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.

22 April 1968

Pyatigorsk Pharmaceutical Institute

UDC 547.918+615, 711, 5

CARDIAC GLYCOSIDES OF JUTE

III. The Structure of Olitoribiose

R. U. Umarova, V. A. Maslennikova, and N. K. Abubakirov

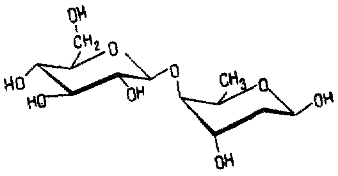
Khimiya Prirodnykh Soedinenii, Vol. 4, No. 5, pp. 325–326, 1968

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:



By determining the structure of olitoribiose we have finally confirmed the structure of olitoriside as strophanthidin 3-(β-D-boivinopyranosido-β-D-glucopyranoside).

REFERENCES

1. N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits, ZhOKh, **28**, 2279, 1958; **29**, 1235, 1959.
2. R. Kuhn, H. Trischmann, and J. Löw, Angew. Chem., **67**, 32, 1955.
3. R. Tschesche, H. J. Wulff, and G. Snatzke, Naturwissen., **46**, 109, 1959. [4] R. Reeves, J. Amer. Chem.
4. R. Reeves, J. Amer. Chem. Soc., **73**, 957, 1951; Advances Carbohydr. Chem., **6**, 107, 1951.

16 May 1968 Institute of the Chemistry of Plant Substances AS UzSSR

UDC 547.597+ 547.918

AMORPHIGENIN β-D-GLUCOSIDE FROM AMORPHA

A. U. Kasymov, E. S. Kondratenko, and N. K. Abubakirov

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 5, pp. 326–327, 1968

We have studied by chromatography ten species of plants of the genus Amorpha in order to ascertain the presence in them of amorphin and amorphigenin. Amorphin has previously been obtained preparatively from seven species [1]. Amorphigenin has been detected chromatographically in the same species. Later, amorphin and amorphigenin were also found in *A. nana*, *A. croceolanata*, and *A. caroliniana*.

Extracts of all the species of seeds of Amorpha studied were chromatographed in a thin layer of silica gel in the benzene–methanol (4 : 1) system. In addition to others, a substance was detected giving a spot with a R_f value intermediate between those of amorphin and amorphigenin.

When a dry chloroform–methanol (9 : 1) extract from the seeds of Amorpha was separated on a column of silica gel in the system mentioned, we succeeded in isolating this substance, with the composition $C_{29}H_{34}O_{12}$, mp 164° C, $[\alpha]_D^{20}$ −122° (c 0.1; ethanol), which showed the reactions characteristic for rotenoids.

Hydrolysis of the new compound with 20% sulfuric acid led to the formation of D-glucose and an aglycone with mp 191°–192° C, $[\alpha]_D^{20}$ −138° (c 0.1; ethanol), identical in physicochemical properties with the 24-hydroxyrotenone (amorphigenin) $C_{23}H_{22}O_4$ that we have studied previously [2].

To determine the dimensions of the oxide ring of the glucose and the configuration of the glycosidic linkage, the differential spectrum of the carbohydrate component of the glycoside was recorded on a UR-10 instrument. An equimolar amount of amorphigenin (in KBr) was previously placed in the comparison channel of the spectrometer.

In the analysis of the differential IR spectrum, three strong absorption bands were found in the 1100–1010 cm^{-1} region (1048, 1085, and 1100 cm^{-1}), these being characteristic for pyranosides [3]. The band at 893 cm^{-1} shows the β-configuration of the glycosidic linkage.

The difference in the molecular rotation of the glycoside ($[M]_D$ −698°) and of amorphigenin ($[M]_D$ −556°) is −132°. For methyl α-D-glucopyranoside, ($[M]_D$ −698° [4]. These results also confirm the β-configuration of the glycoside.

On the basis of what has been said, it may be concluded that the new rotenoid glycoside has the structure of 24-hydroxyrotenone β-D-glucopyranoside.

REFERENCES

1. E. S. Kondratenko and N. K. Abubakirov, DAN UzSSR, no. 10, 35, 1960.
2. E. S. Kondratenko, A. U. Kasymov, and N. K. Abubakirov, KhPS [Chemistry of Natural Compounds], 3, 307, 1967.
33. I. V. Kovalev and V. I. Litvinenko, KhPS [Chemistry of Natural Compounds, **1**, 233, 1965.
4. Tollens-Elsner, Short Handbook on the Chemistry of Hydrocarbons [Russian translation], Moscow-Leningrad, pp. 285, 290, 1938.

20 May 1968 Institute of the Chemistry of Plant Substances AS UzSSR