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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UDC 547.595.9

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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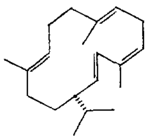
those of an authentic sample of the diol (III), which, from the same solvent mixture, gave crystals with mp 137-137.5°C.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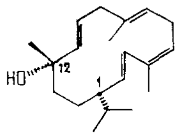
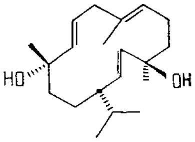


II



III

Thus, alcohol (II) has the 12S-configuration, and the stereochemistries of all the alcohols produced by the photooxidation of cembrene [1], including the stereochemistry of alcohol (II), show that in the reacting cembrene molecule the trisubstituted double bonds are orientated in relation to the ring in the same way as in cembrene molecules present in the crystal lattice [4]. Apparently, in this case the conformation of the cembrene molecule does not change appreciably on passing from the crystalline state into solution.

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3β-HYDROXY-trans-BIFORMENE AND ITS ACETATE AND OTHER DITERPENE ALCOHOLS FROM *Pinus sylvestris* SHOOTS

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For the investigation we used air-dry needle-free shoots of *Pinus sylvestris* L. (Scotch pine) collected in March 1982, in Leningrad Province. They were extracted in a Soxhlet apparatus and the neutral fraction was isolated from the extract (yield, 4.6% on the weight of the shoots; conditions of extraction and isolation as in [1]). The chromatography of this fraction on silica gel gave, successively, a hydrocarbon fraction (4.2% on the initial neutral fraction), an ester fraction (54.7%), and three fractions of monohydric alcohols, the first of which contained mainly triterpenols (TLC), and the third β-sitosterol. The second fraction of alcohols (7.6% on the neutral fraction, 3.6 g) was acetylated with acetic anhydride in pyridine (20°C, 12 h). The acetates formed were separated by chromatography on silica gel from the unchanged components of the initial fraction and were rechromatographed on silica gel with 5% of silver nitrate (using as eluent petroleum ether containing diethyl ether in concentrations rising from 4 to 8%). This gave successively 1.1 g of a mixture of fatty alcohol acetates (IR spectrum) and 0.6 g of a mixture of acetates of diterpene alcohols, the main representatives being the acetates of pimarinol, of isopimarinol, and of dehydroabietinol (46.5%, 25.2%, and 11.2%, respectively, according to GLC on SE-30/Chromaton N-AW-DMCS).

The identification of these compounds was confirmed by the PMR spectrum of the mixture obtained in which the main signals were those corresponding to the substances mentioned. Further elution led to 0.7 g of the acetate of 3β-hydroxy-trans-biformene with mp 118-119°C from acetonitrile, $[\alpha]_D^{20}$ +48° (c 2.30; chloroform); mass spectrum (m/z): 330 (M^+); UV

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