ACYLATED FLAVANONE GLYCOSIDES FROM *Ricinus communis*

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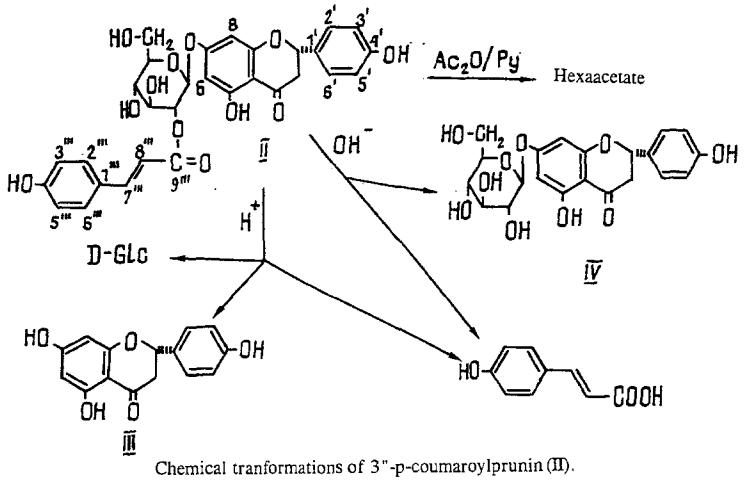
Naringenin 7-O-(6"-O-p-coumaroyl-β-D-glucopyranoside) and the new flavanone naringenin 7-O-(2"-O-p-coumaroyl-β-D-glucopyranoside) have been isolated from the seeds of Ricinus communis L. The structures of the compounds isolated were established on the basis of the results of chemical transformations and spectral characteristics.

The seeds of the castor bean *Ricinus communis* L. (family Euphorbiaceae) are used to obtain castor oil [1]. With the aim of the rational utilization of the plant raw material and finding possibilities for utilization of the wastes, we have studied the chemical composition of the phenolic fraction of the meal obtained after the extraction of the oil.

An investigation of the components of the seed meal led to the isolation of the two acylated glycosides the structures of which are described in the present paper. The two compounds (I) and (II) had the same composition, $C_{30}H_{28}O_{12}$, and, according to their UV and PMR spectra [2], they were flavanone derivatives, while their IR spectra contained absorption bands of ester carbonyl groups (1708 and 1713 cm^{-1}, respectively). The presence in the PMR spectra of compounds (I) and (II) of the signals of the protons of the carbohydrate moieties and the signals of *trans*-olefinic protons with a SSCC of 16 Hz showed that the substances under consideration were flavanone glycosides acylated with cinnamic acid or a derivative of it.

According to the results of hydrolytic cleavage, both compounds contained residues of naringenin [4',5,7-trihydroxyflavanone (III)] [3], glucose, and *p*-coumaric acid. As the result of mild alkaline hydrolysis of both glycoside (I) and glycoside (II), *p*-coumaric acid and one and the same naringenin monoglucoside (IV) were obtained.



Chemical tranformations of 3"-p-coumaroylprunin (II).

The carbohydrate residue in the molecule of compound (II) had to be present at C-7, since its PMR spectrum taken in DMSO-d_6 showed the signals of the protons of phenolic hydroxy groups at C-5 (11.93 ppm) and C-4' (9.85 ppm). This was confirmed by a study of the UV spectra of compound (IV) taken with the addition of diagnostic reagents [2]. By a study of spectral (UV, PMR) characteristics, the results of acid hydrolysis, and comparison with literature information, glycoside (IV) was identified as the known naringenin 7-O-β-*D*-glucopyranoside (prunin) [4].

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TABLE 1. Details of the ^{13}C NMR Spectra of Prunin (IV) and of 2″-*p*-Coumaroylprunin (II) in DMSO-d_6

C	IV	II	C	IV	II	C	II
2	78,7	78,9	3′	115,2	115,8	2‴	130,5
3	42,0	42,4	4′	157,8	157,9	3‴	116,4
4	197,2	197,3	5′	115,2	115,8	4‴	160,1
5	162,9	163,4	6′	128,5	128,6	5‴	116,4
6	96,5	97,1	1″	99,5	98,1	6‴	130,5
7	165,2	165,5	2″	73,1	74,4	7‴	145,6
8	95,4	96,2	3″	76,3	74,2	8‴	114,4
9	162,8	163,0	4″	69,5	70,4	9‴	166,4
10	103,3	104,1	5″	77,1	77,6		
1′	128,8	129,2	6″	60,6	61,1		
2′	128,5	128,6	1‴	—	125,6		

The acetylation of glycosides (I) and (II) led to hexaacetates having different properties, the PMR spectra of which contained the signals of three alcoholic and three aromatic acetoxy groups so that, in both compounds, the *p*-coumaric acid residue was attached to the carbohydrate part of the molecule.

