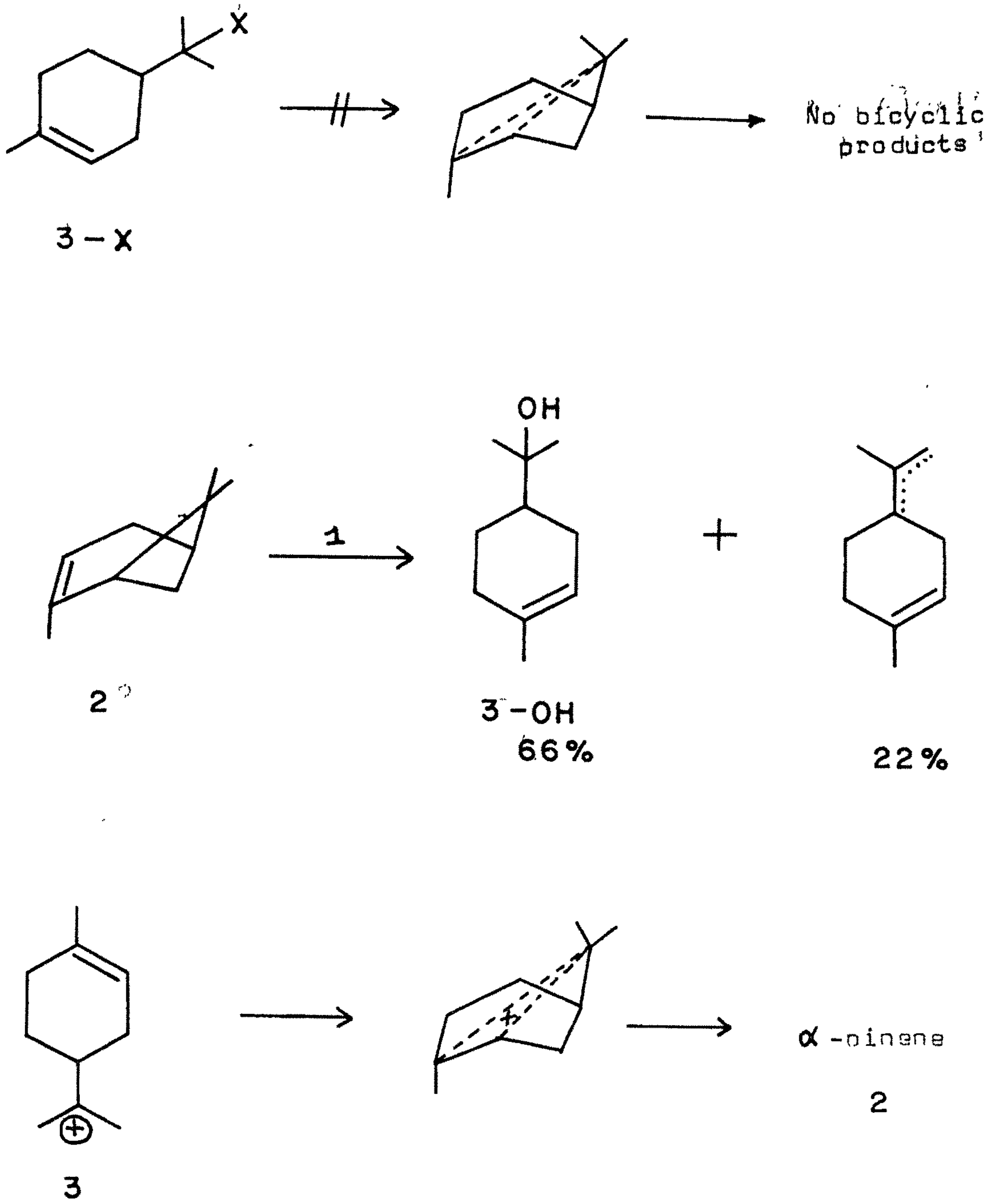
CHAPTER - 2

REVERSION OF (+)-α-LONGIPINENE TO HIMACHALENES

INTRODUCTION

(+)-α-Longipinene (1) has been isolated from various members of family Pinaceae (Chapter 1 of this Part) and as the name indicates, it is the higher isoprenologue of α-pinene (2)[1]. Since (+)-α-longipinene (1) is a high energy molecule because of its strained structure, it was thought worthwhile to examine fate of its cation under various conditions. These reactions may be expected to show some parallelism with the reaction of α-pinene(2).

