Tetrahedron Vol. 48, No. 23, pp. 4905-4918, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

STUDIES IN SESQUITERPENES-LX[a,b] REVERSION OF LONGIPINANE TO HIMACHALANE SYSTEM : REVISION OF STRUCTURE OF ISOCENTDAROL

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(*Received in UK* 1 *October* 1991)

Abstract Longipinene on exposure to acids rapidly rearranges to furnish α-and β-himachalenes, longifolene and isolongifolene. Longipinene epoxide, under acid catalysis, gives several products resulting from fragmentation and Wagner-Meerwein rearrangement. All products have been fully characterised. Formation of isocentdarol in this reaction requires revision of its stereochemistry at the centre carrying tertiary hydroxyl function.

Cyclization of p-menthenyl cation (1) to pinane cation (2) is reflected in sesquiterpene chemistry[1a] in the biosynthesis of copane, longipinane cations (**4**,**6**), and related systems as illustrated in Fig.1. Of course, Fig. 1 has been constructed to emphasise the step **1** to **2**, and is not intended to convey the involvement of such cations (or their equivalents) as discrete species[1]. This process, which generates strained bicyclo [3.1.1]heptane system, is endothermic and has not been duplicated in solvolytic reactions. On the other hand, reversion of this cyclization is a reaction characteristic of pinane system[2]. Thus,

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a Dedicated to Prof. Gabor Fodor on his 75th birthday.

b Part LIX; J. Indian Chem. Soc. **1978**, 55, 1138.

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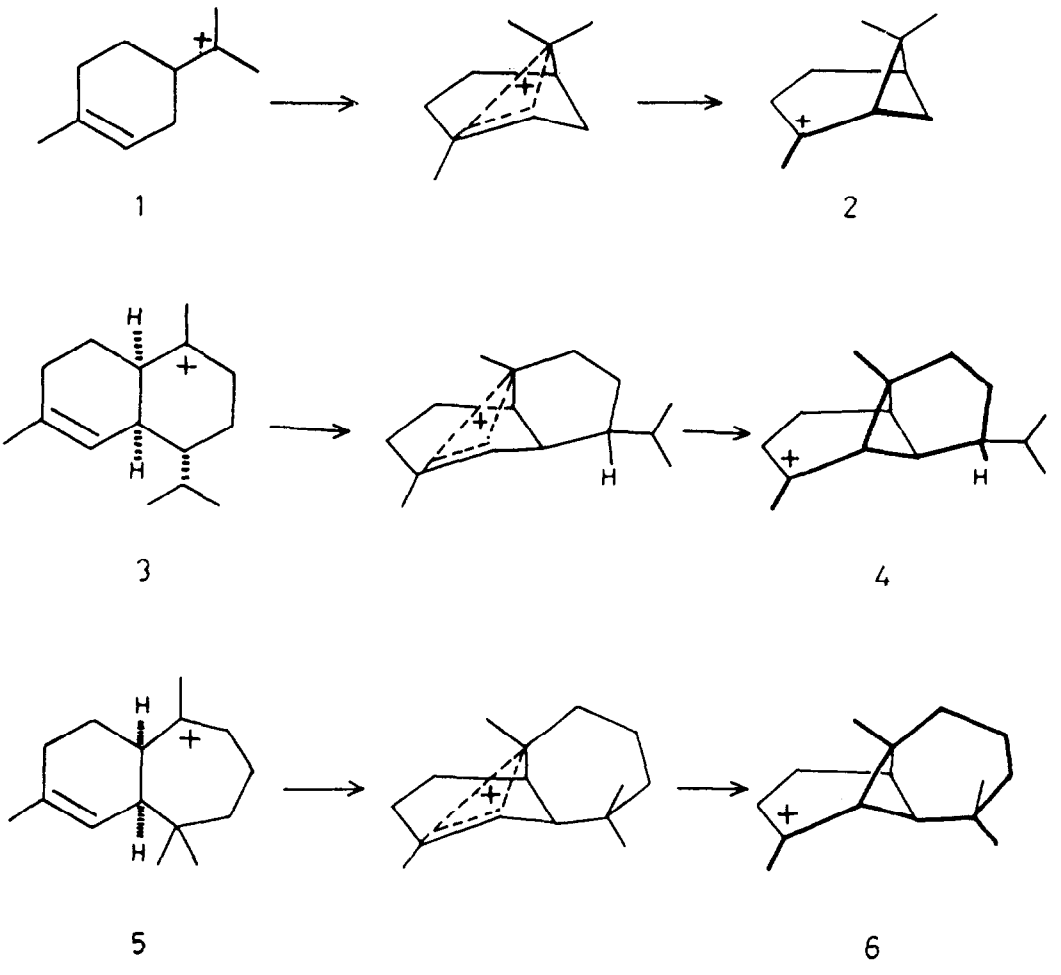

