Sesquiterpenes from *Cedrus* Species *

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Rao, Dew and Guha isolated two bicyclic sesquiterpene hydrocarbons $C_{15}H_{24}$ called a- and β-himachalene from the wood of *Cedrus deodara* [1] and references to earlier work on sesquiterpenes from *Cedrus* species are given in this paper. a-Himachalene (b.p. 124°/10 mm, n_D^{27} 1.507, d^{27} 0.924, $[a]_D^{27} -86.5°$) as well as β-himachalene (b.p. 132°/10 mm, n_D^{27} 1.513, d^{27} 0.9264, $[a]_D^{27} + 196.8°$, gave a dihydrochloride m.p. 118−119°, $[a]_D \pm 0°$, and a monohydrochloride, m.p. 56−57°, $[a]_D \pm 0°$. Selenium dehydrogenation gave mixtures of at least partly aromatic hydrocarbons. The authors concluded that the himachalenes probably belong to a new class of bicyclic sesquiterpenes.

We have obtained similar sesquiterpenes from the wood of *Cedrus atlantica* and *C. libani*. (Commercial essential oils and wood extracts.) However, our best a-himachalene preparation (according to gas-liquid chromatography (G.L.C.) about 96 % pure) obtained by careful fractional distillation followed by chromatography on alumina, had the following constants: b.p. 133°/15 mm, $[a]_D^{20}$ −198° (CHCl₃, $c = 2$), n_D^{25} 1.5073, d^{20}_4 0.9160 (according to its IR absorption it contained one exocyclic double bond). The quantitatively dominating β-himachalene, isolated in the same way, (G.L.C. purity, 99 %) had b.p. 138−139°/15 mm, $[a]_D^{20}$ + 204° (CHCl₃, $c = 4$), n_D^{25} 1.5113, d^{20}_4 0.9244 (no exocyclic double bond in the I.R.). Both gave identical dihydrochlorides (HCl/HAc), m.p. (rapid heating) 115−117° (decomp.), $[a]_D^{20}$ −9° (CHCl₃, $c = 5$) immediately after dissolution, + 13° after 1 h and + 31° after 15 h (HCl liberated). Recrystallisation from methanol afforded the monohydrochloride containing one exocyclic double bond and having m.p. 55−57° but $[a]_D^{20}$ + 106° (CHCl₃, $c = 3$).

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Catalytic hydrogenation of a-himachalene gave mainly one dihydrocompound but hydrogenation of β-himachalene proceeded slowly and nonstoichiometrically. G. L. C. examination of the products indicated the formation of several compounds (2−6). One of these was an aromatic compound, "Ar III" ($C_{15}H_{22}$, (G.L.C. purity, 97 %), n_D^{25} 1.5257, inflexion 261 mμ (ε 342), λ_{max} 267, 276 mμ (ε 420, 380)) which could be isolated by low temperature (−70°) ozonisation followed by chromatography.

Selenium dehydrogenation of β-himachalene gave a large yield of a mixture of aromatic compounds "Ar I" (0−16 %), "Ar II" (27−35 %) and Ar III (56−70 %). "Catalytic selenium dehydrogenation" (β-isomer:Se = 36:1) gave 40 % Ar II, 51 % Ar III and 9 % hydrogenated compounds. a-Himachalene gave similar results.

Ozonisation of the dehydrogenation mixture (1.1 g) followed by oxidation with NaOH + 30 % H_2O_2 furnished evil smelling volatile acids and non volatile acids (270 mg). The latter gave a *cyclo*hexylamine salt, m.p. 140−142°. The m.p. of the corresponding acid, 65−70°, (26 mg) was not depressed (68−71°) on admixture with 2,2,6-trimethylpimelic acid (m.p. 72−73°)[2] kindly provided by Dr. G.F. Wright, Toronto. The I.R.- and mass spectra of the two acids were identical.

Chromic acid oxidation of the dehydrogenation mixture gave neutral products free from Ar III and acids which were chromatographed on silica gel. An acid, $C_{15}H_{20}O_2$, m.p. 135−137° (yield 30 %) was obtained. According to spectral data this was an aromatic acid. A strong "peak" of mass number 217 in the mass spectrum may indicate the loss of one CH_3 (232−15).