An important reaction pathway for pinyl derivative[2] is cleavage of gem-dimethyl bridge to give α-terpinyl products (3-OH) or the corresponding elimination products[3,4], the exact reverse of the cyclization of (3) in the biogenetic scheme (Fig. 1). A quantitative study using α-pinene (2)[4] has delineated two pathways. One is Wagner rearrangement to bornyl and fenchyl ions (5 and 6) by migration of band electrons from the gem-dimethyl and methylene bridges respectively and in the presence of a nucleophile this leads to endo-products together with camphene (Fig. 2). The other route is generally favoured when dilute (0.1-1.0 N) aqueous acid are used, and typically



Reagents: 1. HClO$_4$-95% aq. acetone 75°C

Fig. 1. Reaction pathway for pinyl derivative

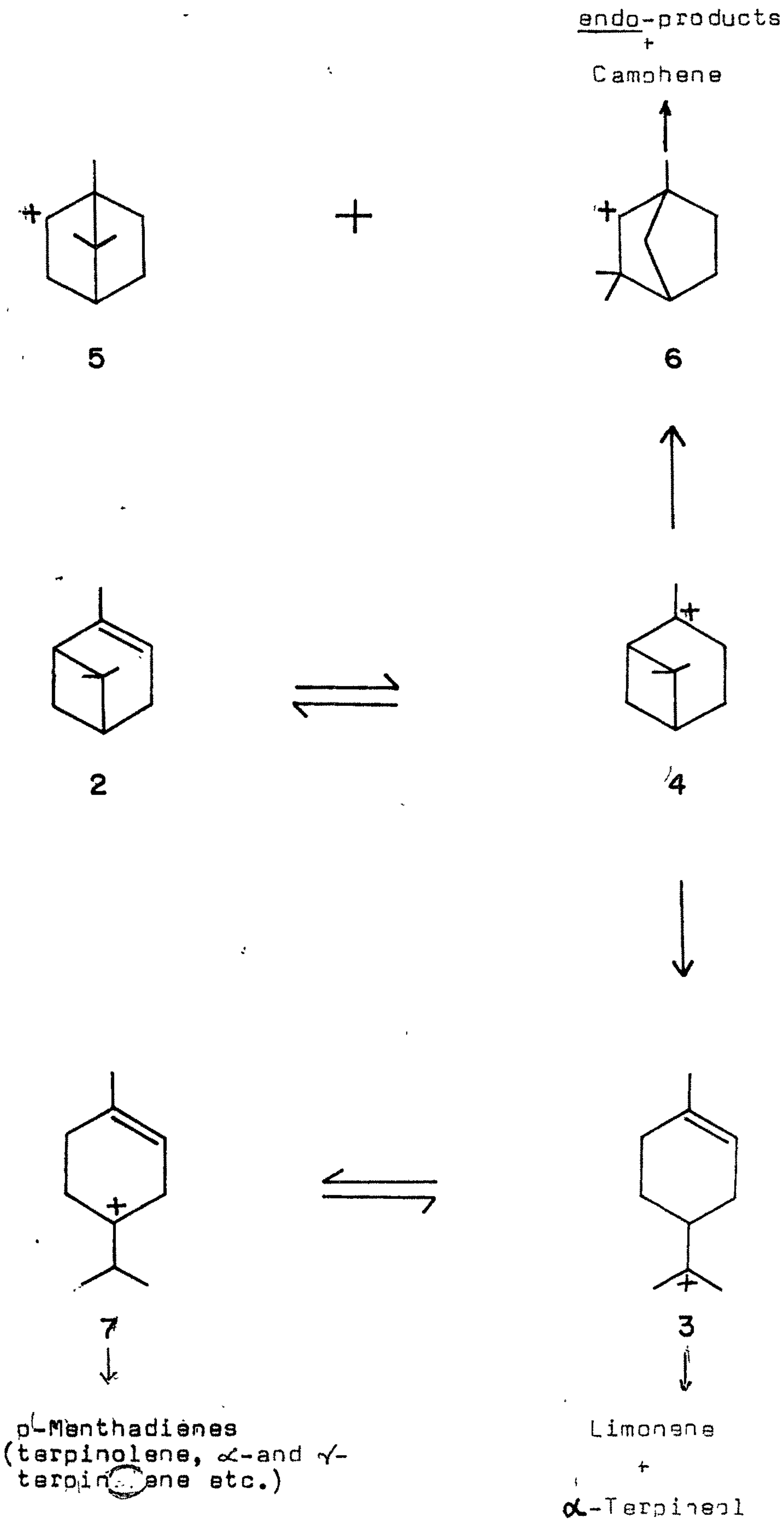


Fig. 2. Rearrangement of α-pinene

limonene and α-terpinolene and isomerization and hydration products resulting from the ions (3) and (7) are formed together with traces of β-pinene and terpene ethers (cineoles)[4,5].

PRESENT WORK

The present work describes the rearrangement of (+)-α-longipinene cation (8) under a variety of conditions. (+)-α-Longipinene cation (8) occupies an unique position at the crossroads to himachalenes (10 and 11)[6,7,8], longifolene (13)/longibornyl systems (12)[9,10]. Protonation of (+)-α-longipinene (1) can, in principle, generate species (8) which has been implicated in the biogenesis[11] of (+)-longifolene (13) and related compounds (Fig. 3).

Rearrangement of (+)-α-longipinene (1) under the influence of various acids has been investigated and the products were separated and identified (Fig. 4). It is shown that a facile reversion of (+)-α-longipinene (1) to α- and β-himachalenes (10 and 11) occurs. A concomitant

