CHAPTER III

A NOVEL FRAGMENTATION REACTION AND ITS APPLICATIONS

A NOVEL FRAGMENTATION REACTION AND ITS APPLICATIONS

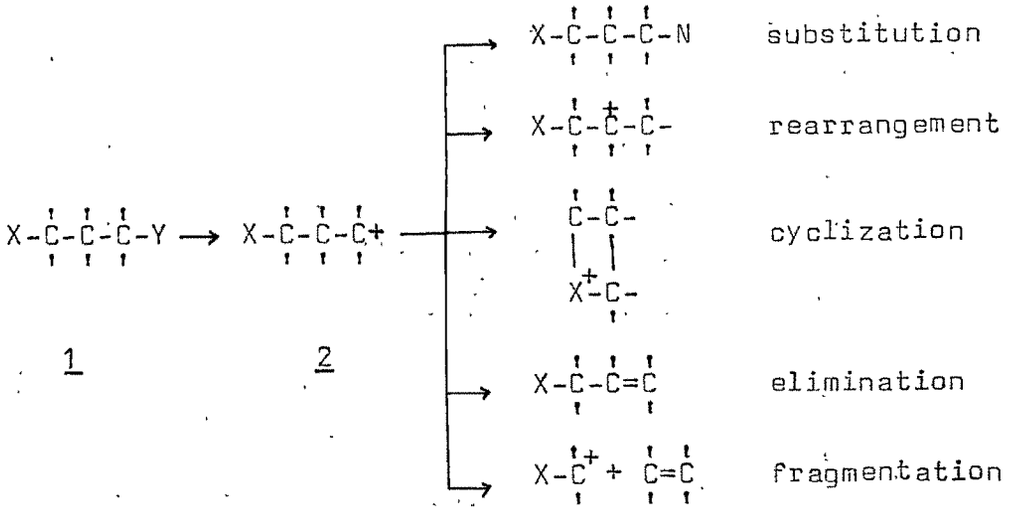
Abstract

A new fragmentation reaction of homoallylic alcohols into carbonyl compounds and allylic halides/alcohols has been demonstrated. Synthesis of a sesquiterpene alcohol, seco-longifolene diol[4], is described by utilization of this fragmentation reaction.

A NOVEL FRAGMENTATION REACTION AND ITS APPLICATIONS

1. INTRODUCTION

The carbonium ion 2 formed during the solvolysis of systems such as 1 (where Y is a leaving group) may quench itself by undergoing substitution, rearrangement, cyclization, elimination or fragmentation. Fragmentation predominates



1 2 3

in cases where $X-\overset{+}{C}$ (3) moiety is highly stabilized by X which may be oxygen, sulphur, or nitrogen atoms carrying unshared pair

of electrons or a carbanion or even olefinic or aryl grouping. Carbonium ion, 2, is easily generated from the corresponding halides, sulfonates, ammonium, diazonium, oxonium or sulphonium groups.

Fragmentation of the above type leading to the formation of alkenes and alkynes will be discussed illustratively rather than exhaustively

1.1. Alkene Forming Fragmentations

The cleavage of carbonium ions into smaller cationic fragments was recognized as early as 1933 as a possible secondary reaction of carbonium ions[1] but the reaction has gained importance comparatively recently only and has been reviewed by Grob[2,3]. A number of other reports[4-23] have also appeared later. The reaction can be illustrated by following examples.

γ-Hydroxy or amino halides or tosylates are solvolysed under suitable conditions to undergo fragmentation to give olefins and carbonyl compounds. For instance, bicyclic γ-hydroxytosylate 4 is cleaved to 5 when treated with strong bases like potassium tert. butoxide, the reactive species being the anion[24] 5a (Chart I).

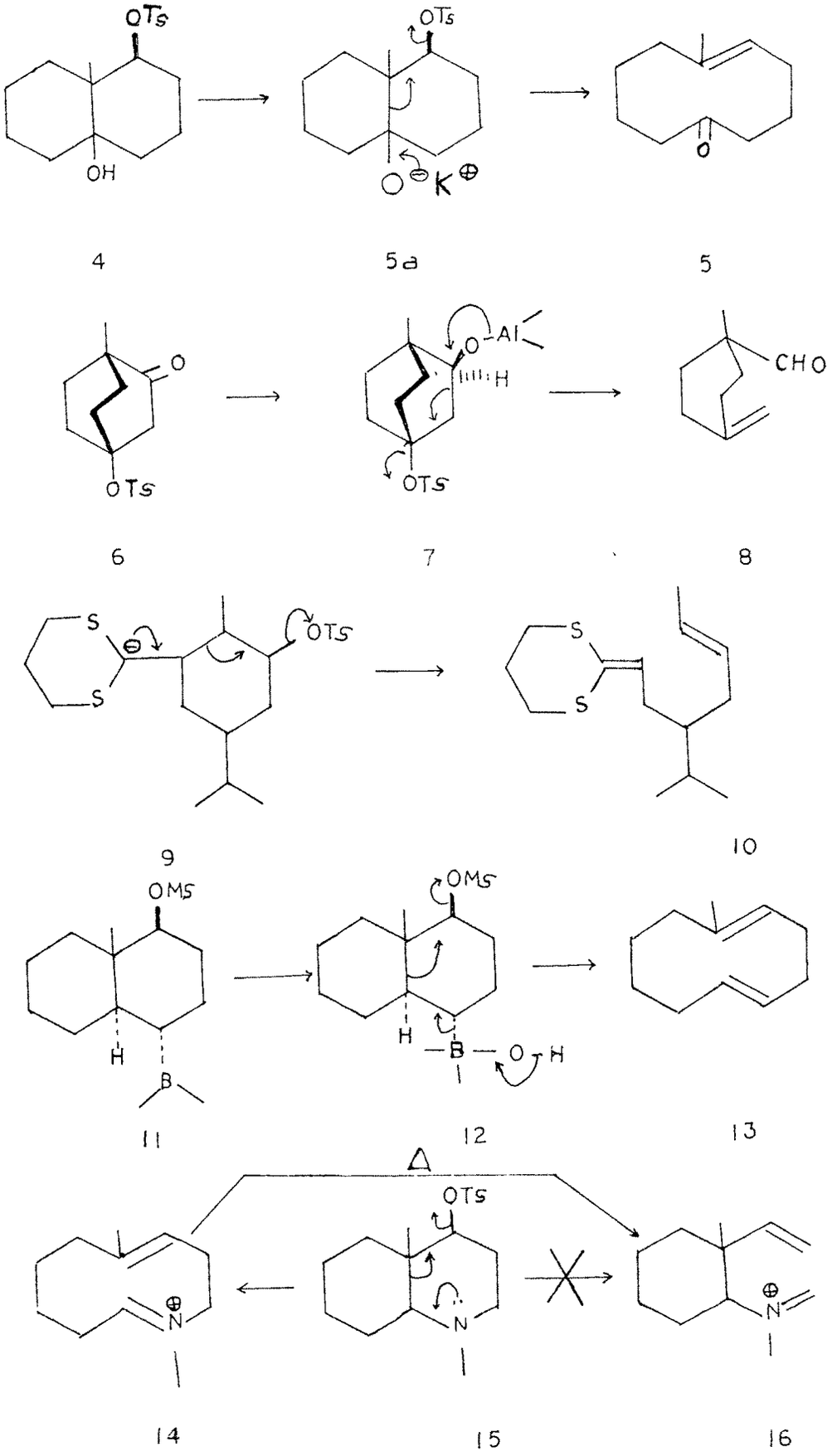

OTs
OH
OTs
O⊖K⊕
O
4
5a
5
O
OTs
6
O-Al
H
OTs
7
CHO
8
S
S
⊖
OTs
S
S
9
10
OMs
H
B
11
OMs
H
B
O
H
12
13
Δ
OTs
⊕N
N
14
15
16

CHART I

Attempted reduction of 4-methyl-3-oxo-bicyclo [2,2,2] octanyl-1-tosylate(6) with lithium aluminium hydride (LAH) results in its fragmentation to 4-methylene-cyclohexane derivative (8) (reduced further to corresponding alcohol) formed via anion 7 which is an intermediate in the reduction[7] (Chart I).

Thioketal 9 when treated with a strong base, fragments to 10. The necessary requirement for the cleavage to occur is the generation of an electron source at the carbon three bonds away from the cationic carbon[19] (Chart I).

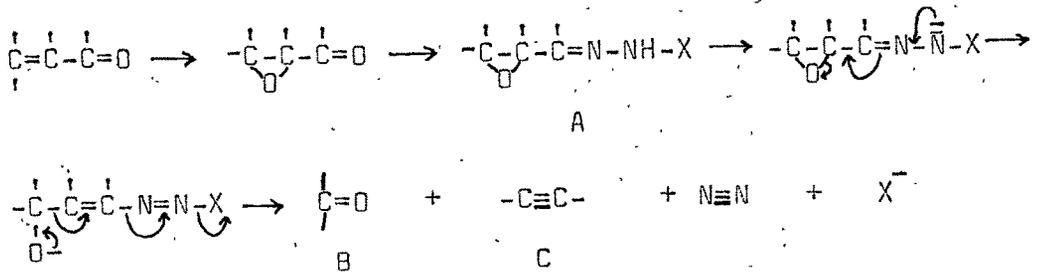
Marshall and coworkers have demonstrated through a series of papers[25-27], the application of fragmentation reaction for the sythesis of medium-sized rings. Homoallylic sulphonate on hydroboration gives the boronate derivative 11, which cleaves on being refluxed with sodium hydroxide, to diene 13. Bicyclo mesylate boronate ester 11 undergoes more substituted internal cleavage to give cyclodecane system[26]. This is in contrast to fragmentation of decahydroquinolyl tosylate 15 to cyclohexane derivative 16, which occurs through an external cleavage[28].

Marshall and coworkers[27] have later established that the fragmentation of decahydroquinolyl tosylate 15 occurs through

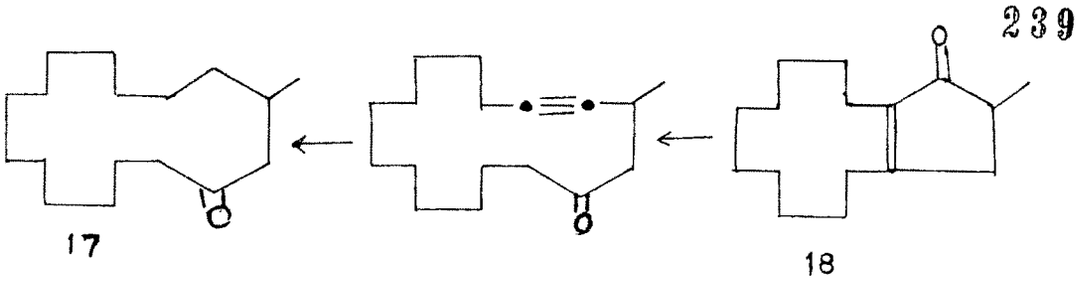
an internal cleavage to 14 which undergoes a 'Cope rearrangement' to give the ultimate product 16. A sharp contrst has been observed in the fragmentation of hydroxyboronate esters by intramolecular hydroxyl participation[29].

1.2. Alkyne Forming Fragmentation

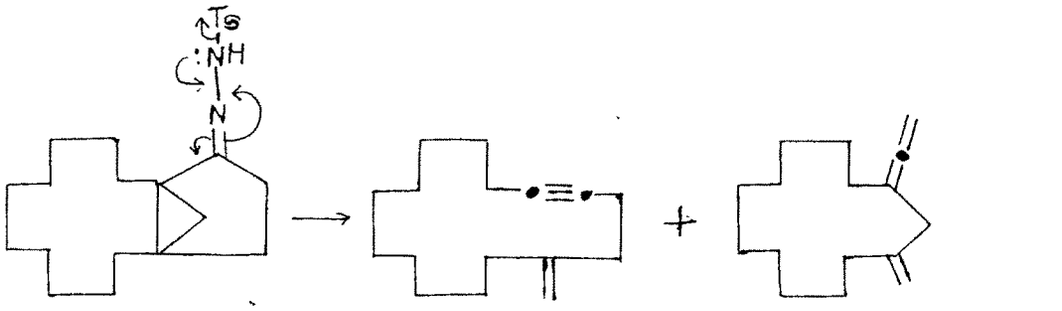
These fragmentations are not as common as the olefin forming fragmentations. In general α,β-unsaturated-β-halo-acids or carbonyl compounds eg. β-bromocinnamic acid[30] and β-chloroacrolein[31] constitute common precursors which fragments to corresponding alkyne on treatment with strong base. Recently, interesting fragmentation of α,β-epoxyketone derivatives (oximes or tosylhydrazones) of the type A→B and C (given below) in presence of a mild base have been reported[32-35].



