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Abstract

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ON NATURAL β-CEDRENE

The isolation of β-cedrene from natural sources has not hitherto been described. In the course of studying the chemical composition of the essential oil of hemispherical juniper (*Juniperus semiglobosa* Rgl.), we established that the sesquiterpene fraction contains cedrol, which is the principal component, and a small amount of hydrocarbons; upon chromatography of these hydrocarbons a fraction with $[\alpha]_D^{20} - 21.0^\circ$ was isolated. The infrared spectrum of this fraction showed considerable similarity to the spectrum of β-cedrene obtained by us earlier synthetically from α-cedrene (^{1}).

More careful chromatography made it possible to isolate β-cedrene with the following constants: n_D^{20} 1.5018; d_4^{20} 0.9330; $[\alpha]_D^{20} - 2.6^\circ$. The infrared spectra of synthetic and natural samples of β-cedrene practically do not differ from one another (cf. Fig. 1).

Oxidation of synthetic β-cedrene with perbenzoic acid gives the α-oxide, which is so unstable that in the course of isolation it isomerizes to the aldehyde cedranal I. The infrared spectrum of cedranal contains a frequency at 1722 cm^{-1}, and the ultraviolet spectrum of a heptane solution of its 2,4-dinitrophenylhydrazone has a maximum of the long-wavelength absorption band at about 341 mμ. It should be noted that the spectrum of the 2,4-dinitrophenylhydrazone of isocedranone II—the ketone from α-cedrene—has a maximum at about 349.5 mμ. According to a known empirical rule (^{2}), the absorption maxima should be located, respectively, at about 337 and 344 mμ. The deviation from the calculated values is probably connected with the presence of a complex tricyclic skeleton. Upon oxidation of natural β-cedrene, cedranal was likewise obtained, identified by the 2,4-dinitrophenylhydrazone with m.p. 195–196°.

Cedranal, synthesized earlier (^{3}) by oxidation of primary cedranol III, gave a 2,4-dinitrophenylhydrazone with m.p. 144–144.5°, which is evidently connected with a different orientation of the formyl group. If, upon oxidation of primary cedranol, which most probably (^{3}) has an equatorial oxymethyl group, cedranal IV was obtained, then in the isomerization of the α-oxide of β-cedrene it is easy to envisage the formation of isomer I with an axial arrangement of the aldehyde group.

Reaction scheme with structures I-IV: β-cedrene is oxidized with $C_6H_5CO_3H$ to an oxide, which under H^+ gives cedranal I; isocedranone II, primary cedranol III, and cedranal IV obtained by CrO_3 oxidation are also shown.

Figure 1: Reaction scheme with structures I-IV: β-cedrene is oxidized with $C_6H_5CO_3H$ to an oxide, which under H^+ gives cedranal I; isocedranone II, primary cedranol III, and cedranal IV obtained by CrO_3 oxidation are also shown.

Fig. 1. Infrared spectra: β-cedrene, synthetic (1), natural β-cedrene (2), and cedranal (3). (IKS-14, NaCl prism)

Figure 2: Fig. 1. Infrared spectra: β-cedrene, synthetic (1), natural β-cedrene (2), and cedranal (3). (IKS-14, NaCl prism)

Experimental Part

The essential oil of hemispherical juniper, in an amount of 1.13 kg, was distilled with a Widmer column to remove monoterpenes. The residue (128 g) was poured into 700 ml of 60% methanol; the cedrol (75 g) that precipitated on cooling was filtered off, and the liquid portion was distilled with a Widmer column.

Fig. 1. Infrared spectra: synthetic β-cedrene *(1)*, natural β-cedrene *(2)*, and cedranal *(3)*. (IKS-14, NaCl prism)

The fraction with b.p. 100–124°/2 mm (18.5 g) was chromatographed on 750 g of aluminum oxide (activity II). The product eluted with petroleum ether (8.6 g) was chromatographed on 600 g of aluminum oxide (activity I), with elution by petroleum ether. The first 60 ml of eluate contained 2.19 g of product with $[\alpha]_D^{20} - 21.0°$.

Repeated chromatography on 400 g of Al_2O_3 (activity I) gave 0.45 g of β-cedrene, which had the following constants: n_D^{20} 1.5018; d_4^{20} 0.9330; $[\alpha]_D^{20} - 2.6°$.

Found, %: C 87.90; H 11.75
$C_{15}H_{24}$. Calculated, %: C 88.17; H 11.83

Oxidation of β-Cedrene

β-Cedrene (0.35 g) was oxidized with perbenzoic acid in benzene solution at 0° for 16 h. After the usual work-up, 0.30 g of cedranal I was isolated.

On interaction of 0.10 g of cedranal I, 0.1 g of 2,4-dinitrophenylhydrazine, and 0.2 ml of sulfuric acid in a solution of 5 ml of alcohol, 0.15 g of the 2,4-dinitrophenylhydrazone was obtained, m.p. 195–196°. The same product was obtained from synthetic β-cedrene; it gave no melting-point depression in a mixed sample with the hydrazone from natural β-cedrene.

Found, %: N 13.76

$C_{21}H_{28}O_4N_4$. Calculated, %: N 13.99

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