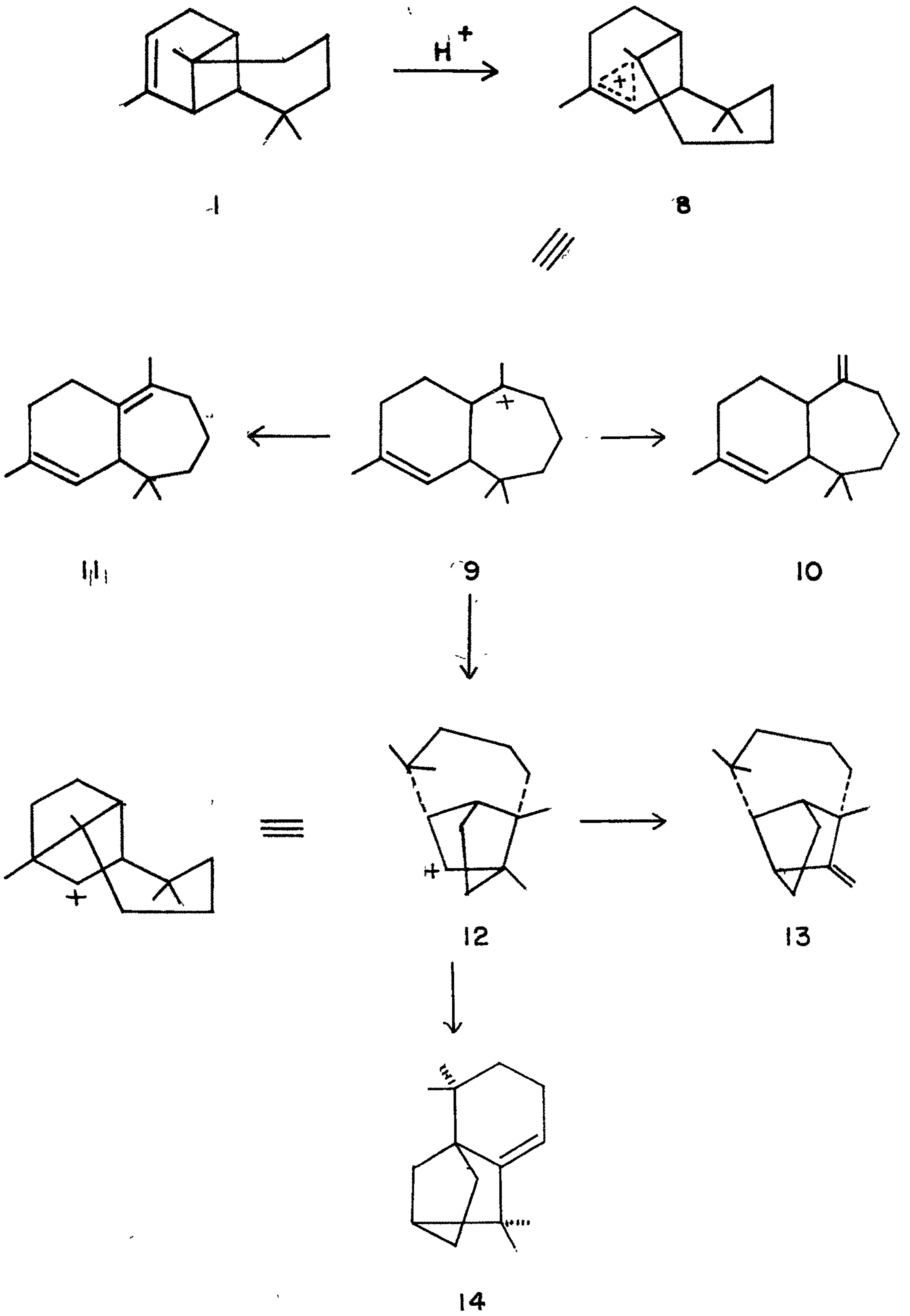
