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BRYONOLIC ACID IN THE ROOTS OF BRYONIA ALBA

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From a chloroform extract of the roots of Bryonia alba collected in the spring of 1967 in the region of the village of Garni in Armenia, we have isolated bryonolic (3β-hydroxyurs-12-en-29-oic) acid. It has been found previously in the roots of Bryonia dioica [1].

For identification, several derivatives were obtained by the usual methods. The melting points and specific rotations of the substances obtained were compared with literature data.

Substance	Values found mp, °C, $[\alpha]_D$, deg		Literature data mp, °C, $[\alpha]_D$, deg		
Byronolic acid	303–305	—	303–305	—	[1]
Methyl ester	149–151	+14	140–142	+19	[1]
Acetate of the methyl ester	159–162	+22	162	+24	[1]
Acetate of the acid	267–270	—	267–268		[1]
3-Dehydro acid	240–242	—	227	—	[2]
Methyl ester of the 3-dehydro acid	154.5–157	—	132–133	—	[2]

The results of the elementary analysis of all the compounds agree with the calculated figures. The acid that we isolated and its methyl ester gave no depression of the melting point with samples kindly provided by Prof. G. Biglino.

REFERENCES

1. G. Biglino, Atti. Ac. Sci. Tornio, **94**, 411, 1959–1960.
2. G. Biglino, Atti. Ac. Sci. Torino, **95**, 106, 1960–1961.

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GLYCOSIDES OF THE LEAVES OF EUONYMUS EUROPAEA

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The dry comminuted leaves of Euonymus europaea L. (European euonymus) were exhaustively extracted with 70% ethanol at the boil in the water bath. By treatment with various solvents, chromatography on Kapron, and preparative separation on paper, individual substances B and C were obtained.

The glycoside C has not been described in the literature and we have called it beresklet in ["beresklet" is the Russian for euonymus]. It is a greenish yellow amorphous substance with R_f 0.35 [n-butanol–CH_3COOH–H_2O (4 : 1 : 5)], which is soluble in water, methanol, and ethanol, and insoluble in ether and chloroform. The hydrolysis of glycoside C with 2% hydrochloric acid in an air bath for 2 hr led to the formation of quercetin, glucose, rhamnose, galactose, and caffeic acid. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 328, 256 mμ; $\lambda_{max}^{CH_3COONa}$ 329, 256 mμ ($\Delta\lambda_1$ + 1, $\Delta\lambda_2$0); $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 330, 254 mμ ($\Delta\lambda_1$ + 2, $\Delta\lambda_2$ – 2); $\lambda_{max}^{C_2H_5ONa}$ 328, 256, mμ ($\Delta\lambda_1$0, $\Delta\lambda_2$0); $\lambda_{max}^{AlCl_3}$ 371, 264 mμ ($\Delta\lambda_1$ + 43, $\Delta\lambda_2$ + 8); $\lambda_{max}^{AlCl_3+HCl}$ 336, 260 mμ ($\Delta\lambda_1$ + 8, $\Delta\lambda_2$ + 4), which shows the presence of a free hydroxy group at C_5 and the presence of substituents at C_3, C_7, and C_4'.

Hydrolysis with 0.5 N methanolic caustic potash for 15 min yielded a glycoside C' and caffeoyl D-galactoside, readily hydrolyzed with 1% hydrochloric acid to D-galactose and caffeic acid.

On acid hydrolysis, glycoside C' with R_f 0.48, mp 192°–196° C, gave quercetin, glucose, and rhamnose in equimolar amounts (amount of aglycone obtained 48.9%, calculated 49.5%). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 358, 256 mμ; $\lambda_{max}^{CH_3COONa}$ 358, 256 mμ ($\Delta\lambda_1$0; $\Delta\lambda_2$0); $\lambda_{max}^{C_2H_5ONa}$ 410, 256 mμ ($\Delta\lambda_1$ + 52; $\Delta\lambda_2$ + 10); $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 376, 261 mμ ($\Delta\lambda_1$ + 18; $\Delta\lambda_2$ + + 5); $\lambda_{max}^{AlCl_3}$ 415, 266 mμ ($\Delta\lambda_1$ + 57, $\Delta\lambda_2$ + 10); $\lambda_{max}^{AlCl_3+HCl}$ 359, 257 mμ ($\Delta\lambda_1$ + 1, $\Delta\lambda_2$ + 1). Consequently, in glycoside

C' the hydroxy groups at C_5, C_4' and C_3' are free and the sugar residues are located at C_3 and C_7. The hydrolysis of glycoside C' (1% H_2SO_4 for 30 min, in the water bath) gave rhamnose and glycoside C", the R_f of which in various systems of solvents, coincided with the R_f of quercimeritrin.

