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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS. LIII. CHEMICAL TRANSFORMATION OF CYCLOARTANES. III. MODIFICATION OF ACKENDOSIDE D

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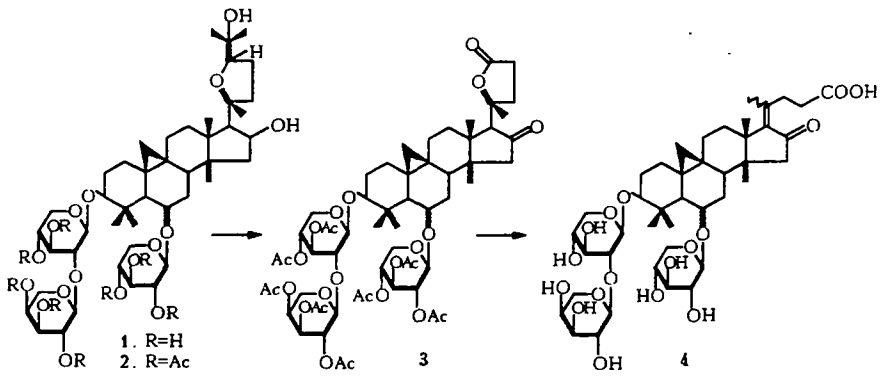
The 17E- and 17Z- isomers of 3β-[O-α-L-arabinopyranosyl-(1→2)-β-D-xylopyranosyloxy]-6α-(β-D-xylopyranosyloxy)-25-norcycloart-17-en-16-on-24-oic acid have been synthesized in four stages from askendoside D.

In continuation of investigations on the chemical transformations of cycloartanes [1, 2], we have synthesized a chromatographically homogeneous mixture of two isomers of the 25-norglycoside (**4**).

Askendoside D (**1**) was converted into the octaacetate (**2**) by acetylation with acetic anhydride in pyridine. Oxidation of the octaacetate (**2**) with the Jones reagent [3] at room temperature gave the previously described ketolactone (**3**) [2]. Alkaline hydrolysis of the latter followed by acidification of the reaction mixture led to products the column chromatography of which gave a homogeneous mixture of the glycosides (**4**).



The IR spectrum of the product obtained lacked the absorption band characteristic for a γ-lactone and contained a broad band at 1707 cm^{-1}. A singlet at 8.49 ppm in the PMR spectrum showed that the above-mentioned band in the IR spectrum was due in part to a carboxy group which must have included the C-24 atom. The lowering of the absorption frequency of the five-membered cyclic ketone at C-16 to 1707 cm^{-1} is connected with the appearance of the C-17−C-20 double bond conjugated with it. The latter was formed by the β-elimination of a water molecule at the expense of the tertiary hydroxy group at C-20 and the hydrogen atom at C-17 in the acidification stage. Actually, the ^{13}C NMR spectrum of product (**4**) showed paired signals from the ketonic carbonyl carbon atom (208.33 and 207.56 ppm), the carbonyl carbon atom of the carboxy group (175.64 and 175.23), and disubstituted sp^2-hybridized carbon atoms (147.09, 146.25; and 142.51, 142.42 ppm). These facts show that the product obtained consisted of two components. Since each of these components contained a double bond conjugated with the keto function at C-16, it must be assumed that they represent 17E- and 17Z- isomers. This was also shown by the presence of paired signals in the PMR spectrum of compound (**4**) from a methyl group present at a double bond (1.72 and 1.88 ppm). It must be mentioned that the signals of the carbon atoms of the monosaccharide residues and also of C-3 and C-6 of the genin moiety were single (Table 1).

