GLYCOSIDES OF Polygonatum stenophyllum

L. I. Strigina and E. V. Kol'chuk

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This paper gives the results of a preliminary chemical study of the steroid glycosides of the endemic plant of the Soviet Far East Polygonatum stenophyllum (family Liliaceae).

The thin-layer chromatography of a methanolic extract from the roots of Polygonatum stenophyllum in the chloroform–methanol (2:1)/H_2O system showed that the plant contains four glycosides, these being detected with a modified Sannié reagent [1]. The glycosides, called in order of increasing polarity polygonatosides A-D, were isolated in the chromatographically homogeneous state by chromatography on silica gel. The isolation of the individual glycosides was associated with great experimental difficulties because of their high lability. Thus, the heating or prolonged (1-2 days) standing at room temperature of a methanolic solution of polygonatosides C and D led, according to two-dimensional thin-layer chromatography, to a partial change in the initial substances. Such changes have been described for sarsaparilloside [2], in which they were due to the presence of a semiacetal hydroxyl in an open side chain of the aglycone. Polygonatoside C, homogeneous on chromatography in a thin layer of silica gel in two systems [chloroform–methanol (2:1)/H_2O (1) and butanol–ethanol (5:1)/H_2O (2)], crystallized from aqueous acetone in the form of needles with mp 281-285°C, $[\alpha]_D^{20}$ −124.9° (c 0.489; aqueous acetone). IR spectrum (KBr): 1650 cm^{-1} (double bond); there were no bands corresponding to any of the forms of a carbonyl group. The acid hydrolysis (3 N H_2SO_4) of each of the polygonatosides led to identical mixtures of aglycones according to thin-layer chromatography in three systems [petroleum ether–chloroform–acetic acid (100:40:4) Sannié's system [3] (1), chloroform–methanol (95:5)/H_2O (2), and chloroform–ethyl acetate–methanol (7:7:1) (3)].

Under the action of the enzymes contained in the digestive juice of the Far-Eastern snail Eulota maakii, polygonatoside D split off glucose and gave a mixture of progenins which, on analysis in a thin layer of silica gel, had the same R_f values as polygonatosides B and C. The enzymatic hydrolysis of polygonatoside C gave an aglycone $C_{27}H_{42}O_4$ with mp 226-231°C (needles from benzene, mol. wt. 430) (mass spectrometry).

The nature of the fragmentation of the aglycone on mass spectroscopy in association with the other properties permits the aglycone to be assigned to the steroid sapogenins. From the facts given above it was not possible to establish the identity of the compound obtained with any known compound. As paper chromatography in the butanol–pyridine–water (6:4:3) system showed, the carbohydrate chains include glucose, arabinose, and rhamnose (polygonatosides B, C, and D) and arabinose (polygonatoside A). Thus, polygonatosides B, C, and D are new glycosides not previously described in the literature.

According to information from K. A. Meshcherskaya and T. M. Goncharova (Medical Institute, Vladivostok), polygonatosides C and D possess a pronounced anticoagulant action.

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