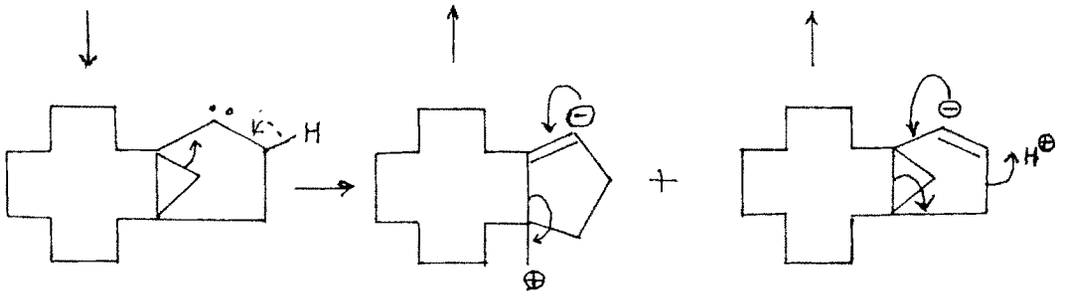
Muskone 17 has been synthesized from 18 using above sequences of reactions[32] (Chart II).



17 18



19 20 21



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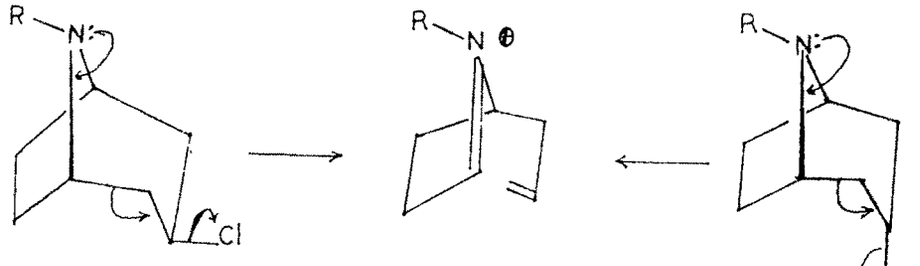
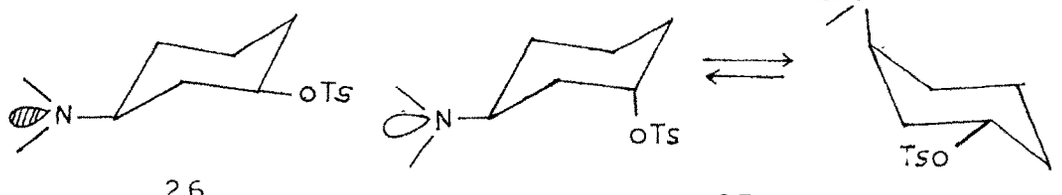


23 R = Me
24 R = H

25



26 27

Tricyclic tosylhydrozone 19 on treatment with base fragments to monocyclic alkyne 20 and allene 21; the mechanism for the formation of 20 and 21 have been proposed via carbene intermediate[36] 22.

1.3. Stereoelectronic Requirements for Fragmentation

3,β-Chlorotropane 23 and 3,β-chloronortropane 24 undergo fragmentation but their α-isomers 25 fail to fragment. It is concluded[37] that fragmentation is synchronous and requires that leaving group and β,γ -bond to be anti to one another. This is further illustrated by the observation that cis-dimethylaminocyclohexyl p-toluene sulphonate (26) is solvolysed about 12 times faster than its trans-isomer 27. Also, conversion in fragmentation is 99% in the former compared to 28% in the latter[38]. The details of stereoelectronic requirement or other factors responsible for fragmentation are discussed elsewhere[3].

Based on the rate of solvolysis of decahydroquinoline derivatives it has been demonstrated that it is necessary for lone pair on the nitrogen as well as the leaving group to be antiperiplanar to the fragmenting bond[39].

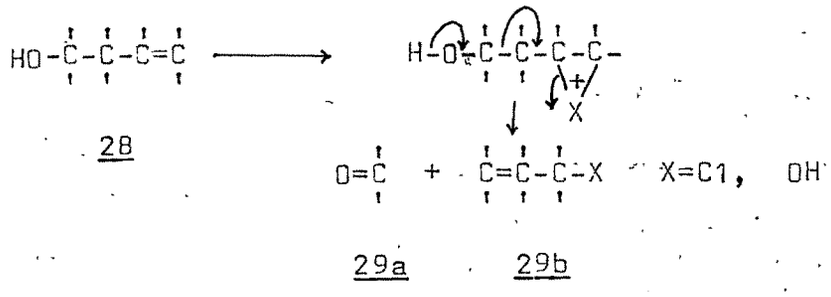
1.4. Synthetic Utility of Fragmentation Reactions

These fragmentation reactions have been put to wide applications and were used for the synthesis of many natural products, eg. caryophyllene, himachalene, juvenile hormone etc.[17,40].

2. CLEAVAGE OF HOMOALLYLIC ALCOHOLS - A NOVEL FRAGMENTATION REACTION

2. Introduction

In the last section we have described some common type of fragmentation which a carbonium ion of the type X-C-C-C$^+$ (2) undergoes. In most cases 2 is generated by the solvolysis of corresponding halides, tosylates or the like. We wish to report a related, yet novel, cleavage of homoallylic alcohols where an electron deficient site is created by electrophilic addition of chlorine on the olefinic bond or acid-catalysed ring opening of the corresponding epoxide. In generalized terms the fragmentation can be depicted as follows (28 → 29a + 29b)



28

29a 29b

This cleavage was first encountered while studying reactions of 30. This cleavage differs from Grob fragmentation[2,3] in producing allylic halides or alcohols instead of olefins and in appropriate cases this can be of distinct value for synthetic operations. The cleavage is thus interesting and potentially useful.

2.1. Results & Discussion

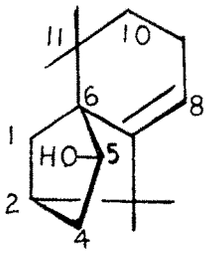
The fragmentation has been studied in homoallylic alcohols 30, 31 and 32. Treatment of alcohol*[41] 30 in carbon tetrachloride with molar equivalent of chlorine in presence of excess lithium carbonate gave a product in almost quantitative yield, which was homogeneous on TLC and PMR (Fig. 1). The PMR spectrum of this product shows four quaternary Me's each as singlets at 0.99, 1.00, 1.01 and 1.03 ppm. and a broad signal at 4.56 ppm (W_H = 7 Hz) and a triplet at 9.78 ppm (J = 1.5 Hz). Its IR spectrum (Fig. 9) shows a carbonyl frequency at 1730 cm^{-1} and an absorption at 2720 cm^{-1} assignable to an aldehyde function. This product gives strong yellow color with TNM indicating the presence of a double bond. This product is unstable and even at room temperature (~30°) slowly tends to decompose to a coloured mass. Its properties had to be studied in CCl_4 soln only, as attempts at purification through distillation or chromatography (SiO_2 or Al_2O_3) led to decomposition. Based on the mechanistic consideration and spectral data, the

*Preparation of this alcohol from isolongifolene is described in Part A, Chapter II.

product can be assigned structure 33. The stereochemistry of C-Cl bond in 33 follows from the known propensity for endo attack (with reference to norbornyl part) in isolongifolene derivatives[42]. Such an approach could lead to chloronium ion type intermediate 42 or an ion pair of the type 43. It is unlikely that chloronium ion 42 will undergo ready cleavage because bond a and bond b involved in fragmentation are syn-clinal[43] (dihedral angle $\sim 50^{0}$) rather than antiperiplanar[3,40c]. It is more probable that the reaction intermediate is the ion pair 43, which undergoes fragmentation fast enough to preclude the formation of any elimination and/or rearranged products.

In order to get more information about its structure, it was treated with lithium carbonate in aq. dioxane under nitrogen, where a mixture of epimeric alcohols 34 and 35 with the latter predominating was obtained (IR: OH 3440, CHO 2705, 1720 cm^{-1}). The epimeric nature of hydroxyaldehydes 34 and 35 was revealed by oxidizing them to a single α,β-unsaturated ketoacid.37 λ_{max}(EtOH), 250.5 nm, (ϵ 15150) (Chart III).

Acid catalysed cleavage of epoxide 36 gave the hydroxy-aldehyde 35 partially epimerized to 34, together with small amounts of dehydrated product 38. The formation of both epimers,[13] rather than only 34, is ascribed to acid-catalysed epimerization



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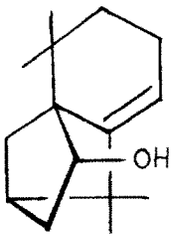

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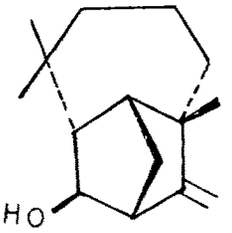

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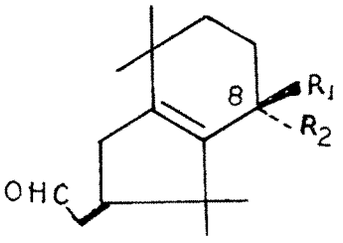
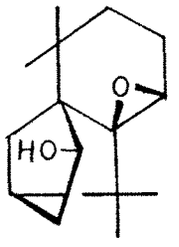


33 R_1=Cl R_2=H
34 R_1=OH R_2=H
35 R_1=H R_2=OH



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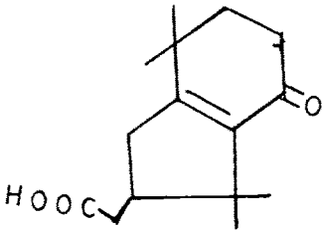

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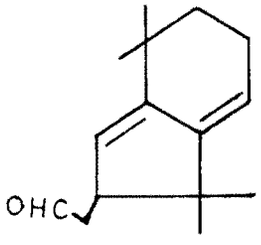

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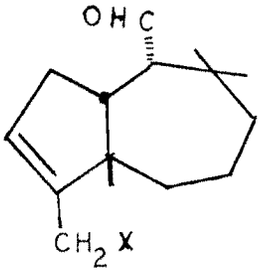
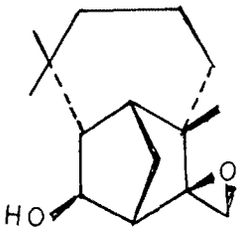


39 X=Cl
41 X=OH



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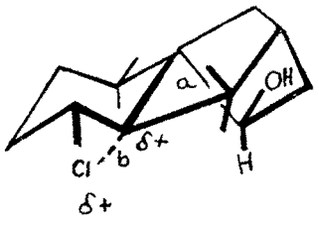

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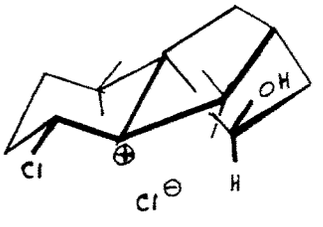

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CHART III

(to some extent) at C-8 under the reaction condition. Even in epoxide 36, the fragmenting bond a is not antiperiplanar with respect to bond b in oxirane ring. It is therefore reasonable to assume that the reaction is not concerted and an intermediate analogous to 43 is first formed, which undergoes fragmentation.

Similarly, the homoallylic alcohol* 32 on exposure to Cl_2 yielded (~90%) the expected chloroaldehyde 39 (PMR: four quaternary Me's 0.97, 1.05, 1.18 ppm; $C\underline{H}_2Cl$, bs, 4.01 ppm; $C{=}C\underline{H}$ broad signal, 5.72 ppm, W_H = 9Hz; $C\underline{H}O$, d, 9.80 ppm, J = 4 Hz, IR: CHO, 2705, 1705 cm^{-1}), while the derived epoxide 40 on acid cleavage furnished (~95%) the anticipated hydroxyaldehyde 41.

