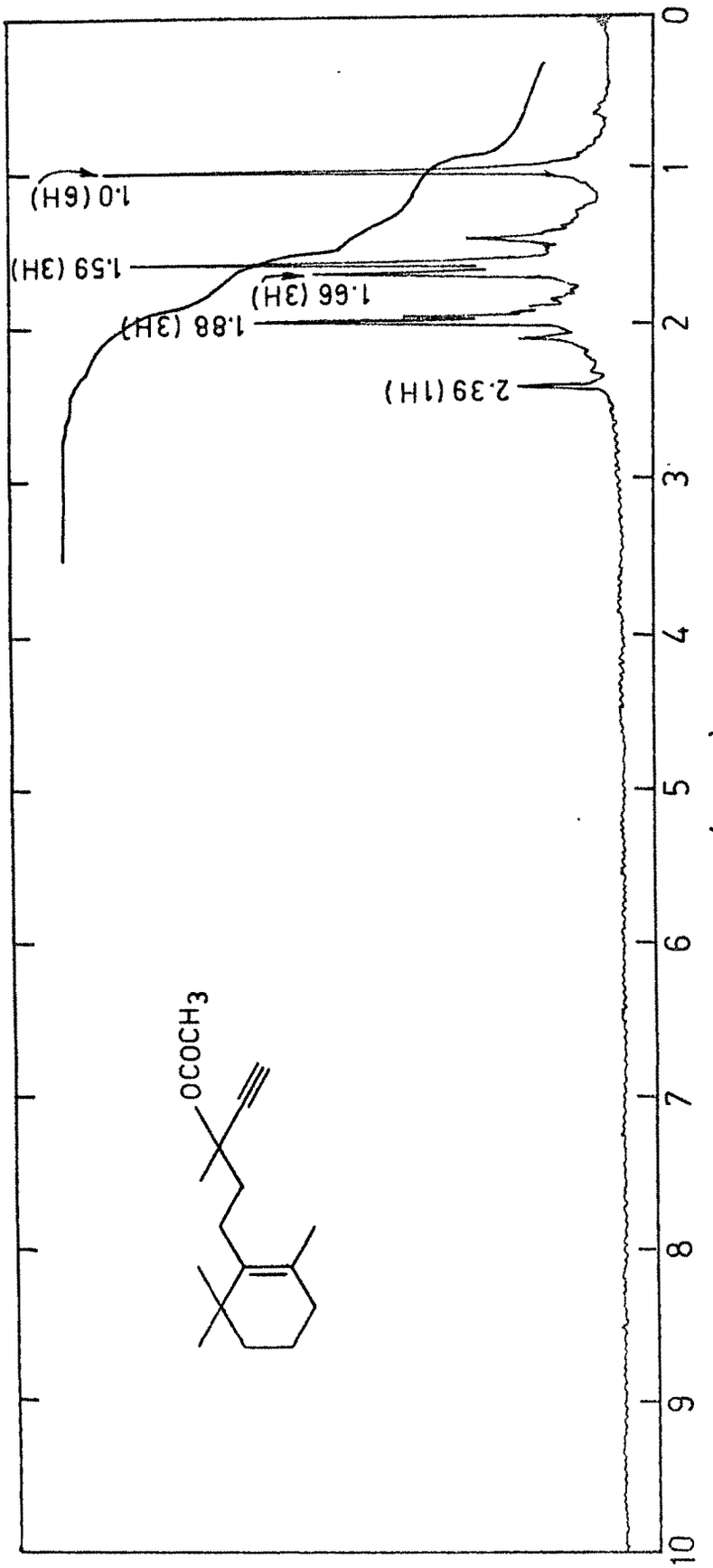
The pet.ether eluate was collected, washed with water, aq.$Na_2S_2O_3$(5 percent, 20 ml x 2) and brine. It was dried(Na_2SO_4) and then evaporated to give a residue(1.46 g) which was distilled (bp 100-110°(bath)/3 mm) to give 1.1 g(70 percent) of a pale yellow distillate and a residue of 0.3 g. A GLC analysis of the distillate (10 percent CW and SE-30, 170°) showed a very complex mixture of atleast fifteen compounds. PMR of the mixture did not show any traces of α- or β- chamigrene even on amplification.



