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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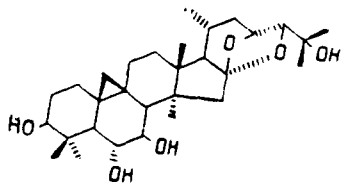
TABLE 1. Chemical Shifts of the Carbon Atoms of Cycloorbigenin B (I) and Cycloorbicoside B (II) (C_5D_5N, δ, ppm, Bruker AM-400)

C atom	Compound		C atom	Compound	
	I	II		I	II
1	32,72	32,42	19	31,37	31,54
2	31,68	28,75	20	27,95	27,93
3	78,05	88,51	21	19,97	19,95
4	42,46	42,70	22	38,34	38,31
5	51,67	51,79	23	71,73	71,73
6	72,88	72,64	24	90,52	90,50
7	75,00	74,94	25	71,01	71,00
8	53,58	53,50	26	23,61*	23,78*
9	19,53	19,64	27	24,64*	24,62*
10	29,03	30,30	28	19,28	19,17
11	26,61	26,53	29	29,15	28,66
12	32,97	32,94	30	16,00	16,52
13	44,19	44,18	β-D-Xylp residue		
14	46,75	46,72	1		107,72
15	48,84	48,74	2		75,65
16	115,15	115,12	3		78,56
17	60,59	60,57	4		71,22
18	18,72	18,67	5		67,08

The assignments of the signals marked by asterisks are ambiguous within a column.

The chemical shifts of the carbon atoms of the D-xylose residue showed the pyranose form of the monosaccharide and the β-configuration of its anomeric center [5]. A calculation of the difference in molecular rotations and the PMR spectrum of glycoside (II), where the signal of the anomeric proton was observed in the form of a doublet with ^3J = 8 Hz were in good agreement with the conclusion of the β-configuration of the glycosidic bond. Consequently, cycloorbicoside B has the structure of (23R,24S)-16β,23; 16α,24-diepoxycycloartane-3β,6α,7β,25-tetraol 3-O-β-D-xylopyranoside.



I R=H

II R=β D-Xylp

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