LABDANE AND CEMBRANE DITERPENOIDS FROM THE OLEORESIN OF THE *Picea ajanensis*

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From the oleoresin of the Yeddo spruce (*Picea ajanensis* Fisch.) have been isolated cis-abienol, isocembrol, geranyllinalool, epimanool, and labd-13E-ene-8α,15-diol. It has been established that the biosynthesis of isocembrol and epimanool in the Yeddo spruce is not accompanied by the formation of epimers of these compounds — 4-epiisocembrol and manool — and that cis-abienol is the main neutral oxygen-containing compound of the oleoresin investigated in terms of content.

Diterpenoids of the cembrane structural group (cembrene), the labdane structural group (isoabienol, manool, epimanool, epimanoyl oxide), and the phyllocladane structural group (phyllocladan-16α-ol and its C_{16}epimer) have been isolated previously from the oleoresin of the Yeddo spruce (*Picea ajanensis* Fisch.) [1]. Continuing an investigation of the diterpenoids of this oleoresin, we have separated it by means of a scheme proposed previously for the group separation of the components of conifer oleoresins [2]. In this process, from the combined neutral oxygen-containing substances, making up 58% of all the neutral substances of the oleoresin, we have isolated the phyllocladan-16α-ol described previously [1], and also a fraction of oxides, polyfunctional compounds, and nonpolar tertiary alcohols with yields of 8, 2, 3, and 15%, respectively. Chromatography of the last fraction on silica gel containing 5% of silver nitrate yielded, successively, epimanool, cis-abienol, and isocembrol. The compounds isolated were identified from their spectral characteristics (IR and NMR spectra) and their constants, corresponding to those given in the literature. The main component of this fraction was cis-abienol (according to the NMR spectrum, it made up about 80% of the fraction, with a yield of 72%), and it also contained smaller amounts of isocembrol (yield 9.2%) and epimanool (yield 4.1%). The same fraction contained, according to the NMR spectrum, about 4% of geranyllinalool, which issued from the column between the cis-abienol and isocembrol. It was identified from its IR and NMR spectra.

No 4-epiisocembrol, which is a usual associate of isocembrol in the oleoresins from the species *Pinus* L. [2-4] and is readily detected by TLC, was found in the oleoresin studied. Another associate of isocembrol — the hydrocarbon cembrene — is present in the hydrocarbon fraction of the oleoresin [1], where its amount as determined by GLC, is 3.6% of the total diterpene hydrocarbons, which, in their turn, make up only 13.8% of all the hydrocarbons of the oleoresin.

From the oxide fraction, chromatography on silica gel yielded 13-epimanoyl oxide, which was identified from its constants and NMR spectrum. This compound, according to GLC, makes up about 90% of all the oxides. Its epimer, manoyl oxide, was not detected in the oleoresin under investigation. In this respect, the Yeddo spruce differs from species of *Pinus* L., in which manoyl oxide is the main component of the oxide fraction [2, 4, 5].

We did not detect isoabienol (trans-abienol [6]) and manool, which have been isolated previously from the oleoresin of the Yeddo spruce [1]. The absence of manool was confirmed by the use of Rowe's method [7].

Geranyllinalool, cis-abienol, and isocembrol are, apparently, normal components of spruce oleoresins [8, 9]. cis-Abienol is the main component of the neutral oxygen-containing substances of the oleoresin, and its amount even exceeds that of phyllocladan-16α-ol,

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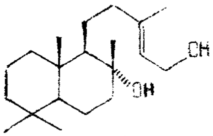
previously described as the main component of the neutral oxygen-containing compounds of Yeddo spruce oleoresin [1]. Such fluctuations in the composition of the Yeddo spruce oleoresin may apparently be explained by the fact that the samples of it were obtained from sites differing markedly in their climatic conditions. The oleoresins studied previously was collected in Khabarovo Territory [1], while we carried out our work on oleoresin from the Kamchatka Province.

From the fraction of polyfunctional compounds of the Yeddo spruce oleoresin we isolated labd-13E-ene-8α,15-diol (I) by chromatography on silica gel. This compound was first obtained by synthesis from sclareol [10], and only its antipode has been found in nature, being isolated from *Beyeria* sp. (Euphorbiaceae) [11], and from *Aphanamixis pollystachya* (Wall) Parker (Meliaceae) [12].



The simultaneous presence of the diol (I) and of cis-abienol in one natural source permits the assumption of the existance of a biogenetic link between them. It is possible that the diol (I), the side chain of which is formally a fragment of the first precursor of all diterpenoids — geranylgeraniol [13] is a precursor of cis-abienol. The latter may apparently be formed from the diol (I) in the enzymatic dehydration of its side chain.

