299. d-*Phellandral and* d-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one.*

By P. A. Berry, A. Killen Macbeth, and T. B. Swanson.

The biogenetic relationship *l*-β-phellandrene, *l*-phellandral, *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, disclosed in the examination of the oil of *E. cneorifolia*, led to the examination of the oil of water fennel (*Phellandrium aquaticum*, L.), since this is a reputed source of *d*-β-phellandrene. It is now found that this oil contains *d*-phellandral (α_D + 116·22°, homogeneous), associated with *d*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one {α_D + 52·16°, homogeneous; $[\alpha]_D$ + 64·57° (alcohol; c = 5·556)}.

Examination of the nitrosite, and oxidation experiments support the previous observation that *d*-β-phellandrene is present in the oil. The occurrence in water-fennel oil of the stereoisomerides of the three related compounds found in *E. cneorifolia* appears to lend support to the biogenesis suggested.

As the examination of the seasonal variation of the oil of *E. cneorifolia* (preceding paper) disclosed the biogenetic relationship *l*-β-phellandrene, *l*-phellandral, *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, it was thought of interest to examine the stereochemical character of phellandral from sources known to contain *d*-β-phellandrene. Attention was accordingly directed to water-fennel oil, obtained from the seeds of *Phellandrium aquaticum*, L., since a phellandrene identified in this oil by Pesci (*Gazzetta*, 1886, **16**, 225) was later considered by Wallach (*Annalen*, 1905, **340**, 2) to be *d*-β-phellandrene.

Water-fennel seeds were obtained for us by Messrs. Stafford Allen & Sons., Ltd., to whom we are greatly indebted, and before distillation they were compared with a specimen in the museum of the Pharmaceutical Society, and found to be undoubtedly genuine fruits, although inferior to the authentic specimen in size and colour. On distillation, the seeds yielded about 1% of oil in which the presence of *d*-β-phellandrene has now been confirmed. The mutarotation of *l*-α-phellandrene-α-nitrosite has been studied by Read and his collaborators (J., 1923, **123**, 1657; 1924, **125**, 930), and a marked change, with reversal of sign of rotation, was observed. In contrast with this, the mutarotation of *d*-β-phellandrene-α-nitrosite is slow and reversal of sign has not been noted. The specimens of the nitrosite prepared had m. p. 102—103° and $[\alpha]_D$ from — 153° to — 165·7° in chloroform, with a mutarotation to about half this value in 200 hours. Similar slow mutarotation has also been observed with *l*-β-phellandrene-α-nitrosite prepared from eucalyptus oils.

The examination of the oil has also confirmed the presence of phellandral, but although this has previously been reported as having a lævorotation of some — 36·3° (Schimmel and Co. Report, October, 1904, 88), we now find it to be the dextrorotatory aldehyde (α_D + 116·22°, homogeneous).

We have also found that the oil contains 4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, and this also is dextrorotatory {$[\alpha]_D$ + 64·57° in alcohol (c = 5·556); α_D + 52·16°, homogeneous}. The biogenetic relationship between these three substances, which has been suggested to hold in the case of eucalyptus oils, would thus appear to receive confirmation from the results now recorded in the case of water-fennel oil, in which the stereoisomerides are in each case found to be present.

EXPERIMENTAL.

The oil was of a deep orange colour and possessed the characteristic odour of water-fennel. It had the following physical constants: $d_{15\cdot5^\circ}^{15\cdot5^\circ}$ 0·880; $n_D^{20^\circ}$ 1·4839; $[\alpha]_D$ + 22·4°, homogeneous; which are in good agreement with those previously recorded, *viz.*, d^{15° 0·85—0·89; $n_D^{20^\circ}$ 1·484—1·495; α_D + 12·42—19° (Gildemeister and Hoffmann, "The Essential Oils," 2nd Edn., III, 358). The aldehyde content of the oil (including the ketone) was approximately 14%.

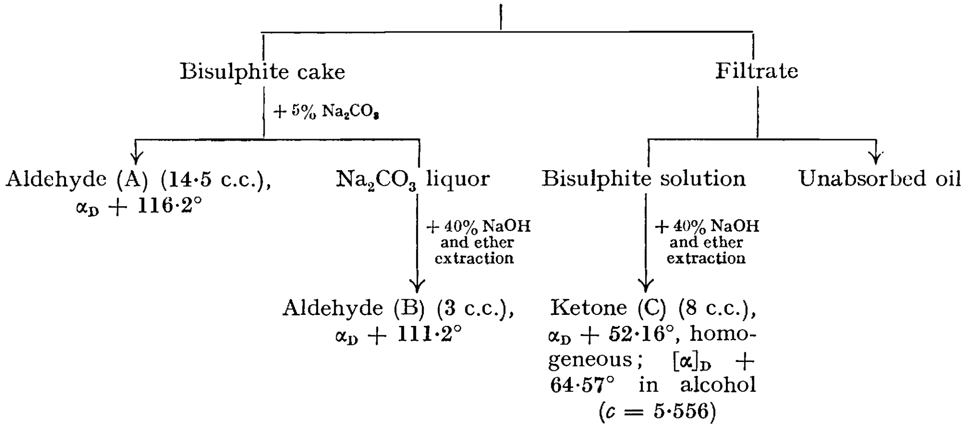
The oil (500 c.c.) was fractionated through a 70-cm. Widmer–Schenck column, and after collection of the main fractions, the residue (136 c.c.) was steam-distilled to separate aldehydes, alcohols, etc., from polymerised products, with the following results:

Fraction.	B. p.	$d_{15\cdot5^\circ}^{15\cdot5^\circ}$.	$[\alpha]_D$.
(1) 15 c.c.	21—41°/7 mm.	0·8523	+20·18°
(2) 64 c.c.	41—47/7 mm.	0·8575	+20·8
(3) 166 c.c.	44/4 mm.	0·8564	+18·85
(4) 89 c.c.	44—59/4 mm.	0·8509	+16·16
(5) 9 c.c.	59/4 mm.	—	—
Steam-distillate (94 c.c.)		0·9400	+43·62

d-β-*Phellandrene.*—The nitrosite was prepared in the usual way from fraction (2), and purified by repeated precipitation from chloroform solution by methyl alcohol. It had m. p. 96° and $[\alpha]_D - 159{\cdot}4°$ in chloroform ($c = 1{\cdot}255$). A solution of the nitrosite in chloroform showed slow mutarotation, finally attaining a value of $[\alpha]_D - 86°$ after 216 hours. The nitrosite was also prepared from fraction (3), and had m. p. 99°, $[\alpha]_D - 162{\cdot}6°$ in chloroform ($c = 1{\cdot}255$). Further purification raised the m. p. to 102—103° and $[\alpha]_D$ to $- 165{\cdot}7°$. The chloroform solution again showed the slow mutarotation, falling to a final value of $- 97{\cdot}2°$ after 288 hours. The optical sign indicates that the substance is an α-nitrosite of *d*-phellandrene, and the slow mutarotation without reversal of sign of rotation, which is in contrast with the behaviour of the α-phellandrene-α-nitrosites, indicates that the derivative is *d*-β-phellandrene-α-nitrosite. This behaviour of the α-nitrosite of β-phellandrene has been confirmed by the examination of the derivatives of *l*-β-phellandrene from *E. cneorifolia* and other sources.

The identity of the terpene as β-phellandrene was also shown by oxidation experiments. The regulated oxidation with 1% permanganate (Wallach, *Annalen*, 1905, **340**, 1) led to the isolation of the glycol, which, when distilled with 10% sulphuric acid, gave an aldehyde in the distillate. This on extraction gave a 2 : 4-dinitrophenylhydrazone, m. p. 203—204° after recrystallisation from chloroform–alcohol, which showed no depression on admixture with the corresponding derivative of *d*-phellandral (below). The ærial oxidation of fraction (4) was also examined. The oil (80 c.c.) was placed in a quartz flask with water (50 c.c.), and oxygen bubbled through at a rate sufficient to mix the two liquids during irradiation by light from a mercury lamp for 6 hours. The aldehyde content (calculated as $C_9H_{14}O$) rose from 3·3% to approximately 14·1%. Extraction with neutral sodium sulphite led to the isolation of the ketone *d*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, $\alpha_D + 46{\cdot}7°$ in alcohol ($c = 20$), which gave a *p*-nitrophenylhydrazone crystallising from methyl alcohol as glistening yellow needles, m. p. 167°, undepressed on admixture with the same derivative from another specimen of the *d*-ketone (below).

Isolation of the Aldehyde and Ketone.—The steam-distillate (86 c.c.) was shaken for 8 hours with sodium bisulphite (175 c.c., 35% solution), and the various aldehyde fractions separated as shown schematically below :



Identification of d-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one.*—The oil (C), separated on treatment of the bisulphite solution, was identified as this ketone by the preparation of the following derivatives : p-*nitrophenylhydrazone*, glistening yellow needles from methyl alcohol, m. p. 167·5° (Found : N, 15·3. $C_{15}H_{19}O_2N_3$ requires N, 15·4%) ; 2 : 4-*dinitrophenylhydrazone*, red needles from alcohol, m. p. 136° (Found : N, 17·3, 17·4. $C_{15}H_{18}O_4N_4$ requires N, 17·6%). Part of the ketone (2·5 g.) in alcohol (25 c.c.) was catalytically reduced in the presence of palladised charcoal (hydrogen absorbed at N.T.P., 416 c.c. ; theory, 396 c.c.), and the reduced ketone identified as 4-*iso*propyl*cyclo*hexanone by preparation of the semicarbazone, m. p. 186°, and the *p*-nitrophenylhydrazone, m. p. 124°, which gave no depression on admixture with the respective derivatives prepared from the reduction product of the *l*-ketone from eucalyptus oils.

Identification of d-*Phellandral.*—The preparation of derivatives showed that aldehydes (A) and (B) were the same, and they were identified as *d*-phellandral by the following compounds : semicarbazone, white leaflets, m. p. 200° ; *p*-nitrophenylhydrazone, yellow needles, m.p. 174—175° ; 2 : 4-*dinitrophenylhydrazone*, deep orange micro-crystals, m. p. 204° (Found : N, 17·0, 17·1. $C_{16}H_{20}O_4N_4$ requires N, 16·9%). The structural identity of the aldehyde with the *l*-

phellandral from eucalyptus oils was shown by oxidation by 4% permanganate solution. The oxidation product, recovered by extraction with ether after removal of the manganese dioxide and concentration and acidification of the filtrate, had, after recrystallisation from water and from chloroform–light petroleum, m. p. 71°, undepressed on admixture with the oxidation product (m. p. 70—72°) similarly prepared from *l*-phellandral from *E. cneorifolia* oil.

THE JOHNSON CHEMICAL LABORATORIES,
UNIVERSITY OF ADELAIDE.

[*Received, July* 12*th*, 1937.]