The substrates investigated for this fragmentation reaction, in the present study, are all based on bicyclo[2,2,1]heptane system. Work is in progress to determine the geometrical requirements, if any, for this reaction and to delineate its scope. Configuration of the OH group, appears to be inconsequential as the epimeric alcohol 31 fragments with equal ease to give the same product.

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*This compound has been synthesized from longicyclene; the details are reported in next section and we call this alcohol as Neolongifol-1-ol.

3. SYNTHESIS OF NATURAL PRODUCTS - APPLICATION OF THE NOVEL FRAGMENTATION REACTION

Exploitation of the just uncovered fragmentation reaction in the synthesis of a monoterpene, α-campholene alcohol[44] (46) and a bicyclic sesquiterpene, secolongifolene diol[45] (47) is described in this section.

3.1. Synthesis of α-Campholene Alcohol (46)

α-Campholene alcohol 46 has been synthesized[46] from α-pinene oxide but recently it has been shown[44] to occur in essential oil of Juniperus communis L. We now describe the synthesis of this alcohol 46 in high yield from camphene alcohol* (44). 44 with chlorine in CCl_4, yielded quantitatively, chloroaldehyde 45 PMR spectrum (Fig. 5): two quaternary Me's each as singlets at 0.92, 1.12 ppm; CH_2Cl, bs, 4.04 ppm; C=CH broad signal, 5.76 ppm W_H= 6Hz; CHO, t, 9.75 ppm, J= 1.5 Hz; IR: CHO 2710, 1725 cm^{-1} . This chloroaldehyde was reduced with LAH to naturally occurring alcohol 46. Its spectral data were consistent with those reported for an authentic sample[49].

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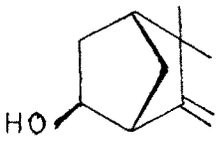
* 44 has been frequently synthesized[47,48] but isolated recently from Chrysanthenum japonense Makino and named as nojigiku alcohol[48b].



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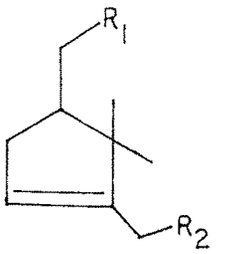
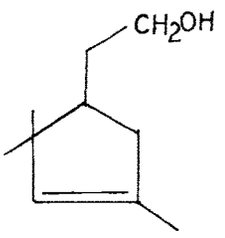


45 R_1=CHO, R_2=Cl
46 R_1=CH_2OH, R_2=H



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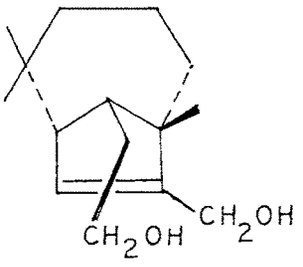

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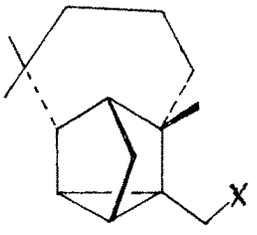
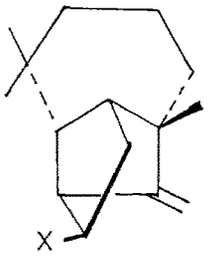
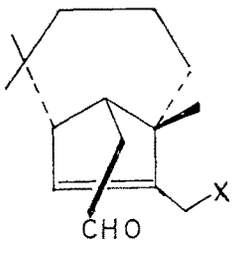


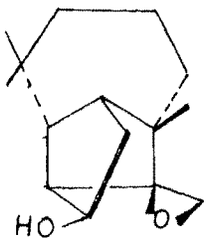
49 X=H
50 X=OH



51 X=OH
52 X=Br



53 X=OH
54 X=Cl



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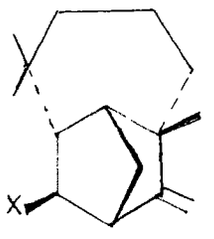
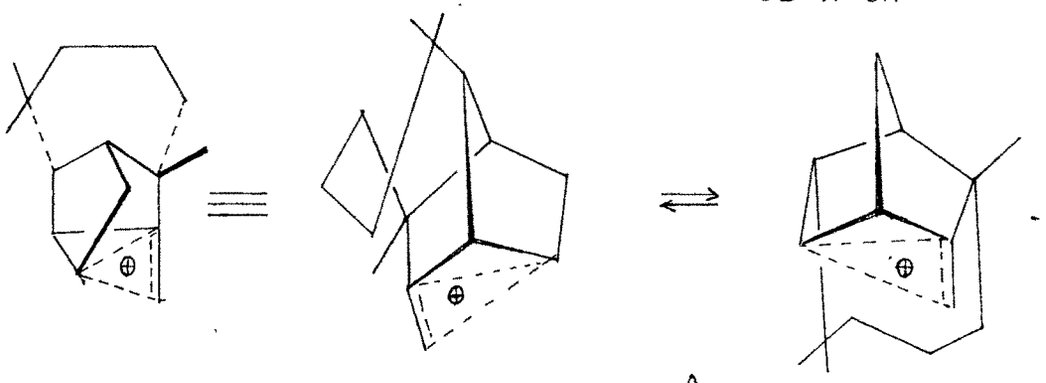


56 X=Br
32 X=OH



A

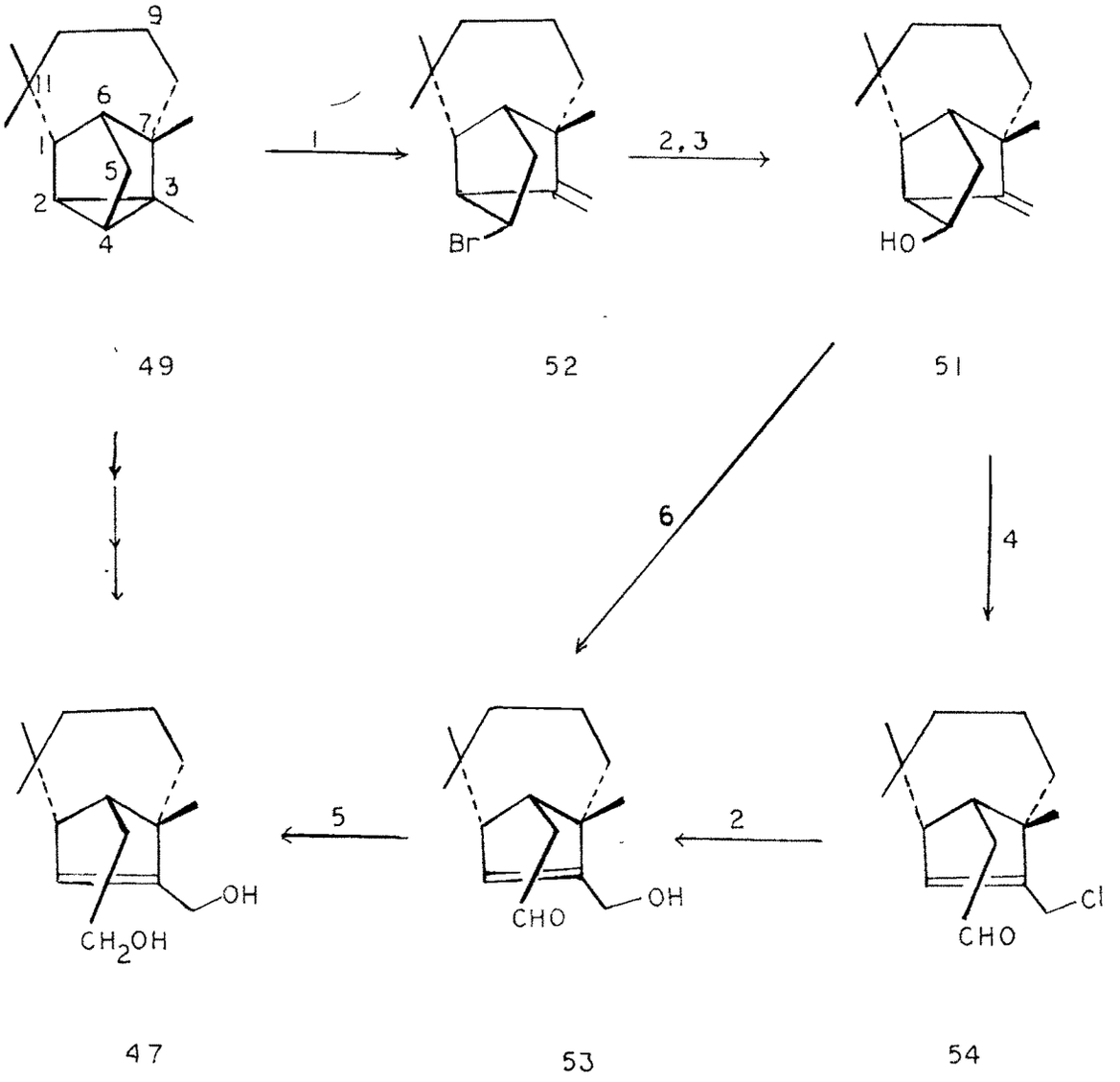
CHART IV

It may be emphasized here that this alcohol 46 has been previously prepared by reduction of α-campholene aldehyde derived from α-pinene epoxide. α-Pinene is known to undergo rearrangement to fenchane derivatives[50], and as a result, the isomeric 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde[51] (48) is always formed as a by-product in varying proportions. This fragmentation reaction precludes such a possibility and gives only the desired intermediate 45 in an excellent yield.

3.2. Biogenetic-type Synthesis of Secolongifolene diol (47)

Secolongifolene diol 47 has been recently isolated from Helminthosporium sativum and H. victoriae by Arigoni et al.[45] The structure of diol 47 has been assigned on the basis of spectral characteristics and its conversion to longifolene. The synthesis of this sesquiterpene has been achieved from longicyclene[52] (49) utilizing the aforementioned fragmentation as the key step.

Homoallylic alcohol 51 is a vital intermediate which is expected to undergo fragmentation with chlorine to produce 54; the latter through standard reactions could be easily transformed to diol 47. The synthetic scheme is delineated in Chart V.



1	$NBS-CHCl_3$	2	Li_2CO_3-aq. Dioxane
3	$HClO_4$ - aq Dioxane	4	Cl_2- Li_2CO_3
5	$NaBH_4$	6	$\Phi COOOH-H^{\oplus}$

CHART V SYNTHESIS OF SECOLONGIFOLENE DIOL (47)

In 1964, Sukh Dev et al.[47] reported an efficient method for opening of cyclopropane with N-bromosuccinimide. In the reaction of N-bromosuccinimide with longicyclene it was expected that the reagent will attack from the exo-side and preferably at the less hindered C-4 rather than C-2 (cf. Chart V). Indeed, homoallylic bromides 52 and 56 were formed in ratio of ca 4:1, which were inseparable on TLC and GLC but clearly distinguishable by their PMR spectra (Fig. 3). The separation of these two bromides in pure form was not attempted.

The structural assignment of the two bromides 52 and 56 was easily made on the basis of difference in splitting pattern of proton α to bromine atom in their PMR spectra. This proton in 52 appears as double doublet (J_1 = 4Hz, J_2 = 7.5 Hz) as expected from dihedral angles of 75°, 15° and 105°, which it subtends with vicinal protons. On the contrary, dihedral angles of proton α to bromine in 56 with two vicinal protons are 90 and 135° and it appears as illresolved doublet. These assignments are further borne out by the PMR spectra (Fig. 4 and 7) of the corresponding alcohols 51 and 32 respectively (Chart IV).

These bromides (52 and 56) on being refluxed with Li_2CO_3 in aq. dioxane for 24 hrs. yielded alcohols 32, 51 and 50 in approximate ratio of 2:3:15, along with an unidentified

alcohol (m.p. 129.5-131°). The solvolysis of bromides takes place with retention of configuration because of known preference of attack from the exo-side in bridge cations of the type A. This is indicated by the close resemblance of PMR spectra of bromides 52 and 56 and alcohols 51 and 32 respectively. But the major product of solvolysis is kinetically formed ψ-longifolol[53] (50), which can be easily derived from the carbonium ions A.

