PLANT POLYPHENOLS

II. Polyphenols of the Flowers of Godetia whitneyi Gray

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Godetia whitneyi is a decorative annual plant. By paper chromatography, a methanolic extract of the flowers has been found to contain two substances of flavonoid structure; both substances were isolated in the crystalline form. The physicochemical constants of one of them correspond to hyperoside [1]. The IR spectrum of the other substance contains bands characteristic of carbonyl (1658 cm^{-1}) and hydroxyl (3302 cm^{-1}) groups [2]. A comparison of the results obtained with the literature data has enabled us to assert that this compound is quercitrin.

The acid hydrolysis of both glycosides gave an aglycone identified by mixed-melting-point test as quercetin. The UV and IR spectra and the constants of its penta-acetate likewise correspond to quercetin.

The sugars were identified by paper chromatography in two solvent systems in the presence of markers, and also by their osazones. It was confirmed that in hyperoside quercetin forms a glycoside with galactose, and in quercitrin with rhamnose.

In order to determine the position of the carbohydrate residue, the glycosides were methylated with dimethyl sulfate and then hydrolyzed with sulfuric acid. After this treatment, hyperoside gave a substance identified as 3', 4', 5', 7-tetramethylquercetin.

Attempts to methylate the second flavonoid gave a pentamethylquercetin in all cases. The rhamnose residue was eliminated in the methylation process, and it was therefore impossible to establish the position of the rhamnose in the molecule by this method. Attachment of the rhamnose in quercitrin in position 3 was demonstrated by the absence of fluorescence in acetic anhydride [3] and by a bathochromic shift in the UV spectra of the maxima at 257 and 355 mμ by the addition of sodium acetate, sodium ethoxide, as well as boric acid and sodium acetate to an ethanolic solution [4, 5].

These statements confirm that we obtained hyperoside and quercitrin.

Experimental

Isolation of hyperoside. One kilogram of the air-dry flowers of Godetia whitneyi were steeped successively in petroleum ether (two 10-liter portions) and methyl alcohol (three 10-liter portions). The methanolic extract was evaporated in vacuum, water was added to the residue, and the solution (0.5 liter) was kept for 24 hr at a temperature of 2-5°. The precipitate which deposited was separated off, and the aqueous solution was exhaustively extracted with ethyl acetate. After the ethyl acetate had been distilled off in vacuum, 15 g (1.5%) of combined flavonoids was obtained. The chromatographic analysis of this on type "M" paper (Leningrad) in the butanol–acetic acid–water (4:1:5; system A) and ethyl acetate–formic acid–water (10:2:3; system B) systems showed the presence of two glycosides of flavonoid structure with R_f 0.59 (A), 0.65 (B), and 0.80 (A), 0.74 (B), respectively.

Recrystallization of 15 g of the combined material from 100 ml of alcohol gave 3.2 g (0.32%) of a substance which, after repeated recrystallization, had mp 235-236°. A mixture with hyperoside obtained from Rhododendron aureum (233-234°) [1] gave no depression of the melting point. $[\alpha]_D^{20}$ −58.94°; literature: $[\alpha]_D^{20}$ −59°. R_f 0.60 (A), 0.65 (B). UV spectrum: λ_{max} 259 and 365 mμ. The IR spectrum was identical with the IR spectrum of hyperoside. Found, %: C 52.43, 53.60; H 4.74, 4.84. Calculated for $C_{21}H_{20}O_{12} \cdot H_2O$, %: C 52.27; H 4.60.

Hydrolysis of hyperoside. A mixture of 0.3939 g of hyperoside and 60 ml of 2% sulfuric acid was heated at 98° for 2 hrs. The aglycone precipitate was filtered off, washed with water, and dried. Yield 0.2584 g or 64%. The theoretical figure for a monoglycoside is 64% . After recrystallization from 20% alcohol, the substance had mp 315-316°. R_f 0.76 (A), 0.71 (B). The substance gave no depression of the melting point in admixture with quercetin. The IR spectra of the aglycone and of quercetin obtained by the hydrolysis of rutin coincided. Found, %: C 59.41; H 3.33. Calculated for $C_{15}H_{10}O_7$, %: C 59.57; H 3.33.

