THE FLAVONOLS OF THE FLOWERS OF GOSSYPIUM HIRSUTUM L. (COTTON VARIETY 108-F)

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Perkin [1, 2] was the first to isolate quercetin, quercimeritrin, isoquercitrin, and gossypitrin from various varieties of cotton. Seshadri et al. [3] isolated gossypin and herbacitrin, in addition to the above-mentioned glucosides, from Indian varieties of cotton. The same authors [4] reported that the qualitative and quantitative composition of the flavonols in cotton flowers depends on variety, seasonal changes, and the soil and climatic conditions of the growth of the plant.

The cotton varieties cultivated in Uzbekistan have not been investigated with respect to their content of flavonols. We have studied the flavonols in the flowers of the cotton variety 108-F. A quantitative determination showed that the flowers contained 4.5% and young leaves 1.5% of flavonols [5]. Paper chromatography [6] established the presence of five flavonols in the cotton flowers.

Boiling methanolic extraction of flowers collected in 1959 yielded quercimetrin [7]. From flowers of the 1962 harvest, in addition to the glucosides mentioned, a new, isomeric quercimetrin was isolated, a glucoside having a lemon-yellow color, mp 228-230°, UV absorption spectrum λ_{max} 368, 253 mμ (in alcohol), and composition $C_{21}H_{20}O_{12}$. Paper chromatography in the isobutanol-acetic acid-water (4:1:5:) system gave R_f = 0.41.

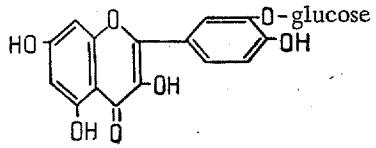
The glucoside fluoresces in ultraviolet light; the quantitative reactions for flavonols with ferric chloride and magnesium in hydrochloric acid are positive; on acetylation with acetic anhydride an octaacetyl derivative is formed. Hydrolysis of the glucoside with 5% H_2SO_4 solution leads to decomposition into the aglycone and glucose. The identity of the aglycone with quercetin has been shown by the preparation of a pentaacetyl derivative, a pentamethyl ether, by comparison of the UV spectra, and also by a mixed-melting-point test with an authentic sample of quercetin. The glucose was identified by the production of the osazone (mp 202°) and by paper chromatography in the ethyl acetate-pyridine-water (2:1:2) system. The staining agent was aniline phthalate.

In order to establish the position of the linkage of the quercetin to the D-glucose, methylation of the glucoside with dimethyl sulfate was carried out. The resulting tetramethyl ether of composition $C_{25}H_{28}O_{12} \cdot 1.5H_2O$ was hydrolyzed with 5% aqueous sulfuric acid. This gave a tetramethyl ether of quercetin of composition $C_{19}H_{18}O_7$ with mp 220-222°.

The following ethers of quercetin have been described in the literature: 5, 7, 3', 4'-tetra-O-methylquercetin, mp 194-195° [3]; 3, 7, 3', 4'-tetra-O-methylquercetin, mp 159-160° [3]; 3, 5, 3', 4'-tetra-O-methylquercetin, mp 282-284° [3]; and 3, 5, 7, 3'-tetra-O-methylquercetin, mp 199-201° [8].

From its physicochemical properties, the tetramethyl ether of quercetin with mp 220-222° differs from the tetramethyl ethers mentioned above. It follows from this that in the glucoside the quercetin is linked to the D-glucose residue through the hydroxyl group in position 3'.

Thus, the flavonol that we have isolated from cotton flowers is a new glycoside of quercetin not previously described in the literature and having the following formula:



EXPERIMENTAL

Quercimeritrin. Five kg of crushed air-dried flowers were extracted three times with boiling methanol. The extract (30 liters) was distilled under vacuum down to 2-3 liters. After 8-10 days' standing, a precipitate deposited which was separated off and washed with water. The precipitate gave no qualitative reaction for flavonols. The mother liquor after the separation of the precipitate was treated with a three-fold volume of water. The resinous substances which precipitated were filtered off. After 10-15 days standing in the refrigerator, greenish yellow crystals deposited with m.p. 234-236°. After three recrystallizations from 70% alcohol using activated charcoal and drying under vacuum, the flavonol had m.p. 246-247°; R_f 0.30. Yield 20 g (0.5% of the air-dry material). The qualitative reaction for flavonols was positive.

Found %: C 54.16, 54.24; H 4.53, 4.60. $C_{21}H_{20}O_{12}$. Calculated %: C 54.31; H 4.31.

Acetyl derivative. A mixture of 0.5 g of the glucoside with acetic anhydride and sodium acetate was heated for 2 hr. This gave white needles with mp 216-217° (from alcohol).

Found %: C 55.51; 5.49; H 4.52; 4.51. $C_{37}H_{36}O_{20}$. Calculated %: C 55.59; H 4.50.

