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FLAVONOIDS OF Thermopsis alterniflora.

CROTONOYLTHERMOPSOSIDE AND CROTONOYLCOSMOSIIN – NEW ACYLATED FLAVONE GLYCOSIDES

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From the epigeal part of Thermopsis alterniflora Rgl.et Schmalh. (Fabaceae), in addition to formononetin, ononin, cynaroside, and rothindin, two new acylated flavone glycosides have been isolated and, on the basis of chemical transformations and spectral characteristics, their structures have been established as 4',5,7-trihydroxy-3'-methoxyflavone 7-O-(6"-O-crotonoyl-β-D-glucopyranoside) and 4',5,7-trihydroxyflavone 7-O-(6"-O-crotonoyl-β-D-glucopyranoside).

Thermopsis alterniflora Rgl. et Schmalh. (family Fabaceae) is a medicinal plant and is used for obtaining cytisine [1]. The flavonoids chrysoeriol, thermopsoside, genistin, and teralin have been obtained from this plant previously [2, 3].

In an investigation of the flavonoids of the epigeal part of T. alterniflora, in addition to chrysoeriol, thermopsoside, and genistin we have isolated another six compounds (I-VI).

Compounds (I-III) were identified on the basis of IR, UV, PMR, and mass spectra and by comparison with authentic samples as, respectively, formononetin [4], ononin [4], and cynaroside [5].

Compound (IV), according to its spectral parameters, was an isoflavone glycoside. On acid hydrolysis, glycoside (IV) was split with the formation of an aglycon, identified as pseudobaptigenin (7-hydroxy-3',4'-methylenedioxyisoflavone), and D-glucose. A study of the mass and PMR spectra of the tetraacetate of (IV) and a comparison of its physicochemical properties with those given in the literature showed that the substance isolated was a monoglycoside identical with rothindin. In the present paper we consider the structure of the two new acylated flavone glycosides (V) and (VI).

The absorption maxima at 254, 259.5, and 351 nm observed in the UV spectrum of compound (V) showed that it was a flavone derivative [7]. This was confirmed by the formation of chrysoeriol (4',5,7-trihydroxy-3'-methoxyflavone (VII) [2]) on the acid hydrolysis of glycoside (V). In addition to chrysoeriol the hydrolysate was found to contain D-glucose and crotonic (trans-β-methylacrylic) acid.

In the IR spectrum of compound (V), in addition to the absorption bands of the functional groups characteristic of the flavonoid class, there was an absorption band at 1719 cm^{-1} showing the presence of an ester function in the molecule. Treatment of glycoside (V) with a 0.5% solution of potassium hydroxide led to the formation of thermopsoside (chrysoeriol 7-O-β-D-glucopyranoside (VIII) [3]) and crotonic acid.

When compound (V) was acetylated with acetic anhydride in pyridine, the pentaacetyl derivative (IX) was formed. The mass spectrum of the latter had the peak of the molecular

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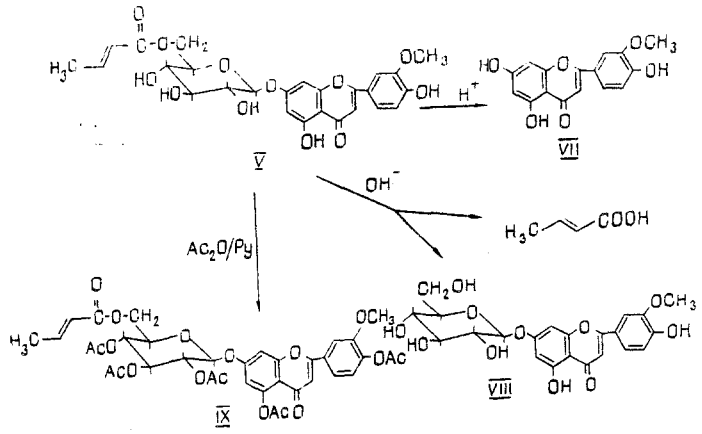
TABLE 1. Details of the PMR Spectra of Crotonoylthermopsoside (V) and of Crotonoylcosmosiin (VI) in C_5D_5N