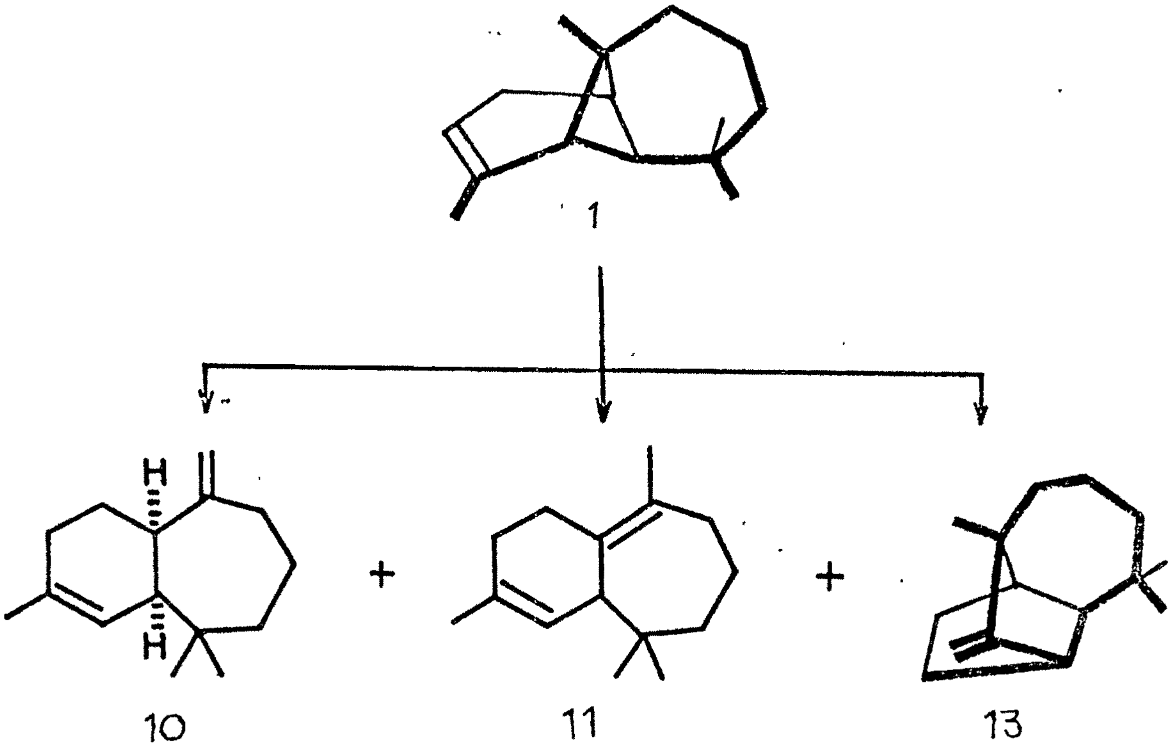