Glycoside C", with R_f 0.30, mp 243°–246° C, λ_{max} 375, 257 mμ, on hydrolysis with 2% hydrochloric acid, gave quercetin and glucose. It was shown by UV spectroscopy that the glucose was located at C_7 and that the hydroxy groups at C_3, C_5, C_4', and C_3' were free.

The aglycone of the glycosides studied had R_f 0.73, mp 310°–314° C, λ_{max} 375, 257 mμ. Chromatographic analysis, the absence of a depression of the melting point of a mixture, and the results of spectroscopic studies permitted the conclusion that the aglycone was identical with quercetin. We assume that the new glycoside C that we have isolated (bereskletin) is quercetin 4'-(caffeoyl-D-galacto)-7-(D-gluco)-3-(L-rhamnoside).

Glycoside B formed yellow crystals with mp 194°–196° C, λ_{max} 357, 257, mμ, R_f 0.48. The acid hydrolysis of glycoside B led to quercetin, glucose, and rhamnose. From the hydrolysis products, the results of paper chromatography, and a study of the UV spectrum, etc., this substance was found to be identical with the glycoside C', ie., it is quercetin 3-(L-rhamno)-7-(D-glucoside) and, possibly, the product of the hydrolysis of glycoside C.

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CARDIAC GLYCOSIDES OF JUTE

III. The Structure of Olitoribiose

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Olitoribiose is the name that has been given to the disaccharide formed in the hydrolysis with 0.1 N sulfuric acid of olitoriside—a cardiac diglycoside from Corchorus olitorius L. [1]. The sugar, obtained in the form of a syrup, gives a crystalline hexaacetate $C_{24}H_{34}O_{15}$ with mp 190°–192° C, $[\alpha]_D^{20}$ −12.5 ± 2° (chloroform), which corresponds to the empirical formula for the bioside of $C_{12}H_{22}O_9$.

It follows from the structure of olitoriside, that the disaccharide contains D-boivinose and D-glucose. The full structure of olitoribiose has been established by exhaustive methylation. For this purpose, the disaccharide was first methylated with dimethyl sulfate by Haworth's method, and then with methyl iodide in dimethylformamide in the presence of silver oxide, by Kuhn's method [2]. Methylation was continued until a chromatogram of the reaction products in a thin layer of silica gel in the chloroform–ethanol (25 : 1) system showed the presence of only one compound. The IR spectrum of this compound had no absorption band for hydroxy groups.

The hexa-O-methylolitoribioside, obtained in the amorphous form, was hydrolyzed by boiling with 2 N sulfuric acid, and the reaction mixture was neutralized on the anion-exchanger EDE-10P. Among the reaction products, by paper chromatography in the systems 1-butanol–acetic acid–water (4 : 1 : 5), methyl ethyl ketone–1% ammonia, and methyl ethyl ketone–1-butanol–borate buffer (1 : 1 : 2) [3], we identified D-sarmentose (a sample of this sugar was kindly given to us by Prof. T. Reichstein, Switzerland) and 2, 3, 4, 6-tetramethylglucose. By preparative separation of the mixture of methylated sugars on Schleicher and Schüll 2043 chromatographic cardboard, we succeeded in isolating 2, 3, 4, 6-tetra-O-methyl-β-D-glucopyranose in the crystalline form (mp 91° C, $[\alpha]_D^{20}$ +80°, water).

The formation of D-sarmentose shows that the D-glucose residue is attached to carbon atom 4 of the D-boivinose and the formation of 2, 3, 4, 6-tetramethyl-β-D-glucose shows that it has the pyranose form and the glycosidic bond has the β-configuration. Thus, olitoribiose has the structure 4-β-D-glucopyranosido-D-biovinopyranose. On the basis of Reeves' investigations [4], it has been established that D-glucose has the C 1 form and that all the hydroxy substituents in it occupy equatorial positions, also, taking into consideration the fact that D-boivinose belongs to the D-gulose series with the hydroxy substituents at C_3 and C_4 in the axial position, the conformation of olitoribiose can be represented in the following way: