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STUDIES IN SESQUITERPENES—XLV

STRUCTURE OF AN ALCOHOL FROM HYDRATION OF LONGIFOLENE*†

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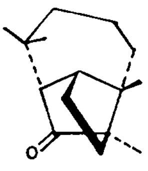
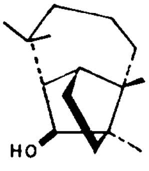
Abstract—Hydration of longifolene under acid catalysis gives, besides longiborneol, one secondary alcohol and a tertiary alcohol. The structure of the secondary alcohol, which is the major alcohol, has now been elucidated. This alcohol, now characterized as longibornan-9-ol, arises by transannular hydration of longifolene.

IT HAS already been reported[1] that longifolene (I) on treatment with Bertram–Walbaum reagent produces three alcohols (as acetates) besides isolongifolene. One of these alcohols on CrO_3 oxidation produced the known[2] longicamphor (II) and the parent alcohol was thus assumed to be longiborneol (III).[2] The structures of other two alcohols remained unelucidated. We now report on the complete analysis of the "acetate" mixture, isolation of longibornyl acetate and the structure elucidation of one of the new alcohols.


I


II



III

GLC of the total oxygenated hydration product showed it to consist of at least five components. Systematic chromatography, along with GLC monitoring, showed that, in fact, six components are present—three acetates (~90%) and the corresponding three alcohols. GLC of the total saponified product showed the three alcohols (with RRT of 1, 1·32 and 1·60) to be present in the approx ratio of 2:3:9 respectively.

During the abovementioned systematic chromatography of the total "acetate" both longiborneol (III; RRT 1·32) and its acetate were obtained pure and identified by comparison (GLC, IR) with authentic samples. Thus, acid-catalysed hydration of longifolene yields longiborneol (III) and not its epimer (longi-isoborneol, IV) in complete contrast to the behaviour of camphene (V) which under the same conditions yields only the *exo*-isomer, isoborneol (VI).[3] However, these results are completely

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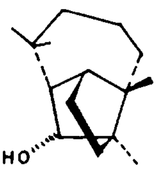
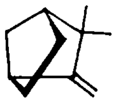
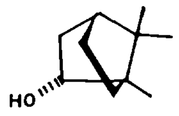


IV



V



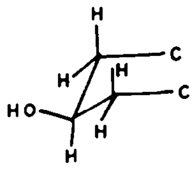
VI

expected in view of the known *endo*-attack of halide ions during exposure of longifolene to hydrogen halides.[2,4]

Structure of solid alcohol A

Fractionation of the total saponified alcohols has been shown[1] to yield a solid alcohol (m.p. 107–108°) in the tail fractions. This alcohol was designated[1] "solid alcohol-A" and corresponds to the GLC component with RRT of 1·60 (GLC of total alcohols). This compound is most conveniently obtained by precise fractionation of the total alcohols, as already described.[1]

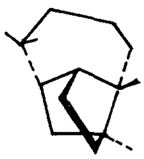
This compound, $C_{15}H_{26}O$, is clearly a secondary alcohol (IR: OH 3300 and 1020 cm^{-1}. PMR: C$\underline{H}$OH, 1H multiplet centred at 236 c/s; CHO$\underline{H}$, 1H singlet at 128 c/s, concentration dependent. 3,5-Dinitrobenzoate,[1] m.p. 144–145°) and since it contains no olefinic linkage (no colour with tetranitromethane, no olefinic proton in PMR spectrum) it must be tricyclic. Its PMR spectrum also shows signals for four quaternary Me's (49, 52·5, 54 and 57·5 c/s) and since the C$\underline{H}$OH signal, centred at 236 c/s, appears as a broad multiplet (essentially a septet) with a large half-band width (W_H = 20 c/s) it must be axially oriented and should be coupled with two neighbouring axial-type protons.[5] The same situation obtains in the PMR spectrum of the derived acetate (quaternary Me signals at 48, 53, 54 and 58 c/s): —C$\underline{H}$OAc, 1H essentially a septet, centred at 303 c/s, W_H = 24 c/s. These results suggest the presence of the grouping VII in alcohol A.

