150. *The Carbonyl Constituents of Eucalyptus Oils. Part III. The Constitution of Phellandral.* d-, l-, *and* dl (*Synthetic*)-*Phellandric Acids.*

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Further evidence for the accepted constitution of phellandral has been obtained.

The constitution of phellandral (4-*iso*propyl-Δ^1-*cyclo*hexene-1-aldehyde, Δ^1-tetrahydrocuminal) is a matter of interest, as the evidence on which the accepted structure rests (Schimmel, *Semi-annual Reps.*, Oct./Nov., 1904, 90) cannot be regarded as a rigid proof. Additional support for this structure follows from the conversion of phellandric acid into hexahydrocuminic acid, the epimeric forms of which have already been characterised by Cooke and Macbeth (J., 1939, 1245). The 1 : 4 positions of the substituents in phellandral are thus established, and the position of the ethylene linkage is fixed by the synthesis of dl-*phellandric acid* from *α-bromohexahydrocuminic acid*, which is also now described.

To complete the proof the resolution of the synthetic acid into antipodes identical with the active acids derived from *d*- and *l*-phellandral is required, but this has not yet been achieved. The conversion of the natural aldehydes into the corresponding active acids is conveniently brought about by oxidation with silver oxide.

Experimental.

d-*Phellandric Acid.*—The spontaneous aerial oxidation of phellandral to phellandric acid is slow and gives rise to gummy products, so the change is better brought about by the action of silver oxide, following the method of Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39).

d-Phellandral (16 g.), isolated from water-fennel oil (Berry, Macbeth, and Swanson, J., 1937, 1448; Macbeth and Winzor, J., 1939, 264) and having a specific rotation of +73°, was dissolved in alcohol (600 c.c.), and silver nitrate added (38 g. in 120 c.c. of water). N/2-Sodium hydroxide (750 c.c.) was gradually added with vigorous shaking during ½ hour, and after further mechanical shaking for 3 hours the mixture was left overnight. The precipitated silver was removed and washed, the filtrate saturated with carbon dioxide, the alcohol distilled off, and the whole concentrated to about 700 c.c. On acidification after cooling, *d*-phellandric acid was precipitated; it was dried on tile and crystallised from dilute ethanol. The pure d-*phellandric acid* had m. p. 144—145° and $[\alpha]_D^{20°}$ +112·8° in methyl alcohol (*c*, 2·083) (Found: C, 71·6; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). The p-*chlorophenacyl* ester formed flat pearly needles from aqueous alcohol, m. p. 78—78·5°, $[\alpha]_D^{20°}$ +71° in chloroform (*c*, 1·967) (Found: C, 67·25; H, 6·45; Cl, 11·25. $C_{18}H_{21}O_3Cl$ requires C, 67·4; H, 6·6; Cl, 11·1%). The p-*bromophenacyl* ester separated in long fine needles from dilute alcohol, m. p. 86°, $[\alpha]_D^{20°}$ +68·1° in chloroform (*c*, 2·041) (Found: C, 59·05; H, 5·8; Br, 21·9. $C_{18}H_{21}O_3Br$ requires C, 59·2; H, 5·8; Br, 21·9%).

l-Phellandric acid formed by oxidation of *l*-phellandral with silver oxide as described above, had m. p. 144—145° and $[\alpha]_D^{20°}$ −112·6° in methanol (*c*, 2·07). It formed a p-*chlorophenacyl* ester, which crystallised in flat pearly needles from dilute alcohol or light petroleum, m. p. 78—78·5°, $[\alpha]_D^{20°}$ −57° in chloroform (*c*, 2·155) (Found: C, 67·2; H, 6·55; Cl, 11·2%). The p-*bromophenacyl* ester separated from dilute alcohol as a mass of fine needles, m. p. 86°, $[\alpha]_D^{20°}$ −52·2° in chloroform (*c*, 2·07) (Found: C, 59·25; H, 5·7; Br, 22·0%). *l*-Phellandric acid formed a p-*nitrobenzyl* ester when the sodium salt was refluxed in aqueous alcohol with a slight excess of *p*-nitrobenzyl bromide. After three crystallisations from methanol the ester was obtained in clusters of short, pale yellow needles, m. p. 56—57° (Found: C, 67·45; H, 6·9; N, 4·65. $C_{17}H_{21}O_4N$ requires C, 67·3; H, 7·0; N, 4·6%).