Fig. 3. Reversion of (+)-α-longipinene



Acid	Solv.	Temp./hr.	PRODUCTS (%) 10	11	13
BF_3	Et_2O	28°/7	46	10	32
$HClO_4$	aq. diox.	90°/2	20	44	21
H_2NSO_2OH	acetone	60°/18	34	26	25

Fig. 4. Reversion products of (+)-α-longipinene

reaction is its rearrangement to (+)-longifolene (13) and isolongifolene (14) .

Acid-catalyzed reversion of (+)-α-longipinene

(i) Using BF$_3$-etherate. (+)-α-Longipinene (1) in dry ether and BF$_3$-etherate were stirred for 6-7 hrs at 28-29°C (or at 39°, 1-1.5 hrs). The product obtained after usual work-up was a mixture of longifolene (13, 32%), α-himachalene (10, 46%), β-himachalene (11, 10%), unreacted (+)-α-longipinene (1, 6.7%) and some other unidentified products (4.2%) along with traces of isolongifolene (14, 2%). The products were isolated by prep. GLC (20% CW, 12', 150°C) and found to be pure by GLC but NMR showed impurities. Finally the products were isolated in a pure form by medium pressure liquid chromatography (MPLC) using AgNO$_3$-SiO$_2$ gel and identified by comparison with authentic samples.

(ii) Using perchloric acid (HClO$_4$) in aq. dioxane. When (+)-α-longipinene (1) in dioxane/water and HClO$_4$ (60%) was stirred for 27 hrs. at R.T.(≈ 30 ± 5°), it remained unreacted. At moderate temperature (60°, 1 hr) poor conversions resulted. Finally, when it was stirred at 90° (2 hr), the product obtained after usual work-up was found to be a mixture of longifolene (<u>13</u>, 21%), α-himachalene (<u>10</u>, 20%), β-himachalene (<u>11</u>, 44%); unreacted (+)-α-longipinene (<u>1</u>, 7%) and traces of isolongifolene (<u>14</u>, 2%) along with some other unidentified products (6%).

(iii) <u>Using sulfamic acid (H_2NSO_3H)</u>: (+)-α-longipinene (<u>1</u>) and sulfamicacid, a strong acid (pH of 1% soln. at 25° is 1.18) in dry acetone when refluxed while stirring, maximum conversion was obtained after 18 hrs, and the product obtained after usual work-up was found to be a mixture of longifolene (<u>13</u>, 25%), α-himachalene (<u>10</u>, 34%), β-himachalene (<u>11</u>, 26%), unreacted (+)-α-longipinene (<u>1</u>, 9.4%) and unidentified products (6%) with no trace of isolongifolene (<u>14</u>).

(iv) <u>Using glacial acetic acid-sulphuric acid.</u> It is well-documented in the literature[12] that the addition of acids to α-pinene (<u>2</u>) involves addition of unionised acid to give an intimate ion-pair, which favours elimination over addition when the counter ion is not strongly nucleophilic. When a catalytic amount (0.2 N) of sulphuric acid is added to 5% soln of α-pinene (<u>2</u>) in acetic acid, the reaction was very rapid, the α-pinene (2) disappeared within 15 min and gave olefins produced by isomerisation of (2) as the main products and the product arising from addition of the counter ion was negligible.