The 3, 5, 3', 4'-tetramethyl ether of quercimeritrin was obtained by methylating the glucoside with dimethyl sulfate. Colorless needles deposited with mp 203-204° (from 70% ethyl alcohol).

Found %: C 56.70; 56.68; H 5.56; 5.47. $C_{25}H_{28}O_{12} \cdot 0.5\ H_2O$. Calculated %: C 56.71; H 5.52.

The 3, 5, 3', 4'-tetramethyl ether of quercetin was obtained by the hydrolysis of the 3, 5, 3', 4'-tetramethyl ether of quercimeritrin with 5% sulfuric acid. It formed pale yellow crystals with mp 282-284° (decomp.).

Hydrolysis of quercimeritrin. A mixture of 0.5 g of quercimeritrin and 10 ml of 5 % sulfuric acid was boiled for 3 hr. The aglycone obtained was recrystallized from dilute alcohol. The aglycone had mp 311-312° (decomp.) and gave no depression of the melting point with a sample of quercetin.

The acidic aqueous mother liquor remaining after the hydrolysis of the quercimeritrin and the separation of the quercetin was neutralized with barium carbonate. The barium sulfate was separated off by centrifuging. The filtrate was concentrated to small volume and then an alcoholic solution of phenylhydrazine hydrochloride, sodium acetate, and acetic acid was added to it. The mixture was heated for 1 hr. The osazone was recrystallized from ethyl alcohol, mp 202-203°; a mixture with glucose osazone gave no depression of the melting point.

Penta-0-acetyl quercetin was obtained by the acetylation of quercetin with acetic anhydride by the usual method. The white silky crystals had mp 195-196° (from dilute ethyl alcohol).

Found %: C 57.87; 58.00; H 3.94; 3.91. $C_{25}H_{20}O_{12} \cdot 0.5\ H_2O$. Calculated %: C 57.77; H 4.03.

The pentamethyl ether of quercetin was obtained by methylating the aglycone with dimethyl sulfate in the usual way; white needles, mp 151-152° (from dilute ethyl alcohol).

Quercetin 3'-glucoside. Air-dried crushed flowers (1.8 kg) were extracted three times with boiling methanol. The extracts were collected in fractions. Each fraction was concentrated separately under vacuum (water-jet pump) to 400-600 ml. The concentrated extracts were treated with a three-fold volume of water. The resinous substances which precipitated were filtered off with suction. The clear filtrates were left to stand in the refrigerator, and after 7-10 days all the fractions had deposited crystals of quercimeritrin (mp 246-247°, R_f 0.30). Five to six days after the quercimeritrin had been separated off, fresh crystals had deposited from all the fractions. A mixture of flavonols was isolated from fractions I-II and from fraction III lemon-yellow crystals which, after recrystallization from dilute alcohol, had mp 228-230°. Yield 2.5 g.

Found %: C 51.47; 51.24; H 4.72; 4.75. $C_{25}H_{28}O_{12} \cdot 1.5\ H_2O$. Calculated %: C 51.32, H 4.68.

The acetyl derivative of quercetin 3'-glucoside was obtained with acetic anhydride by the usual method. Mp 169-170° (from methanol).

Found %: C 55.46; 55.26; H 4.52; 4.60. $C_{37}H_{36}O_{20}$. Calculated %: C 55.50; H 4.50.

The 3, 5, 7, 4'-tetramethyl ether of quercetin 3'-glucoside was obtained by methylation with dimethyl sulfate with heating for 12 hr, mp 219-220° (from dilute alcohol).

Found %: C 54.31; 54.49; H 5.73; 5.88. $C_{25}H_{28}O_{12} \cdot 1.5\ H_2O$. Calculated %: C 54.34; H 5.67.

The 3, 5, 7, 4'-tetramethyl ether of quercetin was obtained by hydrolyzing the 3, 5, 7, 4'-tetramethyl ether of quercetin 3'-glucoside with 5% sulfuric acid. After recrystallization from alcohol, mp 220-222°.

Found %: C 63.56; 63.49; H 5.06; 5.09. $C_{19}H_{18}O_7$. Calculated %: C 63.58; H 5.02.

The hydrolysis of quercetin 3'-glucoside was effected by the method described for quercimeritrin. After recrystallization from dilute ethyl alcohol, the aglycone had mp 311-312° (decomp.), R_f 0.59. The aglycone was identical with quercetin in all its properties.

The sugar obtained after the hydrolysis of quercetin 3'-glucoside yielded an osazone which gave no depression of the melting point in admixture with glucose and osazone.

SUMMARY

Quercimeritrin $C_{21}H_{20}O_{12}$, and a new flavonol glucoside with mp 228-230° and composition $C_{21}H_{20}O_{12}$, which has been shown to be quercetin 3'-glucoside, have been extracted from flowers of the cotton variety 108-F.

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