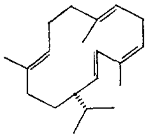
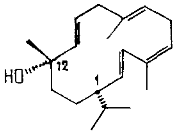
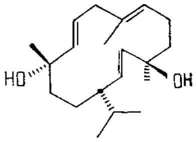
those of an authentic sample of the diol (III), which, from the same solvent mixture, gave crystals with mp 137-137.5°C.



I



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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UDC 547.597

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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spectrum (in ethanol): λ_{max}, 232 nm (ε 28,000); according to the literature [2]: mp 118°C, $[\alpha]_D$ + 51°. This acetate, like the free alcohol, was isolated by Bohlmann [2] from the epigeal part of *Palafoxia rosea* (Bush.) Cory (family Compositae).

The reduction with lithium tetrahydroaluminate in diethyl ether of the acetate obtained gave free 3β-hydroxy-trans-biformene in the form of an unstable oil the PMR spectrum of which (in deuterochloroform) corresponded to that given in the literature [2]. It must be mentioned that in Bohlmann's publication [2] inaccuracies have been admitted in the drawing up of Table 1 with details of the PMR spectra of his substances (I) and (II). Thus, the assignments of the 3β-H and 3α-H signals in the column must change places, since in a labdane compound with a 3β-hydroxy group the H_3 proton should appear in the form of a doublet of doublets and not as a singlet. In the PMR spectrum of a model compound — labda-8(17),13E-diene-3β,15-diol [3] — the H_3 signal coincides in form and position with that for 3β-hydroxy-trans-biformene (doublet of doublets at 3.23 ppm, J = 11.0 and 4.7 Hz).

By the GLC method with the addition of authentic samples, in the ester fraction from the shoots under investigation we established the presence of the native acetate of 3β-hydroxy-trans-biformene (0.2% of the fraction) and of geranylgeraniol acetate. This is the first time that 3β-hydroxy-trans-biformene and its acetate have been detected in a coniferous plant. The other labdane diterpenoids with oxygen-containing functional groups at C_3 have been found previously in the oleoresin of the Japanese stone pine [4].

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HOLOTHURIN A — THE MAIN TRITERPENE GLYCOSIDE OF THE CUVIERIAN ORGANS OF THE HOLOTHURIAN *Bohadschia graeffei*. THE STRUCTURES OF THE NATIVE AGLYCONE AND OF PROGENINS.

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It has been shown previously that the glycosides of *Bohadschia graeffei* (Semper.) differ in their chromatographic behavior and structure from the glycosides of other holothurians of this genus [1, 2]. Recently, Levin et al., on the basis of an analysis of a complex of biochemical morphological, and ecological features of *B. graeffei*, have separated out the species into the newly established genus *Pearsonothuria* Levin [3].

We have studied the glycoside fraction obtained from the Cuvierian organs of this holothurian. The animals were collected in February 1982 on the coast of North Vietnam during the expedition cruise of the Scientific-Research ship "Professor Bogorov." The isolated Cuvierian organs were extracted with 70% ethanol, and the dry extract was dissolved in water and extracted with butanol. Then the butanolic extract (1 g) was separated on Polikhrom (250 g) in the water—ethanol (100:20) system. The main glycoside, with mp 228-230°C, was identified from its ^{13}C spectrum as holothurin A, isolated previously from the holothurians *Holothuria leucospilota* [4] and *Actinopyga agassizi* [5]. Then holothurin A was incubated with glycosidases from the snail *Eulota maackii* (100 mg, 38°C, 4 days), which gave combined genins and progenins. Column chromatography on silica gel in the hexane—ethyl acetate (3:1) system

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