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TABLE 1. Chemical Shifts of the Carbon Atoms of Glycosides (1) and (4) (δ, ppm, C_5D_5N, 0 — TMS)

Atom	Compound	
	1	4
	Genin moiety	
3	87.69	87.52
6	77.59	77.60
16	73.49	208.33; 207.56
17	58.08	147.09; 146.35
20	87.39	142.51; 142.42
24	81.68	175.64; 175.23
	residue 3-O-β-*D*-Xyl_p	
1	105.38	105.29
2	83.73	83.71
3	77.21	76.26
4	71.04	71.04
5	66.67	66.62
	residue α-*L*-Ara_p	
1	106.64	106.62
2	73.77	73.74
3	74.35	74.33
4	69.21	69.19
5	66.97	66.95
	residue 6-O-β-*D*-Xyl_p	
1	105.80	105.94
2	75.52	75.43
3	78.42	78.43
4	71.15	70.99
5	67.17	67.11

Thus, compound (4) consisted of the 17E- and 17Z- isomers of 3β-[O-α-*L*-arabinopyranosyl-(1→2)-β-*D*-xylopyranosyloxy]-6α-(β-*D*-xylopyranosyloxy)-25-norcycloart-17-en-16-on-24-oic acid. Judging from the integral intensities of the H-19 signals at 0.00 and 0.02 ppm, the isomer to which the second signal belonged predominated in the mixture approximately twofold.

EXPERIMENTAL

General observations are given in [4]. The following solvent systems were used: 1) chloroform–methanol (100:1); 2) chloroform–methanol–water (70:23:4).

^1H and ^{13}C NMR spectra were taken on a Bruker AM 400 instrument in deuteropyridine with the internal standard TMS (δ, ppm). The ^{13}C NMR spectra were obtained with complete decoupling of C–H interactions, and also under J-modulation conditions. IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer.

Askendoside D Octaacetate (2) from (1). Askendoside D (2 g) was acetylated with 10 ml of acetic anhydride in 10 ml of pyridine at room temperature. The reaction mixture was poured into ice water, and the resulting precipitate was filtered off and washed with water. The products were chromatographed on a column with elution by system 1. This gave 2.6 g of the amorphous octaacetate (2), $C_{61}H_{90}O_{25}$. $[\alpha]_D^{24}$ 0 ± 3° (*c* 1.3; MeOH) [2].

3β-[O-α-*L*-Arabinopyranosyl-(1→2)-β-*D*-xylopyranosyloxy]-6α-(β-*D*-xylopyranosyloxy)-25-norcycloartan-16-one-20,24-olide Octacetate (3) from (2). The octaacetate (2) (1 g) in 40 ml of acetone was treated with 1 ml of the Jones reagent [3], the mixture was stirred and was left at room temperature for 20 min, and the excess of oxidant was destroyed by the addition of 5 ml of methanol. The reaction mixture was poured into water and treated with chloroform. The chloroform extract was washed with water and was evaporated, and the residue was chromatographed on a column, with elution by system 1. This gave 0.818 g of the lactone acetate (3), $C_{58}H_{80}O_{25}$, mp 150-152° (from ethanol), $[\alpha]_D^{24}$ −54 ± 2° (*c* 0.6; MeOH) [2].

3β-[O-α-*L*-Arabinopyranosyl-(1→2)-β-*D*-xylopyranosyloxy]-6α-(β-*D*-xylopyranosyloxy)-25-norcycloart-17E- and 17Z-en-16-on-24-oic Acids (4) from (3). Compound (3) (0.818 g) in 40 ml of methanol was treated with 50 ml of a 2% methanolic solution of sodium hydroxide. The mixture was stirred, and after a short time it was acidified with a methanolic solution of sulfuric acid. It was then diluted with water, the methanol was evaporated off, and the aqueous solution was

treated with *n*-butyl alcohol. The residue after evaporation of the butanolic extract was chromatographed on a column with elution by system 2. This led to the isolation of 260 mg of the noncrystalline product (**4**), $C_{42}H_{64}O_{17}$. IR spectrum (KBr, ν, cm^{-1}): 3403 (OH), 1707 (CO at C-16 and CO of the carboxy group). PMR spectrum (δ, ppm, C_5D_5N, 0 — TMS): 0.00, 0.02, and 0.64 (2 × 2H-19, d, ^2J = 4 Hz), 1.21, 1.26, 1.28, 1.29 × 4, 1.31, 1.72, 1.88 (10 × CH_3, s), 4.75 and 4.77 (2H-1 of *D*-xylose, d, ^3J = 8 Hz), 5.16 (H-1 of *L*-arabinose, d, ^3J = 8 Hz), 8.49 (H of the C-24 carboxy group, s).

For the ^{13}C NMR spectrum, see Table 1.

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