PARTIAL SYNTHESIS OF QUERCETIN 4'-β-D-GLUCOPYRANOSIDE

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We have performed an investigation on the selective introduction of a sugar component into a predetermined position of a flavonoid. For this purpose, we have obtained preparatively 3,3',5,7-tetraacetylquercetin by the hydrolysis of quercetin pentaacetate under mild conditions. From the 3,3',5,7-tetraacetylquercetin (3,3',5,7-tetraacetoxy-4'-hydroxyflavone) and tetraacetylglucopyranosyl bromide in acetone in the presence of silver oxide followed by saponification of the product we have synthesized 3,3',4',5,7-pentahydroxyflavone 4'-O-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$ (I).

Substance (I) gives the cyanidin reaction, and on a chromatogram in filtered UV light if fluoresces yellow, which shows the absence of substituents in position 3 of the flavonoid.

In the products of the acid hydrolysis of this substance, D-glucose and quercetin (3,3',4',5,7-pentahydroxyflavone) (II) were detected.

Sodium acetate caused a bathochromic shift of 15 nm in band I of the UV spectrum of substance (I), while band (II) remained unchanged under these conditions. Sodium acetate caused a bathochromic shift of both bands in the UV spectrum of substance (II). It is interesting to note that the UV spectra of substance (I) are identical with the UV spectra of quercimeritrin (quercetin 7-glucoside) both in neutral solutions and after the addition of diagnostic reagents to the solution under study, although the R_f values of these substances in the ethyl acetate–formic acid–water (10 : 2 : 3) system differ. Under analogous conditions, the UV spectra of 4'-O-methylquercetin do not differ from the UV spectra of 7-O-methylquercetin (I), which is obviously a result of a similarity of the electronic systems of these substances. Thus, the replacement of either the hydroxy group in position 7 or that in position 4' leads to a disappearance of the bathochromic shift of band (II) caused by sodium acetate in the UV spectra as compared with the unsubstituted substance.

What has been said above permits the conclusion that the sugar component in the substance synthesized is present in the 4' position. On the basis of the results of a comparison of the molecular rotations of substance (I) and the corresponding phenyl glucosides, it has been established that substance (I) contains a β-D-glucopyranose residue.

EXPERIMENTAL

The elementary analyses of all the substances corresponded to the calculated figures.

Pentaacetylquercetin. With heating, 2 g of quercetin was dissolved in a 50-fold amount of acetic anhydride, a drop of concentrated sulfuric acid was added, and the mixture was poured into cold water. The precipitate that deposited was filtered off, washed with water, and recrystallized from concentrated ethanol, mp 202-204°C.

3,3',5,7-Tetraacetylquercetin. A solution of 2 g of pentaacetylquercetin in 100 ml of a 0.4% solution of hydrochloric acid in acetone was heated at 73-75°C for 5 h. Then the excess of acid was neutralized with silver carbonate and after the removal of the resulting precipitate the filtrate was evaporated to dryness. After the dry residue had been recrystallized from strong ethanol, 1 g of acicular crystals with mp 180-183°C was obtained.

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Quercetin 4'-O-β-D-Glucopyranoside. 3,3',5,7-Tetraacetylquercetin (1 g) was dissolved in 200 ml of acetone containing 0.2 g of caustic potash in solution, and then 6 g of silver oxide and 6 g of tetraacetylglucopyranosyl bromide were added, and the mixture was stirred with a magnetic stirrer. After 5 h, the solution was filtered, the same amounts of reagents were added, and stirring was continued for another 5 h. After filtration and evaporation, the residue was dissolved in 30 ml of 10% caustic potash solution; after 10 min the resulting solution was neutralized with sulfuric acid. After evaporation and dissolution of the residue in aqueous ethanol the solution was deposited on a column of polyamide (100 g of polyamide) and eluted first with water and then with 35% ethanol. The 35% ethanol eluates were evaporated to dryness and the residue was recrystallized from aqueous acetone, mp 255-257°C, $[\alpha]_D^{20}$ −20° (c 1; methanol), R_f 0.40 in ethyl acetate–formic acid–water (10 : 2 : 3) system.

SUMMARY

The reaction of 3,3',5,7-tetraacetylquercetin with tetraacetylglucopyranosyl bromide has given quercetin 4'-O-β-D-glucopyranoside, and the substance has been characterized.

LITERATURE CITED

1. V. S. Batyuk, Khim. Prirodn. Soedin., 36, 368 (1970).