The Penta-acetate of the aglycone. This had mp 199-200° and showed no depression of the melting point in admixture with penta-acetate of quercetin from rutin. Found, %: C 58.85; H 4.19. Calculated for $C_{25}H_{20}O_{12}$, %: C 58.60; H 3.93.

After the separation of the aglycone, the filtrate was neutralized with "Dowex" 1 × 2 ion-exchanger (HCO_3^-) and was concentrated in vacuum to a volume of 10 ml. On chromatography on type "M" paper in the butanol–benzene–pyridine–water (5:1:3:3) (C and A) systems by the descending method, the R_f values for the sugar obtained and for

galactose coincided. The chromatogram was detected with aniline phthalate and heating to 105°.

The osazone (mp 187-188°) gave no depression of the melting point in admixture with galactose osazone.

Methylation of hyperoside. A mixture of 0.3 g of the flavonoid (mp 235-236°), 4 g of calcined potassium carbonate, 50 ml of anhydrous acetone, and 1.5 ml of redistilled dimethyl sulfate was boiled for 35 hr until the ferric chloride reaction was negative. The precipitate was filtered off, and the solution was treated with 40 ml of 2% sulfuric acid and boiled again for 3 hr. The acetone was evaporated off and the aqueous solution was cooled. The precipitate which deposited was recrystallized from alcohol. Mp 194-195°. A mixture with 3', 4', 5, 7-tetramethylquercetin had mp 193-195°. Found, %: C 63.61, 63.53; H 5.33, 5.33. Calculated for $C_{19}H_{18}O_7$, %: C 63.68; H 5.06.

Isolation of quercitrin. The mother liquors after the separation of the hyperoside were combined and the solvent was distilled off in vacuum; the residue was dissolved in water and transferred to a polyamide column [6] (column diameter 3.2 cm, height 35 cm). The column was washed with plain water and then with water containing 5-10% of alcohol. This gave 2.7 g (0.27%) of the flavonoid. Mp 186-187°. R_f 0.80 (A), 0.74 (B). UV spectrum λ_{max}: 257 and 355 mμ. IR spectrum: 1658, 3302 cm^{-1}, etc. Found, %: C 52.43; H 4.97; H_{act} 3.01; 2.96. Calculated for $C_{21}H_{20}O_{11} \cdot 2H_2O$, %: C 52.06; H 4.89; H_{act} 2.71.

Hydrolysis of quercitrin. The hydrolysis of 0.205 g of the substance with mp 185-187° in 25 ml of 2% sulfuric acid under conditions similar to those for hyperoside gave 0.133 g, or 66.5%, of the aglycone. The theoretical figure is 67.3%. The substance gave no depression of the melting point with quercetin from rutin and from hyperoside. Their IR spectra coincided; R_f 0.75 (A), 0.71 (B). Found, %: C 59.35; H 3.73. Calculated for $C_{15}H_{10}O_7$, %: C 59.57; H 3.33.

The acetate had mp 198-199° and gave no depression of the melting point in admixture with the penta-acetate of quercetin.

Rhamnose was found in the hydrolyzate after the separation of the quercetin.

Methylation of quercitrin. 0.4 g of the substance with mp 185-187° was methylated with 3 ml of freshly-distilled dimethyl sulfate in the presence of 4 g of anhydrous potassium carbonate and 55 ml of acetone under the conditions described for hyperoside. This gave 0.28 g of a substance with mp 151-152°. A mixture with 3', 4', 5, 7-tetramethylquercetin (mp 194-195°) had mp 130-132°.

Shortening the time of boiling with dimethyl sulfate from 35 to 18 and 5 hr led in all cases to the formation of pentamethylquercetin. Mp 151.5-152.5°. R_f 0.87 (B). UV spectrum λ_{max}: 249 and 338 mμ. Found, %: C 64.80, 64.49; H 5.82, 5.43; OCH_3 44.65, 45.02. Calculated for $H_{act}O \cdot C_{20}H_{20}O_7$, %: C 64.52; H 5.41; OCH_3 41.7 H_{act}.

Summary

Hyperoside and quercitrin have been isolated from the flowers of Godetia whitneyi and identified.

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