The results obtained enabled us to consider that flavonoids (I) and (II) were position isomers differing from one another by the positions of attachment of the acyl residues to the carbohydrate moieties.

The positions of attachment of the acyl residues were determined by a study of the ^{13}C NMR spectra of prunin (IV) and of flavonoids (I) and (II). On passing from prunin to glucoside (I), the signal of the C-6 carbon atom of the *D*-glucose residue underwent a paramagnetic shift by +3.2 ppm, while the signal of the C-5 carbon shifted upfield by —2.7 ppm. This showed attachment of the *p*-coumaric acid residue to the $-CH_2OH$ group of *D*-glucose.

Thus, compound (I) had the structure of naringenin 7-O-(6″-O-*p*-coumaroyl-β-*D*-glucopyranoside). A substance with this structure has been described in the literature [5]. The melting points of the compound (I) that we had isolated and of its acetate agreed with the figures given in the literature.

As can be seen from Table 1, an α-effect of acylation was experienced by C-2 of the β-*D*-glucopyranoside residue of glycoside (II), and its signal underwent a downfield shift by +1.3 ppm compared with its position in the spectrum of prunin. As was to be expected, the C-1 and C-3 atoms of the carbohydrate residue underwent a β-effect of acylation and the signals were shifted upfield by —1.4 and —2.1 ppm in comparison with the corresponding signals of the spectrum of glycoside (IV). This means that the *p*-coumaroyl group in glycoside (II) was located at C-2 of the β-*D*-glucopyranose residue.

Consequently, compound (II) was the previously undescribed narigenin 7-O-(2″-O-*p*-coumaroyl-β-*D*-glucopyranoside).

EXPERIMENTAL

General Observations. For thin-layer chromatography (TLC) we used Silufol UV-254 plates. Column chromatography was conducted on KSK and Woelm (FRG) silica gels. In TLC, the substances were revealed by the action of ammonia vapor and by spraying with a 1% solution of vanillin in sulfuric acid. Glucose was detected in TLC by spraying with *o*-toluidine salicylate, followed by heating at 100-105°C for 2-5 min.

We used the following solvent systems: 1) chloroform—methanol (85:15); 2) chloroform—methanol (92:8); and 3) *n*-butanol—methanol—water (5:3:1).

PMR spectra were taken on a Tesla BS-567A spectrometer in Py-d_5, and ^{13}C NMR spectra on a Bruker WP200S instrument in DMSO-d_6. Mass spectra were obtained on a MKh-1310 instrument at an ionizing energy of 50 eV, IR spectra on a UR-20 instrument in KBr, and UV spectra on a Specord UV-Vis spectrophotometer.

Isolation of the Flavonoids. The dried and comminuted meal (4.4 kg, waste from the production of castor oil in the Belorechensk oil-extracting factory) was extracted at room temperature with 85% ethanol six times. The alcoholic extract was concentrated in vacuum to a viscous consistency and was treated with chloroform. The chloroform-insoluble part was evaporated to dryness. This gave 46.0 g of purified extract, of which 35.0 g was chromatographed on a column (4.5 × 150 cm) of silica gel (500 g) in the chloroform—methanol (97:3)-(80:2) system. On elution from the column by the solvents chloroform—methanol (95:5)-(90:10), 1.0 g of (I) and 0.8 g of (II) were isolated.

6″-O-*p*-Coumaroylprunin (I). White crystalline substance with a creamy tinge having mp 152-153°C, ν_{max}^{KBr}, cm^{-1}: 3515-3200 (OH group), 1707 (α,β-unsaturated C=O); 1646 (C=O of a γ-pyrone); 1614, 1520 (C=C); 1100-1000 (C—O of glycosides); λ_{max}^{EtOH} 212, 227, 283, 315 nm.

PMR spectrum in Py-d_5 (δ, ppm): 2.50-3.30 (m, 2H-3), 3.37-4.50 (m, H-2″, 3″, 4″, 5″), 4.88 (m, 2H-6″), 5.20 (d, 7 Hz, H-1″), 5.77 (dd, 11.0 and 3.0 Hz, H-2), 6.37 (br.s. H-6), 6.43 (d, 16.0 Hz, H-α), 6.44 (br.s. H-8), 6.91 (d, 8.0 Hz, H-3′, 5′), 7.00 (d, 8.5 Hz, H-3‴, 5‴), 7.22 (d, 8.0 Hz, H-2′, 6′), 7.34 (d, 8.5 Hz, H-2‴, 6‴), 7.84 (d, 16.0 Hz, H-β).