Fig.1

Typical cyclizations in terpene biosynthesis generating bicyclo[3.1.1] heptane system

α-pinene (**7**) on exposure to aqueous mineral acids gives, in good yield, a mixture of terpineols, in which α-terpineol (**8**) predominates[2b]. Likewise, (-)- α-copaene (**9**) on treatment with hydrogen chloride gas furnishes as the major product (-)-cadinene dihydrochloride (**10**)[3]. However, α-longipinene (**11**) has been reported[4] to yield under similar conditions longibornyl chloride (**12**) as the only isolable product. In view of this rather unexpected behaviour of longipinene, it appeared of interest to investigate its reactions under acid catalysis.

(+)- α-Longipinene on treatment with a variety of acids ($BF_3.Et_2O$, $HClO_4$ in aqueous dioxane, H_2NSO_2OH in acetone, and H_2SO_4 in glacial acetic acid) underwent both fragmentation (to himachalane system) and Wagner-Meerwein rearrangement (to longifolane system) to yield α-himachalene (**13**)[5], β-himachalene (**14**)[5], longifolene (**15**)[6], and isolongifolene (**16**)[7]. From the relevant data summarised in Table I, it is clear that in fragmentation versus rearrangement, the former pathway predominates. In all these reactions, some 6-7% longipinene remained unchanged and about 4-6% of other unidentified products were formed. This is reflected in the product composition shown in Table I. Perchloric acid in aqueous dioxane had practically no effect on longipinene at room temperature (30 ± 5^{o}) even after prolonged exposure (27 hr).

Thus, longipinene, as expected, does undergo fragmentation to the himachalane skeleton. Longifolene arises from a series of 1,2-shifts, and the two pathways must be mutually exclusive, even though himachalene cation (**5**) is central to the biosynthesis of longifolene[6]. As a matter of fact, it was also demonstrated that himachalenes on exposure to H_2SO_4-AcOH ($50-51^{o}$, 1 h; cf last entry Table I) do not give any longifolene/isolongifolene.

The reaction was next extended to longipinene epoxide as its fragmentation should be more facile, due to additional driving force being provided by the protophilicity of the epoxy oxygen and cleavage of the strained oxirane ring. Furthermore, the product(s) could be of structural interest as being likely to occur in nature. Longipinene epoxide was prepared by the action of peracetic acid on (+)- α-longipinene. Since in longipinene (**17**=**11**), the endo face is less hindered like that in α-pinene, one would expect the epoxy ring to be oriented as shown in **18** [8,9]. When the epoxide was treated with $HClO_4$ in

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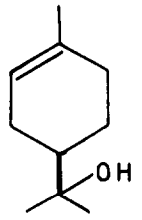

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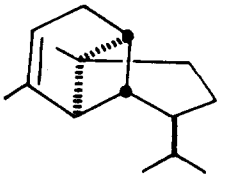

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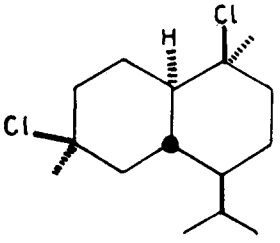

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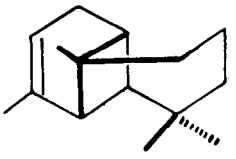

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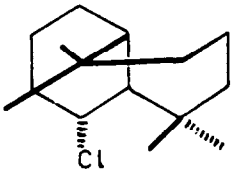

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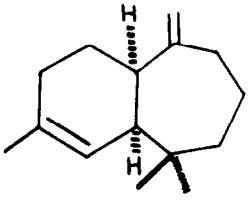