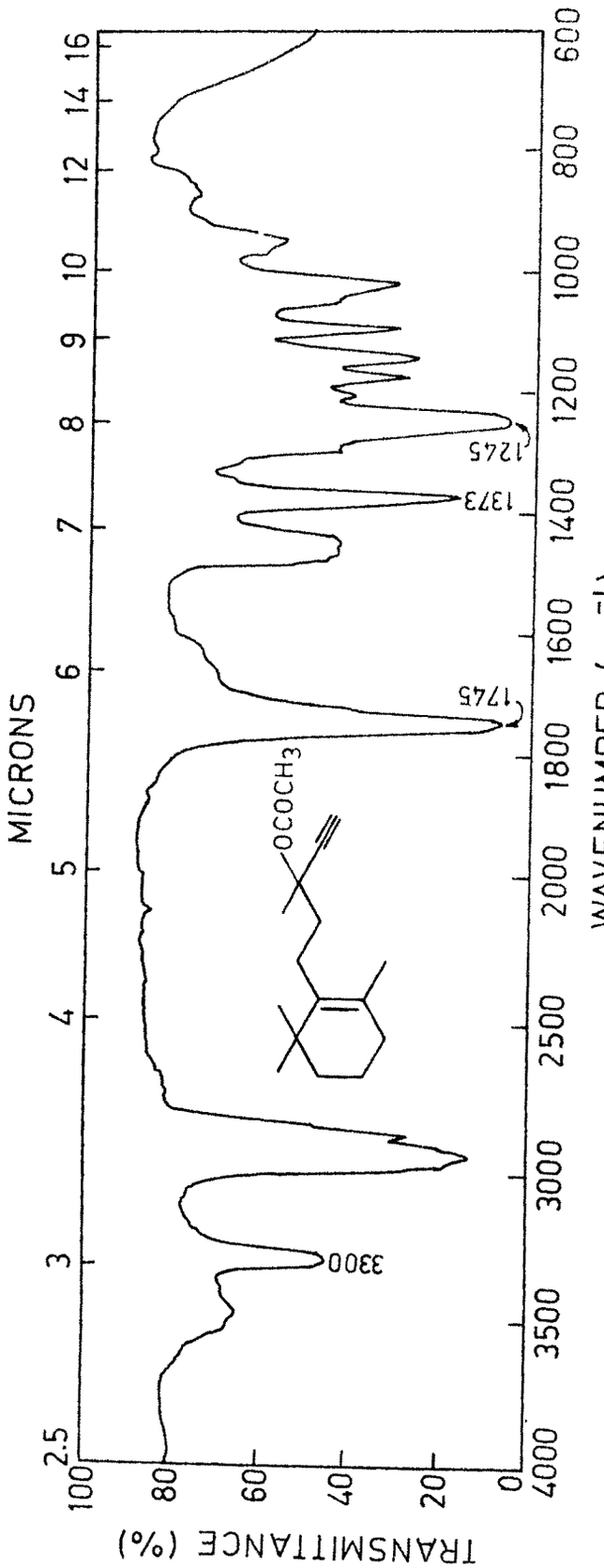
Sp.1a: PMR spectrum of the acetylene addition product(12)



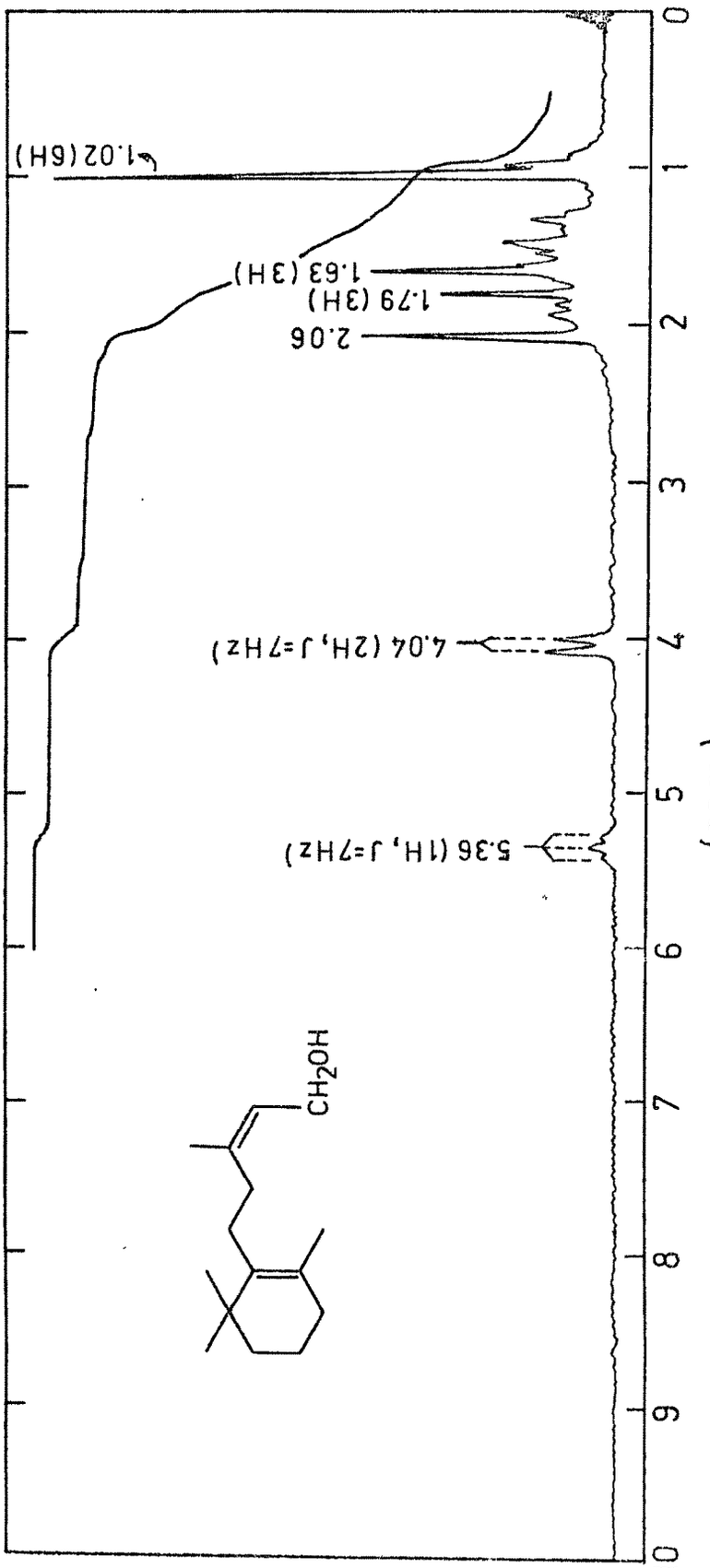