Proton	Crotonoylthermopsoside (V)		Crotonoylcosmosiin (VI)	
	δ, ppm	J, Hz	δ, ppm	J, Hz
H-3	6,86 s		6,76 s	
H-6	6,74 d	^4J=2,5	6,70 d	^4J=2,0
H-8	6,90 d	^4J=2,5	6,85 d	^4J=2,0
H-2′	7,48 br.s		7,79 d	^3J=8,0
H-3′	—		7,08 d	^3J=8,0
H-5′	7,16 d	^3J=9,0	7,08 d	^3J=8,0
H-6′	7,51 dd	^3J=9,0; ^4J=2,5	7,79 d	^3J=8,0
H-1″	5,61 d	^3J=6,5	5,58 d	^3J=6,5
2H-6″	5,00 d	^2J=12,0	4,96 d	^2J=12,0
	4,62 q	^2J=12,0; ^3J=6,0	4,60 q	^2J=12,0; ^3J=6,5
H-α	5,85 dd	^3J=16,0; ^4J=1,5	5,81 dd	^3J=16,0; ^4J=1,5
H-β	6,91 dq	^3J=16,0; ^3J=6,5	6,88 dq	^3J=16,0; ^3J=6,5
=C–CH_3	1,42 dd	^3J=6,5; ^4J=1,5	1,42 dd	^3J=6,5; ^4J=1,5
CH_3O—	3,72 s		—	
H-2″–5″	3,96–4,32		3,84–4,30	

ion with m/z 740 and also intense peaks of ions with m/z 698 $(M - CH_2{=}C{=}O)^+$, 656 $(M - 2 \times CH_2{=}C{=}O)^+$, 357, 300 (100%), 270, 195, 169, 149 and others. The PMR spectra of compounds (V) and (IX) contained the signals of the protons of one methyl group on a double bond and of two trans-olefinic protons (Table 1), which are characteristic for the PMR spectra of crotonic acid [8]



The facts given above showed the presence in glycoside (V) of one crotonic acid residue. The position of the acyl group in compound (V) was established by an intercomparison of the PMR and ^{13}C NMR spectra (Table 2) of thermopsoside (VIII) and the glycoside (V). The PMR spectrum of compound (V) contained the signals of the protons of a gem-acyl methylene group (see Table 1), which showed the attachment of the acyl residue to the CH_2OH group of the glucose residue [9, 10].

On passing from thermopsoside (VIII) to glycoside (V), the chemical shifts of the carbon atoms of the aglycon moiety scarcely changed. At the same time, definite changes were observed in the positions of the resonance signals of the carbon atoms of the sugar residue. Thus, in the spectrum of thermopsoside the signals of the C-5" and C-6" carbon atoms of the glucopyranose residue resonated at 76.9 and 60.6 ppm, respectively, while in the spectrum of compound (V) the signals of these atoms were found at 73.7 and 62.9 ppm. Consequently, on passing from glycoside (VIII) to compound (V) the chemical shift of the C-6" carbon underwent a paramagnetic shift by 2.3 ppm and the signal of the C-5" carbon an upfield shift by 3.2 ppm.

The facts given above unambiguously showed that the acyl group in compound (V) was located in the C-6" position [11].

Thus, substance (V) had the structure of 7-(6"-O-crotonoyl-β-D-glucopyranosyloxy)-4', 5-dihydroxy-3'-methoxyflavone.

TABLE 2. Chemical Shifts of the Carbon Atoms of Rothindin (IV), Thermopsoside (VIII), and Crotonoylthermopsoside (V) in DMSO-d_6 (δ, ppm, 0 – TMS).

Atom	Rothindin (IV)	Thermopsoside (VIII)	Crotonoylthermopsoside (V)	Atom	Rothindin (IV)	Thermopsoside (VIII)	Crotonoylthermopsoside (V)
2	153,8 d	163,6s	163,9 s	5′	108,3d	115,6 d	115,5 d
3	123,7 s	102,7d	103,5 d	6′	122,7d	120,2** d	120,0 d
4	175,0 s	181,2s	181,9 s	1″	100,4d	99,7* d	99,5 d
5	127,2 d	160,7s	160,9 s	2″	73,4d	72,4 d	72,8d
6	115,9 d	99,1*d	99,5 d	3″	76,7d	76,0 d	76,2d
7	161,8 s	162,4 s	162,4 s	4″	70,0d	69,5 d	69,9d
8	103,7d	94,7 d	94,6 d	5″	77,4d	76,9d	73,7 d
9	157,3s	155,8 s	157,0 s	6″	60,9t	60,6t	62,9 t
10	118,7s	104,8 s	105,0 s	C=O	—	—	166,8 s
1′	125,8s	120,6** s	121,3 s	C-α	—	—	121,8 d
2′	109,6d	109,6 d	110,0 d	C-β	—	—	145,3 d
3′	147,3s	150,2 s	150,8 s	$-CH_3$	—	—	17,7 q
4′	147,3s	147,4 s	148,0 s	OCH_3	—	55,8 q	55,7 q
				O_2CH_2	101,3 t	—	—