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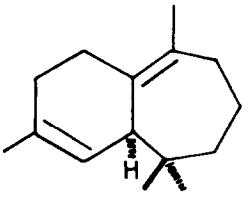

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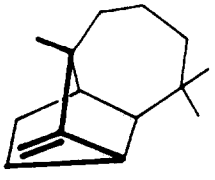

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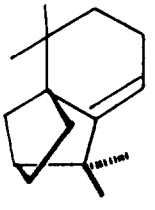

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aqueous dioxane at 0° for first 1/2 h, a number of products resulted with complete disappearance of longipinene epoxide. This may be contrasted with the behaviour of α-longipinene when no reaction occurs under identical conditions. The total reaction product showed by TLC and GLC (after acetylation) at least five compounds, and all of these could be obtained pure by systematic chromatography. Two of these, an aldehyde and a monohydric alcohol, constituted some 85% of the total product, while the three minor products were diols.

TABLE I Products from exposure of longipinene to acids

Acid	Solvent	Reaction Temp.(°C)	Reaction Time (hr)	Products (%)[a] 12	14	15	16
BF_3	Et_2O	28-29°	7	46	10	32	2
$HClO_4$	Aq. dioxane	90-92°	2	20	44	21	2
H_2NSO_2OH	Acetone	reflux	18	34	26	25	-
H_2SO_4	AcOH	25-26°	1	32	28	25	7
		50-51°	1	-	52	4	32

[a] Balance is unreacted longipinene and unidentified products

13 : α-himachalene **15** : longifolene

14 : β-himachalene **16** : isolongifolene

The major product (45-50% by GLC), which was least polar, was readily recognized (IR, ^{1}H NMR) as the known 'secolongifolene aldehyde' **19**, which we had obtained earlier[11,12] as a product resulting from heterolytic cleavage of homoallylic alcohol **20**. The aldehyde (antipode?), since then, has been found to occur as a secondary metabolite of Artemisia filifolia[13]. It may be recalled that pinene epoxide (**22**) is known to furnish the related aldehyde, α-campholene aldehyde (**23**), on treatment with a variety of acids[14,15], including active silica gel[16]. Formation of aldehyde **19** from α-longipinene epoxide is readily rationalized as shown in Fig. 2.

The next major compound (35% by GLC), was a crystalline solid, m.p. 109-110°C characterized as the expected fragmentation product **21**,