Sp. 1b: IR spectrum of the acetylene addition product(12)



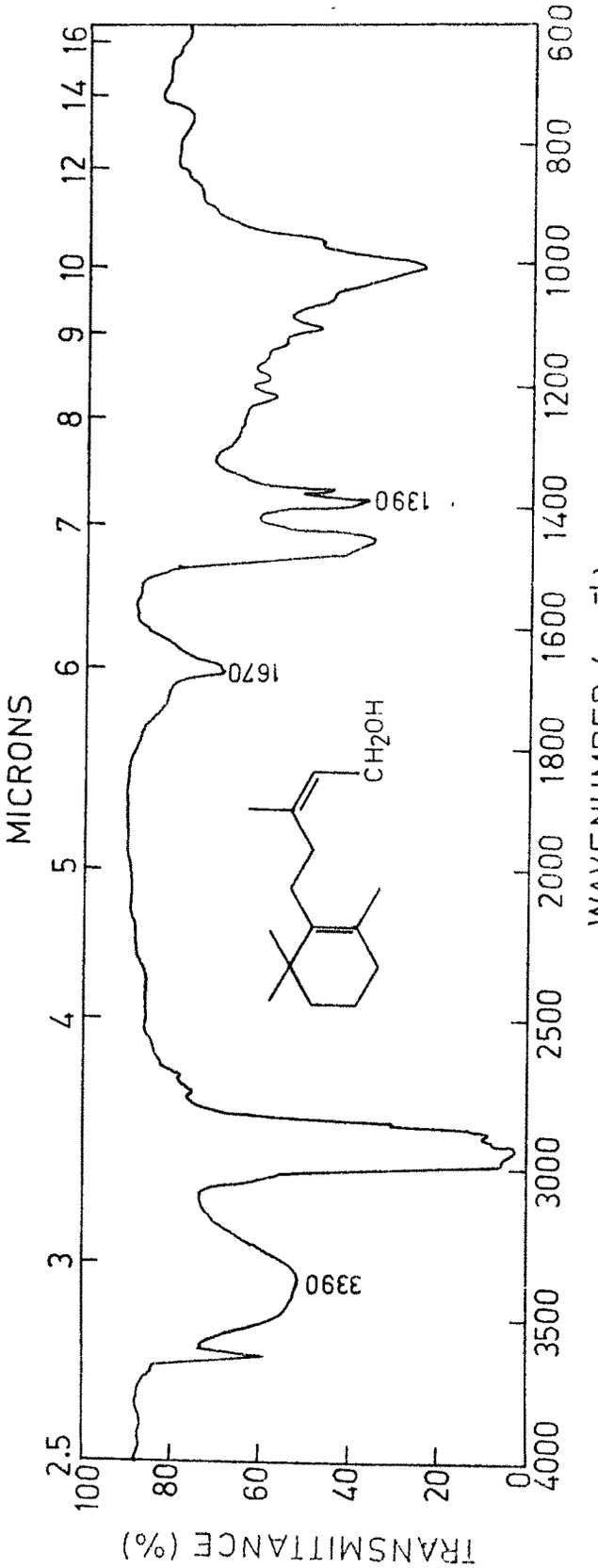
Sp. 2a: PMR spectrum of the acetate (13)