The unidentified alcohol (m.p. 129.5-131°) and 32 could be isolated pure by chromatography over silica gel by eluting them with benzene, but alcohols 50 and 51 were inseparable on ordinary silica gel column and eluted with 5% ethyl acetate in benzene. The equilibration of alcohols' mixture with .35% $HClO_4$ in 90% aq. dioxane at 45 ± 1 for 60 hrs resulted in increasing the proportion of alcohol 32, and to some extent, that of 51 at the expense of ψ-longifolol (50). The equilibration proved beneficial in two ways: (a) it provided substantial amount of alcohol 32 which was needed for separate study (described in above section) (b) it reduced proportion of ψ-longifolol (50) and made the separation of alcohols 50 and 51 easier over $AgNO_3$/silica gel chromatography. Required alcohol 51 was obtained pure in about 10-12% overall yield from longicyclene.

The alcohol 51 was converted to secolongifolene diol 47 in excellent yield by following sequence of reactions. Alcohol 51, on treatment with molar equivalent of chlorine solution, yielded chloroaldehyde 54 (PMR spectrum; Fig. 6), which on solvolysis with Li_2CO_3 in 90% aq. dioxane at 42° under nitrogen gave the hydroxyaldehyde 53 (Data vide Experimental), which was reduced with $NaBH_4$ to naturally occurring seco-longifolene diol (47), whose PMR spectrum (Fig. 8) was identical with the reported values[45] (vide Experimental)*.

The same hydroxyaldehyde 53 was also obtained by treatment of 51 with perbenzoic acid in toluene benzene mixture (1:4) at -5°. The intermediate epoxide 55 could not be isolated. In analogy[54] with longifolene, epoxidation should take place from its endo face of the bornyl part and endo epoxide, being unstable, instantaneously opens to hydroxyaldehyde 53. The extraordinary labile character of 55 is understandable in view of the known properties of longifolene epoxide[56]. The yield of reaction is only moderate, as hydroxy aldehyde undergoes further oxidation.

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* Longicyclene used for the synthesis was partially racemized. Therefore all the intermediates in the scheme are also optically impure and hence the difference in the rotation and m.p. of the final product. Work is in progress to get(-)-secolongifolene diol(47)using optically pure starting material.

Arigoni *et al.*[45] have indeed implicated the fragmentation of a hypothetical precursor longifolene epoxide in the proposed biogenesis of secolongifolene diol (47) from longifolene.

It seems plausible that genesis of longifolene alcohol (51) from longifolene is mediated through ψ-longifolol (50), formed from longifolene by epoxidation and rearrangement, which may be isomerized to longifolene alcohol (51) by an *in vitro* reaction parallel to acid catalyzed equilibration of alcohol's mixture 32, 51 and 50 discussed above.

Our results thus constitute first biogenetic-type synthesis of secolongifolene diol (47)

4. EXPERIMENTAL

For general remarks see Part B, Chapter I of this Thesis.

4.1. Preparation of Homoallylic Alcohols

4.1.1. 5, exo-Hydroxyisolongifolene (30)

The preparation of this alcohol is described in Part A, Chapter II, Section 6.3.4 of this Thesis.

4.1.2. 5, endo-Hydroxyisolongifolene (31)

To a stirred slurry of LAH (300 mg) in ether (30 ml) was added dropwise, a solution of 5-oxo-isolongifolene* (1.2 gm) in ether (25 ml) during 15 min. It was stirred for additional half an hour and excess of LAH was destroyed by adding water (0.5 ml). It was worked up by adding 15% aq. NaOH (0.5 ml) followed by addition of water (0.5 ml). Inorganic materials were filtered off and washed with ether (10 ml x 2). Solvent removal gave a residue (1.2 gm) which was chromatographed over silica gel (IID, 50 gm, 1.5 x 45 cm):

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*For preparation of this ketone see Part A, Chapter II, Section 6.3.5. of this Thesis.

Frac. 1	pet ether	(50 ml)	nil
Frac. 2	50% benzene in pet ether	(25 ml x 3)	950 mg,
Frac. 3	50% benzene in pet. ether	(25 ml x 1)	31 mg mixture rejected.
Frac. 4	benzene	(2 ml x 2)	100 mg, solid. m.p. 82-85° characterized as 30

Frac. 2 was distilled to get pure 31 (900 mg), which, on standing, crystallized (m.p. 48.5-49.5°). IR (neat): OH 3455, 1120, 1080, 1040, C=CH, 870, 840, 810 cm^{-1}; PMR: $-\overset{|}{C}-$Me each as singlet at 0.79, 0.99, 1.03, 1.11ppm; CHOH (1H, dd, 4.05 ppm, J_1 = 3Hz, J_2 = 8.5 Hz), =CH (1H, t, 5.56 ppm, J = 3.5 Hz). Microanalysis: $C_{15}H_{24}O$ requires C, 81.76; H, 10.98; found C, 81.49; H, 10.59%.

4.1.3. Camphene Alcohol (44)

This alcohol was prepared from tricyclene according to the procedure reported by Sukh Dev et al.[47]

4.1.4. Homoallylic Alcohols (32) and (52)

4.1.4.1. Action of N-Bromosuccinimide on Longicyclene (49):

A mixture of longicyclene (49) (4.08 gm; 20 mmol) and NBS (3.6 gm, 20 mmol) in alcohol free, purified chloroform[55] (50 ml) was refluxed on a waterbath for 2 hr under N_2. When the NBS was consumed (tested with KI soln), it was cooled to room temperature and succinimide was washed with water (20 ml x 3) and dried. Removal of solvent gave a yellow coloured liquid (5.8 gm) which was distilled to give bromides (52) and (56) (5.5. gm) in ratio of 4:1 respectively. IR (liq): (total bromides): C=CH-1640, 880, 815, 750 cm^{-1}. PMR: -$\overset{|}{C}$-Me each as singlet at 0.96, 0.96, 1.04 ppm, CH_2=$\overset{|}{C}$-C$\underline{H}$- (1H, bs, 2.88 ppm, W_H = 5Hz), C$\underline{H}$Br (1H, dd, 3.84 ppm, J_1= 4Hz, J_2= 7.5 Hz), =CH_2(1H, s, 4.72 ppm, 1H, s, 5.02 ppm); these values are assigned for bromide (52). The bromide (56), which was present as a minor product, was characterized by its one signal at 3.80 ppm, J= 4Hz (C$\underline{H}$Br) and two singlets at 4.70 and 4.99 ppm for exo-methylene protons. Microanalysis (total bromides): $C_{15}H_{23}Br$ requires C, 63.60; H, 8.18; Br, 28.21; found C, 64.38; H, 8.23; Br, 27.50%.

4.1.4.2. Action of aq. Li_2CO_3 on Bromides (52) and (56)

A mixture of bromides (5.0 gm) and Li_2CO_3 (2.3 gm) in 50% aq. dioxane (60 ml) was plunged in an oil bath at 95 ± 2° and stirred at same temperature for 48 hours. The reaction mixture was brought to room temperature, diluted with 2% aq.

AcOH (50 ml) and extracted with ether (30 ml x 3). The organic extracts were washed with water (20 ml x 3) and dried (Na_2SO_4). Removal of solvent offered a gummy residue (4.3 gm). A portion (1.2 gm) of this residue was chromatographed over silica gel (IIB, 40 gm, 1.5 x 38 cm) with tlc monitoring (SiO_2, solvent 5% EtOAc in C_6H_6).

Frac.	1	pet ether (20 ml x 3)	200 mg, a mixture of bromides & hydrocarbon rejected.
Frac.	2	50% benzene in pet ether (20 ml x 1)	nil
Frac.	3	50% benzene in pet ether (20 ml x 3)	110 mg, solid, m.p. 109-115°.
Frac.	4	50% benzene in pet ether (20 ml x 2)	50 mg mixture
Frac.	5	50% benzene in pet ether (20 ml x 3)	150 mg, solid m.p. 155-165°.
Frac.	6	50% benzene in pet ether (20 ml x 1)	10 mg, gummy
Frac.	7	benzene (50 ml)	610 mg gummy material.

Frac.3 was crystallized (MeCN) upto constant m.p. 129-131° (55 mg). Its structural elucidation will be published elsewhere.

Frac. 5 was crystallized (MeCN) to give needles of alcohol 32

(m.p. 171.5-172.5°, 100 mg). IR ($CHCl_3$): OH 3580, 1015, C=CH 882 cm^{-1}. PMR (Fig. 7): -$\overset{|}{\underset{|}{C}}$-Me each as singlet at 1.02, 1.04, 1.04 ppm; CH_2=$\overset{|}{C}$-$\overset{|}{C}$H- (1H, bs, 2.56 ppm, W_H = 8Hz); CHOH (1H, d, 3.80 ppm, J= 5Hz); =CH (1H, s, 4.55 ppm; 1H, s, 4.91 ppm). Microanalysis: $C_{15}H_{24}O$ requires C, 81.76; H, 10.98; found C, 81.77; H, 11.00%.

Frac. 7 was homogeneous on SiO_2-gel tlc but showed two compounds on $AgNO_3$-SiO_2 plate. This fraction was chromatographed over silica gel containing 15% $AgNO_3$ (30 gm, 1.2 x 35 cm).

Frac. 1	50% benzene in pet ether	(10 ml x 2)	nil
Frac. 2	50% benzene in pet ether	(10 ml x 3)	408 mg, solid m.p. 68-72°.
Frac. 3	50% benzene in pet ether	(10 ml x 1)	40 mg mixture
Frac. 4	benzene	(10 ml x 3)	108 mg, solid m.p. 82-86°

Frac. 2 was crystallized (MeCN) to give alcohol (50) (m.p. 76-77.5°, 320 mg). Its IR and PMR were superimposable with those of the authentic sample[53].

Frac. 4 was crystallized (MeCN), to give alcohol (51) (m.p. 88-92°, 50 mg). IR($CHCl_3$): 3450 cm^{-1}. PMR (Fig. 4): ($CDCl_3$):

-C(Me)- each as singlet at 0.92, 0.92, 1.01 ppm; CH_2=C(Me)-CH-(1H bs, 2.61 ppm, W_H= 8Hz); CHOH (1H, dd, 3.81 ppm, J_1 = 4Hz, J_2= 8Hz); =CH (1H, s, 4.70 ppm, 1H, s, 4.90 ppm). Microanalysis: $C_{15}H_{24}O$ requires C, 81.76; H, 10.98; found C, 81.42; H, 11.27%.

4.1.4.3. Action of aq. $HClO_4$ on ψ-Longifolol (50)

To a mixture of alcohols 32, 51 and 56 (2.1 gm) obtained from the solvolysis of bromides was introduced to a 0.35%* solution of $HClO_4$ in aq. dioxane (40 ml) and kept at 45 ± 1° 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% aq $NaHCO_3$ (70 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). A part of the residue obtained (1.4 out of 1.8 g) was chromatographed over silica gel (50 gm, 1.5 x 45 cm).

Frac. 1	pet ether	(25 ml)	nil
Frac. 2	50% benzene in pet ether	(10 ml x 3)	110 mg, liquid.
Frac. 3	50% benzene in pet ether	(10 ml x 1)	nil

*0.35% aq. $HClO_4$ was prepared by adding 70% $HClO_4$ (0.5 ml) to dioxane (90 ml) and water (10 ml). This solution was used for our studies in this chapter.

Frac. 4	75% benzene in pet ether	(10 ml x 4)	150 mg, solid m.p. 116-121°.
Frac. 5	75% benzene in pet ether	(10 ml x 2)	60 mg, mixture
Frac. 6	benzene	(10 ml x 3)	400 mg, solid m.p. 160-167°
Frac. 7	benzene	(10 ml x 2)	50 mg, mixture gum.
Frac. 8	5% EtOAc in benzene	(20 x 2)	520 mg, gummy material.

