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FURTHER ACYLATED KAEMPFEROL RHAMNOSIDES FROM *PLATANUS ACERIFOLIA* BUDS[1]

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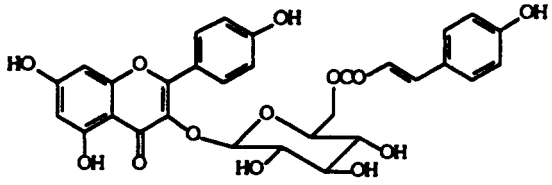
ABSTRACT.—The EtOAc extract of fresh *Platanus acerifolia* buds afforded a mixture of two new acylated flavonol monoglycosides. Separations were achieved by cc on polyamide and Sephadex LH-20 as well as by centrifugal tlc on Si gel and reversed-phase hplc. Structural elucidations were performed by uv, ^{1}H nmr, and ms. The two new compounds **3** an **4** were identified as kaempferol 3-(2-*p*-coumaroyl-α-L-rhamnopyranoside) in the *E* and the *Z* form, respectively. This is the first report of *Z*- and *E*-2″-cinnamoyl flavonoid rhamnosides.

Earlier phytochemical analysis of the EtOAc extract of fresh *Platanus acerifolia* Willd. (Platanaceae) buds revealed the presence of acylated and non-acylated kaempferol monoglycosides (2). Tiliroside [**1**] and platanoside [**2**] were shown to be the most dominant *p*-coumaroyl kaempferol glycosides. In continuation of this work, two further minor *p*-coumaroyl kaempferol rhamnosides in the *E* and the *Z* form have been isolated together from the same extract. Such a mixture of unseparable cinnamoyl isomers occurs in nature (3–5), as recently reported for loganin (6) and quinic acid derivatives (7). Attempts to separate the two components by polyamide and Sephadex LH-20 cc, centrifugal tlc on Si gel, and hplc on reversed-phase column were unsuccessful. However, small amounts of the mixed isomers have been obtained for spectroscopic analysis.

RESULTS AND DISCUSSION

Fresh buds collected in November were exhaustively extracted with *n*-hexane, C_6H_6, EtOAc, and MeOH. Isolation of glycosides **3** and **4** from the EtOAc-soluble fraction was performed by Sephadex LH-20 and polyamide cc, centrifugal tlc on Si gel, and hplc on reversed phase (see Experimental). The mixture of components **3** and **4** was obtained as a single sharp peak by hplc (aqueous MeOH 70%). However, tlc analysis of Si gel revealed two compounds, with a similar chromatographic behavior, that were slightly more polar than platanoside [**2**]. On the other hand, the uv spectra of the mixture with the usual shift reagents (8,9) were identical to those of tiliroside [**1**]. These results suggested a structure for **3** and **4** based on 3-glycosylated kaempferol containing only one *p*-coumaric acid type acylation, and they were confirmed by ms and ^{1}H-nmr spectroscopy. The negative fabms of the mixture exhibited the highest peak at *m/z* 577 $[M-H]^-$. This agreed with the presence of a kaempferol unit, a *p*-coumaric residue, and a rhamnose moiety in these molecules. Thus, compounds **3** and **4** were characterized as kaempferol coumaroyl rhamnosides showing peaks at *m/z* 431 $[M-H-146]^-$ and 285 $[M-H-292]^-$, consequent to the successive elimination of one rhamnose and one *p*-coumaroyl unit. Further evidence

[1]Part 8 in the series "Polyphenols from *Platanus acerifolia* Buds." For part 7, see Kaouadji and Ravanel (1).



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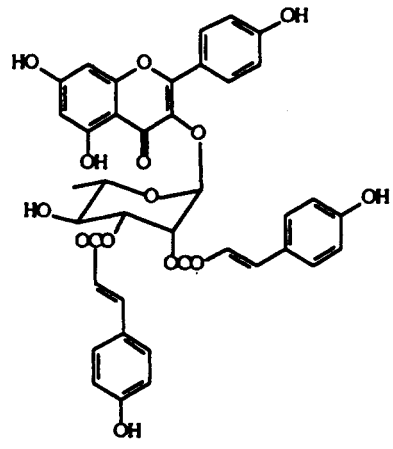

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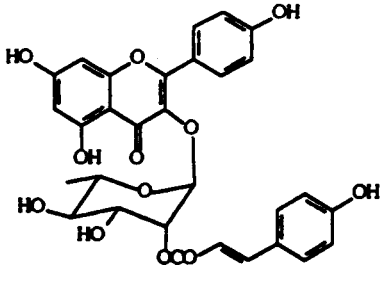