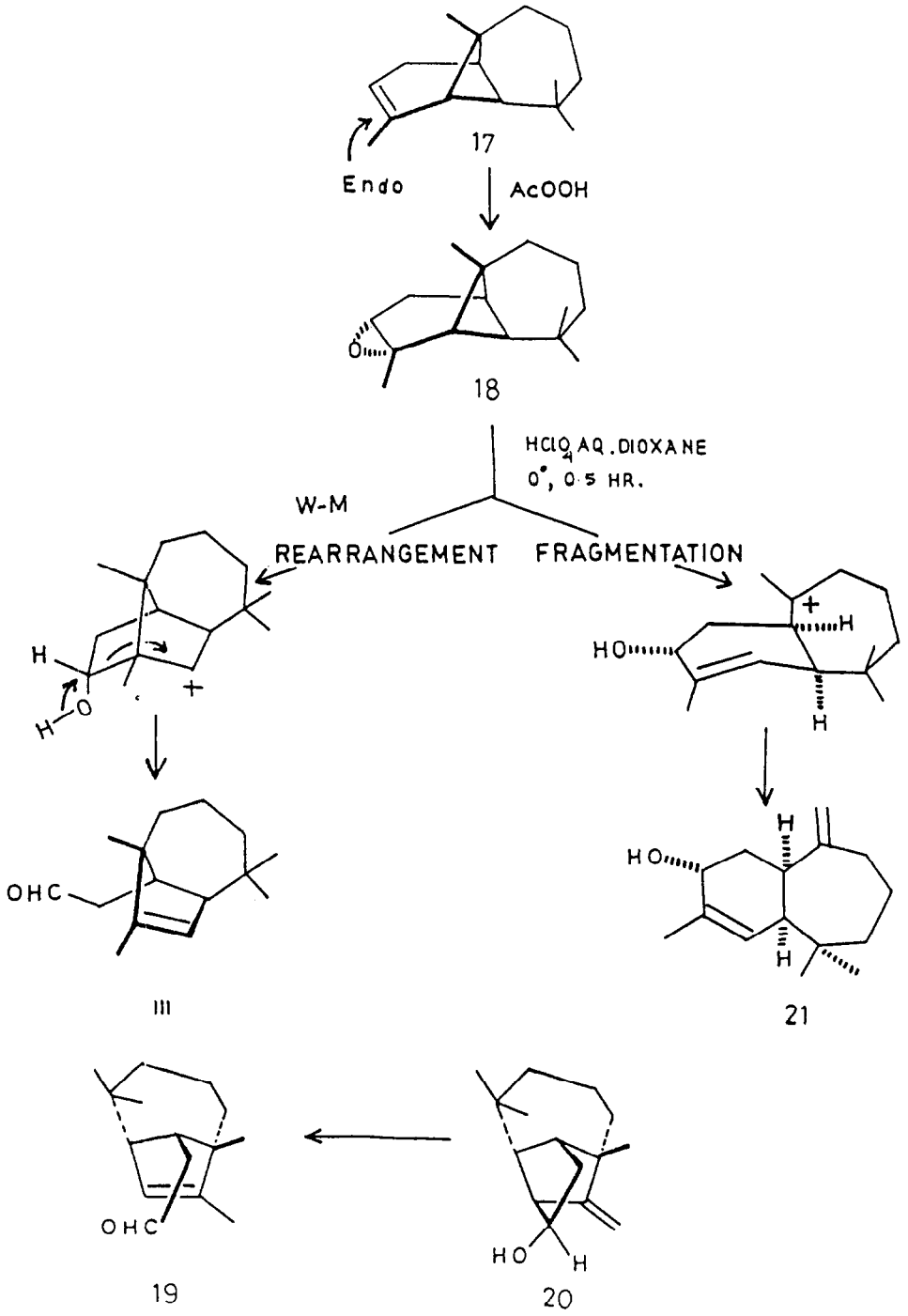


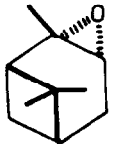
Fig.2
Rearrangement of (+)- α-longipinene epoxide.

as shown in Fig. 2. The spectral data (vide Experimental) are fully consistent with structure **21**. Though, in Fig.2 free carbocations have been depicted, the transformations of longipinene epoxide (**18**) to the products **19** and **21**, must be concerted and the pathways mutually exclusive.

The first diol in order of polarity was a crystalline compound of m.p. 153-154°C, isolated in 2% yield and has been labelled diol-I. From spectral data (^{1}H NMR) of the diol and the derived diacetate, it is clear that both hydroxyls are secondary. On oxidation with pyridinium chlorochromate, a dione (m.p. 105-106°C; IR, C=O 1736, 1704 cm^{-1}) was obtained. Wolff-Kishner reduction of this dione furnished longibornane (**24**)[17]. Taking all these facts into account, structure **25** is considered appropriate for this diol. The coupling constants of the two CHOH/CHOAc protons are consistent with their environment (vide Experimental). This diol arises by transannular hydride shift as shown in **26**, for which there is a precedence[6,17].

The next diol (diol-II, m.p. 148-149°C; yield, 2-4%) has one tertiary and one secondary hydroxyl (^{1}H NMR; monoacetate; CrO_3 oxidation to hydroxy ketone) and has been formulated as **27**, a product of trans-cleavage of the oxirane ring in **28**. Structure **27** has been confirmed by its synthesis from (-)-marsupellol **28**[9] by oxymercuration-demercuration hydration procedure, and will be reported elsewhere.