Frac. 2 was distilled to give an aldehyde. IR (liq.): CHO 2700, 1720, C=CH 1640, 878, 815 cm^{-1}, PMR: $-\overset{|}{C}-\underline{Me}$ each as singlet at 0.99, 1.06, 1.06 ppm; $CH=C\underline{Me}$ (3H, t, 1.65 ppm, J = 2Hz); $=C\underline{H}$ (1H, b.sig, 5.50 ppm, W_H= 7Hz); $C\underline{H}O$ (1H, dd, 9.76 ppm; J_1=Hz, J_2= 3Hz); on the basis of these spectral data it was assigned the structure 53 (where X = H, instead of OH).

Frac. 4 was crystallized (MeCN) to get an alcohol (m.p. 129-131°) whose structure will be published later.

Frac. 6 was crystallized (MeCN) to get pure alcohol (32) (m.p. 171.5-172.5°, 350 mg).

Frac. 8 was rechromatographed over silica gel containing 15% $AgNO_3$ (24 gm, 1.1 x 35 cm^{-1}).

Frac. 1	50% benzene in pet ether	(20 ml x 2)	nil
Frac. 2	50% benzene in pet ether	(10 ml x 3)	205 mg, solid m.p. 72-76°
Frac. 3	50% benzene in pet ether	(10 ml x 2)	10 mg gum
Frac. 4	benzene	(10 ml x 3)	235 mg solid 80-85°

Frac. 2 and 4 were characterized as alcohols (50) and (51) respectively as described above.

4.2. Cleavage of Homoallylic Alcohols

4.2.1. Fragmentation of 5,exo-Hydroxyisolongifolene (30)

To a cooled soln. (ice-salt bath, internal temp. -5 ± 2°) of homoallylic alcohol (30) (660 mg, 3 mmol) in carbon tetrachloride (20 ml) containing Li_2CO_3 (610 mg, 9 mmol), was introduced a cold solution of chlorine (4.2%, 5 ml; 210 mg of chlorine; 3 mmol) during 5 min, keeping the temperature -5±3°. The yellow colour of chlorine was discharged immediately as the addition of Cl_2 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 (780 mg) of chloroaldehyde (33). IR (Fig. 9) (CCl_4): CHO 2730, 1730 cm^{-1}. PMR (Fig. 1): -C(Me)- each as singlet at 0.99, 1.0, 1.01, 1.03 ppm;

C<u>H</u>Cl (1H, b.sig, 4.56 ppm, W_H= 7Hz); C<u>H</u>O (1H, t, 9.78 ppm, J=1.5 Hz).

Similarly, 5-<u>endo</u>-hydroxyisolongifolene (<u>31</u>) (200 mg) was treated with 4.2% chlorine soln in CCl_4 (1.25 ml) under identical condition mentioned above. It gave chloroaldehyde (<u>33</u>) (210 mg) whose PMR and IR were identical with those of the product described above.

4.2.1.1. <u>Hydrolysis of Chloroaldehyde (33) with Li_2CO_3-aq.dioxane</u>

The chloroaldehyde (<u>33</u>) was stirred with Li_2CO_3 (580 mg) in 50% aq. dioxane (20 ml) at 40 ± 1° for three hours under N_2 atmosphere and when all chloride was hydrolysed (monitored by tlc), it was cooled to room temperature (28 ± 2°). Li_2CO_3 was filtered off and washed with ether (10 ml x 2). The filtrate was diluted with water (10 ml) and extracted with ether (10 ml x 3). The ether layer was washed with water (10 ml x 2) and dried. The solvent removal gave a residue (613 mg) which was chromatographed over silica gel (IIIB, 15 gm, 1 x 25 cm).

Frac. 1.	pet ether (50 ml)	nil
Frac. 2	50% pet ether in benzene (25 ml x 2)	120 mg liquid.

Frac. 3	benzene	(25 ml x 1)	nil
Frac. 4	5% EtOAc in benzene	(25 ml x 4)	434 mg, viscous liq.

Frac. 2 was distilled b.p. 110-125° (bath)/0.5 mm, to give olefinic aldehyde 38 (100 mg); IR(liq.): CHO 2715, 1725 cm^{-1}, PMR: $-\underset{|}{C}-Me$ each as singlet at 0.90, 1.04, 1.05, 1.09 ppm; $=CH$ (1H, it 5.28 ppm, J = 4Hz; 1H, bs, 5.44 ppm, W_H = 3Hz); CHO (1H, t, 9.78 ppm, J= 1.5 Hz). UV: λ_{max} (EtOH) 245 nm (ϵ 8215).

Frac. 4 was homogeneous on tlc but it was a mixture of two alcohols 34 and 35 in which 35 dominated as shown by its PMR: $-\underset{|}{C}-Me$ each as singlet at 0.79, 0.89, 1.05, 1.13 ppm; CHOH (1H, b.sig 4.04 ppm, W_H= 8Hz); CHO (1H, t, 9.76 ppm, J= 1.5 Hz).

4.2.1.2. Oxidation of Hydroxyaldehydes (34) and (35)

Hydroxyaldehydes (34 and 35) (180 mg) were taken in acetone (1 ml) and cooled to 0°. To this cooled solution, Jone's reagent (0.5 ml) was added dropwise during five minutes and then the reaction mixture was kept at that temperature for one hour. The ketoacid (37) was extracted with ether (10 ml x 3) after diluting the reaction mixture with water (10 ml). The extracts were washed till neutral with water (10 ml x 2)

and dried (Na_2SO_4). The solid residue (m.p. 140-151°, 170 mg) was crystallized (acetonitrile) to get crystalline 37 (m.p. 162-164°, 120 mg). IR (Fig. 10) (Nujol): CO 1725, 1705 cm^{-1}. PMR (Fig. 2): ($CDCl_3$): -C(Me)- each as singlet at 0.96, 1.12, 1.18, 1.28 ppm. UV: λ_{max} (EtOH) 250.5 nm (ϵ 15150). Microanalysis: $C_{15}H_{22}O_3$ requires C, 71.97; H, 8.86; found C, 71.74, H, 8.87%.

4.2.1.3. Epoxidation of 5,exo-Hydroxyisolongifolene (30)

Perbenzoic acid (420 mg) in benzene (5 ml) was added dropwise to a precooled (25°) solution of alcohol 30 (490 mg) in 20% toluene in benzene (5 ml) and kept at -5 ± 1° for 48 hours. Then the reaction mixture was diluted with ether (15 ml) and benzoic acid was removed with 5% aq. $NaHCO_3$ (10 ml x 3). Excess of perbenzoic acid was removed by washing with 10% aq. $NaHSO_3$ (10 ml x 1). It was washed neutral and dried. Residue (480 mg), after removal of solvent was crystallized (pet ether) to get epoxide 36 (m.p. 102-103°, 400 mg). IR($CHCl_3$): OH 3610, 3495, 1040, epoxide, 3045, 1220, 880 cm^{-1}. PMR ($CDCl_3$): -C(Me)- 0.68, 0.94, 1.03, 1.10 ppm; CHOC (1H, t, 3.12 ppm, J= 4Hz); CHOH (1H, dq, 4.21 ppm, J_1=1.5 Hz, J_2= 3Hz, J_3= 6.5 Hz). Microanalysis: $C_{15}H_{24}O_2$ requires C, 76.22; H, 10.24; found C, 75.94; H, 10.09%.

4.2.1.4. Action of $HClO_4$ on Epoxide 36

To a solution of 0.35% $HClO_4$ in 90% aq. dioxane (10 ml) at 10°C was introduced the epoxide 36 (315 mg) in one lot. The reaction mixture was stirred at the same temperature for 15 minutes, then quenched with 5% aq. $NaHCO_3$ (15 ml) and extracted with ether (15 ml x 3). The ether extracts were washed till neutral, with water (10 ml x 3) and dried (Na_2SO_4). The residue (312 mg) obtained was homogeneous on tlc but it was a mixture of hydroxyaldehydes (34) and (35), in which now 34 predominated. IR ($CHCl_3$): CHO 2705, 1720, OH 3440, 1020 cm^{-1}. PMR ($CDCl_3$): -C(Me)- each as singlet at 0.94, 0.97, 0.97, 1.00 ppm; CHOH (H, b.sig 4.21 ppm, W_H= 9 Hz); CHO (1H, t, 9.83 ppm, J= 1.5 Hz). This mixture of epimeric alcohols 34 and 35 after oxidation with Jone's reagent, gave the same ketoacid (37)

4.2.2.1. Cleavage of 2-Hydroxyneolongifolene (32)

To a cooled (-2 ± 1°) and agitated soln of alcohol 32 (220 mg, 1 mmol) in $CHCl_3$ (2 ml) containing Li_2CO_3 (210 mg, 3 mmol) was introduced a cold soln of 3.6% chlorine in CCl_4 (2 ml, 72 mg) during 3 minutes and stirred at the same temp. for 5 minutes. Inorganic salts were filtered off and washed with chloroform (1 ml x 2). Removal of solvent gave a residue

(255 mg) of chloroaldehyde (39). IR ($CHCl_3$): CHO 2705, 1705 cm^{-1}, PMR (CCl_4): $-\underset{|}{C}-\underline{Me}$ each as singlet at 0.97, 1.05, 1.28 ppm; $C\underline{H}Cl$(2H, bs, 4.01 ppm, W_H= 5 Hz), $=C\underline{H}$ (1H, b.sig, 5.72 ppm, W_H = 9Hz), $C\underline{H}O$ (1H, d, 9.80 ppm, J= 4Hz).

4.2.2.2. Cleavage of Epoxide (40)

To a cooled soln of alcohol 32 (70 mg) in a mixture of toluene and benzene (1:1, 2 ml) was introduced perbenzoic acid (5 mg) in benzene (0.6 ml) and kept at -5 ± 1^{o} for 4 days. Usual work up (described above) gave epoxide (40) (72 mg). PMR($CDCl_3$): $-\underset{|}{C}-\underline{Me}$ each as singlet at 0.89, 1.08, 1.08 ppm, $C\underline{H}OC$ (2H, ABq, 2.23, 2.44 ppm, J= 5 Hz), $C\underline{H}OH$ (1H, d, 4.07 ppm, J= 6Hz).

The above epoxide (40) (72 mg) was treated with 0.35% $HClO_4$ in aq. dioxane (5 ml) at 10 ± 1^{o} for 15 min. Usual work up (described above) gave hydroxyaldehyde (41). PMR($CDCl_3$): $-\underset{|}{C}-\underline{Me}$ each as singlet at 0.97, 1.05, 1.13 ppm; $C\underline{H}OH$ (1H, bs, 4.14 ppm, W_H= 6Hz); $=C\underline{H}$ (1H, b.sig, 5.50 ppm, W_H = 7Hz); $C\underline{H}O$ (1H, d, 9.91 ppm, J= 4.5 Hz).

4.3. Synthesis of Natural Products.

4.3.1. Synthesis of α-Campholene Alcohol (46)

A 4.2% soln of chlorine in CCl_4 (6 ml, 252 mg of chlorine, 3.6 mmol) was introduced to a cooled (-2 ± 1^{o}) and stirred soln of alcohol 44 (540 mg, 3.6 mmol) in CCl_4 (10 ml) containing Li_2CO_3 (500 mg) during 5 min. Usual work up (described above) gave chloroaldehyde (45). IR (Fig. 11) (CCl_4): CHO 2710, 1725, C=CH 885, 700 cm^{-1}. PMR (Fig. 5): $-\overset{|}{C}-Me$ each as singlet at 0.92, 1.12 ppm; CHCl (2H, bs, 4.04 ppm, W_H = 4Hz); =CH (1H, b.sig, 5.76 ppm, W_H= 6Hz); CHO (1H, t, 9.75 ppm, J= 1.5 Hz).