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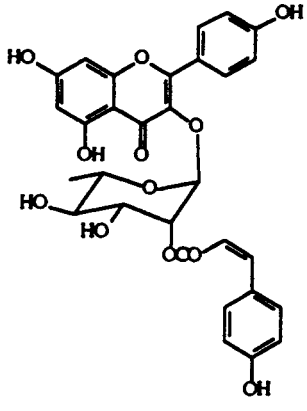

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for these structures was given by the 400 MHz ^{1}H-nmr spectrum, which differed from that of tiliroside [**1**] in the sugar portion and in the supplementary cinnamic acid signals (Table 1). Being close to that of platanoside [**2**] except for the *Z*-cinnamic acid moiety, this spectrum showed the two components **3** and **4** in the ratio 2:1 with a kaempferol portion, a *p*-coumaroyl unit, and an α-rhamnose. The kaempferol moiety was indicated by two meta-related signals (J=2 Hz) at δ 6.16/6.17 and δ 6.34 assigned to H-6 and H-8, respectively, and two groups of ortho-coupled protons (J=8.8 Hz) at δ 7.76 and δ 6.92 identified with H-2′, -6′ and H-3′, -5′. Only one *p*-coumaric acid was present in these molecules with the *E* and the *Z* configuration. This was deduced from two pairs of doublets at δ 7.60 (H-7 coum.) and 6.31 (H-8 coum.) (J=15.8 Hz) in **3** and δ 6.83 (H-7 coum.) and 5.75 (H-8 coum.) (J=12.8 Hz) in **4** for the side chain, the aromatic ring being responsible for the remaining four doublets (J=8.7 Hz) at δ 7.42 (H-2, -6 coum.) and 6.76 (H-3, -5 coum.) in **3** and δ 7.58 (H-2, -6 coum.) and 6.72 (H-3, -5 coum.) in **4**. As suggested by the uv spectrum, the α-rhamnose was attached at the 3 position of the kaempferol. The well-resolved ^{1}H-nmr spectrum in the sugar region displayed resonances spread over 4.5 ppm, thus allowing unambiguous assignments. In comparison with platanoside [**2**], which exhibited three

TABLE 1. ^{1}H-nmr Data of Tiliroside [**1**], Platanoside [**2**], and Glycosides **3** and **4** (δ ppm, 400 MHz)[a].

Proton	Compound			
	1	**2**	**3**	**4**
H-6	6.05 d, J=2 Hz	6.10 br s	6.16 d, J=2 Hz	6.17 d, J=2 Hz
H-8	6.19 d, J=2 Hz	6.26 br s	6.34 d, J=2 Hz	6.34 d, J=2 Hz
H-2′, -6′	7.91 d, J=8.6 Hz	7.81 d, J=8.8 Hz	7.76 d, J=8.8 Hz	7.76 d, J=8.8 Hz
H-3′, -5′	6.76 d, J=8.6 Hz	6.93 d, J=8.8 Hz	6.92 d, J=8.8 Hz	6.92 d, J=8.8 Hz
H-1″	5.19 d, J=7.6 Hz	5.55 d, J=1.6 Hz	5.45 d, J=1.6 Hz	5.39 d, J=1.5 Hz
H-2″	3.45 m	5.77 dd, J=3.4 and 1.6 Hz	5.49 dd, J=3.4 and 1.6 Hz	5.47 dd, J=3.4 and 1.5 Hz
H-3″	3.45 m	5.25 dd, J=9.6 and 3.4 Hz	3.90 dd, J=9 and 3.4 Hz	3.88 dd, J=9 and 3.4 Hz
H-4″	3.45 m	3.59 t, J=9.6 Hz	3.35 t, J=9 Hz	ca. 3.38 m
H-5″	3.50 m	3.50 m	ca. 3.42 m	ca. 3.42 m
H-6″		0.99 d, J=6 Hz	0.96 d, J=5.8 Hz	0.93 d, J=6.2 Hz
H_A-6″	4.29 dd, J=11.9 and 1.9 Hz			
H_B-6″	4.15 dd, J=11.9 and 6.8 Hz			
H-2, -6 coum. .	7.21 br d, J=8.5 Hz	7.42 and 7.33 br d, J=8.6 Hz	7.42 d, J=8.7 Hz	7.58 d, J=8.7 Hz
H-3, -5 coum. .	6.71 d, J=8.5 Hz	6.76 and 6.71 d, J=8.6 Hz	6.76 d, J=8.7 Hz	6.72 d, J=8.7 Hz
H-7 coum.	7.34 br d, J=15.9 Hz	7.58 and 7.56 br d, J=15.9 Hz	7.60 br d, J=15.8 Hz	6.83 br d, J=12.8 Hz
H-8 coum.	6.02 br d, J=15.9 Hz	6.33 and 6.24 d, J=15.9 Hz	6.31 d, J=15.8 Hz	5.75 d, J=12.8 Hz