Fractional distillation of the dehydrogenation mixture (spinning band column) gave 12 fractions. Fraction 1 contained (G.L.C.) 28 % Ar I and 72 % Ar II and gave a large yield of terephthalic acid and some isophthalic acid on oxidation with 30 % HNO₃ at 170°. Fraction 4 contained 15 % Ar I, 82 % Ar II and 3 % Ar III. G.L.C. comparison with dihydro-*ar*-curcumene using 5 different columns conclusively demonstrated the identity of Ar II and dihydro-*ar*-curcumene and the comparison of the I.R.- and U.V.-spectra corroborated this. Fraction 12, b.p. 135−136°/14 mm, d^{20}_4 0.9212, n_D^{25} 1.5295 contained 1 % Ar II and 99 % Ar III and gave on nitric acid oxidation 3,3-dimethylphthalide-5-carboxylic acid (decarbonylation) m.p. 264−266°
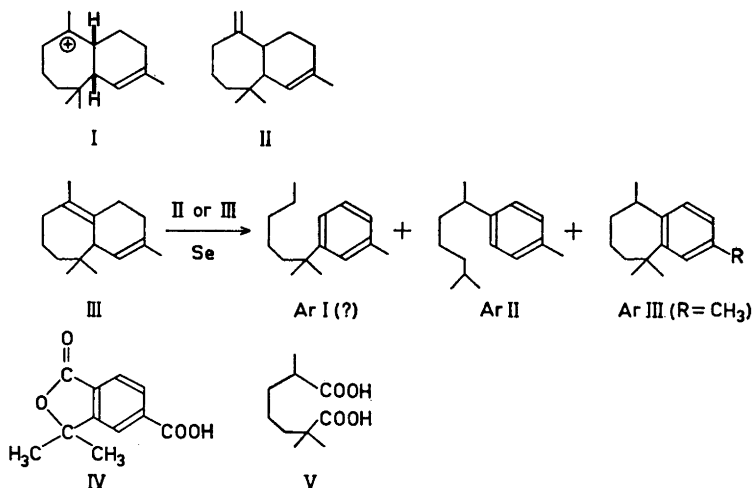
(I.R., mix. m.p.) and trimellitic acid (anhydride, m.p. 161−163°, I.R., mix. m.p.).

From the above results structure(II) and (III) may be tentatively proposed for α- and β-himachalene respectively.

Ar I could be the source of isophthalic acid, Ar II of terephthalic and Ar III (R = CH$_3$) of trimellitic acid, 3,3-dimethyl-phthalide-5-carboxylic acid (IV), 2,2,6-trimethylpimelic acid(V),and acid C$_{15}$H$_{20}$O$_2$, m.p. 135−137° (Ar III, R = COOH). The himachalenes would then appear to be formed by deprotonation of the cation (I) postulated by Hendrickson to be an intermediate in the transformation of cis-farnesol into longifolene [3] (and juniperol) [4]. If this assumption is correct the steric orientation of the hydrogen atoms at the assymmetric carbon atoms of (II) and (III) would be as in (I).

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Synthetic Aminosugar Derivatives as Potential Antimicrobials; Oxazolidine Derivatives of 1-Arylamino-1-deoxy-D-fructopyranose

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Amadori compounds such as 1-arylamino-1-deoxy-D-fructoses,which have interested the authors as potential antimicrobials (unpublished work), are known to be labile in solution because of their high reducing power. The first non-reducing derivative of an Amadori compound (1-(4-methylphenyl)-amino-1-deoxy-D-fructose) was prepared by condensation with benzaldehyde and tentatively described as 2,3-O-benzylidene-1-(4-methylphenyl)-amino-1-deoxy-D-fructopyranose [1]. Kuhn et al. [2] proved this condensation product to be 1,2-N,O-benzylidene-1-(4-methylphenyl)-amino-1-deoxy-D-fructopyranose (I), using methylation and degradation to 1,3,4,5-tetra-O-methyl-D-fructose. Formula (I) represents an aminosugar derivative in which the reducing function is blocked by ring formation and one of the parent sugar's