^{13}C NMR spectrum (DMSO-d_6): 42.7 (C-3), 63.8 (C-6″), 70.6 (C-4″), 73.4 (C-2″), 73.9 (C-53″), 76.6 (C-3″), 79.0 (C-2), 96.3 (C-8), 97.0 (C-6), 99.9 (C-1″), 103.9 (C-10), 114.4 (C-8‴), 115.8 (C-3′, 5′), 116.4 (C-3‴, 5‴), 125.7 (C-1‴), 128.5 (C-2′, 6′), 129.2 (C-1′), 130.5 (C-2‴, 6‴), 145.4 (C-7‴), 157.9 (C-4′), 160.1 (C-4‴), 162.9 (C-9), 163.4 (C-5), 165.4 (C-7), 167.1 (C-9‴), 197.4 (C-4).

2″-O-*p*-Coumaroylprunin (II). White crystalline substance with mp 181-182°C, ν_{max}^{KBr}, cm^{-1}: 3510-3200 (OH groups); 1708 (α,β-unsaturated C=O); 1648 (C=O of a γ-pyrone); 1616, 1519 (C=C); 1110-1005 (C—O of a glycoside); λ_{max}^{EtOH}: 212, 226, 288, 313 nm.

PMR spectrum in Py-d_5: 2.55-3.35 (m, 2H-3), 3.90-4.51 (m, H-2″, 3″, 4″, 5″), 5.27 (t, 9.0 Hz, H-2″), 5.69 (d, 6.5 Hz, H-1″), 5.89 (dd, 12.0 and 3.5 Hz, H-2), 6.40 (br.s. H-6), 6.41 (d, 16.0 Hz, H-α), 6.46 (br.s, H-8), 6.87 (d, 8.0 Hz, H-3′, 5′), 7.03 (d, 8.5 Hz, H-3‴, 5‴), 7.25 (d, 8.0 Hz, H-2′, 6′), 7.38 (d, 8.5 Hz, H-2‴, 6‴), 7.74 (d, 16.0 Hz, H-β); for the ^{13} C NMR spectrum, see Table 1.

Acetylation. A mixture of 40 mg of (I) or (II), 1 ml of pyridine, and 3 ml of acetic anhydride was kept at room temperature for 4 h.

On the addition of ice water, a precipitate deposited, and this was recrystallized from ethanol. A white amorphous powder was obtained.

Hexaacetate of (I). Crystalline substance with mp 113-114°C. Mass spectrum: M^+ 832, 790, 748, 477, 435, 417, 375, 356, 331, 315, 272, 257, 189(100), 147, and others. PMR spectrum in $CDCl_3$: 1.96 (s, $OCOCH_3$), 1.98 (s, 2 × $OCOCH_3$), 2.22 (s, 3 × Ar—$OCOCH_3$).

Hexaacetate of (II). Crystalline substance with mp 107-108°C, M^+ 832; PMR spectrum in $CDCl_3$: 1.93 (s, 3 × $OCOCH_3$), 2.20 (s, 3 × Ar—$OCOCH_3$).

Acid Hydrolysis. A mixture of 30-40 mg of compound (I) or (II) and 15 ml of 5% hydrochloric acid was heated in the boiling water bath for 3-4 h. The precipitate that had deposited was filtered off and recrystallized from ethanol, and it was identified as naringenin (TLC and UV, IR, and mass spectra) [3]. Glucose (PC) and *p*-coumaric acid (TLC, mass spectrum) were detected in the evaporated hydrolysate.

Alkaline Hydrolysis. A solution of 20-30 mg of compound (I) or (II) in 6 ml of 1% KOH was kept at room temperature for 6 h. The reaction mixture was then acidified with 5% hydrochloric acid and was shaken with diethyl ether. After the solvent had been distilled off, *p*-coumaric acid was detected (GLC and mass spectrum). The remainder of the hydrolysate was chromatographed on polyamide in the water—ethanol (8:2) system. This gave 8-11 mg of compound (IV).

Naringenin 7-O-β-*D*-Glucopyranoside (IV). Crystalline substance with mp 223-224°C (from methanol); composition $C_{21}H_{22}O_{10}$. ν_{max}^{KBr}: 3540-3821 (OH groups); 1650 (C=O of a γ-pyrone); 1616, 1522 (C=C), 1120-1020 (C—O of glycosides). λ_{max}^{EtOH}: 283, 323* (sh), nm; +CH_3COONa: 284, 327; +$AlCl_3$: 311, 376; +CH_3ONa: 287, 418.

PMR spectrum in Py-d_5: 2.54-3.28 (m, 2H-3), 3.90-4.60 (m, H-2″, 3″, 4″, 5″, 6″), 5.23 (d, 6.5 Hz, H-1″), 5.61 (dd, 12.5 and 3.0 Hz, H-2), 6.37 (br.s, H-6), 6.44 (br.s, H-8), 6.86 (d, 8.2 Hz, H-5′, 3′), 7.36 (d, 8.2 Hz, H-2′, 6′), 11.63 (5-OH).

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