STEROID GLYCOSIDES FROM THE ROOTS OF Polygonatum stenophyllum. POLYGONATOSIDES C^1 AND C^2

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We have previously reported the isolation from the roots of Polygon turn stenophyllum Maxim. of a series of steroid glycosides — polygonatosides A-E [1], the acid hydrolysis of which formed the steroid aglycone pennogenin [2]. A further investigation has shown that polygonatoside C is a difficultly separable mixture of two glycosides of extremely similar polarities which we have called C¹ and C². In the present paper we report the isolation of the individual polygonatosides C¹ and C² and give the results of a study of their structures.

Polygonatoside C¹, mp 299-300°C, $[\alpha]_D^{2\circ}$ -129.6° (c 0.36; pyridine), was obtained by the chromatography of a butanol extract of the roots of *Polygonatum stenophyllum* on silica gel in the chloroform-ethanol (100:0+75:25) system.

Polygonatoside C², mp 292-294°C, $[\alpha]_D^{25}$ -107.9° (c 0.38; pyridine) was obtained by the saponification with 5% KOH in ethanol of its acetate isolated by chromatography on silica gel in the benzene-diethyl ether (100:0+65:35) system from a mixture of the acetates of C¹ and C² obtained in the usual way.

The IR spectra of the acetates of C^1 and C^2 each have the peak of a free hydroxyl (3560 cm⁻¹) and bands corresponding to spiroketal side chains of steroid sapogenins (870, 900, 922, 980 cm⁻¹).

A qualitative and quantitative determination of the monosaccharides in C¹ and C² by the GLC of the corresponding aldononitrile peracetates showed that C¹ contained glucose, rhamnose, and arabinose (1:1:1) and C² contained glucose and rhamnose (1:2). When a mixture of C¹ and C² was incubated with the digestive juice of the snail *Eulota maachii*, pennogenin was isolated, mp 226-231°C, $[\alpha]_D^{2\circ}$ -93.0° (c 0.18; chloroform).

The acetates of C¹ with $[\alpha]_D^{2^5}$ -79.4° (c 0.41; ethanol) and of C² with $[\alpha]_D^{1^8}$ -60.0 (c 0.67; ethanol) were prepared.

The PMR spectrum of the acetate of C¹ had signals (δ , ppm) at 0.818 s; 0.895, J = 7.2 Hz; and 1.014 s; and that of C² at 0.822 s; 0.90, J = 7.2 Hz, and 1.016 s, which were identical with the signals of the C-18, C-21, and C-19 methyl groups of pennogenin.

The facts given permit the statement that polygonatosides C^1 and C^2 are pennogenin triosides. Since no pennogenin glycoside containing arabinose has been known hitherto, it can be stated that C^1 is a new pennogenin glycoside. The study of the structures of C^1 and C^2 will be continued.

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