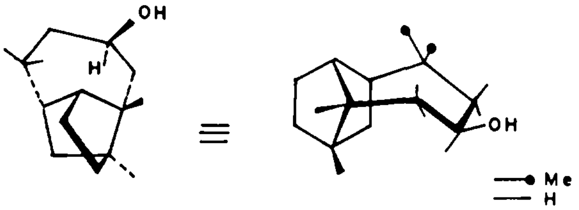


VII

Pyridine-chromic acid oxidation of alcohol-A furnished the corresponding ketone, reported earlier.[1] From it $\nu^{C=O}$ 1692 cm^{-1}, it is clear that the ring containing the C=O function should be 6-membered or larger. On base-catalyzed D-exchange, the ketone incorporated four D-atoms as was clear from a comparison of the mass and PMR spectra of the non-deuterated (M^+, $m/e = 220$; PMR: a total of 5H signals located between 120–152 c/s, region in which protons α to a C=O are normally observed) and deuterated (M^+, $m/e = 224$; PMR: signals in the 120–152 c/s region integrate for ~1·5 protons) samples. These results clearly support the part structure, VII, deduced above.

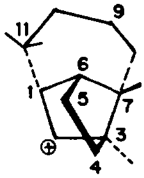
On Wolff–Kishner reduction, the above ketone furnished a hydrocarbon, identified as longibornane (VIII) by comparison (IR, PMR) with an authentic sample prepared from longibornyl bromide.[2] This finding taken in conjunction with the conclusions drawn earlier lead to the only possible structure IX for alcohol A. The configuration (and conformation) of the OH group is dictated by the PMR spectral evidence (cf. VII) discussed earlier, as well as by the mechanistic considerations obtained below.


VIII

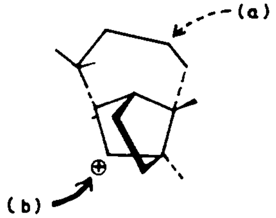


IX

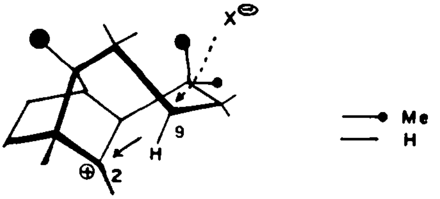
The alcohol-A evidently arises from the carbonium ion (X) by a transannular attack by the nucleophile ($X^{\ominus}$) on C_9 with the simultaneous migration of the α-hydrogen (hydride ion) at C_9 to the electron-deficient centre (XII). It must be noted that the vacant *p*-orbital at C_2 is well-oriented in the direction of the α-H at C_9 which is in close proximity to electron-deficient centre. Thus, both longiborneol (III) and alcohol-A (IX), henceforth called longibornan-9-ol, arise from the same species X,



X



XI



XII

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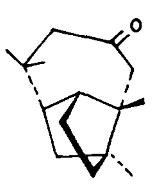
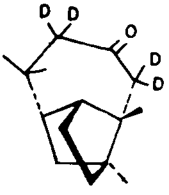
* Transannular shifts (initiated by free radicals) have been observed earlier in the longifolene chemistry.[6]

front side attack (b, XI) leading to longiborneol and backside nucleophilic attack (with concomitant hydride shift) generating longibornan-9-ol.

Mass spectrum of longibornan-9-one. Mass spectrum of longibornan-9-one (XIII) is shown in Fig. 1. The fragmentation pattern of this ketone, briefly discussed below, is readily rationalized in terms of its structure, thus providing additional support for the structure of alcohol-A.

