TRITERPENE GLYCOSIDES FROM *Androsace septentrionalis*. THE STRUCTURE OF ANDROSEPTOSIDES C_1 AND D_1

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The results of study of the total glycosides from *Androsace septentrionalis* L. [northern rock jasmine] (family *Primulaceae*) and the structures of oleanolic acid monosides and biosides and of primulagenin A have been given previously [1, 2]. On isolating the main individual glycosides by column chromatography on silica gel, we obtained a fraction containing two substances. On rechromatography in chloroform–methanol–water (61:32:7) and chloroform–methanol (8:2), systems, we obtained individual glycosides which we have called androseptosides C_1 (I) and D_2 (II): (I) – mp 208-210°C, $[\alpha]_D^{17}$ –50° (c 1.0; methanol); (II) mp 195-197°C, ($[\alpha]_D^{20}$ –19.5° (c 1.3; pyridine).

As the result of the complete acid hydrolysis of glycosides C_1 and D_1 with 2.5% sulfuric acid (110°C, 6 h), D-glucose and α-arabinose were identified in the neutralized hydrolysate by paper chromatography in the butanol–pyridine–water (5:1:3) system. The ratio of the monosaccharides determined by gas–liquid chromatography of the acetates of the aldononitriles was 1:2 for each anhydroseptoside.

The melting point of the aglycone of glycoside C_1, its specific rotation and its R_f value in several solvent systems, and also its IR spectra coincided completely with those for oleanolic acid [mp 305-307°C, $[\alpha]_D^{20}$ +80° (c 1.0; CH_3OH)].

As the aglycone for androseptoside D_1, from its physicochemical constants, we identified primulogenin A [mp 248-250°C, $[\alpha]_D^{20}$+55° (c 1.0; $CHCl_3$)]. The IR spectra of an authentic sample of primulogenin A and of the genin coincided completely.

The stepwise hydrolysis of C_1 (1% H_2SO_4, 90°C, 1.5 h) gave progenins which coincided chromatographically with the androseptosides A and C obtained previously from rock jasmine [2]. The identity of the progenins and of the natural glycosides A and C was confirmed by their physiochemical constants.

The partial hydrolysis of glycoside D_1 yielded progenins coinciding in chromatographic mobility and physicochemical constants with androseptosides B and D.

When androseptosides C_1 and D_1 were methylated by Hakomori's method [3], followed by methanolysis of the permethylated androseptosides with 72% perchloric acid in methanol (1:10), methyl 2,3,4-tri-O-methyl-L-arabinopyranoside, methyl 3,4-di-O-methyl-L-arabinoside, and methyl 2,3,6-tri-O-methyl-D-glucopyranoside were obtained. The methyl glycosides were identified with the aid of GLC in the presence of markers (3.2-m column filled with 5% of XE 60 on Chromaton NAW HMDS, temperature of the thermostat 170°C, of the evaporator 240°C, and of the detector 240°C, carrier gas helium at a rate of 60 ml/min).

Alkaline saponification with a 10% aqueous ethanolic solution of KOH (100°C, 5 h) did not change the chromatographic mobility of glycoside C_1 in a thin layer, which indicates the absence of an O-acyl glycosidic bond and, consequently, the attachment of the carbohydrate components at C_3 of the aglycone. The configurations of the glycosidic centers were found on the basis of Klyne's rule and were established from molecular rotation differences between the initial glycosides and their progenins. The deduction of the position of attachment of the carbohydrate chain to the aglycone in glycoside D_1 was based on analogy with other glycosides of the β-amyrin series.

On the basis of the results presented above, the following structures are proposed for androseptosides C_1 and D_1:

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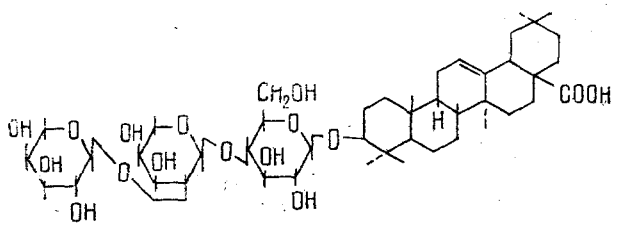
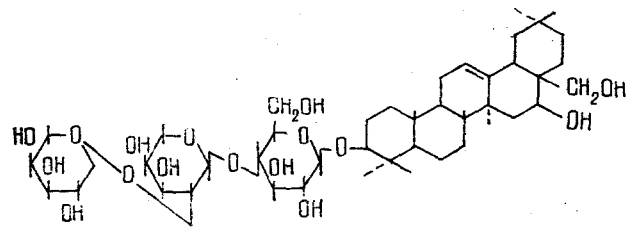


Androseptoside C_1



Androseptoside D_1

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TRITERPENE GLYCOSIDES OF *Androsace septentrionalis*

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We have reported previously [1] that eleven glycosides have been detected in *Androsace septrionalis*, four of which are quantitatively predominant. By column chromatography on silica gel in the chloroform–methanol–water (61:32:7) system we have isolated androseptoside F with mp 197-200°C, $[\alpha]_D^{17}$ −60° (c 1.0; methanol), making up 15% combined dominant glycosides.

After glycoside F had been hydrolyzed with 2.5% sulfuric acid, in the neutralized hydrolysate we detected — by paper chromatography and by GLC of the acetates of aldononitrile derivatives — glucose, arabinose, and rhamnose in a ratio of 1:2:1. The melting point of the aglycone obtained and its specific rotation and IR spectrum coincided with those for primulogenin A [mp 248-250°C, $[\alpha]_D^{20}$ +55° (c 1.0; chloroform)].

To determine the positions of attachment of the manosaccharides to one another, partial hydrolysis was performed with 1% sulfuric acid for an hour. The hydrolysis products were chromatographed on a column in the system mentioned above, which yielded three progenins coinciding in melting points, specific rotations, and R_f values on thin-layer chromatograms with androseptosides B, D, and D_1 [2, 3].

As a result of the methylation of androseptoside F followed by methanolysis of the permethylate and thin-layer chromatography [benzene–acetone (2:1)] and methyl 2,3,4-tri-O-methyl-α-rhamnopyranoside, methyl 2,3,6-tri-O-methyl-D-glucopyranoside, and methyl 3,4-di-O-methyl-α-arabinopyranoside. The periodate oxidation of the glycoside under investigation followed by acid hydrolysis of the oxidized product and paper chromatography yield not one monosaccharide, which confirms the results of methylation.

The position of attachment of the carbohydrate chain to the aglycone was established by analogy with other glycosides of the β-amyrin series, and the configurations of the glycosidic centers according to Klyne's rule.

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