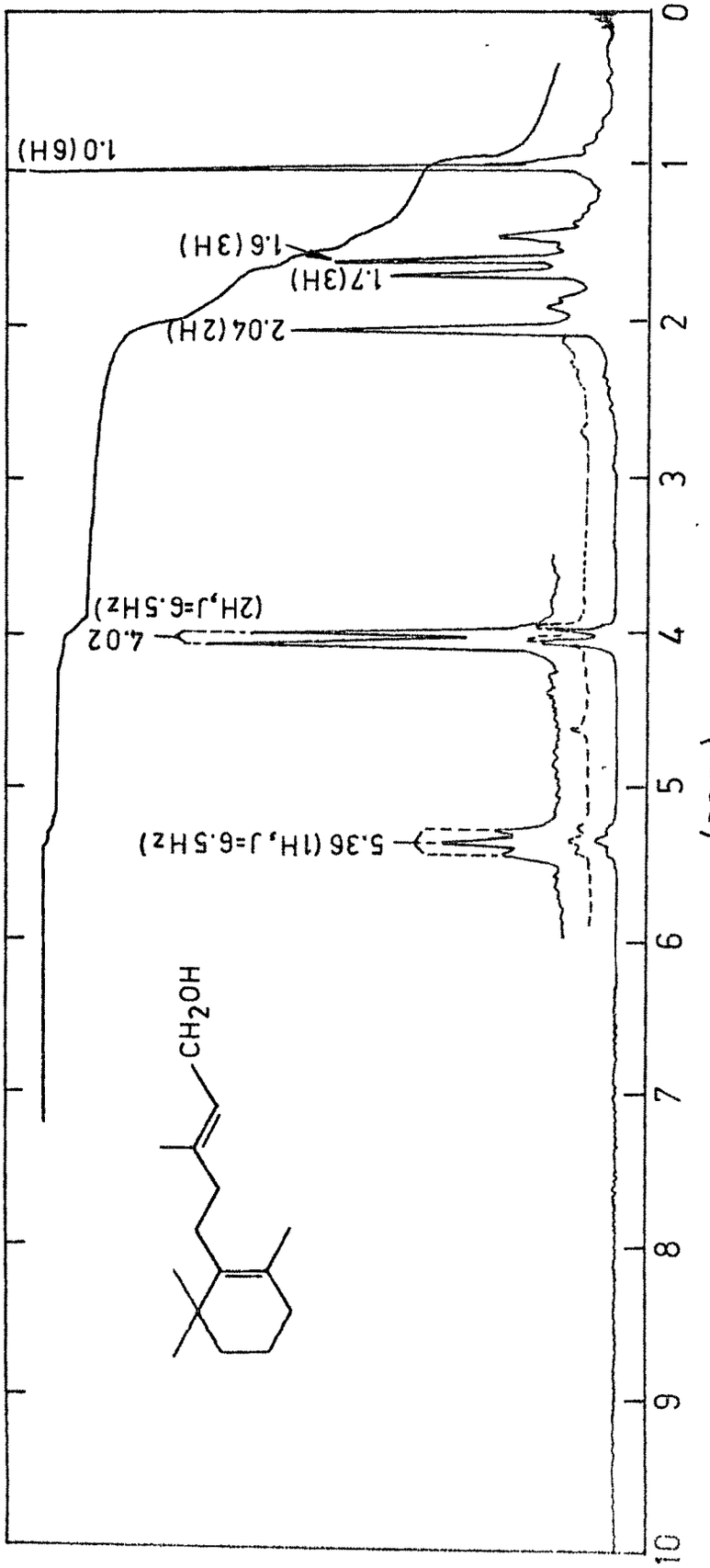
Sp.2b: IR spectrum of the acetate(13)



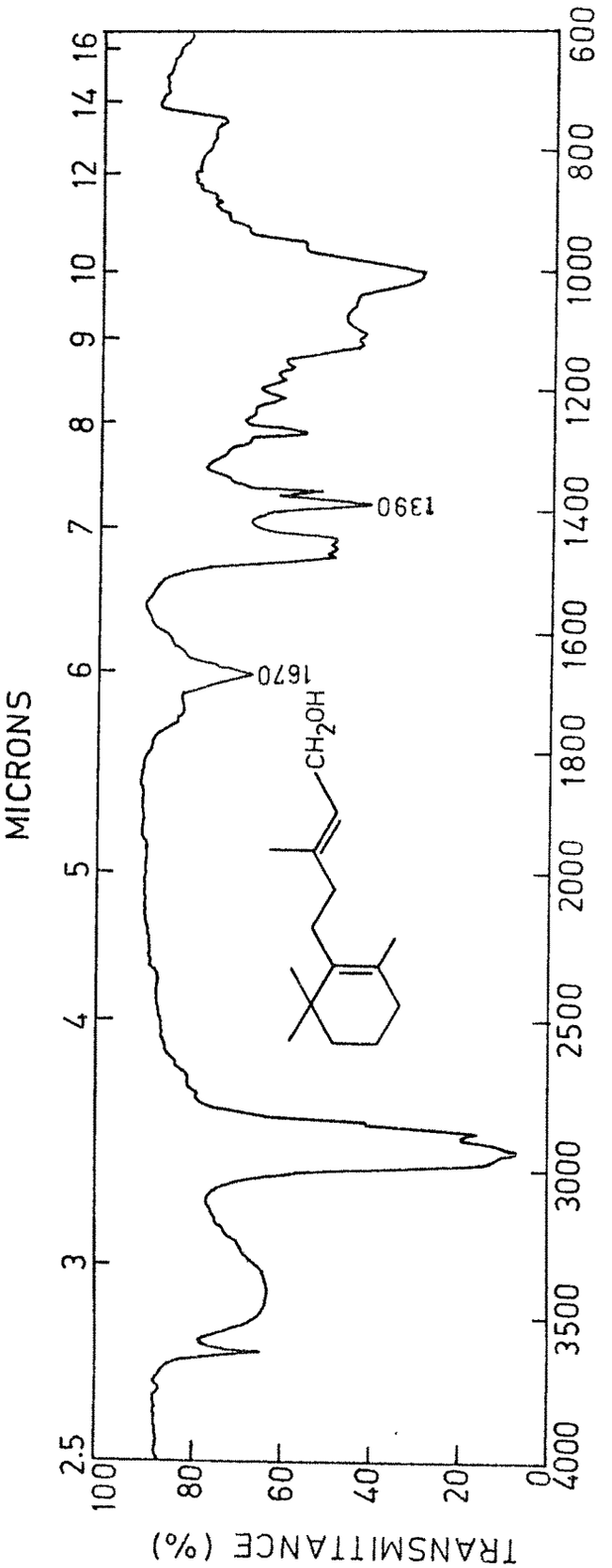