The above chloroaldehyde (45) (350 mg) in THF (10 ml) was added dropwise to a stirred slurry of LAH (250 mg) in THF (10ml) and stirred at room temperature (30 ± 1^{o}) for 36 hours under N_2. This excess of LAH was destroyed by adding EtOAc (1ml), followed by 15% aq. NaOH (0.5 ml) and water (1 ml). The inorganic salts were filtered off and washed with THF (5 ml x 2). Removal of solvent offered a residue (300 mg) which was distilled to give α-campholene alcohol (46), b.p. 110-115^{o} (bath)/2.5 mm, n_D^{25}1.4678. IR (liq.): OH 3340, 1050, C=CH 800 cm^{-1}. PMR: $-\overset{|}{C}-Me$ each as singlet at 0.76, 0.97 ppm; $-CH=\overset{|}{C}-Me$ (3H, m, 1.61 ppm); CHOH (2H, m, 3.59 ppm); =CH (1H, b.sig, 5.20 ppm, W_H= 8Hz). These spectral values are consistent with the value reported by Sukh Dev et al.[49]

4.3.2. Synthesis of Secolongifolene diol (47)

4.3.2.1. Action of Cl_2 on 4-Hydrolongifolene (51)

A 3.6% soln of chlorine in CCl_4 (0.4 ml, 14.4 mg of chlorine, 0.2 mmol) was introduced to a cold soln (-5 ± 1^{o}) of alcohol 51 (44 mg, 0.2 mmol) in CCl_4 (1 ml) in presence of Li_2CO_3 (100 mg) during 2 min and was stirred for 5 min. at the same temperature. Usual work up gave chloroaldehyde (54) (48 mg). IR (Fig. 12) (CCl_4): CHO 2700, 1715 cm^{-1}. PMR (Fig.6): $-\overset{|}{C}-Me$ each as singlet at 0.93, 0.97, 1.06 ppm, CHCl (2H, bs, 3.99 ppm, W_H= 4 Hz); =CH (1H, b.sig, 5.94 ppm, W_H= 7Hz); CHO (1H, t, 9.73 ppm, J= 2 Hz).

4.3.2.2. Hydrolysis of Chloroaldehyde (54)

Chloroaldehyde (54) (44 mg) was stirred with Li_2CO_3 (105 mg) in 90% aq. dioxane (5 ml) at 40 ± 2^{o} for 3 hours under N_2. The reaction mixture was brought to room temperature (30 ± 1^{o}), diluted with water (15 ml) and extracted with ether (10 ml x 4). The organic extracts were washed till neutral with water and dried. Then solvent was flashed off to get hydroxyaldehyde (53) (38 mg). IR($CHCl_3$): CHO 2705, 1715;

OH 3450 cm^{-1}. PMR: $-\underset{|}{C}-Me$ each as singlet at 0.92, 0.97, 1.01 ppm, CHOH (2H, bs, 4.08 ppm), =CH (1H, b.sig, 5.73 ppm, W_H= 7Hz), CHO (1H, t, 9.73 ppm, J= 2Hz).

4.3.2.3. Action of Peroxybenzoic Acid on Alcohol (51)

To a cooled soln of 4-hydroxylongifolene (51) (100 mg) in a mixture of toluene and benzene (1:1, 2 ml) was added perbenzoic acid (78 mg) in benzene (2 ml) and kept at -5 ± 1° for 3 days. The reaction mixture was diluted with ether (10 ml) and benzoic acid was extracted with 5% aq. $NaHCO_3$ (5ml x 4). The organic layer was washed, till neutral, with water (10 ml x 2) and dried (Na_2SO_4). The residue* (60 mg), obtained after removal of solvent, was purified to get hydroxyaldehyde (53) (30 mg), eluting with benzene through a column of silica gel (3 gm, 0.5 x 5 cm).

4.3.2.4. Secolongifolene diol (47)

A mixture of hydroxyaldehyde (53) (45 mg) and $NaBH_4$ (100 mg) in EtOH (5 ml) was stirred for 3 hrs at room temperature (32 ± 1°) under N_2. Then excess of $NaBH_4$ was destroyed by adding (15% aq. AcOH) (1 ml); then it was diluted with water

*The presence of epoxide 55 was not detected in the PMR spectrum of the residue.

(10 ml) and extracted with ether (15 ml x 3). The organic extracts were washed till neutral, with water (10 ml x 2) and dried. Solvent removal offered a residue (35 mg) which was crystallized from acetonitrile, m.p. 101-105° (reported[45] m.p. 117° for (+)- diol 47). PMR (Fig. 8) ($CDCl_3$): -$\overset{|}{C}$-Me each as singlet at 0.93, 0.93, 1.04 ppm; CHOH (2H, m, 3.68 ppm, W_H= 20Hz; 2H, bs, 4.10 ppm); =CH (1H, m, 5.74 ppm). Reported[45] PMR ($CDCl_3$): -$\overset{|}{C}$-Me each as singlet at 0.94, 0.94, 1.04 ppm; CHOH (2H, m, 3.67 ppm, W_H= 20Hz; 2H, s, 4.08 ppm); =CH (1H, m, 5.71 ppm).

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FIG.1

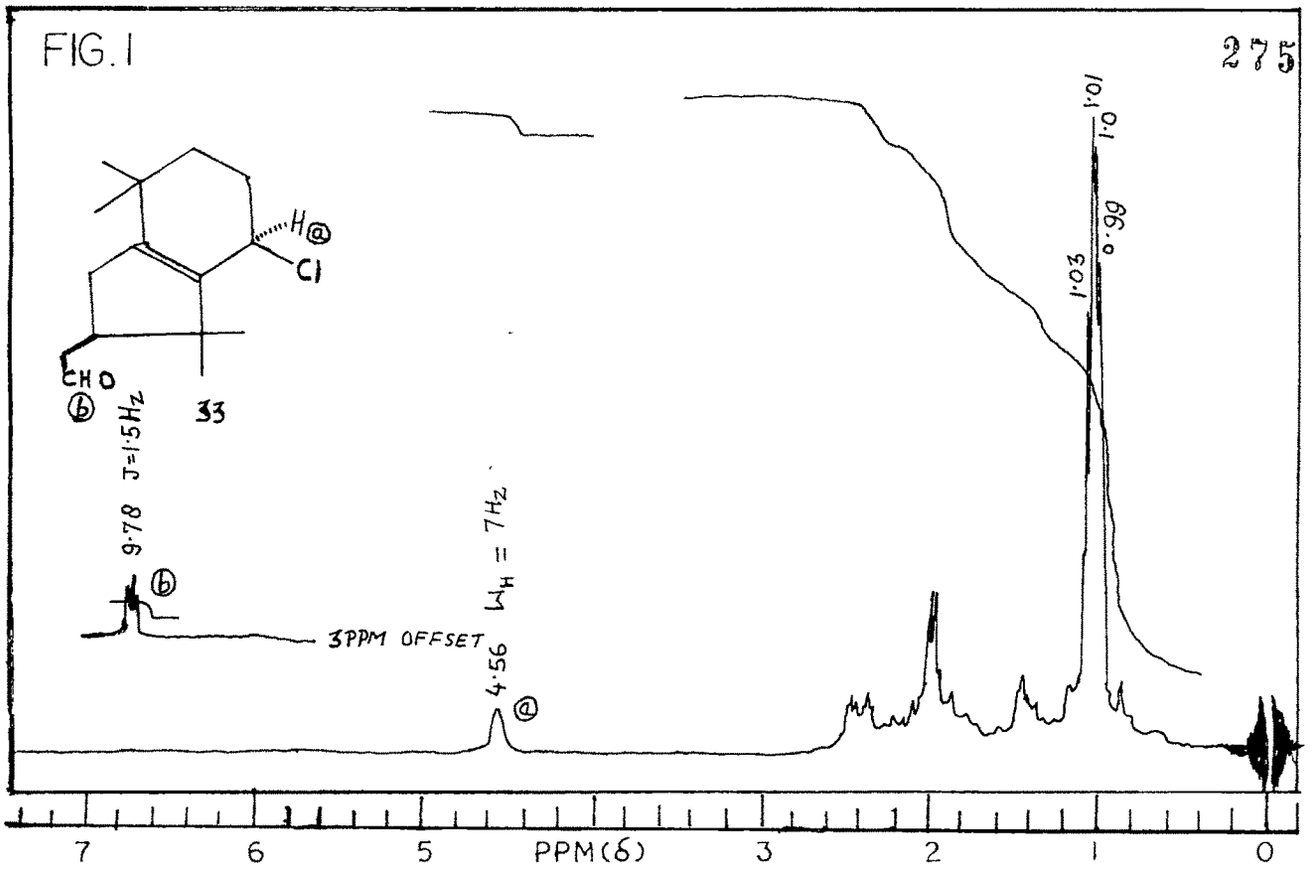

H@
Cl
CHO
ⓑ
33
9·78 J=1·5Hz
ⓑ
3PPM OFFSET
4·56
@
W_H = 7Hz
1·03
1·01
1·0
0·99
7
6
5
PPM(δ)
3
2
1
0

FIG.2

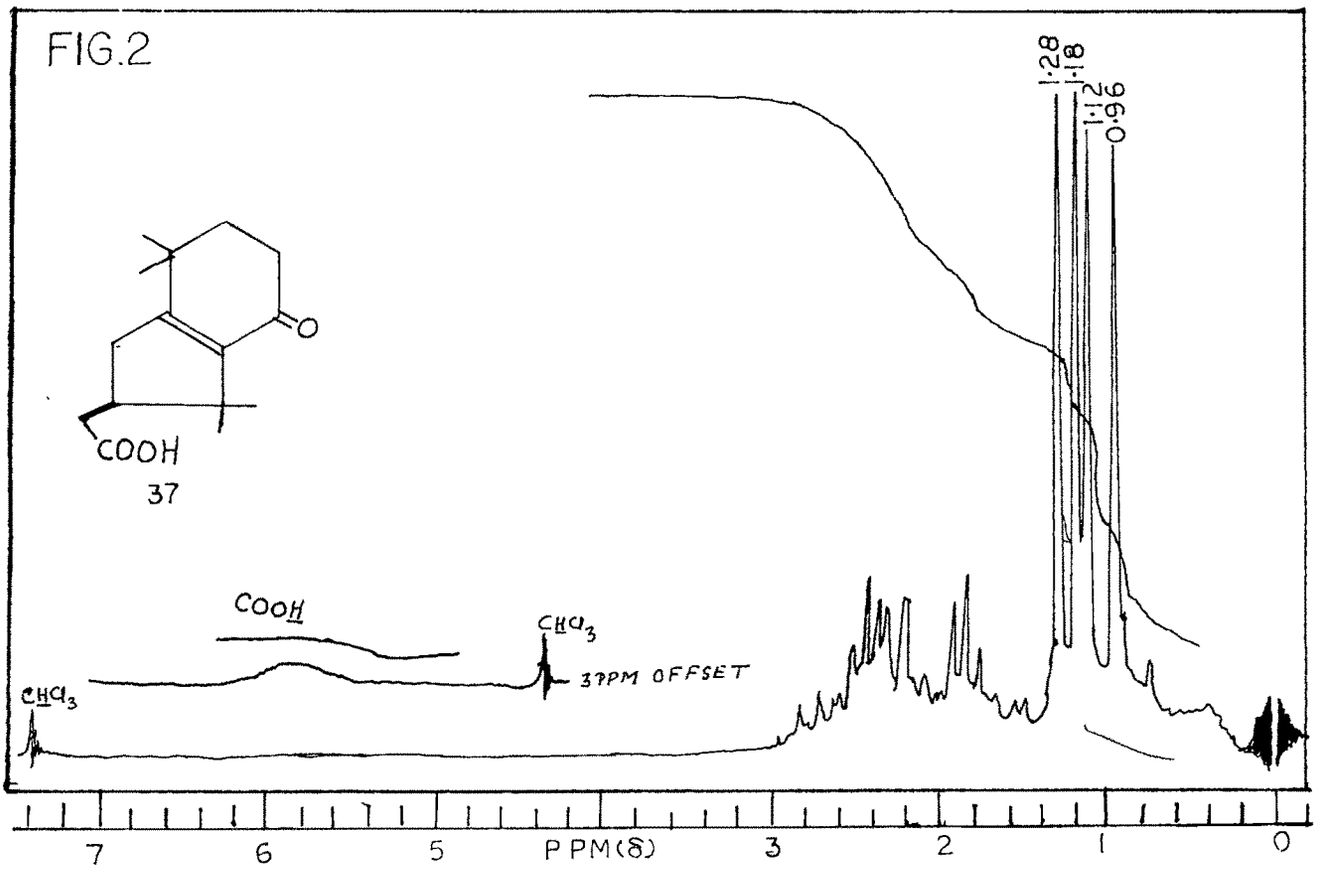
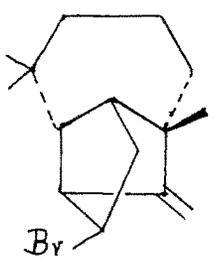
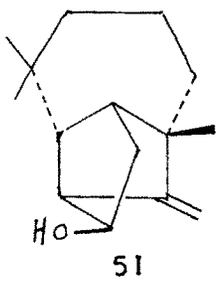