The sample of labd-13E-en-8α,15-diol was kindly supplied by P. F. Vlad (Institute of Chemistry of the Academy of Sciences of the Moldavian SSR).

EXPERIMENTAL

The oleoresin of the Yeddo spruce was collected in 1978 in the Kamchatka province. The instruments and chromatographic conditions were the same as in our previous work [4], and the primary treatment of the oleoresin was performed as described by Shmidt et al. [1]. The isolation of the fractions of oxides, of tertiary nonpolar and tertiary polar alcohols, and of polyfunctional compounds was also carried out as described previously [2].

Separation of the Fraction of Tertiary Nonpolar Alcohols. This fraction (1.20 g) was chromatographed on 80 g of silica gel containing 5% of silver nitrate. Gradient elution with mixtures of petroleum ether and diethyl ether containing from 10 to 50% of the latter eluted successively 0.01 g of a mixture of substances in which the main component, according to TLC and NMR spectroscopy, was T-cadinol [14]; 0.05 g of epimanool with n_D^{20} 1.5152 and $[\alpha]_D^{20}$ +60.5° (c 9.91) (according to the literature [1]: n_D^{20} 1.5280 and $[\alpha]_D^{20}$ +53°); 0.86 g of cis-abienol with mp 40-41°C (from hexane) and $[\alpha]_D^{18}$ +21° (c 5.0) (according to the literature [5]: mp 40-41°C, $[\alpha]_D^{20}$ +22°); 0.02 g of geranyllinalool, the IR and PMR spectra of which coincided with those for an authentic sample; and 0.11 g of isocembrol with n_D^{20} 1.5135 and $[\alpha]_D^{23}$ +72°C (c 10.7) (according to the literature [8]: $[\alpha]_D^{20}$ +78.4°).

Labd-13E-ene-8α,16-diol. The chromatography of 2.0 g of the fraction of polar polyfunctional compounds of the Yeddo spruce oleoresin on 80 g of silica gel yielded successively 0.7 g of a complex mixture of unidentified hydroxy esters (IR spectrum: 1740 and 3610 cm^{-1}), 0.4 g of a mixture of substances among which, according to TLC, the hydroxyketone oplopanone found previously in Yeddo spruce oleoresin [14] was present, and 0.2 g of the diol (I) with mp 129-129.5°C (from diethyl ether). A mixture with an authentic sample of the diol (I) having mp 128-129°C melted at 128-129°C. The NMR spectrum of the diol (I) (in deuterochloroform) coincided with that given in the literature [11] and with the spectrum of the authentic sample.

Phyllocladan-16α-ol. The chromatography of 2.0 g of the fraction of tertiary (nonacetylatable) polar alcohols on 50 g of silica gel yielded 1.5 g of phyllocladan-16α-ol, which sublimed completely at 170-180°C (0.1 mm Hg) with the formation of crystals having mp 181-181.5°C and $[\alpha]_D^{20}$ +17° (c 5.0); (according to the literature [1]: mp 181-181.5°C, $[\alpha]_D^{20}$ +17.3°).

SUMMARY

1. cis-Abienol, epimanool, isocembrol, geranyllinalool, and labd-13E-en-8α,15-diol have been isolated from the oleoresin of the Yeddo spruce.

2. It has been established that, in contrast to species *Pinus* L., in the Yeddo spruce the biosynthesis of isocembrol is not accompanied by the formation of 4-epiisocembrol.

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GLYCOSIDES OF MARINE INVERTEBRATES.

X. THE STRUCTURE OF STICHOPOSIDES A AND B FROM THE HOLOTHURIAN *Stichopus cloronotus*

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The structures of two triterpene oligosides from the holothurian *Stichopus cloronotus* (Brandt) have been established; they are: 23ξ-acetoxy-3β-[O-β-D-quinovopyranosyl-(1→2)-β-D-xylopyranosyloxy]holost-7(8)-ene and 23ξ-acetoxy-3β-[O-β-D-glucopyranosyl-(1→2)-β-D-xylopyranosyloxy]holost-7(8)-ene.

The physiologically active glycosides of holothurians (class *Holothurioidea*) have now been investigated for more than two decades, but the complete structures of only four of them have been established [1-3]. The present paper gives the structures of two more such glycosides — stichoposides A (I) and B (II) from *Stichopus cloronotus* (Brandt) (Coetivy island, Seychelles archipelegro).

The glycosides of *S. cloronotus* after acid hydrolysis give the genin (III) [4], and differ from one another in their monosaccharide compositions. We have recently established that (III) is not the native genin but is formed from the 23-acetate of holost-7(8)-ene-3β,23ξ-diol (IV) as the result of 7(8)→8(9)→9(11) migration in the acid medium [5]. After this, the structural study of compounds (I) and (II) reduced in the main to determining the structures of their carbohydrate chains.

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