Sp.3a: PMR spectrum of Z-Monocyclofarnesol



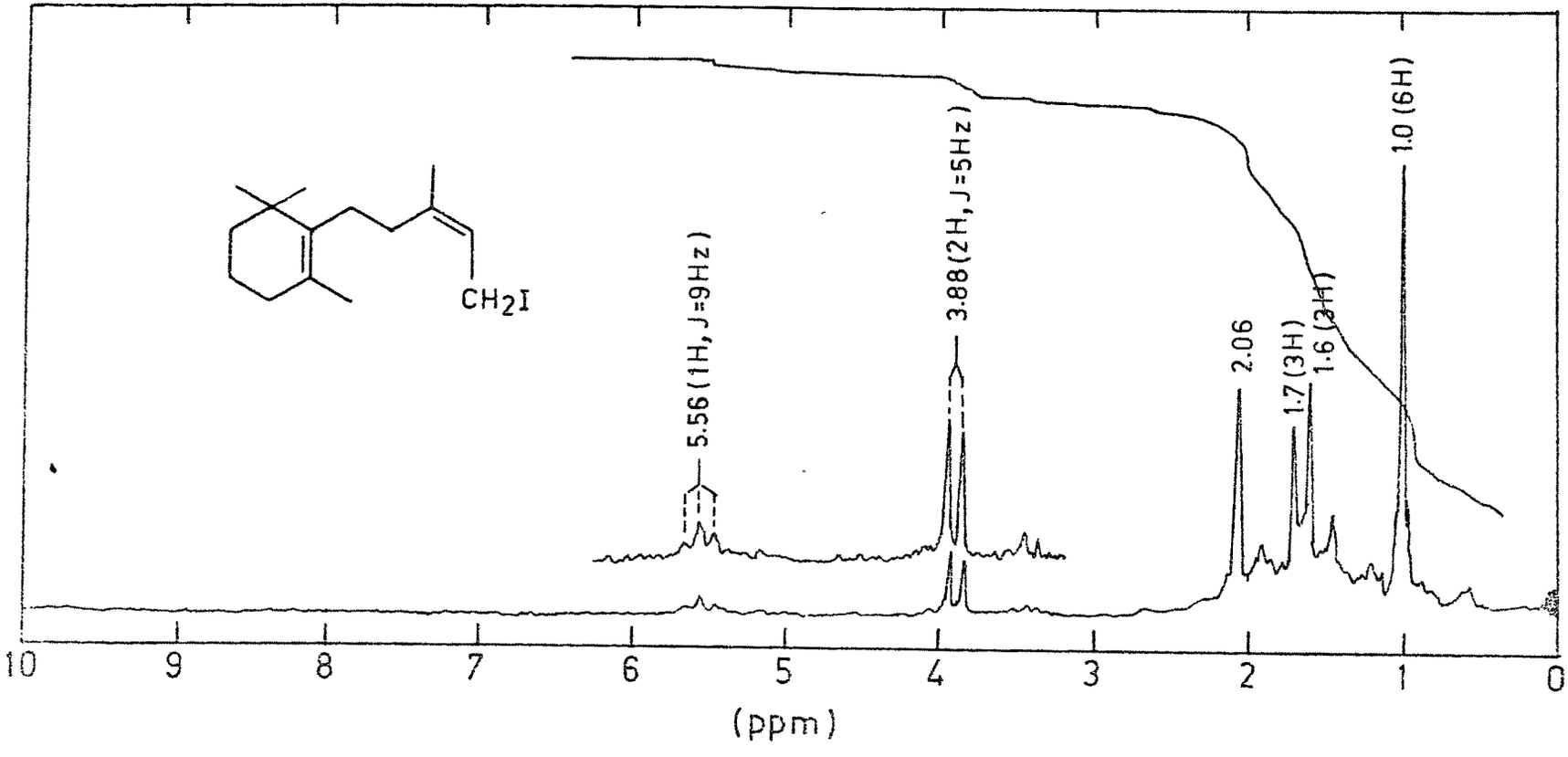
Sp.3b: IR spectrum of Z-Monocyclofarnesol