The third and the most polar diol (diol-III, m.p. 174-177°C; $[\alpha]_D$ +94°, c 1.7% in EtOH) was obtained in a yield of 6-8%. From its spectral data, (vide Experimental) it has been formulated as **29**, arising by way of **30**. A survey of literature showed that a compound isocentdarol (m.p. 165°C; $[\alpha]_D$+5°, c 1% in EtOH) had been isolated[18] from wood of Cedrus deodar Loud. and assigned structure **31**. Though its physical constants (m.p., $[\alpha]_D$) were quite different from our diol-III, their ^{1}H NMR spectral data appeared close. An authentic sample of isocentdarol was obtained by courtesy of Dr. Rastogi, when it was found that its IR and ^{1}H NMR spectra were essentially identical with those of diol-III. A m.p. determination of isocentdarol gave a value 169-174°C and mixed m.p was 171-175°. From these we conclude that diol-III is a purer version of isocentdarol. Considering its mode of formation (cf. **30**) from longipinene epoxide, the structure of isocentdarol stands revised to **29**.



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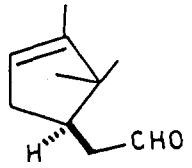

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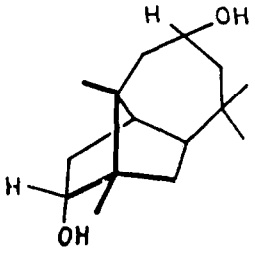

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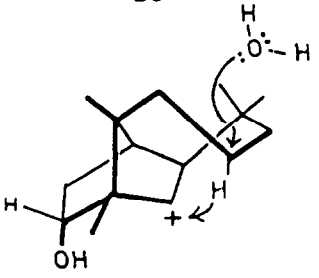

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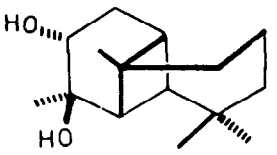

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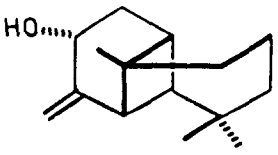

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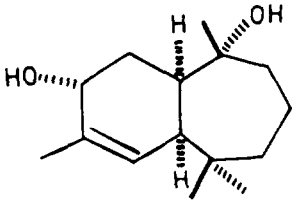

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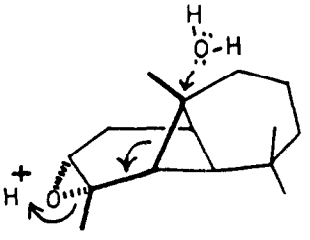

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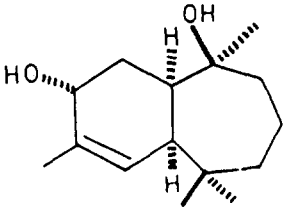

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EXPERIMENTAL

All melting points and boiling points are uncorrected. Petroleum ether refers to fraction of b.p. 60-80°. Alumina used for chromatography was made neutral by the HNO_3 method[19] and graded according to Brockmann[20]. TLC was carried out on silica gel layers (0.25 mm) containing 15% gypsum and activated at 110-115°C (2 h); 1% vanillin in 50% H_3PO_4 aqueous was used as the spray reagent.

The following instruments were used for spectral/analytical data: Schmidt +Haensch electronic polarimeter model Polatronic 1; Perkin-Elmer model 402 Infrared Spectrophotometer; Perkin-Elmer model R32 (90 MHz) NMR Spectrometer; Varian Mat CH7 Mass Spectrometer (70 eV, direct inlet system); Hewlett-Packard 5712A and 7624A Gas Chromatographs (A1 columns, 180 x 0.6 cm; support 60-80 mesh Chromosorb W; carrier gas, H_2). All ^1H NMR spectra were recorded with 10-15% solution in CCl_4 with TMS as internal reference; signals are reported in ppm (δ); while citing ^1H NMR data, following abbreviations have been used: s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet), b(broad). While summarising mass spectral data, besides the molecular ion, only abundant ions (m/z) are reported with their relative intensities. IR spectra were taken on films for liquids and in KBr pellets for solids; values are given in cm^{-1}.