Applying similar conditions to (+)-α-longipinene (1), the reaction favoured elimination over addition furnishing reversion products, α-himachalene (10), β-himachalene (11), longifolene (13) and isolongifolene (14). The product formation varies with the temperature. At room temp. (25°, 1 hr) α-himachalene (10, 32%) and β-himachalene (11, 28%) predominates in the product mixture along with longifolene (13, 7%) and isolongifolene (14, 7%). At slightly higher temp. (50°C, 1 hr), it gave β-himachalene (11, 52%) and isolongifolene (14, 32%) as the major products. At higher temp. (87 ± 1°, 1 hr), it gave complex mixture as the product, isolongifolene (14, 58%) being the major one along with other unidentified products. At higher temperature α-himachalene (10) or β-himachalene (11) were not found to be present in the product mixture, so it was thought that β-himachalene (11) may be getting converted into isolongifolene (14). However, applying these conditions to β-himachalene (11) resulted in a complex mixture with only traces of longifolene (13) and isolongifolene (14). Results are summarized in Table 1 (Fig. 5).

Hydration of Longipinene

Sr. No.	(+)-α-Longipinene gr.	mole	Temp.[a] °C	Products Crude gm(%)	Dist. gm(%)	Res. gm(%)	GC analysis[d] Low boilers %	Unreacted Longipinene 1 %	Isolongifolene 14 %	Longifolene 13 %	α-himachalene 10 %	β-himachalene 11 %	others (%)	Recovery[e] (%)
1.	1	0.005	25 ± 2[b]	00.94 (94%)	00.87 (86.58)	00.06 (6.69)	1.08	6.76	6.76	24.77	31.53	28.38	-	93.27
2.	1.05	0.005	50 ± 1[b]	1.03 (98)	00.87 (82.85)	00.12 (11.42)	8.7		32.3	4.35	-	51.55	7.45	94.27
3.	1.08	0.005	87 ± 1[b]	1.04 (96.3)	00.76 (70.37)	00.24 (22.3)	16.89		57.43	trace	-	1.35	24.27	92.67
4.	β-Himachalene 1.00	0.005	67[c]	00.85 (85.2)	00.55 (55)	00.29 (29.1)	......		complex mixture					84.1

[a] gla. acetic acid (4 ml) and sulphuric acid (0.4 ml, 50% v/v) were used on hydration

[b] Reaction time (1 hr)

[c] Reaction time (7 hr)

[d] GC analysis was performed by 10% CW column (12', 170°, H_2 as carrier gas)

[e] Recovery = distillate + residue.

Fig. 5

EXPERIMENTAL

For general remarks, see page No. 71

Acid catalyzed reversion of (+)-α-longipinene

(i) Using BF_3-ethereate. A solution of (+)-α-longipinene (1, 5.0 g, 0.035 mole) in dry ether (50.0 ml) and BF_3-ethereate (2.5 g) were stirred at 28 ± 2° till GLC (10% CW, 12', 150°) of an aliquot showed maximum conversion (7 hr). The reaction mixture was washed with water (10 ml x 4), 20% sodium carbonate (5 ml x 1), dried and evaporated. The residue (4.8282 g, 96.6%) was distilled and the distillate (4.43 g, 88.6%, b.p. 96-110°/1-2 mm) was shown by GLC (Fig. 6) to be a mixture of α-himachalene (10, 46%), β-himachalene (11, 10%), longifolene (13, 32%), unreacted (+)-α-longipinene (1, 6%) and some other unidentified products (6%). α- and β-Himachalenes (10 and 11) separated by preparative GLC (20% CW, 12', 150°) were found to be GLC pure but ^{1}H-NMR showed impurities. Finally, they were isolated in pure state by medium pressure liquid chromatography.

Adsorbent : 10% $AgNO_3$-SiO_2-gel* (90 g)
Column dimensions : 100 x 1.5 cm
Pressure : 40 psi

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*Silica gel used was TLC grade without binder, mesh 100-200.

Eluent : Light petroleum

Vol. of the fraction : 100 ml

Pool No.	Fraction No.	Wt.(g)	Remarks
1.	1-3	0.200 g	Unreacted 1 and other unidentified products.
2.	4-8	0.7425 g	1 and longifolene
3.	11-25	0.7201 g	α-himachalene (pure)
4.	37-40	0.0471 g	β-himachalene (pure)

Recovery: 80%

Pure longifolene (13) was isolated from pool No. 2 by preparative GLC (20% CW, 12', 150°). The identity of (+)-longifolene (13), α-himachalene (10) and β-himachalene (11) were established by comparison of physical and spectral data. The pure samples had the following characteristics.