*, **Assignment of the signals uncertain.

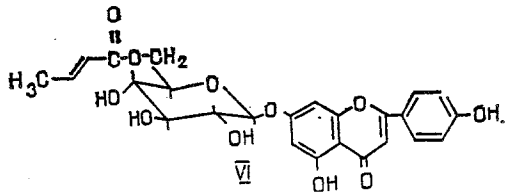
Compound (VI) was also a flavone derivative, and on acid hydrolysis it gave D-glucose and an aglycon which was identified as apigenin (4',5,7-trihydroxyflavone) [12].

The IR spectrum of glycoside (VI) contained the absorption band of an ester carbonyl group at 1705 cm^{-1}. The presence in the PMR spectrum of the signals of protons at (ppm) 1.42 (dd, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 5.81 (dd, ^3J = 16 Hz, ^4J = 1.5 Hz), and 6.88 (dq, ^3J = 16 Hz, ^3J = 6.5 Hz) showed that the compound under consideration contained one crotonic acid residue [8].

The mass spectrum of compound (VI) contained the peak of the molecular ion with m/z 500 and, among the peaks of fragmentary ions, that of the aglycon with m/z 270 and that of a crotonic acid residue with m/z 69.

The alkaline hydrolysis of glycoside (VI) led to the formation of apigenin 7-O-β-D-glucopyranoside [13] and crotonic acid.

In the PMR spectrum of substance (VI) there were the signals of the protons of a geminal methylene group (4.60 ppm, dd, ^2J = 12 Hz, ^3J = 6.5 Hz; 4.95 ppm, br.d., ^2J = 12 Hz), which determined the location of the acyl group at the C-6" carbon atom of the glucopyranose residue of the molecule of (VI) [9, 10]. Consequently, compound (VI) corresponded to the structure of 7-(6"-O-crotonoyl-β-D-glucopyranosyloxy)-4',5-dihydroxyflavone.



VI

Flavonoid glycosides acylated with crotonic acid have not been detected previously. There is a report of the isolation of a xylofuranoside of the arylnaphthalene lignan diphyllin acylated with crotonic acid in the C-5 position of the carbohydrate residue [14].

EXPERIMENTAL

General Remarks. Silufol plates were used for thin-layer chromatography (TLC). Column chromatography was carried out on type KSK silica gel with a grain size of 100-160 μm. The substances in TLC were revealed by the action of ammonia vapor.

The following solvent systems were used: 1) chloroform–methanol (97:3); 2) chloroform–methanol (19:1); 3) chloroform–methanol (9:1); 4) chloroform–methanol (4:1); 5) butan-1-ol–methanol–water (5:3:1); and 6) benzene–ethanol (21:2).

PMR and ^{13}C NMR spectra were taken on a Tesla BS-567A spectrometer (δ, ppm; for PMR, 0 – HMDS; for ^{13}C NMR, 0 – TMS) at frequencies of 100 MHz for protons and 25.142 MHz for carbon in Py-d_5 and DMSO-d_6, respectively.

Mass spectra were obtained on a MKh-1310 instrument at an ionizing voltage of 50 V. IR spectra were taken on a UR-20 instrument in KBr, and UV spectra on a Hitachi EPS-3T spectrometer in ethanol.

