at 1.90 ppm (methyl group on a carbon with a double bond).

The signal of the lactone proton consisted of a doublet at 4.75 ppm with J = 10 Hz, the spin–spin coupling constant of which showed the trans-linkage of the lactone ring.

The structure deduced from the above facts corresponded to the known lactone taurin [2].

Compound (II), obtained in very low yield by the rechromatography of the mother solutions from (I), was a stereoisomer of taurin.

This conclusion followed from the results of a comparison of their mass and PMR spectra. The mass-spectrometric fragmentations of lactones (I) and (II) were completely identical, while the PMR spectra differed mainly by the chemical shifts (CSs) of the signal of the lactone proton: in (I) it was a doublet at 4.75 ppm, J = 10 Hz, and in (II) a doublet at 4.50 ppm, J = 10 Hz. Such a difference in the CSs of the lactone protons is characteristic for lactones differing by the orientation of a methyl group in the γ-lactone ring. With the β-orientation of the methyl group, through the screening effect the signal of the lactone proton is shifted upfield. Consequently compound (II) was the β-isomer of taurin at the C-11 center and corresponded to the lactone 1-oxo-6β,7α,11β-eudesman-6,12-olide [3].

Compound (III) was identified as β-sitosterol [4], and (IV) as 7-hydroxycoumarin (umbelliferone) [5].

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ACID SUCCINATES OF DITERPENE ALCOHOLS – A NEW TYPE OF COMPONENTS OF CONIFER OLEORESINS

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In recent years groups of compounds previously unknown for the oleoresins of coniferous plants of the family Pinaceae have been found in them – ferulates of monoterpene alcohols [1], triterpene acids [2], and acid succinates of labdane acids [3, 4].

On continuing an investigation of the chemical composition of the oleoresin of the Schrenk spruce (Picea schrenkiana Fisch.) [5], we found that this fraction contained a compact mixture, readily isolated by chromatography in the form of methyl esters, of acid 18-O-succinates of diterpene alcohols – abietinol, palustrol, dehydroabietinol, neoabietinol (the main components, present in approximately equal amounts), levopimarinol, isopimarinol, and pimarinol. A mixture of the methyl esters of these succinates giving a single spot in TLC on SiO_2 and a set of overlapping spots in TLC on SiO_2 + 5% of $AgNO_3$ was isolated by the chromatography on silica gel of the methylated total acids of the oleoresin (yield 1.7% on the total acids).

The IR spectrum of the resulting methyl esters of acid succinates had no absorption band of a free hydroxy group but there was a band at 1730 cm^{-1} of approximately double the intensity of that in the IR spectrum of palustrol acetate. The PMR spectrum (400 MHz, $CDCl_3$) exhibited the signals of the olefinic protons that are characteristic for the above-mentioned alcohols, and also the singlet signal of the protons of the $COOCH_3$ group (3.66 ppm), a multiplet due to

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the $-C\underline{H}_2-OCO-$ protons (3.6-4.0 ppm), and a signal at 2.62 ppm split into singlet components of unequal intensity. The last-mentioned signal could be assigned quite unambiguously to the protons of the $ROOC-C\underline{H}_2-C\underline{H}_2-COOR'$ group [3], and its splitting was due to the presence of different succinates in the mixture. The ratio of the integral intensities of the signal at 2.62 ppm and of the multiplet in the 3.6-4.0 ppm region ($COOC\underline{H}_3$ + $-C\underline{H}_2-OCO-$) was approximately 4:5, which corresponds to the theoretical ratio.

Saponification of the mixture being analyzed with an ethanolic solution of sodium hydroxide (1 h with boiling) led to a mixture of diterpene alcohols and succinic acid, which was identified in the form of its dimethyl ester by GLC. The mixture of diterpene alcohols contained those mentioned above (PMR spectrum). Neoabietinol, palustrol, and levopimarinol were present in it only in trace amounts, which can be explained by their isomerization into abietinol under the conditions of severe saponification.

Thus, in coniferous plants during the biosynthesis of diterpenoids the succinylation may take place not only of labdane acids but also of tricyclic primary alcohols.

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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS

XXXIII. CYCLOORBICOSIDE B FROM Astragalus orbiculatus

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We have previously [1] reported the isolation from the epigeal part of Astragalus orbiculatus Ledeb. (Leguminosae) of a new substance 2 (a glycoside of the cycloartane series [2, 3]) and the structure of its genin cycloorbigenin B (I). The present communication is devoted to a determination of the structure of substance 2, which we have called cycloorbicoside B (II).

Cycloorbicoside B, $C_{35}H_{56}O_{10}$, mp 242-244°C (from methanol) $[\alpha]_D^{24}$ + 20.6 ± 2° (c 0.87; methanol). By the GLC method [4], using D-glucose as standard, it was shown that glycoside (II) contained one D-xylose residue. ν_{max}^{KBr} cm^{-1}: 3600-3190 (OH), 3045 (CH_2 of a cyclopropane ring). PMR spectrum (C_5D_5N, δ, ppm, O-TMS, AM-400, Bruker): 0.33 and 0.69 (2H-19, d, ^2J = 4 Hz), 0.85 (CH_3-21, d, ^3J = 6 Hz), 1.18; 1.32; 1.36; 1.42; 1.44; 2.00 (6 × CH_3, s), 2.55 and 2.77 (2H-15, d, ^2J = 15 Hz), 3.67 (H-24, s), 4.74 (H-23, d, ^3J = 9 Hz), 4.91 (anomeric proton of D-xylose, d, ^3J = 8 Hz).

The ^1H and ^{13}C NMR spectra (Table 1), containing the signals of one anomeric proton at 4.91 ppm and of one anomeric carbon at 107.72 ppm, respectively, confirmed the conclusion that cycloorbicoside B was a monoside.

A comparative analysis of the ^{13}C NMR spectra of compounds (I) and (II) unambiguously determined the position of the D-xylose residue at C-3. As can be seen from Table 1, the signal of the C-3 atom in cycloorbicoside B (88.51 ppm) had undergone a downfield shift by 10.46 ppm in comparison with the corresponding signal in the spectrum of cycloorbigenin B (78.05 ppm). At the same time, the chemical shifts of the two carbonyl carbon atoms were practically identical.

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