O
COOH
37
1·28
1·18
1·12
0·96
COOH
CHCl3
3PPM OFFSET
CHCl3
7
6
5
PPM(δ)
3
2
1
0

FIG.3



52

FIG.4



51

FIG 5

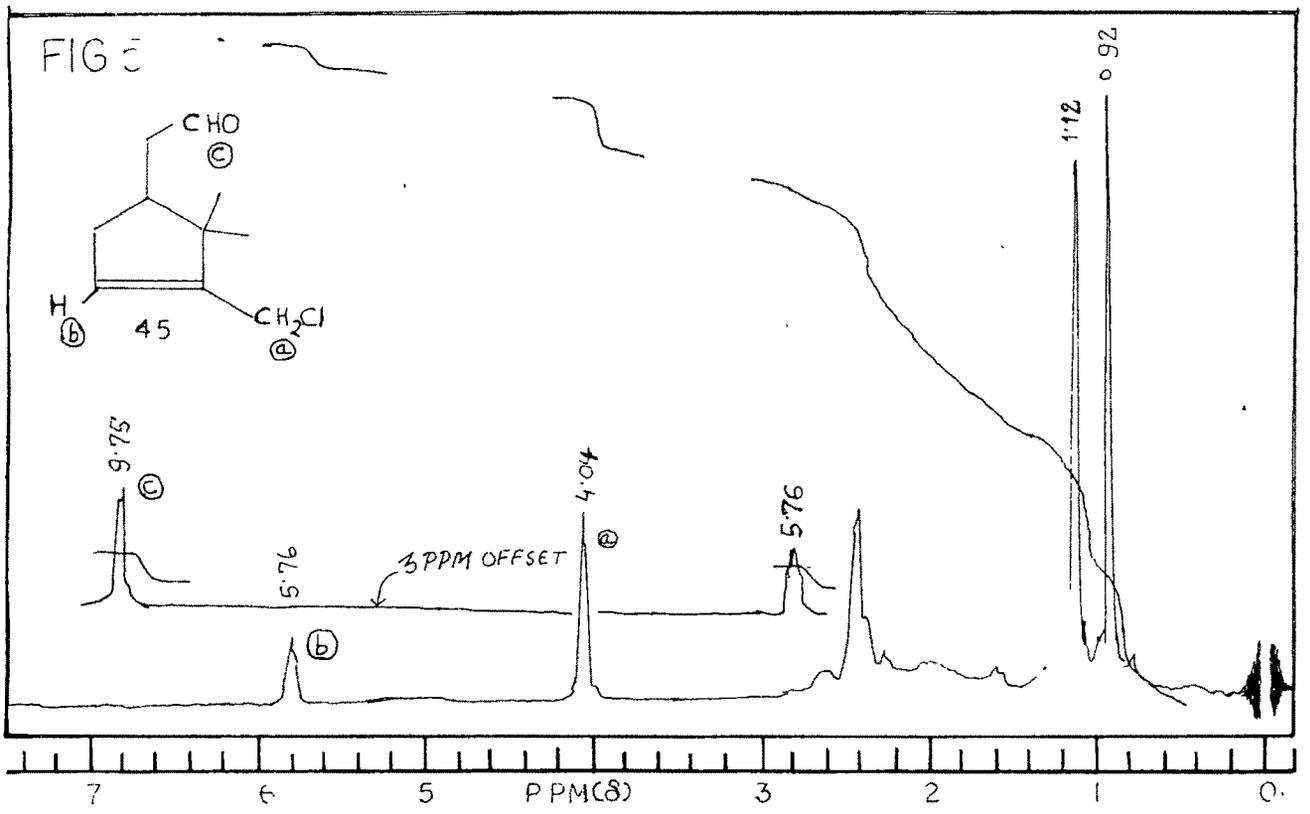

CHO
©
H
ⓑ
45
CH_2Cl
@
9·75
©
5·76
3PPM OFFSET
4·04
@
5·76
1·12
0·92
ⓑ
7
6
5
PPM(δ)
3
2
1
0

FIG.6

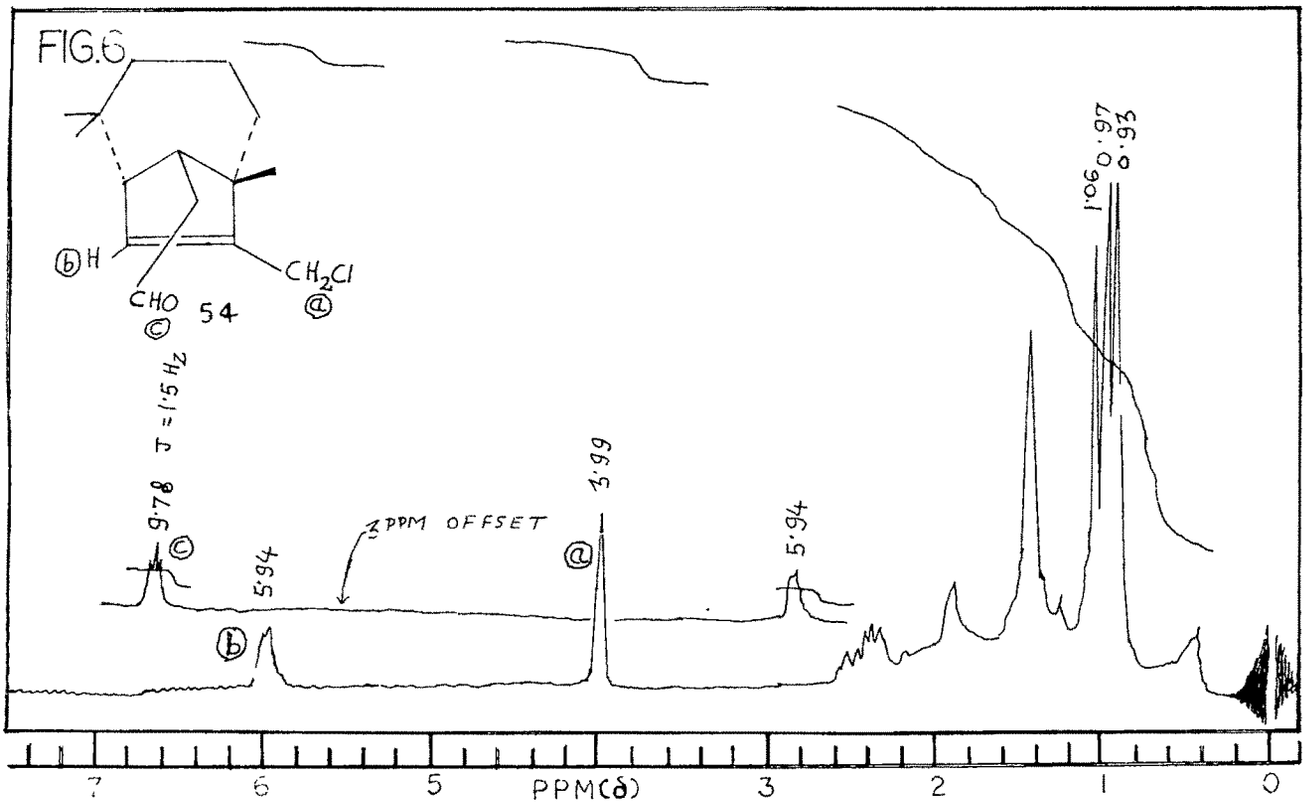

ⓑH
CH_2Cl
CHO
©
54
@
9·78
J = 1·5 Hz
©
5·94
3PPM OFFSET
3·99
@
5·94
1·06
0·97
0·93
ⓑ
7
6
5
PPM(δ)
3
2
1
0

FIG.7

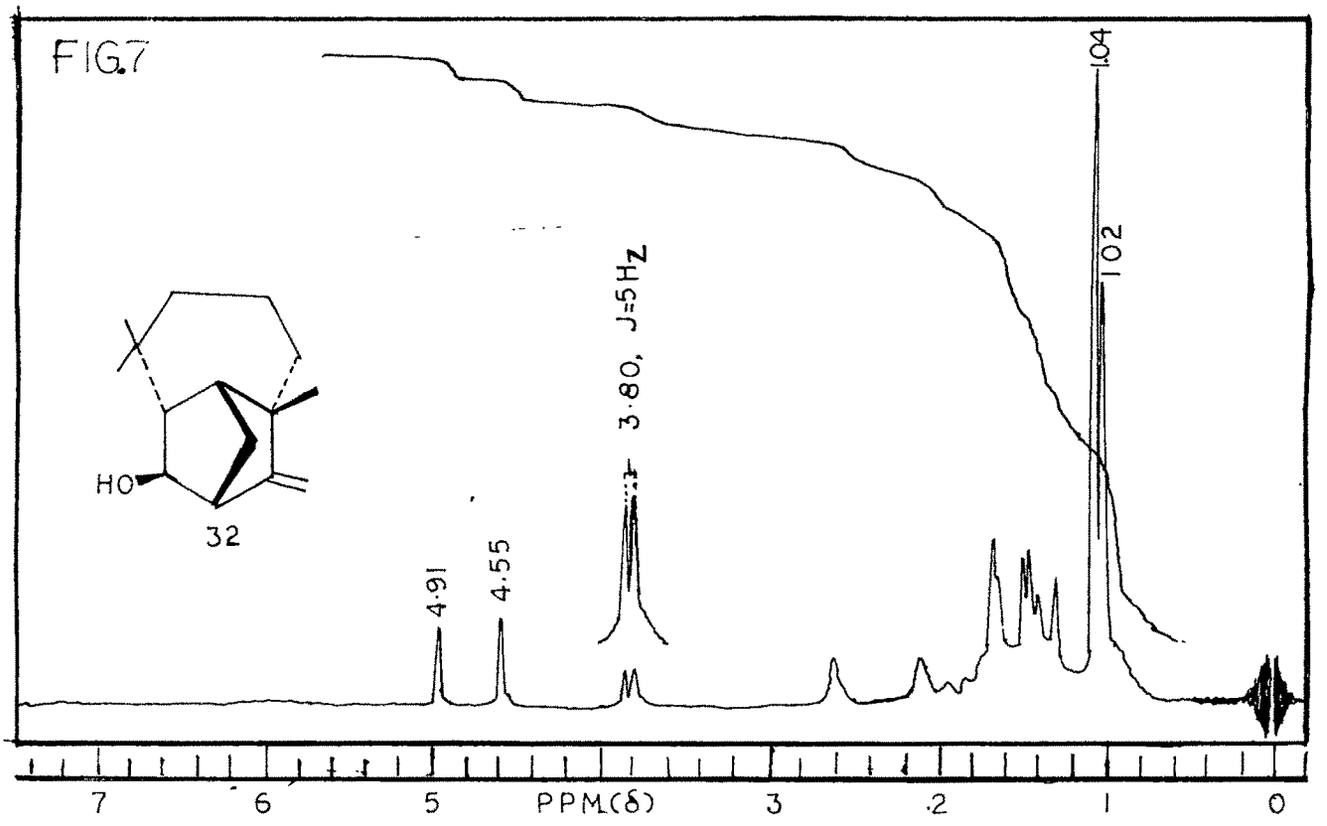
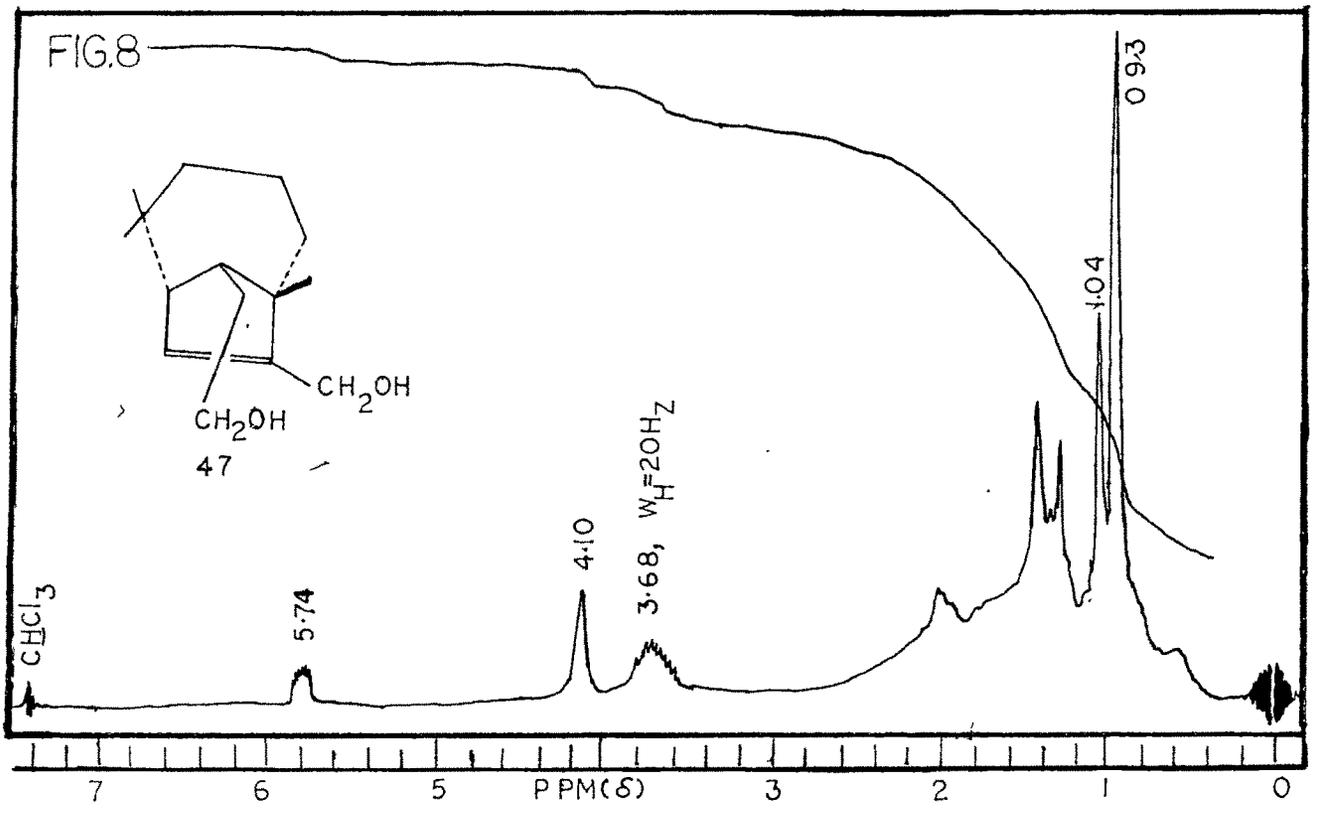
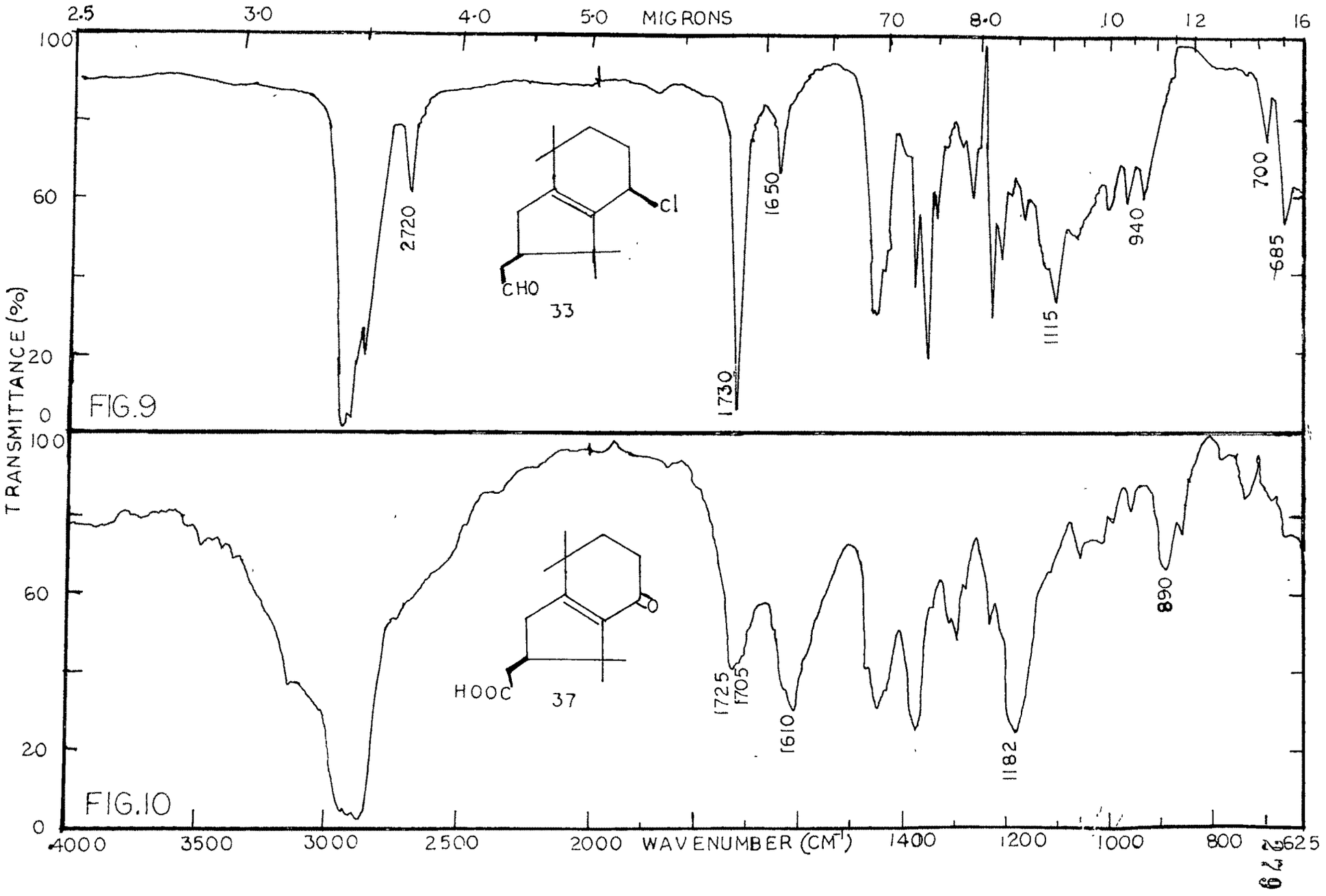
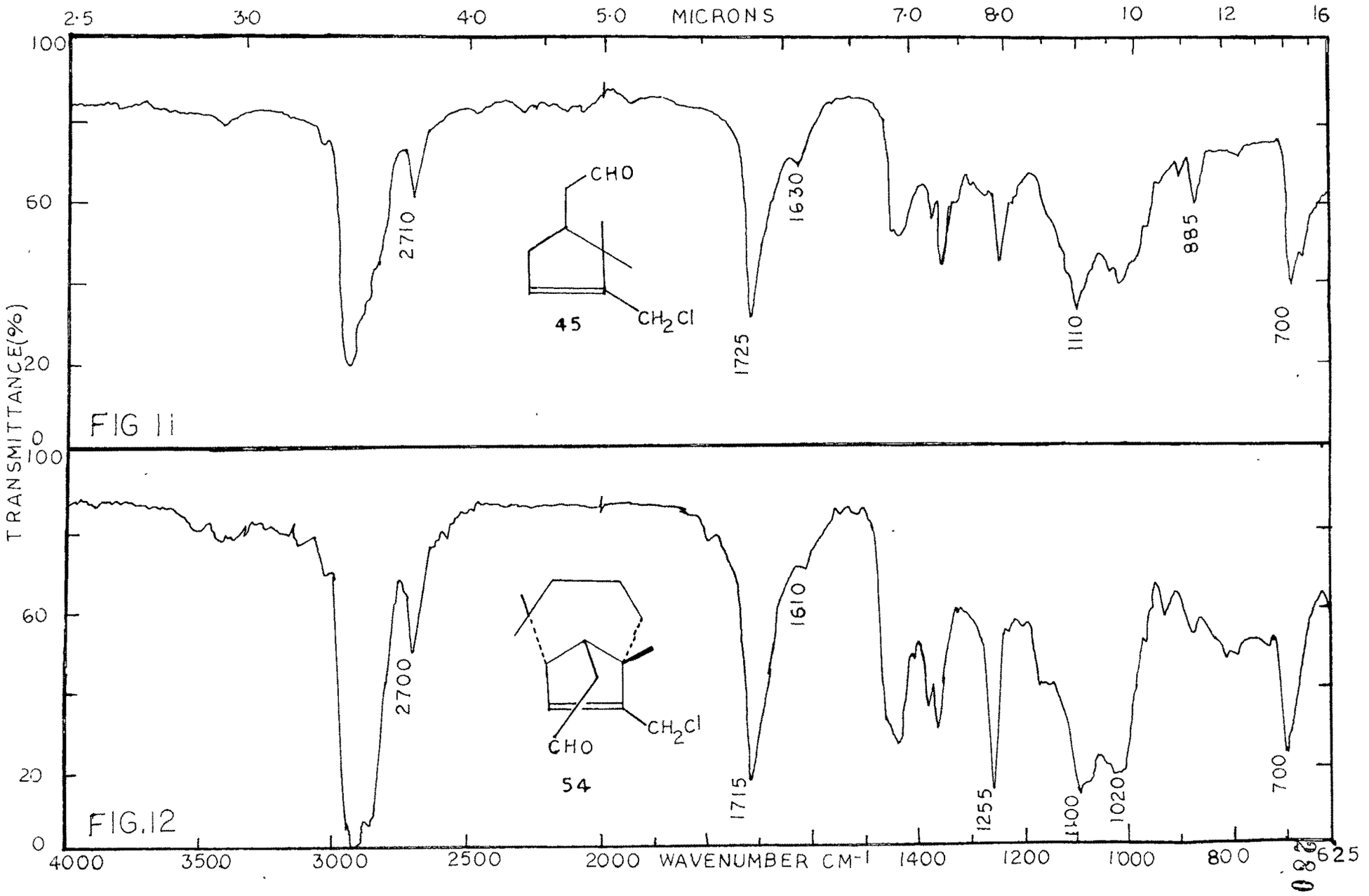

1.04
1.02
3.80, J=5Hz
HO
32
4.91
4.55
7
6
5
PPM(δ)
3
2
1
0

FIG.8


0.93
1.04
CH2OH
CH2OH
47
CHCl3
5.74
4.10
3.68, WH=20Hz
7
6
5
PPM(δ)
3
2
1
0


2.5
3·0
4·0
5·0
MICRONS
7·0
8·0
10
12
16
100
60
20
0
TRANSMITTANCE (%)
2720
1730
1650
1115
940
700
685
Cl
CHO
33
FIG.9
100
60
20
0
HOOC
37
1725
1705
1610
1182
890
FIG.10
4000
3500
3000
2500
2000
WAVENUMBER (CM⁻¹)
1400
1200
1000
800
625


2·5
3·0
4·0
5·0
MICRONS
7·0
8·0
10
12
16
100
60
20
0
TRANSMITTANCE(%)
2710
1725
1630
1110
885
700
CHO
CH2Cl
45
FIG 11
100
60
20
0
2700
1715
1610
1255
1100
1020
700
CHO
CH2Cl
54
FIG.12
4000
3500
3000
2500
2000
WAVENUMBER CM-1
1400
1200
1000
800
625