(+)-α-Longipinene (11)

A 'prefraction' (3.34 Kg) from commercial production (Camphor and Allied Products, India) of longifolene from Indian turpentine oil (ex Pinus roxburghii Sarg. Syn. P. longifolia Roxb.), which contained some 20% longipinene (GLC) was carefully fractionated to get a rich (>90%) cut of longipinene (450 g). This was purified by chromatography over Al_2O_3/I to get pure (+)-α-longipinene, b.p. 78-80°C/1.5 mm, n_D^{25} 1.4959, $[\alpha]_D^+$ 40°($CHCl_3$, c 1.5%). Mass spectrum: 204(22%), 161(16%), 136(11%), 133(45%), 119(100%), 107(32%), 105(54%), 93(42%), 91(37%), 55(37%). IR spectrum: 1649, 1430, 1360, 1139, 781. ^1H NMR spectrum: 0.84s, 6H(CH_3); 0.90s, 3H(CH_3); 1.65dd, 3H(CH_3-C=C); 5.14m, 1H(C=CH). (Lit.[4,21,22]).

Action of acids on longipinene

(a) Boron trifluoride etherate. To a solution of $BF_3.Et_2O$ (2.5 g) in

dry ether (50 ml), longipinene (5.1 g, 0.025 mole) was added with stirring and the reaction mixture stirred at 28±2° till GLC (10% Carbowax, 150°C) of an aliquot showed maximum conversion (7 h). The reaction mixture was washed with water (10 ml x 4), 20% Na_2CO_3 aq. (10 ml x 1), dried (Na_2SO_4) and freed of solvent to get a product which was distilled, yield 4.5 g, b.p. 96-110°C/1.5 mm. GLC indicated the composition shown in Table 1. Products were separated by preparative GLC and further purified by chromatography over 10% $AgNO_3$-silica gel[23]. Products were identified by comparison of their spectral data with those of authentic samples.

(b) Perchloric acid. To a mixture of dioxane (4 ml), water (1 ml)and $HClO_4$ aq. (60%, 45 mg), longifonene (0.4 g) was added and stirred at 90° (2 h) and worked up as above.

(c) Sulphamic acid. A solution of longipinene (2.0 g) in dry acetone (50 ml) containing H_2NSO_2OH (1g) was refluxed for 18 h, bulk of solvent was removed and the residue diluted with water and the product taken up in ether (25 ml x 2) and further worked up as under (a).

(d) Sulphuric acid. To a solution of longipinene (1.0 g) in glacial AcOH (4 ml), H_2SO_4 aq. (50% v/v, 0.4 ml) was added and the mixture stirred at 25± 2° for 1 h, and then worked up as under (a).

(+)- α-Longipinene epoxide (18)

To a solution of longipinene (52 g, 0.255 mole) in $CHCl_3$ (156 ml) containing suspended $NaHCO_3$ (42 g), 30% peracetic acid aqueous (100 ml, 0.4 mole) was introduced with stirring and cooling at -5° to -3°C. After stirring for a total of 4 h at that temperature, the product was worked up as usual to get 57 g of crude epoxide. This was purified by precise fractionation on a spinning band column (45 theoretical plates) to furnish pure longipinene epoxide (44 g) b.p. 100°C/1.5 mm, n_D 1.4936, $[\alpha]_D$ + 69.6° ($CHCl_3$, c 4.6%). Mass spectrum: 220(M^+, 8%), 204(25%), 161(24%), 105(100%). IR spectrum: 1465, 1450, 1376, 1350, 1208, 913, 828. ^1H NMR spectrum: 0.84s, 3H(CH_3); 0.86s, 3H(CH_3); 0.90s, 3H(CH_3); 1.31s, 3H(CH_3-C - C); 2.91bs, 1H(C - CH).

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Action of acid on longipinene epoxide

To a stirred solution of above epoxide (7.0 g, 0.032 mole) in dioxane (21 ml) and water (5 ml), $HClO_4$ aq. (60%, 0.2 ml) was added with stirring and cooling (0-2°C) till TLC (solvent: 25% EtOAc in toluene) showed essentially complete disappearance of epoxide (1.5 h). The reaction mixture was worked up with ether in the usual manner to give a crude product (7.0 g). Analysis of an aliquot after acetylation (Ac_2O/pyridine, 30-35°, 16 h) by GLC (10% SE30, 200°) revealed at least five components. This product (7.0 g) was chromatographed over Al_2O_3/II (65 cm x 2.2 cm) with TLC/GLC monitoring. Elution was carried out with petroleum ether and petroleum ether containing increasing amounts of EtOAc. After rejecting a material (0.358 g) eluted with petroleum ether, the following compounds were finally isolated:

(a) Secolongifolene aldehyde (19). This product (2.1 g) was eluted with 2-3% EtOAc in petroleum ether (100 ml x 8), and was purified by distillation, b.p. 130-32°C/2 mm, n_D^{25} 1.4985, $[\alpha]_D$ + 15.54° ($CHCl_3$, c 3.8%). Mass spectrum: 220(M^+, 48%), 205(17%), 105(100%). IR spectrum: 2961, 2871, 1725, 1462, 1362, 832. ^1H NMR spectrum: 0.88s, 3H(CH_3); 0.95s, 6H(CH_3); 1.54bs, 3H(Me-C=C); 5.4bs, 1H(C=CH); 9.66dd, 1H(CHO, J_1=3 Hz, J_2=2 Hz).

(b) Mono-ol (21). This product (2.1 g) was eluted with 5% EtOAc in petroleum ether (100 ml x 8) and was further purified by two crystallizations from CH_3CN, m.p. 109-110°C, $[\alpha]_D$-117.65° ($CHCl_3$, c 1.3%). Mass spectrum: 220(M^+, 43%), 205(34%), 149(37%), 109(100%). IR spectrum: 1630, 1452, 1065, 1021, 890. ^1H NMR spectrum: 0.95s, 3H(CH_3); 1.76bs, 3H(CH_3-C=C); 3.94m, 1H(CHOH); 4.76s, 2H($C=CH_2$); 5.48m, 1H(CH=C). For $C_{15}H_{24}O$ (220.34) calculated: 81.76%C, 10.98%H; found: 81-82%C, 10.91%H.

(c) Diol-I (25). The material (0.81 g) eluted with 6-50% EtOAc in petroleum ether (100 ml x 15) was essentially a mixture of three components. It was rechromatographed over silica gel/IIA^{24} (34cm x 2.5 cm) and fractions collected as before. 10% EtOAc in petroleum ether (35 ml x 10) furnished 80 mg of a solid which was crystallized from CH_3CN to give pure XXV, m.p. 153-154°. Mass spectrum: 220(M^+-H_2O, 68%), 191(31%), 133(50%), 107(100%). IR spectrum: 1362, 1280, 1117, 1049. ^1H NMR spectrum: 0.80s, 3H(CH_3); 0.98s, 6H(CH_3); 1.03s, 3H(CH_3); 3.87bs,

1H(CHOH): 4.10dd, 1H(CHOH). For $C_{15}H_{26}O_2$ (238.36) calculated: 75.58%C, 11.00%H; found: 75.54%C, 11.20%H.

(d) Diol-II (27). In the above chromatography, this product (80 mg) was eluted with 12% EtOAc in petroleum ether (35 ml x 16), and was recrystallized from CH_3CN: m.p. 148-149°, $[\alpha]_D$- 33.33°($CHCl_3$, c 1.8%). Mass spectrum: 220(M^+-H_2O, 16%), 177(40%), 136(30%), 135(33%), 123(54%), 109(83%), 95(100%). IR spectrum: 1361, 1205, 1100, 1022. ^1H NMR spectrum: 0.90s, 6H(CH_3); 1.03s, 3H(CH_3); 1.33s, 3H(CH_3); 4.28dd, 1H(CHOH, J_1=10 Hz, J_2=4 Hz). For $C_{15}H_{26}O_2$ (238.36) calculated: 75.58%C, 11.00%H; found: 75.51%C, 11.05 %H.

(e) Diol-III (Isocentdarol, 29). This fraction (0.5 g) was eluted with EtOAc (35 ml x 4) and was recrystallized from CH_3CN: m.p. 174-177°, $[\alpha]_D$ + 94° (EtOH, c 1.7%). Mass spectrum: 220(M^+-H_2O, 11%), 133(86%), 136(77%), 109(100%). IR spectrum: 1630, 1282, 1044, 1020, 908. ^1H NMR spectrum: 0.82s, 3H(CH_3); 1.01s, 3H(CH_3); 1.28s, 3H(CH_3); 1.67d 3H(CH_3-C=C, J=1.5 Hz); 4.05bs, 1H(CHOH); 5.75dd, 1H(C=CH, J_1=5 Hz, J_2=1.5 Hz). For $C_{15}H_{26}O_2$ (238.36) calculated: 75.58%C, 11.00%H; found: 75.45%C, 11.10%H.

