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Chun-Nan Lin, and Bai-Luh Wei

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FLAVONOL AND NAPHTHALENE GLYCOSIDES FROM *RHAMNUS NAKAHARAI*[1]

CHUN-NAN LIN*

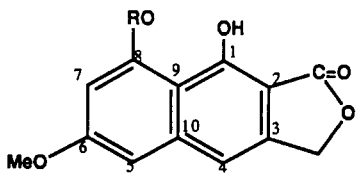
Natural Products Research Center, Kaohsiung Medical College, Kaohsiung, Taiwan 807, Republic of China, and National Research Institute of Chinese Medicine, Taipei, Taiwan 231, Republic of China

and BAI-LUH WEI

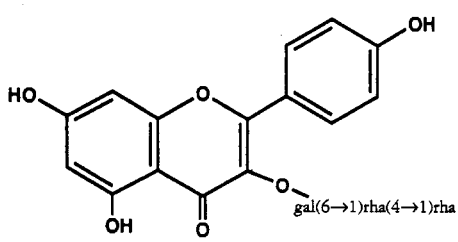
Ta-Jen Pharmaceutical Junior College, Ping Tung Hsien, Taiwan 907, Republic of China

ABSTRACT.—A new naphthalene glycoside and a new flavonol triglycoside have been isolated from the root bark of *Rhamnus nakaharai*. These compounds have been characterized as 6-methoxysorigenin-8-*O*-α-L-rhamnosyl (1→6)-glucoside [**2**] and kaempferol 3-*O*-[α-L-rhamnopyranosyl (1→4)-α-L-rhamnopyranosyl (1→6)]-β-D-galactopyranoside (kaempferol 3-isorhamninoside) [**3**].

In a previous paper (1), we reported the isolation and characterization of a new anthraquinone glycoside, chrysophanol 8-*O*-xylosyl-(1→6)-glucoside, and a new naphthalene glycoside, 2-acetyl-3-methyl-6-methoxynaphthalene-1,8-diol 8-*O*-xylosyl-(1→6)-glucoside, from the root bark of *Rhamnus nakaharai* (Rhamnaceae). In a continuation of this work, a known naphthalene glucoside, 6-methoxysorigenin-8-*O*-β-D-glucoside [**1**] (2), a new naphthalene glycoside [**2**], a new flavonol triglycoside [**3**], and five known compounds, taraxerol, chrysophanol, physcion, rhamnocitrin, and kaempferol, were further isolated from the root bark and leaf of this plant. In this paper, we report the isolation and characterization of the two new glycosides **2** and **3** and the characterization of **1** by more detailed spectroscopic methods.



1 R=glc
2 R=glc(6→1)rha



3

Compound **1** showed uv absorption maxima similar to 6-methoxysorinin (3). The ^{1}H-nmr spectrum of **1** showed a MeO signal at δ 3.79, a lactonic methylene signal at δ 5.28 (s), a glucosyl anomeric proton at δ 5.71 (d, J=7.1 Hz), a pair of meta-coupled 1H doublets at δ 6.99 (J=2.0 Hz, H-7), and δ 7.59 (J=2.0 Hz, H-5), and an aromatic proton at δ 7.14 (s, H-4). The ^{13}C nmr of **1** (Table 1) was assigned by ^{1}H-decoupling spectra, the DEPT pulse sequence, comparison with the chemical shifts of 6-methoxysorinin (3), and reported values in the literature (4). The above ^{1}H- and ^{13}C-nmr spectra further supported the characterization of **1** as 6-methoxysorigenin-8-*O*-β-D-glucoside.

Compound **2** showed a blue fluorescence under uv light, similar to the uv absorption of 6-methoxysorinin (3). The presence of a chelated carbonyl group absorption at 1645 cm^{-1} and a bathochromic shift with $AlCl_3$ in the ir and uv spectrum of **2**, respectively, sug-

[1]Part 8 in the series "The Constituents of Formosan *Rhamnus* Species." For part 7 see ref. (1).