Isolation of the Flavonoids. The dried and comminuted epigeal part (5 kg) of the plant Thermopsis alterniflora collected in the flowering period in May, 1986 (village of Khumsan, Tashkent oblast) was extracted at room temperature with 90% ethanol five times. The ethanolic extract was concentrated in vacuum to 1.5 liters and was then diluted with water to 3 liters. The aqueous ethanolic extract was shaken with chloroform (5 × 0.5 liter) and the chloroform extract was treated with a 1% solution of KOH (3 × 0.5 liter), after which the combined alkaline solution was washed with chloroform, acidified with 10% HCl solution, and extracted exhaustively with chloroform. The final chloroform extract was dried with anhydrous Na_2SO_4, filtered, and evaporated to small volume. The precipitate that then deposited was filtered off and recrystallized from ethanol. This gave 0.51 g of formononetin.

The chloroform-purified aqueous solution was passed slowly through a column (5 × 120 cm) containing polyamide sorbent (560 g). The column was washed with water (20 liters), and then the flavonoids were desorbed with ethanol. The ethanolic eluate was evaporated in vacuum and the residue was dried. This gave 73.5 g (1.46% on the weight of the raw material) of total flavonoids. Part of this total (38.0 g) was chromatographed on a column (6 × 80 cm) containing silica gel (800 g) with elution successively by chloroform and by systems 1, 2, 3, and 4. Fractions with a volume of 500 ml each were collected. When the column was eluted with system 1, individual fractions yielded 2.9 g of chrysoeriol, 1.0 g (0.02% on the weight of the raw material) of crotonoylthermopsoside and 0.27 g (0.0054%) of crotonoylcosmosiin. Then eluting the column with system 2 gave 1.6 g of ononin and 1.4 g of rothindin. Elution of the column in system 3 led to 5.8 g of thermopsoside and 0.6 g of genistin. Elution of the column with system 4 yielded 8.9 g of cynaroside.

Formononetin (I). $C_{16}H_{12}O_4$, M^+ 268, mp 261-263°C, $\lambda_{max}^{C_2H_5OH}$, nm: 239* (inflection), 251, 260* 305 (lg ε 4.28; 4.31; 4.28; 4.00); ν_{max}^{KBr}, cm^{-1}: 3150 (OH), 1641 (C=O), 1624, 1613-1600 (aromatic C=C), 1573, 1518, 1458, 1031.

Ononin (II). $C_{22}H_{22}O_9$, M^+ 430, mp 215-216°C, $[\alpha]_D$ –58.8° (c 0.2; methanol), $\lambda_{max}^{C_2H_5OH}$, nm: 261, 303 (log ε 4.03, 3.55). PMR spectrum (C_5D_5N): 3.60 (s, OCH_3), 4.05-4.57 (protons of the sugar moiety), 5.74 (d, 6.5 Hz, H-1"), 6.95 (d, 9 Hz, H-3',5'), 7.11 (d, 2 Hz, H-8), 7.30 (m, H-6), 7.68 (d, 9 Hz, H-2',6'), 8.05 (s, H-2), 8.32 (d, 9 Hz, H-5).

Cynaroside (III), $C_{21}H_{20}O_{11}$, M^+ 448, mp 240-242°C (decomp.), $\lambda_{max}^{C_2H_5OH}$, nm: 256, 268, 350; ν_{max}^{KBr}, cm^{-1}: 3480-3300 (OH), 1665 (C=O), 1560, 1510 (C=C), 1095, 1050, 1030, 900.

Rothindin (IV), $C_{22}H_{20}O_{10}$, mp 234-236°C, $[\alpha]_D^{22}$ –38.2° (c 0.5; methanol); $\lambda_{max}^{C_2H_5OH}$, nm: 263, 293* (inflection) (log ε 4.46, 4.14).

PMR spectrum (C_5D_5N): 4.00-4.60 (protons of the carbohydrate moiety), 5.68 (d, 6.5 Hz, H-1"), 5.88 (s, OCH_2O), 6.80-7.34 (m, H-6,8,2',5',6'), 8.00 (s, H-2), 8.21 (d, 9 Hz, H-5).

Acid Hydrolysis of Rothindin (IV). A solution of rothindin (60 mg) in 10 ml of methanol was treated with 10 ml of a 5% solution of HCl and was boiled in the water bath for 4 h. Then the methanol was distilled off in vacuum and the precipitate that had deposited was filtered off and was recrystallized from aqueous methanol. This gave 27 mg of pseudobaptigenin with mp 292-293°C. Mass spectrum, m/z (%): M^+ 282 (100), 281 (27); 267 (21), 253 (8), 137 (6), 136 (5), 108 (7), 146 (57).