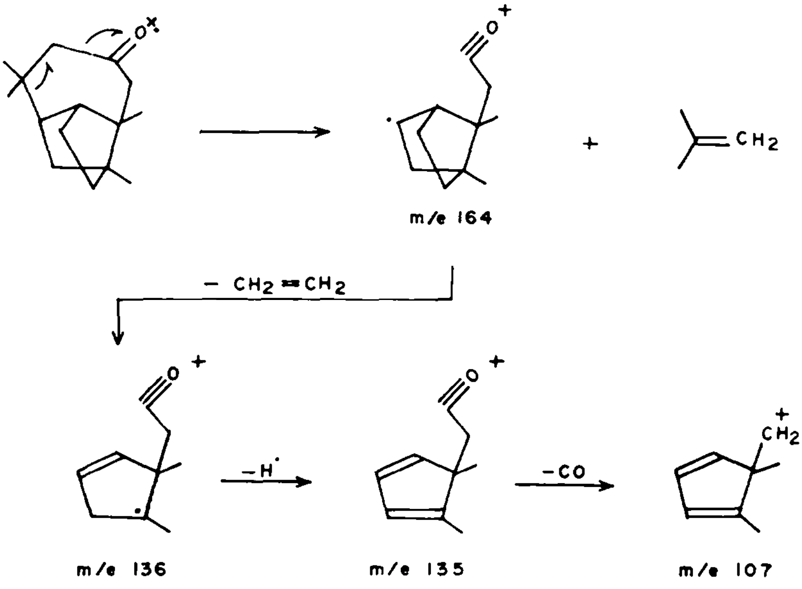


XIII

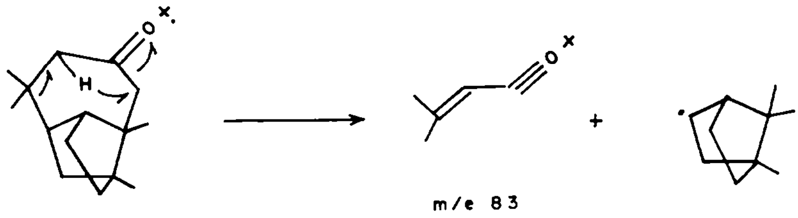


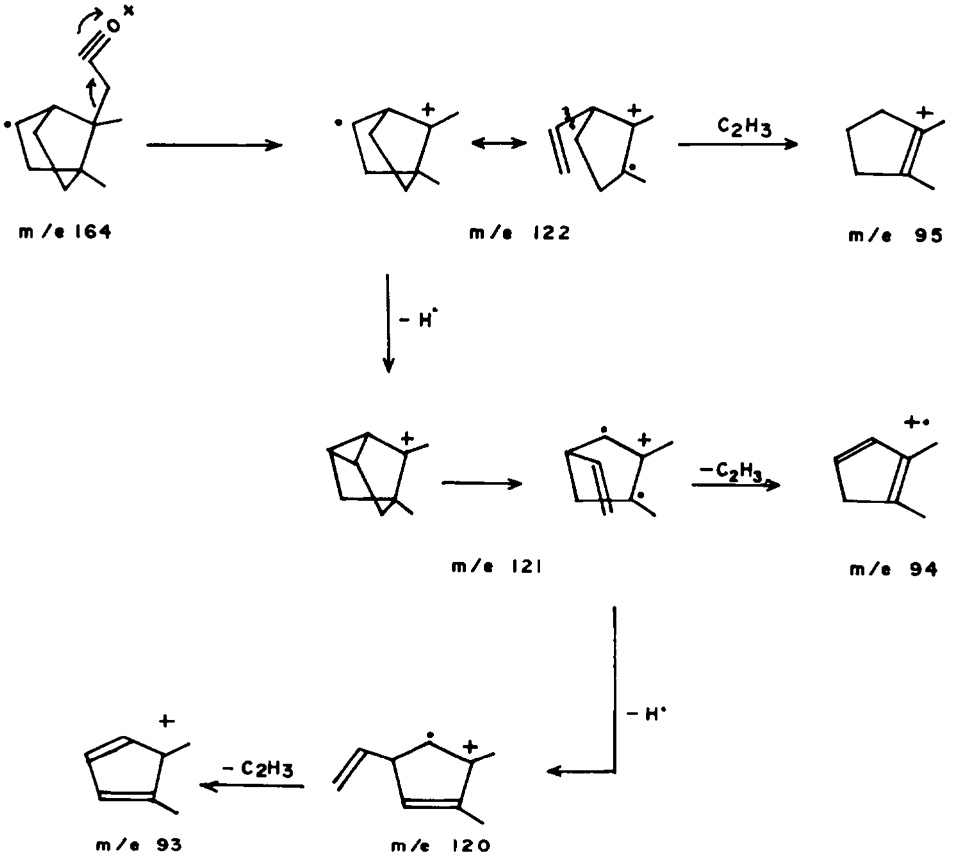
XIV

As expected from the number of quaternary Me's, M-15 ion (at m/e 209 in the mass spectrum of d_4-analog XIV) is quite intense. A comparison of the mass spectra of XIII and XIV reveals that ions at m/e 164, 136, 135 and 107 (for XIII) must retain one of the α-methylene groups in tact (ions at m/e 166, 138; 137 and 109 for XIV) and possibly arise as under:[7]



The ion corresponding to *m*/*e* 83 in XIII occurs at *m*/*e* 84 in the spectrum of XIV:





The ions *m*/*e* 122, 121, 120, 95, 94 and 93 are common in the spectra of both XIII and XIV, and one possible mode of genesis of these ions is indicated above.

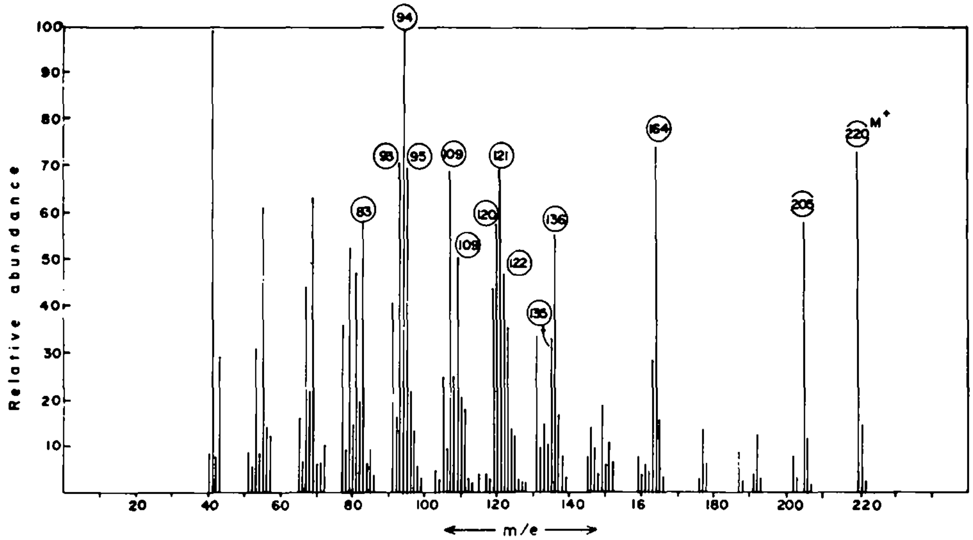


FIG. 1 Mass spectrum of longibornan-9-one (XIII)

EXPERIMENTAL

For general remarks see Part XL of this series. GLC was carried out on "Aerograph" model A-350-B using a 300 cm × 5 mm column packed with 20% diethylene glycol polysuccinate on Chromosorb W (60–80 mesh) with H_2 as carrier gas (30 ml/min) at 200°. The mass spectra were recorded on a CEC mass spectrometer, model 21-110B, using an ionizing potential of 70 eV and a heated inlet system.

Separation of total "acetates"

GLC of the total acetate mixture,[1] from the hydration of longifolene, showed 5 components (a, b, c, d and e) with RRT respectively of 1, 1·18, 1·40, 1·61 and 2·05 and having areas in the approx ratio 20:55:12:7:1. Peak b contains two components (b′ and b″) as shown by column chromatography described below.