[a]In CD_3OD (δ 3.27).

lowfield signals at δ 5.77 (dd, J=3.4 and 1.6 Hz, H-2″), δ 5.55 (d, J=1.6 Hz, H-1″), and δ 5.25 (dd, J=9.6 and 3.4 Hz, H-3″), the H-2″ and H-3″ deshielding being due to the acylation at C-2″ and C-3″, glycosides **3** and **4** gave only two resonances in this zone at δ 5.49/5.47 (H-2″) and δ 5.45/5.39 (H-1″). Disappearance of one *p*-coumaric acid in these isomers was clearly indicated by the H-3″ upfield shift at δ 3.90/3.88 (Table 1). Consequently, compounds **3** and **4** were identified, respectively, with kaempferol 3-*O*-α-L-(2-*E*-*p*-coumaroyl rhamnopyranoside) and kaempferol 3-*O*-α-L-(2-*Z*-*p*-coumaroyl rhamnopyranoside), two new natural products.

Acylated flavonoid rhamnosides are rare in nature. Up to now, only five such glycosides with the rhamnose acylated by an aromatic acid have been reported: the above-mentioned platanoside [**2**] with a 2″,3″-di-acylation by *p*-coumaric acid from *Pl. acerifolia*, the unusual glycoside quercetin 3-(2-*p*-hydroxybenzoyl 4-*p*-coumaroyl rhamnoside) with mixed acylation from *Libocedrus bidwillii* leaf (Cupressaceae) (10), quercetin 3-(2-galloyl rhamnoside) from *Polygonum filliforme* (Polygonaceae) (11), and gossypetin 3′-methyl ether 3-(2-galloyl rhamnoside) along with the 4″-galloyl isomer from *Desmanthus illinoenis* (Leguminosae) (12). The two new *p*-coumaroyl kaempferol rhamnosides **3** and **4** are the first 2″-cinnamoyl flavonoid rhamnosides reported in the plant kingdom.

EXPERIMENTAL

PLANT MATERIAL.—Collection data were previously reported (13).

GENERAL EXPERIMENTAL PROCEDURES.—Tlc was carried out on pre-coated microcrystalline cellulose plastic sheets (Macherey Nagel) and Si gel 60F-254 plastic sheets (Merck). Cc was achieved on Sephadex LH-20 (Pharmacia). For separation by centrifugal tlc on Si gel (2 mm layer thickness), we used a Chromatotron apparatus (Harrison Research). Purification was performed by semi-preparative hplc on a Waters model equipped with a 6000A pump, a variable wavelength detector, and a Lichrosorb RP-18 column (7 μm, 250×10 mm) (Merck). Recording of the uv spectra with the usual shift reagents was made according to standard procedures (8,9). Nmr spectra were recorded with an AM400 Bruker spectrometer; the solvent signal was used as reference.

EXTRACTION AND ISOLATION OF THE FLAVONOL GLYCOSIDES.—The general extraction of the acylated flavonoid glycosides has been previously reported (2). A portion of the EtOAc extract (1 g) was dissolved in hot MeOH. The filtrate was introduced onto a Sephadex LH-20 column eluted with MeOH. Glycosides **3** and **4** were obtained along with platanoside [**2**] and after tiliroside [**1**], which was discarded. The above mixture (175 mg) was successively subjected to polyamide cc with a gradient of MeOH in toluene and then to centrifugal tlc on Si gel [*n*-hexane–$CHCl_3$–iPrOH–MeOH (80:15:2.5:2.5 to 20:50:15:15)]. This procedure yielded 12 mg of the mixed glycosides **3** and **4**. Final purification was achieved by semi-preparative hplc on reversed phase with 70% MeOH, affording 5.2 mg of platanoside [**2**] and 3.8 mg of **3** and **4**.

Kaempferol 3-O-α-L-(2-E-p-coumaroyl rhamnopyranoside) [**3**] *and Kaempferol 3-O-α-L-(2-Z-p-coumaroyl rhamnopyranoside)* [**4**].—Uv λ max (MeOH) nm 266, 296 sh, 311, 360 sh; ($AlCl_3$) 274, 305, 322 sh, 360 sh, 397; ($AlCl_3$+HCl) 272, 305, 322 sh, 360 sh, 397 sh; (NaOMe) 273, 305 sh, 367; (NaOAc) 273, 298 sh, 308, 372 sh; (NaOAc+H_3BO_3) 268, 300 sh, 313, 360 sh. Fabms data are discussed above. ^{1}H nmr see, Table 1.

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