PMR spectrum (C_5D_5N): 5.80 (s, OCH_2O), 6.70-7.13 (H-6,8,2',5'), 7.34 (d, 8.5 Hz, H-6'), 7.95 (s, H-2), 8.25 (d, 8.5 Hz, H-5).

The filtrate was evaporated to small volume, neutralized with $BaCO_3$, and filtered, and the filtrate was evaporated to dryness. D-Glucose was detected in the residue by TLC on Silufol in system 5.

Rothindin Tetraacetate. Rothindin (35 mg) was acetylated with 2 ml of acetic anhydride in 1 ml of pyridine at room temperature for 3 h. After working up by the usual method and recrystallization of the product from ethanol, 21 mg of tetraacetate with mp 217-219°C was obtained. Mass spectrum, m/z (%): M^+ 612 (2.6), 331 (21), 282 (18), 271 (7), 211 (9), 169 (100), 146 (8.5), 137 (6), 136 (5), 107 (73).

PMR spectrum ($CDCl_3$): 1.97-2.03 (4 CH_3CO groups), 3.67-4.22 (H-5", 2H-6"), 4.92-5.40 (H-2",3",4"), 5.87 (s, OCH_2O), 6.73 (d, 9 Hz, H-5'), 6.80-6.96 (H-6,8,2',6'), 7.80 (s, H-2), 8.13 (d, 9 Hz, H-5).

Crotonoylthermopsoside (V), $C_{26}H_{26}O_{12}$, mp 228-229°C, $[\alpha]_D^{22}$ −77.1° (c 0.52; dimethylformamide); ν_{max}^{KBr}, cm^{-1}: 3495-3330 (OH); 1719 (C=O, ester); 1664 (C=O, γ-pyrone); 1616, 1578 (C=C); 1522, 1501, 1264. For the PMR and ^{13}C NMR spectra, see Tables 1 and 2.

Acid Hydrolysis of Crotonoylthermopsoside (V). Glycoside (V) (25 mg) was hydrolyzed with 20 ml of 50% aqueous methanol containing 2.5% of hydrogen chloride on the water bath for 4 h. The precipitate of the aglycon that deposited was filtered off and recrystallized from methanol. This gave 8 mg of substance (VII) with mp 335-337°C, $\lambda_{max}^{C_2H_5OH}$, nm: 253, 270, 350 (log ε 4.18; 4.16; 4.29), identical with chrysoeriol (IR spectrum, mixed melting point).

The filtrate was concentrated in vacuum to small volume, extracted with ether (4 × 30 ml), neutralized on AV-10G anion-exchanger, and evaporated to dryness. D-Glucose was detected in the residue by TLC on Silufol in system 5.

The ethereal extract was evaporated, and crotonic acid was found in the residue by TLC on Silufol in system 6.

Crotonoylthermopsoside Pentaacetate (IX). A solution of 35 mg of glycoside (V) in 1 ml of pyridine was treated with 1.5 ml of acetic anhydride, and the reaction mixture was left at room temperature for 3 h. After working up by the usual method and recrystallization of the product from methanol, 28 mg of the pentaacetate was obtained with mp 109-110°C.

Mass spectrum, m/z (%): M^+ 740 (0.4), 698 (8.4), 672 (0.6), 656 (2), 412 (3.5), 384 (4), 357 (61), 342 (26), 300 (100), 270 (29), 195 (97), 169 (35.5), 149 (61), 109 (29), 97 (39), 69 (96.5).

Alkaline Hydrolysis of Crotonoylthermopsoside (V). A solution of 30 mg of the glycoside in 8 ml of 0.5% KOH solution was kept at room temperature for 1 h. Then the reaction mixture was neutralized with a 5% solution of hydrogen chloride and was exhaustively extracted with ether. The ethereal extract was dried with anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was recrystallized from hexane, giving a substance with mp 69-70°C identical with an authentic sample of crotonic acid (TLC, mixed melting point).