TABLE 1. ^{13}C-nmr Spectral Data of Compounds **1–3**.[a]

Carbon	**1**[b]	**2**[b]	Carbon	**3**[c]
1	157.1[d]	157.1[d]	2	158.7[d]
2	111.3	111.3	3	136.1
3	141.9	142.0	4	179.8
4	110.2	110.3	5	163.1
5	105.0	105.4	6	100.4
6	160.7	161.0	7	166.3
7	104.6	104.9	8	95.3
8	158.4[d]	158.4[d]	9	159.6[d]
9	105.5	105.6	10	106.1
10	144.3	144.3	1′	122.8
OMe	55.6	55.7	2′	132.8
Lactone-CH_2-	68.3	68.3	3′	116.4
Lactone-CO	169.3	169.3	4′	161.9
1′	102.6	102.4	5′	116.4
2′	74.7	74.6	6′	132.8
3′	78.4	78.5	1″	105.9
4′	71.2	71.6	2″	72.5
5′	79.7	77.8	3″	75.4
6′	62.3	67.8	4″	70.3
1″		102.5	5″	75.5
2″		72.9	6″	67.7
3″		72.0	1‴	102.1
4″		74.2	2‴	72.2
5″		69.9	3‴	72.4
6″		18.6	4‴	79.9
			5‴	70.3
			6‴	18.3
			1⁗	104.2
			2⁗	73.4
			3⁗	73.5
			4⁗	74.4
			5⁗	70.5
			6⁗	18.3

[a]The number of directly attached protons to each individual carbon was verified with the DEPT pulse sequence.

[b]Measured in pyridine-d_5.

[c]Measured in MeOH-d_4.

[d]This signal may be reversed in each column.

gested that it possessed an aromatic *O*-hydroxycarbonyl moiety and the sugar moiety was located at C_8-OH. On acid hydrolysis, it gave glucose and rhamnose, detected by tlc. In the fabms spectrum (negative mode) of **2**, peaks at *m/z* 553 $[M-H]^-$, 407 $[M-(\text{rhamnose}-OH)]^-$ and 244 $[\text{aglycone}-2H]^-$ indicated the $[M]^+$ of **2** to occur at *m/z* 554 and the sugar sequence to be glucose-rhamnose.

The ^{1}H-nmr spectrum of **2** showed a MeO signal at δ 3.87, a lactonic methylene signal at δ 5.25 (s), a rhamnosyl anomeric proton at δ 5.49 (d, J=1.0 Hz), a glucosyl anomeric proton at δ 5.62 (d, J=7.5 Hz), a pair of meta-coupled 1H doublets at δ 6.96 (J=2.0 Hz, H-7) and δ 7.71 (J=2.0 Hz, H-5) and an aromatic proton at δ 7.12 (s, H-4). The aromatic proton signals of **2** were almost identical with those of **1**. Based on the above evidence, **2** was partially characterized as 6-methoxysorigenin-8-*O*-glycoside.

In the ^{13}C-nmr spectrum of **2** (Table 1), the chemical shift values of C-1 to C-10, and the lactone-CO and lactone-CH_2-resonances were almost identical with those of the corresponding data for

1 (Table 1), and the chemical shift values of the glucosyl and rhamnosyl carbons of **2** were also identical with those of the corresponding data for physcion 8-*O*-β-rutinoside (5). According to the above results, **2** was characterized as 6-methoxy-sorigenin-8-*O*-α-L-rhamnosyl (1→6)-glucoside [**2**].

Compound **3** was characterized as a flavonol glycoside from its color reactions and spectral properties. On acid hydrolysis, it afforded galactose and rhamnose, as detected by tlc, and kaempferol, identified by its mp and spectral behavior. In the positive-ion fab and eims spectra of **3** and **3** peracetate, peaks at *m/z* 741 $[M+H]^+$, 577 $[741-164]^+$, 431 $[577-146]^+$, and 287 $[aglycone+H]^+$ and an intense peak of *m/z* 273, respectively, indicated the $[M]^+$ of **3** to occur at *m/z* 740 and the sugar sequence to be galactose-rhamnose-rhamnose.