α-Himachalene:	B.p.	93-4°/1.5 mm (Lit.[8] 93-94°/2mm)
	n_D^{25}	1,5082 (Lit.[8], 1,5082)
	$[\alpha]_D$	-84 ($CHCl_3$, c, 1.3%) (Lit.[8] -192.3, $CHCl_3$)
	IR (liq.)	3060, 1770, 1665, 1625, 1388, 1377, 1362, 885 and 855 cm^{-1}.

^{1}H-NMR : Me-C (6H, s, 0.966 and 0.988 ppm)
Me-C=C (3H, s, 1.8 ppm)
H_2C=C (2H, s, 4.7 ppm)
HC=C-Me (1H, s, 5.41 ppm).

β-Himachalene: B.p.(bath) : 130-40°/1-2mm (Lit.[7] 121-122°/4 mm)
n_D^{25} : 1.5105 (Lit.[8] 1.5130)
$[\alpha]_D^{25}$: + 181.8° ($CHCl_3$, c, 3%) (Lit.[8] + 224.7, $CHCl_3$).

IR (liq.): 1665, 857, 1360 cm^{-1}.

^{1}H-NMR : Me-C (6H, s, 0.73 and 0.977 ppm).
Me-C=C (6H, s, 1.73 ppm)
H-C=C-Me (1H, partly splitted, 5.36 ppm).

(+)-Longifolene: B.p. - 86-87°/1.5 mm (Lit.[13] 150-1°/36 mm)
n_D^{25} - 1.5027 (Lit.[13]. 1.4950)
$[\alpha]_D^{25}$ - + 51.14 ($CHCl_3$, c, 1.76%) (Lit.[13] + 54.06, $CHCl_3$)

IR (liq.): 3070, 2948, 1660, 1456, 1375, 1364, 1296, 871 cm^{-1}.

^{1}H-NMR : Me-C (9H, s, 0.90, 0.95, 0.98)
C=CH_2 (2H, s, 4.72, 4.46).

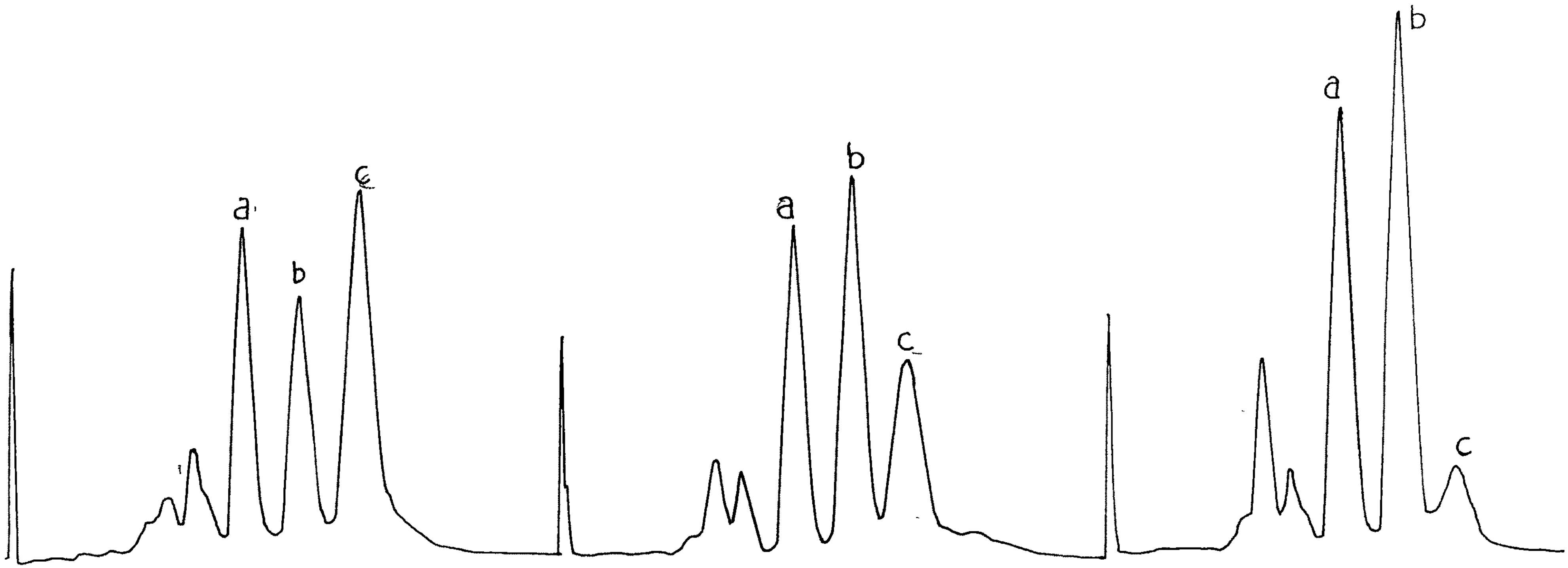
(ii) Using $HClO_4$-aq. dioxane. A solution of (+)-α-longipinene (1, 0.4 g, 0.009 mole) in dioxane: water (4:1; 5.0 ml) and $HClO_4$ (0.045 g, 0.075 ml, 60%) were stirred at 70° (2 hr). The reaction mixture was allowed to attain room temperature (28°) and was extracted with ether (5 ml x 4). The combined ether layer was washed with water (3 ml x 2), 20% sodium carbonate (2 ml x 1), dried and evaporated. The residue (0.38 g, 95%) was distilled and the distillate (0.36g, 90%, b.p., bath, 110-120°/1-2 mm) was shown by GLC analysis (Fig. 6), to be a mixture of α-himachalene (10, 20%), β-himachalene (11, 44%), longifolene (13, 21%), the unreacted (+)-α-longipinene (1, 6%) and some other minor products (9%).