Chromatography of the acetate mixture (12 g) over SiO_2-gel (grade II;[8] 500 g, 52 cm × 7 cm) gave the following fractions:

Fraction 1: light petroleum	9 × 200 ml traces of isolongifolene
Fraction 2: 5% C_6H_6 in light petroleum	10 × 200 ml
10% C_6H_6 in light petroleum	10 × 200 ml
25% C_6H_6 in light petroleum	10 × 200 ml
Fraction 3: 50% C_6H_6 in light petroleum	4 × 200 ml 0·9 g of essentially a
Fraction 4: 50% C_6H_6 in light petroleum	8 × 200 ml 4·32 g, mix. of a, b′ and c
Fraction 5: 50% C_6H_6 in light petroleum	9 × 200 ml 2·75 g, b′ with some c.
Fraction 6: 50% C_6H_6 in light petroleum	4 × 200 ml 0·19 g, partly crystalline, mostly d.
Fraction 7: C_6H_6	4 × 200 ml 0·66 g, crude d.
Fraction 8: C_6H_6	1 × 200 ml 0·59 g, crude b″.
Fraction 9: C_6H_6	1 × 200 ml 0·28 g, mix. of b″ and e
Fraction 10: C_6H_6	4 × 200 ml 0·49 g, crude e
Fraction 11: 5% EtOAc in C_6H_6	5 × 200 ml 0·18 g, crude e.

GLC component a (*longibornyl acetate*). Rechromatography of fraction 3 (0·88 g) over SiO_2-gel (grade II; 50 g, 45 cm × 1·5 cm) gave on elution with light petroleum C_6H_6 (1:1) 230 mg of pure a, identified (IR, mixed GLC) as longibornyl acetate.

GLC component d (*longiborneol*). Fraction 7 on recrystallization from light petroleum gave longiborneol (330 mg), m.p. 106–107°.

GLC component b″ (tertiary alcohol[1]*).* Fraction 8, after three crystallizations from acetonitrile furnished the so-called alcohol-B[1] (280 mg), m.p. 94–95°.

GLC component e (longibornan-9-ol). Fraction 10, 11 were mixed and crystallized from acetonitrile to give 382 mg of alcohol-A,[1] m.p. 105–106°.

It was demonstrated by mixed GLC that GLC component b′ is acetate of alcohol-A, while GLC component ċ is acetate of alcohol-B.

Deutero-longibornan-9-one

The ketone[1] (100 mg), derived from alcohol-A (longibornan-9-ol), was added to EtOD (5 ml) containing EtONa (from 15 mg of Na) and the mixture refluxed, under anhydrous conditions, for 1 hr. Excess EtOD was then flashed off, under vacuum at room temp and the residue treated with EtOD (2·5 ml) refluxed and worked up as above. This operation was carried out six times in all. In the final exchange reaction, after refluxing, two drops of gl AcOH were added, followed by dilution with water (10 ml) and extraction with light petroleum (3 × 15 ml). The extract was washed once with brine (10 ml) and dried (Na_2SO_4). Removal of solvent and distillation of residue gave 100 mg of longibornan-9-one-d_4.

Wolff-Kishner reduction[9] *of longibornan-9-one*

The ketone[1] (510 mg) dissolved in diethylene glycol (5 ml) was added to diethylene glycol (15 ml) in which Na (200 mg) and anhyd hydrazine (250 mg) had been earlier dissolved. The reaction mixture was first heated at 170° (10 hr) and then at 220° (24 hr). The product was cooled, diluted with water (50 ml) and acidified with HClaq to Congo red. This was extracted with ether (4 × 25 ml), the extract washed with brine and dried. Solvent was flashed off and the residue taken up in light petroleum (15 ml) and filtered through Al_2O_3 (grade I, 10 g), the column being washed with light petroleum. The solvent was removed and the residue distilled to give a colourless liquid (460 mg): b.p. 115°/3 mm; PMR spectrum: quaternary Me signals at 44, 49, 52 and 57 c/s.

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[5] e.g. see: N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry* pp. 77–85. Holden-Day, San Francisco (1964).

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[7] e.g. cf. H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* pp. 1–26, 140–160, Holden-Day, San Francisco (1964).

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