The ^{1}H-nmr spectrum of **3** in MeOH-d_4 indicated the presence of two rhamnosyl Me signals at δ 1.13 and δ 1.19 (3H, each J=6.2 Hz), two rhamnosyl anomeric protons at δ 4.53 (1H, d, J=2 Hz) and δ 4.93 (1H, d, J=2 Hz), a galactosyl anomeric proton at δ 5.02 (1H, d, J=7.8 Hz), a pair of meta-coupled ^{1}H doublets at δ 6.17 (J=2.0 Hz, H-6) and δ 6.34 (J=2.0 Hz, H-8), and a pair of meta-coupled 2H doublets at δ 6.87 (J=8.5 Hz, H-3′ and H-5′) and δ 8.07 (J=8.5 Hz, H-2′ and H-6′). In the ^{13}C-nmr spectrum of **3** in MeOH-d_4 (Table 1), the chemical shift values were assigned by comparison with the corresponding data for rhamnocitrin 3-*O*-isorhamninoside and kaempferol (6). From Table 1, it is clear that the sugar moiety in **3** is attached at C-3 because the C-2 signal of **3** produced a larger than anticipated effect (4). The sugar signals of **3** were almost identical with those of corresponding data for rhammocitrin 3-*O*-isorhamninoside. Thus, **3** is kaempferol 3-*O*-[α-L-rhamnopyranosyl (1→4)-*O*-α-L-rhamnopyranosyl (1→6)]-β-D-galactopyranoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All mps are uncorrected. Ft-nmr were performed on a Varian Gemini-200 spectrometer; ir spectra were recorded on a Hitachi model 260-30; uv spectra were measured on a Jasco model 7800; and ms were obtained on a JMS-HX 110 mass spectrometer.

EXTRACTION AND SEPARATION.—Fresh root bark (0.7 kg) and leaves (2 kg) of *R. nakaharai* Hayata were collected at Ali, Wu-Tai Shian, Ping-Tung Hsien, Taiwan, during July 1990, and extracted and separated, as described previously (1). The MeOH extract was chromatographed over Si gel. Elution with CH_2Cl_2-MeOH (5:1) yielded **1**. Elution with CH_2Cl_2-MeOH (3:1) yielded **2**. Elution with CH_2Cl_2-MeOH (2:1) yielded **3**. Elution with C_6H_{12} yielded taraxerol. Elution with C_6H_{12}-C_6H_6 (1:4) yielded chrysophanol and physicion. Elution with C_6H_{12}-C_6H_6-EtOAc (4:10:1) yielded rhamnocitrin and kaempferol. Compound **1** and taraxerol were identified by uv, ir, nmr, ms, and chemical reactions (2,7), respectively. Chrysophanol, physcion, rhamnocitrin, and kaempferol were identified by comparison of mmp, uv, ir, nmr, and ms with those of authentic samples, respectively.

Compound **2**.—Brownish needles (MeOH), mp 227–228°; ir ν max (KBr) 3400, 1740, 1645 cm^{-1}; uv λ max (MeOH) (log ε) 206 (4.38), 250 (sh) (4.32), 258 (4.45), 305 (sh) (3.36), 320 (3.48), 350 (3.61) nm; λ max (MeOH+$AlCl_3$) 208, 266, 296 (sh), 375 nm; ^{1}H nmr (200 MHz, pyridine-d_5), see text; ^{13}C nmr (pyridine-d_5), see Table 1; fabms (glycerol) (negative mode) *m/z* 553 (33), 407 (3), 324 (6), 280 (11), 244 (100), 155 (6), 79 (45). Acid hydrolysis (2N HCl-MeOH) of **2** yielded sugars, examined by ppc, R_f 0.20 (glucose); 0.42 (rhamnose) (*n*-BuOH-HOAc-H_2O, 4:1:2).

Compound **3**.—Orange-yellow powder (MeOH), mp 192–194°; ir ν max KBr 3375, 1660, 1618 cm^{-1}; uv λ max (MeOH) (log ε) 207 (4.09), 275 (3.78), 295 (sh) (3.48), 353 (3.69) nm; λ max (MeOH+$AlCl_3$) 273, 303, 350, 397 nm; λ max (MeOH+NaOAc) 274, 304, 350, 400 nm; ^{1}H nmr (200 MHz, CD_3OD), see text; ^{13}C nmr (CD_3OD) see Table 1; fabms (*m*-nitrobenzyl alcohol) (positive mode) *m/z* $[M+Na]^+$ 763 (740+23) (1), 741 (1), 577 (1), 431 (1), 287 (7), 154 (42), 137 (49), 69 (93), 57 (100). Acid hydrolysis (2N HCl) of **3** yielded kaempferol, yellow needles (MeOH), mp 276–278°; the mmp, ir, nmr and ms were identified as those of authentic kaempferol. Galactose and rhamnose were detected as described previously [6]. Compound **3** peracetate, pale yellow powder (MeOH), mp 122–124° eims *m/z*: no

molecular ion peak, *m/z* 792 (0.1), 641 (0.2), 503 (10), 286 (10), 273 (13), 153 (73), 111 (76), 43 (100).

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