(iii) Using sulphamic acid: A solution of (+)-α-longipinene (1, 2 g, 0.0099 mole in dry acetone (50 ml) and sulphamic acid (1.0 g) were refluxed under dry conditions for 18 hrs while stirring. Acetone(45 ml) was then removed and the product was taken up in ether (25 ml x 2). The usual work followed by the distillation of the residue (1.8 g, 90%) left after evaporation of solvent, gave the distillate (1.65g, 82.5%, bath 120-130°/2-3 mm). The distillate was shown by GLC (Fig. 6) to be a mixture of α-himachalene (10, 34%), β-himachalene (11, 28%), longifolene (13, 25%), the unreacted (+)-α-longipinene (1, 9.5%) and some other minor products (5.5%).

(iv) Using glacial acetic acid-sulphuric acid. To the solution of (+)-α-longipinene (1, 1.0 g, 0.005 mole) in glacial acetic acid (4.0 ml) was added sulphuric acid (0.4 ml, 50% v/v) and the contents were stirred at 25 ± 2° for 1 hr. The product was taken up in ether (25 ml x 2) and the usual work up followed by the distillation of the residue (0.94g, 94%), left after solvent evaporation, gave the distillate (0.86g, 86%, b.p. 82-92°/1-2 mm). The distillate was shown by GLC to be a mixture of α-himachalene (10, 31.0%) β-himachalene (11, 28.0%), longifolene (13, 25%), isolongifolene (14, 7%), the unreacted starting material (1, 7%) and some other minor products (2%). The similar experiment was repeated at higher temperatures. The results are summarised in Table 1 (Fig. 5).

Acid catalyzed rearrangement of β-himachalene (using glacial acetic acid-sulphuric acid)

β-Himachalene (11, 1.0 g, 0.005 mole) under similar conditions as described earlier, after usual work up gave complex mixture as the product (Table 1, Fig. 5).



Column: 10% CW 20M (360 cm x 0.6 cm, Al. column)
Hydrogen flow: 60 ml/min., Temp. 150°
a) Longifolene (13), b) α-Himachalene (10)
c) β-Himachalene (11)

Fig. 6. GLC OF REVERSION PRODUCTS OF (+)-α-LONGIPINENE

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