Acetylation of diols

To a solution of the diol (0.0001 mole) in dry pyridine (1 ml), Ac_2O (1 ml) was added and the reaction mixture left aside at room temperature (30°) for 16 h. Ac_2O and pyridine were removed under reduced pressure from a water bath (60-70°C), the residue taken up in $CHCl_3$ (10 ml) and worked up in the usual manner.

(a) Diol-I diacetate: viscous liquid, $[\alpha]_D$-45.68°($CHCl_3$, c 3.94%). Mass spectrum: 322(M^+, 4.5%), 262(100%), 220(100%), 242(90%), 176(80%), 161(90%), 91(100%). IR spectrum: 1710, 1355, 1250, 1025, 910. ^1H NMR spectrum: 0.78s, 3H(CH_3); 0.88s, 3H(CH_3); 0.94s, 3H(CH_3); 0.95s, 3H(CH_3); 1.97s, 6H(CH_3CO); 4.97dt, 1H(CHOAc, J_1=10 Hz, J_2=2.5 Hz); 5.34dd, 1H(CHOAc, J_1=5 Hz, J_2=1.5 Hz). For $C_{19}H_{30}O_4$ (322.43) calculated: 70.77%C, 9.38%H; found: 70.23%C, 9.41%H.

(b) Diol-II hydroxyacetate: viscous liquid, $[\alpha]_D$+ 65.59° ($CHCl_3$, c 0.93%). Mass spectrum: 280(M^+, 4.5%), 220(100%), 177(80%), 121(75%), 109(80%). IR spectrum: 1710, 1362, 1230, 1010, 950, 915. ^1H NMR

spectrum: 0.89s, 3H(CH_3); 0.90s, 3H(CH_3); 1.04s, 3H(CHOAc, J_1=10 Hz, J_2=4 Hz). For $C_{17}H_{28}O_3$ (280.39) calculated: 72.82%C, 10.06%H; found: 72.53%C, 10.00%H.

Oxidation of diols

To a stirred solution of the diol (0.0001 mole) in CH_2Cl_2 (3 ml) was added pyridinium chlorochromate (0.0003 mole). The reaction mixture was stirred at room temperature (30-35°) till TLC indicated disappearance of the starting diol (5h). The reaction mixture was passed through a column of silica gel (3 cm x 1.7 cm) and the product eluted with ether (50 ml). Evaporation of the solvent gave tthe crude product, which was purified further by preparative TLC (solvent: 15% EtOAc in toluene).

(a) Diol-I diketone: m.p. 105-106°(CH_3CN), $[\alpha]_D$-240°($CHCl_3$, c 0.25%). Mass spectrum: 234(M^+, 100%), 123(90%), 121(96%), 110(75%). IR spectrum: 1740, 1708, 1446, 1000, 940. ^1H NMR spectrum: 0.92s, 3H(CH_3); 0.94s, 3H(CH_3); 1.06s, 3H(CH_3); 1.18s, 3H(CH_3). For $C_{15}H_{22}O_2$ (234.33) calculated: 76.88%C, 9.46%H; found: 76.23%C; 9.41%H.

(b) Diol-II hydroxyketone: m.p. 140-141°(CH_3CN). Mass spectrum: 236(M^+, 12%), 208(82%), 123(80%), 109(85%), 81(100%). IR spectrum: 3450, 1709, 1445, 1106, 1083, 915. ^1H NMR spectrum: 0.92s, 3H(CH_3); 0.94s, 6H(CH_3); 1.22s, 3H(CH_3). For $C_{15}H_{24}O_2$ (236.34) calculated: 76.22%C, 10.24%H; found: 76.00%C, 9.90%H.

Longibornane (24)

The diol-I diketone (50 mg), dissolved in diethylene glycol (0.5 ml) was added to diethylene glycol (3 ml) in which Na (40 mg) and anhyd. hydrazine (50 mg) had been earlier dissolved. Reaction was carried out and worked up as earlier reported for Wolff-Kishner reduction of longibornan-9-one[17].

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