TRITERPENE GLYCOSIDES FROM Arenaria graminifolia

V. G. Bukharov and S. P. Shcherbak

UDC 547.597+547.918

Arenaria graminifolia Schrad. (grass-leaf sandwort) is a perennial plant of the family Caryophyllaceae. Some species of sandwort contain large amounts of saponins which have not been studied chemically [1].

We have investigated the saponins from grass-leaf sandwort collected in the Tatar ASSR. The roots of the plant, previously defatted by boiling with chloroform, were exhaustively extracted with methanol. By thin-layer chromatography on silica gel in the systems 1) butan-1-ol–acetic acid–water (4:1:5) and 2) butan-1-ol–25% ammonia–ethanol (7:5:2) two predominating glycosides, which have been called arenarioosides A and B, have been found in the extract. For their isolation, a methanolic extract was poured into water and extracted with butan-1-ol. The aqueous extract was purified from reserve sugars and oligosaccharides by gel filtration on Sephadex G-25, and the mixture of saponins was separated on a column of silica gel in solvent system 1.

Arenarioside A, mp 255-260°C, $[\alpha]_D^{20}$ −11° (c 1.47; pyridine) was obtained with a yield of ~1% of the weight of the raw material. The glycoside consists of a white amorphous powder readily soluble in water and aqueous alcohols. Acetate: mp 163-165°C, $[\alpha]_D^{20}$ −20° (c 1.0; methanol). The hydrolysis of arenarioside A with 5% hydrochloric acid formed the aglycone, with mp 265-267°C, $[\alpha]_D^{20}$ +90° (c 1.0; ethanol), the constants and chromatographic behavior of which were identical with those of gypsogenin. In addition to gypsogenin, the glucosiduronic acid vaccaroside [2] with mp 220-223°C, $[\alpha]_D^{20}$ +24° (c 1.0; pyridine) was isolated. The carbohydrate moiety of the glycoside was found by paper chromatography (PC) in system and in benzene–butan-1-ol–pyridine–water (1:5:3:3) in comparison with authentic samples to contain galactose, xylose, and rhamnose in a ratio of 1:2:2 and glucuronic acid.

Arenarioside A was saponified with 10% alkali. The glycoside formed [mp 290-295°C, $[\alpha]_D^{20}$ +20° (c 1.0; pyridine)] was extracted with butanol and purified by chromatography on silica gel in water-saturated butan-1-ol. After the acid hydrolysis of the glycoside, galactose and xylose (1:1) and glucuronic acid were identified.

The acid hydrolysis of the oligosaccharide split off gave xylose and rhamnose. Arenarioside A was oxidized with sodium periodate and the product was hydrolyzed. Xylose and glucuronic acid were identified in the hydrolyzate by PC.

Arenarioside B, mp 248-252°C, $[\alpha]_D^{20}$ −26° (c 1.0; pyridine) was obtained with a yield of ≈ 0.2%. After hydrolysis of the glycoside with 5% hydrochloric acid, galactose, glucose, xylose, and rhamnose (1:1:2:1) and glucuronic acid and gypsogenin were found.

LITERATURE CITED

1. V. I. Vereshchagin, K. A. Sobolevskaya, and A. I. Yakubova, Useful Plants of Western Siberia [in Russian], Moscow–Leningrad (1959), p. 203.
2. N. K. Abubakirov and K. Amanmuradov, Zh. Obshch. Khim., 34, 1961 (1964).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR.
Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 123-124, January-February, 1973. Original article submitted July 17, 1972.