TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XIV. ASKENDOSIDE A FROM Astragalus taschkendicus

M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov

A new glycoside of the cycloartane series — askendoside A — has been isolated from the roots of Astragalus taschkendicus Bge. (family Leguminosae), and on the basis of chemical transformation and spectral characteristics its structure has been established as 3β-{O-α-L-arabinopyranosyl-(1→2)-(3′-O-acetyl-β-D-xylopyranosyl)-oxy}-24R-cycloartane-6α,16β,24,25-tetraol.

We have continued a study of the isoprenoids of the plant Astragalus taschkendicus Bge. (family Leguminosae) [1-5]. The present paper is devoted to a proof of the structure of compound (I), which we have called askendoside A [1].

The presence in the PMR spectrum of compound (I) (Fig. 1) of two one-proton doublets at 0.16 and 0.45 ppm interacting in the manner of an AB system has enabled us to assign askendoside A to derivatives of isoprenoids of the cycloartane series [6]. This was confirmed by the production of cycloasgenin C (II) by the acid hydrolysis of glycoside (I).

It was found with the aid of TLC that that the askendoside A molecule contains D-xylose and L-arabinose residues. According to GLC [7] the ratio of the monosaccharides is 1:1.

The IR spectrum of askendoside A has absorption bands at 1735 and 1258 cm⁻¹ showing the presence of an ester grouping. In the PMR spectrum of the substance under consideration, a singlet signal corresponding to three proton units appears at 2.03 ppm. The facts given show that askendoside A contains one acetate group.

The alkaline hydrolysis of askendoside A (I) led to the formation of glycoside (III), which was found to be identical with askendoside C [3]. Askendoside A (I) was subjected to periodate oxidation followed by acid hydrolysis. This gave D-xylose and compound (VI). The formation of D-xylose shows that it is this particular sugar residue that contains the acetate group.


© 1984 Plenum Publishing Corporation
Substance (VI) had a molecular mass of $M^+ 466$, i.e., 14 mass units greater than the derivative (V) described previously ($M^+ 432$). The latter was obtained by the periodate oxidation of cycloasgenin C (II) [2]. The PMR spectrum of compound (VI) showed at 3.29 ppm the three-proton singlet of an OCH₃ group. These facts permitted the assumption that compound (VI) was the 24-O-methyl ether of the triol (V). To confirm this, cycloasgenin C (II) was converted by periodate oxidation into substance (V) [2], the treatment of which with a methanolic solution of sulfuric acid led to the isolation of a compound identical with (VI).

The Smith degradation [8] of askendoside A led to a glycoside (IV) having in its PMR spectrum the signal of an OCH₃ group at 3.25 ppm. As was to be expected, D-xylose was detected in the products of the methanolysis of glycoside (IV). A compound identical with substance (VI) was isolated from the genin fraction of the hydrolysate. The facts given determine glycoside (IV) as 24-methoxy-3β-β-D-xylopyranosyloxy-25-nor-16β,255-epoxycycloartan-6α,6β,24,25-tetraol.

EXPERIMENTAL

General Observations. For general observations see [1]. The following solvent systems were used: 1) chloroform-methanol (15:1); 2) butanol-methanol-water (5:3:1); 3) ethyl acetate-acetic acid-water (6:3:2); 4) chloroform-methanol-water (70:23:4); and 5) benzene-methanol (15:1).

PMR spectra were taken on JNM-4H-100 and XL-200 spectrometers in deuteropyridine or deuterochloroform (δ, ppm; 0 -- HMDS), and 13C NMR spectra on a CFT-20 instrument (Varian) in deuteropyridine (δ, ppm; 0 -- TMS). The isolation of the isoprenoids of Astragalus tashkendicus Bge. has been described previously [1, 2].

Askendoside A (I) — substance C [1], C₄₂H₇₀O₁₈, mp 213-214°C (from methanol), $\alpha$ $^D$ 0±3° (c 0.8; methanol); $\nu_{max}$, cm⁻¹: 3520-3325 (OH), 3040 (CH₂ of a cyclopropane ring); 1735, 1258 (ester group). PMR (CD₂N), ppm: 0.16 (1 H at C-19, d, 2J = 4.4 Hz); 0.45 (1 H at C-19, d, $^2J = 4.4$ Hz); 0.89 (3 H, s, CH₃); 0.98 (3 H, d, $^3J = 6.6$ Hz, CH₃ at C-20); 1.27 (6 H, s, 2 × CH₃); 1.36 (3 H, s, CH₃); 1.38 (3 H, s, CH₃); 1.70 (3 H, s, CH₃); 2.03 (3 H, s, OCCOCH₃ at C-3'); 3.34 (1 H at C-3, m); 4.59 (1 H at C-16, m); 4.88 and 4.89 (2 anomeric protons, d, $^2J = 5.8$ and 7.0 Hz, respectively); 5.54 (1 H at C-3', t, $^3J_1$ ≈ $^3J_2$ ≈ 7.5 Hz).

Cycloasgenin C (II) from Askendoside A (I). A solution of 50 mg of askendoside A in 15 ml of 0.5% methanolic sulfuric acid was boiled on the water bath for 1.5 h. Then the reaction mixture was diluted with water to a volume of 100 ml and the methanol was evaporated off. The precipitate that had deposited was filtered off, washed with water, and dried. Then it was chromatographed on a column with elution by system 1. This gave 19 mg of cycloasgenin C (II) with mp 244-246°C (from acetone), $\alpha$ $^D$ +34 ± 2° (c 1.2; methanol), which was identical with an authentic sample [2] both according to its chromatographic mobility on TLC in various solvent systems and according to a comparison of IR spectra.