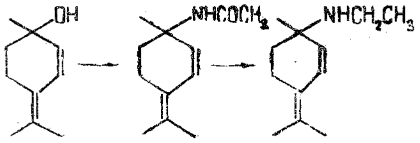

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THE NATURE OF THE DITERPENE DIOL FROM THE OLEORESIN OF LARIX SIBIRICA

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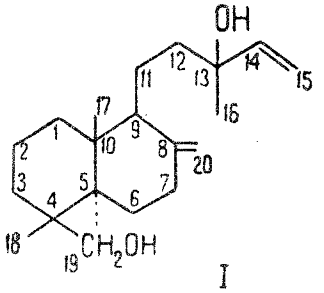
We have previously [1] isolated a diterpene diol $C_{20}H_{34}O_2$ with mp 108.5° C from the neutral fraction of the oleoresin of Larix sibirica Lebd. (Siberian larch). From the results of hydrogenation and dehydrogenation and from the identity of the IR spectrum of the monoacetate of the diol with the IR spectrum of larix acetate [2], we assumed that the diol isolated was larixol [2–6], although its melting point was somewhat higher than that of larixol (101° C).

A further study of the diol has shown that its NMR specturm (taken on an instrument with an operating frequency of 60 MHz and with tetramethylsilane as internal standard) has three signals of equal intensity in a strong field at 9.30 τ, 8.82 τ, and 8.58τ, which are due to methyl groups at C_{17}, C_{18}, and C_{13}, respectively. From its chemical shift, a multiplet with its center at 6.30 τ corresponds to a methylene group connected to an atom of oxygen (CH_2O). This multiplet, consisting of four lines at 6.59 τ, 6.41 τ, 6.19 τ, and 5.99 τ, is characteristic for two nuclei of the AB type (C_{19}). In a weak field, it is possible to isolate, in the 5.20–3.78 τ region, the signal of an exocyclic methylene group (C_{20}) and also a group of signals belonging to a AB_2 system of nuclei (C_{14}–C_{15}).

These results suggest structure (I) for the diol:



I

Oxidation of the diol with chromic anhydride in pyridine gave an aldehyde with n_D^{20} 1.5210, the semicarbazone of which had mp 193–195° C.

The IR spectrum of the aldehyde shows characteristic absorption bands at 1710, and 2720 (CO) cm^{-1}. From its refractive index and IR spectrum, the aldehyde is similar to torulosal [7] but it did not give the crystalline complex with carbon tetrachloride that is characteristic for the latter.

Reduction of the aldehyde with hydrazine hydrate led to a monohydric alcohol $C_{20}H_{34}O$ with mp 38.5–39.5° C, $[\alpha]_D^{20}$ + 50° (c 2.65; chloroform), the IR spectrum of which and a mixed melting point showed that it was identical with epimanool [4]. On direct comparison, the initial diol proved to be 13-epitorulosol [8, 9], and not larixol.

Hydrogenation of the epitorulosol gave the previously undescribed tetrahydroepitorulosol $C_{20}H_{38}O_2$ with mp 77–79°C, $[\alpha]_D^{20}$ + 18.8° (c 2.62; chloroform). IR spectrum: 1020, 3610, 3640 cm^{-1}. The oxidation of tetrahydroepitorulosol with chromic anhydride in pyridine led to a saturated aldehyde $C_{20}H_{36}O_2$. IR spectrum: 1710, 2720 (CO) and 3610 (OH) cm^{-1}.

We obtained the samples of epimanool (mp 36.5–38.5°C) and epitorulosol (mp 109–112°C) from Dr. Rowe (Wood Products Laboratory, Wisconsin, USA).

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TRITERPENES IN PLANTS OF THE FAMILY ERICACEAE

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In an investigation of the defoliated shoots of Ledum palustre L. var. angustum E. Fisch., collected in the Transbaikalia and Cassandra calyculata Don. collected in Leningrad Oblast, we have found three triterpene compounds in them.

From L. palustre we isolated uvaol, taraxerol, and ursolic acid. The uvaol was identified from its melting point, IR spectrum, and acetylation products. A sample of uvaol for a mixed melting point test was obtained by reducing the acetate of methyl ursolate with lithium aluminum hydride.

The taraxerol was identified from its melting point, mixed melting point, UV spectrum, and the preparation of the acetate. This substance has been found previously [1] in L. palustre L. var. vulgare.

The ursolic acid was identified by a direct comparison with an authentic sample. The methyl ester, the acetate of the methyl ester, and the diol obtained from the acid had properties corresponding to those described in the literature for the corresponding derivatives of ursolic acid.

From Cassandra calyculata Don, in addition to uvaol and ursolic acid we have isolated and identified β-amyrin.

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