Conversion of l-*Phellandric Acid into Hexahydrocuminic Acid.*—(a) *l*-Phellandric acid (5 g.) in glacial acetic acid (30 c.c.) in the presence of platinum oxide (Adams's catalyst, 0·2 g.) was shaken with hydrogen in a flask attached to a shaking machine and warmed by a jet of steam. The theoretical amount of hydrogen was absorbed in about ¾ hour; after filtration from the catalyst and removal of acetic acid under reduced pressure, the residual oil was distilled at 138°/3 mm. The *cis*-hexahydrocuminic acid (3·5 g.) was identified by conversion into the *p*-chlorophenacyl ester, m. p. 61°, and the *p*-bromophenacyl ester, m. p. 85°, which showed no depression of m. p. when mixed with authentic derivatives (Cooke and Macbeth, *loc. cit.*). (b) *l*-Phellandric acid (8 g.), dissolved in 10% sodium hydroxide solution (50 c.c.), was hydrogenated in presence of Raney nickel at 120°/1360 lb. After 3 hours' shaking, the catalyst was filtered off on cooling, and the hexahydrocuminic acid precipitated by hydrochloric acid. The product solidified in the refrigerator after some hours, and was crystallised from formic acid. It had m. p. 94—95° and was identified as *trans*-hexahydrocuminic acid by preparation of the *p*-chlorophenacyl ester, m. p. 97·5° (Cooke and Macbeth, *loc. cit.*).

Cuminic Acid from Cuminal.—The following method is more convenient and gives better yields than the hydrogen peroxide method (Cooke and Macbeth, *loc. cit.*). A solution of cuminal (100 g.) in acetone (500 c.c.) was cooled in ice and mechanically stirred while potassium permanganate was added until a permanent pink coloration was obtained (about 70 g.). The manganese sludge was filtered off and washed with hot water, and cuminic acid precipitated from the filtrate by acidification and recrystallised from ethanol or dilute acetic acid.

α-*Bromohexahydrocuminic Acid.*—*trans*-Hexahydrocuminic acid (20 g.), obtained by hydrogenation of cuminic acid in alkaline solution with Raney nickel as a catalyst (Cooke and Macbeth, *loc. cit.*), was treated with phosphorus pentachloride (40 g.). The mixture was finally heated on the water-bath for 20 minutes and allowed to cool somewhat, bromine (1·25 mols.) added, and the heating continued until the colour of the bromine had practically disappeared (about 2 days). The product was poured into formic acid (75%, 4—5 vols.), heated on the water-bath for ½ hour, and allowed to cool. The *bromo-acid* which separated became crystalline after some days; recrystallised from light petroleum (b. p. 59—60°) (charcoal), it formed small pearly plates, m. p. 91° (Found: C, 48·3; H, 6·8; Br, 32·0. $C_{10}H_{17}O_2Br$ requires C, 48·2; H, 6·9; Br, 32·1%).

Ethyl α-*Bromohexahydrocuminate.*—It is convenient to prepare the ester of the bromo-acid for the synthesis of *dl*-phellandric acid (Δ^1-tetrahydrocuminic acid), as the crude ester can be subjected to simultaneous debromination and hydrolysis. The mixture of *cis*- and *trans*-cuminic acids can be used for its preparation. After conversion into the acid chloride and bromination as described above, the cooled product was poured slowly into an excess of well-

cooled alcohol. After some hours the mixture was poured into water, and the ester extracted with ether. The extract was washed with water, then with dilute sodium carbonate solution, and dried over calcium chloride. After removal of the solvent, the crude ester was used for the next step without further purification (the ester boiled at 126—128°/3 mm. with considerable decomposition).

dl-*Phellandric Acid* (4-iso*Propyl*-Δ^1-cyclo*hexene*-1-*carboxylic Acid*).—The crude bromo-ester, in in the first experiments, was debrominated and hydrolysed by refluxing with potassium hydroxide in methanol; water was then added, and the methyl alcohol removed. From the oily acid obtained on acidification, only a small yield of crystalline phellandric acid was isolated. The product evidently consisted largely of α-hydroxyhexahydrocuminic acid, as dihydrocryptone (4-*iso*propyl*cyclo*hexan-1-one) was isolated when the oil was gradually added to concentrated sulphuric acid cooled in a freezing mixture; carbon dioxide was given off, and on dilution and steam-distillation the ketone was collected and identified by its 2 : 4-dinitrophenylhydrazone (m. p. 119·5—120°) (compare the conversion of α-hydroxyhexahydrotoluic acid into 4-methyl-*cyclo*hexanone; Perkin, J., 1906, **89**, 835). In later experiments the crude bromo-ester (65 g.) was simultaneously debrominated and hydrolysed by gradual addition to a solution of sodium (25 g.) in methyl alcohol (200 c.c.) boiling under reflux; sodium bromide separated. After an hour's refluxing, the mixture was diluted with water, and the methyl alcohol distilled off. The aqueous residue was acidified in the cold with concentrated hydrochloric acid, and the precipitated acid recrystallised from aqueous methyl alcohol. The average yield of crystalline *dl*-phellandric acid was about 50% of the weight of hexahydrocuminic acid initially used, the more soluble fractions obtained from the crystallisations being mainly oily. These contained the α-hydroxy-acid, which, although not obtained pure, was shown to be present by its decarboxylation to dihydrocryptone. The pure dl-*phellandric acid* had m. p. **143—144°** (Found : C, 71·3; H, 9·55. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). The p-*bromophenacyl* ester had m. p. 86—86·5° (Found : C, 59·0; H, 5·85; Br, 22·1. $C_{18}H_{21}O_3Br$ requires C, 59·2; H, 5·8; Br, 21·9%).

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