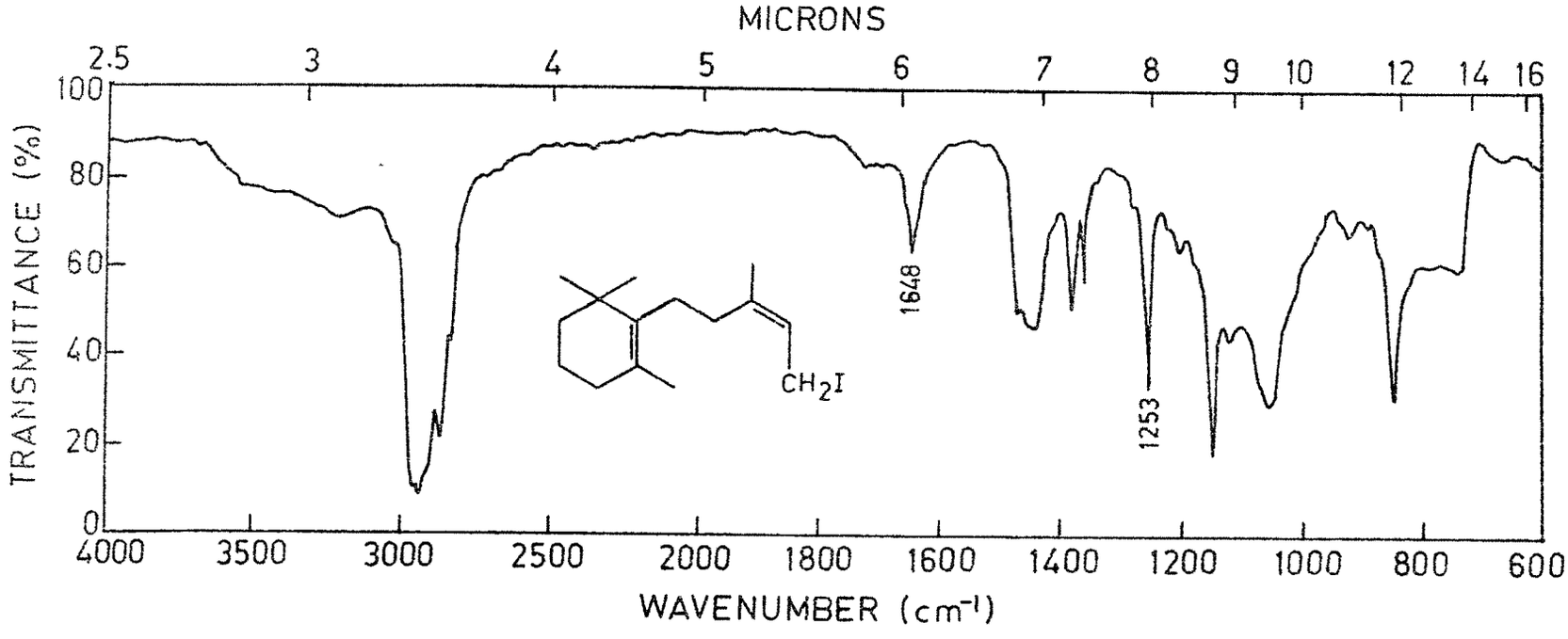
Sp.4a: PMR spectrum of E-Monocyclofarnesol



Sp.4b: IR spectrum of E-Monocyclofarnesol



Sp.5a: PMR spectrum of Z-Monocyclofarnesyl Iodide(5a)



Sp.5b: IR spectrum of Z-Monocyclofarnesyl Iodide(5a)

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