The aqueous solution was evaporated to small volume and was chromatographed on a column of polyamide sorbent. The column was washed with water and then with methanol. The methanolic eluate was evaporated to dryness and the residue was recrystallized from methanol to give 13 mg of thermopsoside with mp 174-175°C, $[\alpha]_D$ −35.3° (c 0.3; ethanol), $\lambda_{max}^{C_2H_5OH}$, nm: 255, 268, 348 (log ε 4.16; 4.16; 4.14), ν_{max}^{KBr}, cm^{-1}: 3450-3280 (OH); 2930, 1666 (C=O); 1614, 1504 (C=C).

PMR spectrum (C_5D_5N): 3.70 (s, OCH_3), 3.82-4.55 (protons of the carbohydrate moiety), 5.65 (d, 6 Hz, H-1"), 6.70 (br. s, H-6), 6.80 (br. s, H-8), 6.95 (s, H-3), 7.08 (d, 8.5 Hz, H-5'), 7.47 (m, H-2',6').

Crotonoylcosmosiin (VI), $C_{25}H_{24}O_{11}$, mp 265-267°C, $[\alpha]_D^{22}$ −161.5° (c 0.53; dimethylformamide); $\lambda_{max}^{C_2H_5OH}$, nm: 258.5* (inflection), 269.5, 342 (log ε 4.08; 4.15; 4.22); ν_{max}^{KBr}, cm^{-1}: 3480-3300 (OH), 1705 (C=O, ester); 1660 (C=O, γ-pyrone); 1606, 1567 (C=C); 1498, 1250. Mass spectrum, m/z (%): M^+ 500 (0.7), 338 (2.8), 323 (2.3), 270 (100), 256 (6.7), 242 (3.7), 204 (3), 153 (2.8), 152 (2.5), 129 (8), 124 (3), 121 (5), 118 (3), 97 (14), 83 (15.3), 69 (0.6), 60 (10), 55 (9.3). For the PMR spectrum, see Table 1.

Acid Hydrolysis of Crotonoylcosmosiin (VI). A solution of 16 mg of glycoside (VI) in 8 ml of methanol was treated with 6 ml of a 3% solution of hydrogen chloride and the mixture was boiled on the water bath for 5 h. The resulting precipitate was filtered off and was recrystallized from aqueous ethanol. This gave 6 mg of an aglycon with mp 346-347°C, M^+ 270, $\lambda_{max}^{C_2H_5OH}$, nm: 270, 298* (inflection), 339, which was identical with apigenin (TLC, IR spectrum).

The filtrate was evaporated to small volume, neutralized on AV-10G anion-exchange resin, and evaporated to dryness. D-Glucose was detected in the residue by TLC on Silufol in system 5.

Alkaline Hydrolysis of Crotonoylcosmosiin (VI). A solution of 43 mg of glycoside (VI) in 15 ml of 0.5% KOH solution was kept at room temperature for 30 min. Then the reaction mixture was acidified with 5% HCl solution and was exhaustively extracted with ether. The ethereal extract was washed with water, filtered, and evaporated. Crotonic acid was detected in the residue by TLC in system 6 with an authentic sample.

The aqueous solution was chromatographed on polyamide. Elution was performed with water and then with ethanol. When the ethanolic eluate was concentrated in vacuum, a precipitate of cosmosiin deposited, with mp 227-229°C, $\lambda_{max}^{C_2H_5OH}$, nm: 270, 341; $+CH_3COONa$ 269, 388; $+AlCl_3$ 274, 383; $+AlCl_3$ + HCl 275, 381; $+CH_3ONa$ 271; 397.

PMR spectrum (C_5D_5N): 3.57-4.62 (protons of the sugar moiety), 5.60 (d, 7 Hz, H-1"), 6.62 (d, 2 Hz, H-6), 6.71 (s, H-3), 6.78 (d, 2 Hz, H-8), 7.09 (d, 9 Hz, H-3',5'), 7.84 (d, 9 Hz, H-2',6').

SUMMARY

From the epigeal part of Thermopsis alterniflora have been isolated formononetin, ononin, cynaroside, rothindin, and two new acylated flavone glycosides for which the structures of 7-(6"-O-crotonoyl-β-D-glucopyranosyloxy)-4',5-dihydroxy-3'-methoxyflavone and 7-(6"-O-crotonyl-β-D-glucopyranosyloxy)-4',5-dihydroxyflavone have been established.

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