The essential oils of these varieties differ mainly with respect to the amounts of the components.

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BIOMIMETIC SYNTHESIS OF 7α-HYDROXYSANDARACOPIMARINOL — THE ANTISPASMATIC PRINCIPLE OF *Iboza riparia*

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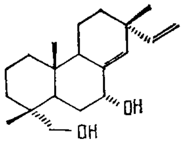
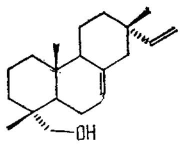
7α-Hydroxysandarcopimarinol (isopimara-8(14),15-diene-7α, 18-diol)* (I) has been isolated from the leaves of the Central African plant *Iboza riparia* (Hochst) N. E. Br., which is used in folk medicine [1]. Continuing studies on biomimetic syntheses [2] and the photooxidation of natural terpenoids [3], we have performed the synthesis of this compound from isopimarinol (II) [4] by sensitized photooxidation. The conditions of photooxidation and of the subsequent working up and separation of the products were similar to those used previously [3] except that the time of the reaction was increased to 8 h. Under these conditions, from 2.20 g of isopimarinol 1.95 g of combined products was obtained the chromatography of which led to the isolation of 1.66 g of the initial compound, 0.05 g of a mixture of by-products, and 0.22 g of the diol (I) with mp 76-82°C (from acetone), $[\alpha]_D^{20}$ −82° (c 8.37; methanol) (according to the literature [1]: mp 76-81°C (from acetone), $[\alpha]_D$ −87.1° (methanol)). By drying *in vacuo* at 100°C, acetone of solvation was eliminated from the crystals obtained [1] and the product was recrystallized from pentane to give fine needles of the diol (I) with mp 96-98°C. The PMR spectrum (in C_6D_6) corresponded to that given in the literature [1].

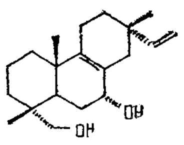
Mass spectrum (70 eV, 100°C, direct introduction): m/z 304 (M^+, 65), 286 ($(M-H_2O)^+$, 4), 255 (22), 164 (26), 151 (85), 123 (100), 81 (41). As has been shown by Fourrey [6], on photooxidation methyl isopimarate gives the corresponding 7α-hydroxy ester.



I



II



III

The mixture of by-products contained ~80% of the isomeric diol (III) (PMR spectrum), which it was possible to isolate by crystallization from a mixture of acetonitrile and diethyl ether. The PMR spectrum of this diol, which had mp 118-120°C, differed qualitatively from that for the diol (I) (solutions in $CDCl_3$) only by the absence of the signal of a proton at a trisubstituted double bond. The methyl groups in them gave singlets at 0.70, 0.92, and 0.95 ppm, and the components of a AB system formed by the protons of the CH_2—OH group were observed at 2.89, 2.94, 3.46, and 3.51 ppm. The H_7 signal (3.78 ppm) had the form of a

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*The name of compound (I) given in [1] does not agree with the accepted nomenclature of cyclic diterpenoids [5].

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narrow ($W_{1/2}$ = 6.5 Hz) multiplet, which showed the α-configuration of the secondary hydroxy group [7]. For the diol (I), the H_7 proton gave in the PMR spectrum (in $CDCl_3$) a similar multiplet ($W_{1/2}$ = 6.5 Hz), but with an ill-defined triplet splitting. The considerable downfield shift of one of the methyl group signals (0.92 ppm) as compared with that for the diol (I) [1] confirmed that the C_{10}-methyl group in the molecule of compound (III) was of allyl nature.

The small amount of diol (III) in the reaction products indicates that the main direction of the migration of the C_7 double bond of isopimarinol is to the C_8—C_{14} position. A similar situation apparently exists in the biosynthetic process — the diol (III) or its derivatives have not yet been detected in plants.

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STEREOCHEMISTRY OF CEMBRA-2E,4Z,7E,10E-TETRAEN-12-OL — A PRODUCT OF THE PHOTOOXIDATION OF CEMBRENE

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As has been shown previously [1], the photosensitized oxidation of the diterpene hydrocarbon cembrene (I) takes place completely stereoselectively. The structures and stereochemistries of the four products of this reaction have been shown unambiguously, with the exception of the configuration of the asymmetric center at C_{12} in the molecule of the alcohol (II). It was taken as S by analogy with the stereochemistry of the product of the epoxidation of cembrene at the C_{11} double bond [1]. In order to prove it, we have performed a chemical correlation of the alcohol (II) with the diol (III), the structure of which has been established [2] with the aid of x-ray structural analysis. Here we used the same approach as in the synthesis of isocembrol from cembrene [3] — the alcohol (II) (0.23 g) was epoxidized with perbenzoic acid (1.8 equivalents) in benzene solution in the presence of sodium bicarbonate and the combined reaction products (according to TLC, a mixture of the initial compound and its mono- and diepoxides), without separation, were reduced with lithium tetrahydroaluminate in tetrahydrofuran (boiling under reflux for 1.5 h). By using authentic samples of the diol (III) and of its C_{12}-epimer [2], it was established with the aid of TLC on Silufol that the diol (III) was present in the mixture of products formed. By chromatographing it on silica gel (with, as eluent, petroleum ether containing amounts of diethyl ether rising from 20 to 100%), 0.02 g of the initial alcohol (II), 0.02 g of the diol (III) and 0.12 g of a mixture of more polar products, which were not identified, were obtained. The diol (III) crystallized from a mixture of petroleum ether and moist diethyl ether (1:1) in the form of prisms with mp 137-137.5°C. The PMR spectrum and TLC behavior of the product obtained coincided with

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