A NEW FLAVONE GLYCOSIDE FROM ANTITOXICUM FUNEBRAE

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In an investigation [1] of the alkaloids of the plant Antitoxicum funebrae (Boiss. et Ky.) Pobed. (family Asclepiadaceae) it was found that after the isolation of the weak bases by making the mother liquor alkaline with ammonia, a yellow amorphous precipitate formed in the mother liquor, and on treatment with dilute acetic acid the former was converted into the crystalline state.

Our investigation of this substance has shown that it is a flavone glycoside and is decomposed on acid hydrolysis into quercetin, glucose, and rhamnose. The molecular weight of the glycoside calculated from the amount of quercetin obtained from it showed that it contained equimolecular amounts of all three components, as was also confirmed by elemental analysis, the results of which corresponded to the formula $C_{27}H_{30}O_{16}\cdot H_2O$. Methylation of the glycoside with diazomethane with subsequent acid hydrolysis led to 5,3',4'-tri-O-methylquercetin, which has been described by Kuhn [2]. It follows from this that the flavone in the glycoside was substituted by sugar residues in positions 3 and 7.

We have not been able to answer the question of the distribution of the glucose and rhamnose residues between the positions mentioned in view of the small amount of the glucoside under consideration in the plant material and the exhaustion of the latter. Consequently, the glycoside that we have isolated, undoubtedly a new one, is quercetin-3(7)-glucosido-7(3)-rhamnoside, and for it we have proposed the name of antoside.

Experimental

The plant (epigeal parts) was collected by the botanical expedition of the Ordzhonikidze All-Union Scientific Research Chemical and Pharmaceutical Institute under the leadership of P. S. Massagetov in the summer of 1959 in the Caucasus. The analyses were carried out in the microanalytical laboratory of the Institute by V. V. Kolpakova and her colleagues.

Isolation of the glycoside. 1.2 kg of the comminuted air-dry plant material was extracted three times with 3 *l* portions of methanol for 18 hr in a Jena-Therm extractor. The methanol was distilled off from the combined extracts, under slightly reduced pressure towards the end of the distillation, and the semiliquid residue was treated with 200 ml of water and 200 ml of chloroform. On the following day, the chloroform was separated off, the aqueous phase was treated with 50 ml of 20% ammonia solution, and the mixture was left at −5° C for a day, after which the amorphous yellow precipitate that had deposited was filtered off on a paper filter with suction, pressed out, transferred to a flask, and treated with 20 ml of 10% acetic acid, in which it dissolved. On the following day (−5° C) the crystals that had deposited were filtered off, washed with 10% acetic acid, and dried. The yield of unpurified glycoside was 0.21 g or 0.018%. After two recrystallizations from 70% alcohol, 0.14 g of a substance with mp 226°-228° C (decomp.) was obtained. To determine the specific rotation and for analysis (here and below) the substances were dried over P_2O_5 at 100° C and 1 mm, $[\alpha]_D^{25}$ −114.2° (c 0.888; pyridine).

Found, %: C 51.63, 51.60; H 5.10, 5.10. Calculated for $C_{27}H_{30}O_{16}\cdot H_2O$, %: C 51.60; H 5.13.

Hydrolysis of the glycoside; isolation of quercetin. A mixture of 0.470 g of the dried glycoside (see above) and 20 ml of 1 N H_2SO_4 was heated on a boiling water bath for 3 hr. On the following day the aglycone was filtered off on a weighed glass filter, washed with water, and dried. This gave 0.223 g of quercetin; found mol. wt. 636; for the formula given above, calculated mol. wt. 628.5.

The hydrolysate was neutralized with barium carbonate, and the filtrate was concentrated in vacuum. Chromatography on paper in the butan-1-ol–acetone–water (2:7:1) system gave two spots corresponding to glucose and rhamnose.

The aglycone was recrystallized from 70% alcohol, mp 309°-310° C (decomp.); it gave no depression of the melting point in admixture with an authentic sample of quercetin. Acetylation of the aglycone with acetic anhydride in pyridine led to the acetate with mp 194°-195° C, which gave no depression of the melting point in admixture with penta-O-acetylquercetin.

Methylation of the glycoside; isolation of 5,3',4'-tri-O-methylquercetin. A suspension of 1.6 g of the glycoside in 70 ml of methanol was treated with 70 ml of an ethereal solution of diazomethane (from 4 g of nitrosomethylurea). After a day, and then again after 2 days, the same amount of diazomethane was added again, after which the mixture was left for 3 days. The solvent was distilled off and the residue was hydrolyzed by heating it with 1 N H_2SO_4. This gave 0.8 g of a methylated product which was recrystallized from 90% alcohol and from methanol. Yield 0.33 g, mp 293°-294° C. Literature data: mp 292°-294° C [2].

Found, %: C 62.75; H 4.78; CH_3O 26.75. Calculated for $C_{18}H_{16}O_7$, %: C 62.77; H 4.70; 3 CH_3O 27.03.

The substance was acetylated by boiling with acetic anhydride in the presence of anhydrous sodium acetate. After the usual working up and recrystallization from methanol, 3,7-di-O-acetyl-5,3',4'-tri-O-methylquercetin with mp 148°–150° C was obtained. Literature data: mp 148°–149° C [2].

Found, %: C 61.17; H 4.71. Calculated for $C_{22}H_{20}O_9$, %: C 61.68; H 4.71.

Summary

A new flavonoid, antoside, which is the 3(7)-glucoside-7(3)-rhamnoside of quercetin has been isolated from Antitoxicum funebrae.

REFERENCES

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