

STEROIDS AND TRITERPENOIDS FROM *ROSA LAEVIGATA*

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Key Word Index—*Rosa laevigata*; Rosaceae; aerial parts; ursolic acid derivatives; euscaphic acid derivatives; oleanolic acid derivatives; sitosteryl glucosides; stigmastadiol glucoside.

Abstract—An acetone extract of aerial parts of *Rosa laevigata* was found to contain 16 components, including derivatives of ursolic, euscaphic and oleanolic acids as well as glucosides of sterols. Among them, 2 α -methoxyursolic acid, 11 α -hydroxytormentic acid, tormentic acid 6-methoxy- β -glucopyranosyl ester and stigmasta-3 α ,5 α -diol 3-O- β -D-glucopyranoside are new compounds. Their structures were established by chemical and spectral methods.

INTRODUCTION

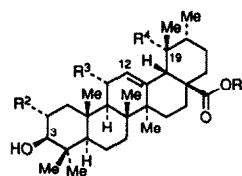
Rosa laevigata is a shrub, very common in thickets at low altitudes, from China, Japan and Taiwan [1]. This plant has been used as a traditional folk medicine [2], an extract of the root of *R. multiflora* has been shown to have hypolipidemic activity [3]. The chemical constituents of *R. laevigata* have not been investigated, but a survey of the literature shows that plants of the same genus are rich in triterpenoid acids, sitosterol and their glycosides [3-5]. We describe here constituents isolated from *R. laevigata* for the first time.

RESULTS AND DISCUSSION

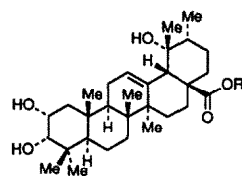
An acetone extract of air-dried aerial parts of *R. laevigata* was concentrated to give semi-solids. Chromatography of the semi-solids and combination of appropriate fractions (monitored by TLC analyses) led to four fractions A-D. Fraction A was found to contain ursolic acid (1) [6], oleanolic acid (10) [7] and hederagenin (11) [7]. Fractions B and C also consisted of related triterpenoid acids, but no methyl esters by analyses of ¹H NMR spectra, which showed no signal between δ 3.5 and 3.8 attributable to CO₂Me. Fractions B and C were separately treated with diazomethane and subjected to chromatography to give methyl ursolate (1a) [8, 9], methyl 2 α -hydroxyursolate (2a) [8-10], methyl 2 α -methoxyursolate (3a), methyl tormentate (4a) [10], methyl 11 α -hydroxytormentate (5a), methyl euscaphate (8a) [11, 12], methyl oleanolate (10a) [9], and the methyl ester of hederagenin (11a) [9]. Fraction D was triturated with ethyl ether and the soluble components were composed of tormentic acid β -D-glucopyranosyl ester (6) [3], tormentic acid 6-methoxy- β -D-glucopyranosyl ester (7), euscaphic acid β -D-glucopyranosyl ester (9) [12] and methyl β -D-glucopyranoside (16) [13]. The insoluble residue of fraction D, which showed no proton resonances for acetates MeCO₂R at δ 2.0, was subjected to peracetylation and separated by HPLC to give sitosteryl- β -D-glucopyranoside tetraacetate (12Ac) [14, 15], 7-oxositosteryl- β -D-glucopyranoside tetraacetate (13Ac) [15], 7-hydroxysitosteryl-3-O- β -D-glucopyranoside tetraacetate

(14Ac) [15] and stigmasta-3 α ,5 α -diol 3-O- β -D-glucopyranoside tetraacetate (15Ac).

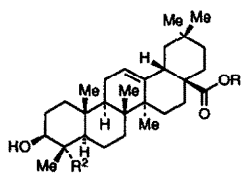
Identification of the known compounds was based on comparison of the physical and spectral properties (mp, $[\alpha]$, mass spectrum, IR, ¹H and ¹³C NMR) with those reported in literature. Compounds 3, 5, 7 and 15 are new



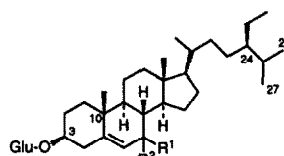
	R ¹	R ²	R ³	R ⁴
1	H	H	H	H
2	H	OH	H	H
2a	Me	OH	H	H
3	H	OMe	H	H
3a	Me	OMe	H	H
4	H	OH	H	OH
4a	Me	OH	H	OH
5	H	OH	OH	OH
5a	Me	OH	OH	OH
6	Glu	OH	H	OH
7	6-MeO-Glu	OH	H	OH



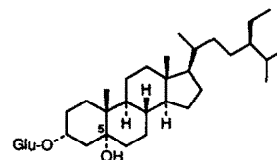
8	R = H
8a	R = Me
9	R = Glu



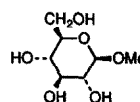
	R ¹	R ²
10	H	Me
10a	Me	Me
11	H	CH ₂ OH
11a	Me	CH ₂ OH



	R ¹ , R ²
12	H, H
13	O
14	OH, H



15



16

compounds. The methyl ester **3a** (C₃₂H₅₂O₄) showed a parent peak at *m/z* 500 and a base peak at *m/z* 262 attributable to the fragment derived from retro-Diels–Alder reaction [16]. The H-3 resonance at δ 3.02 exhibited as a doublet with a large coupling constant 9.4 Hz, which indicated the *trans*-diaxial relationship between H-2 and H-3. Compound **3a** was further proved to be a methylation product of **2a** (2 equiv NaH, 1 equiv MeI). Complete assignment of the proton and carbon resonances for the methyl ester **5a** (Tables 1 and 2) was obtained with the assistance of the ¹H–¹H and ¹H–¹³C correlation spectra. The 11-hydroxy group was inferred to be on the α -face (equatorial position) because the axial H-11 at δ 4.84 had a large coupling constant (8.6 Hz) with H-9. The allylic alcohol **5a** (C₃₁H₅₀O₆) was prone to autoxidation on standing to give the corresponding enone (C₃₁H₄₈O₆) which showed the exact mass for [M]⁺ at *m/z* 516.3427 (calcd 516.3452).

In addition to the 30 carbons for triterpenes of the ursolic acid type, compound **6** displayed another six signals at δ 62.2, 71.1, 73.9, 78.8, 79.2 and 95.7 attributable to the carbons of glucopyranose. The FAB mass spectrum of **6** showed negative ions at *m/z* 649 for [M–1][–] and at *m/z* 487 owing to cleavage at the glycoside bond. Com-

pound **6**, namely rosamultin, has been reported once as a constituent of roots of *R. multiflora* [3]. The FAB mass spectrum of **7** showed a [M–1][–] ion at *m/z* 663 and an intense peak at *m/z* 487 for the aglycone. The structure of **7** was assigned by comparison of the ¹³C NMR spectrum with that of **6** (Table 2). The values of ¹³C resonance of the two compounds were similar except for **7**, which showed an additional signal for the methoxy group at δ 57.0 and the C-6 resonance occurring at a lower field of δ 72.6. The proton of the anomeric carbon (C-1') appearing at δ 6.21 (*d*, *J* = 7.8 Hz) was in agreement with an axial α -orientation.

Compounds **13** and **14** are the first report in nature although synthetic samples have already been used in pharmacological studies [15]. Compound **14Ac** actually consisted of the *7* α and *7* β epimers in nearly equal amounts as indicated by the H-7 signals at δ 3.78 (*m*) and 3.82 (*m*). Unlike the sitosterol derivatives **12Ac**–**14Ac**, compound **15Ac** has no C=C double bond by analyses of its ¹H and ¹³C NMR spectra (Table 3). The parent peak at *m/z* 762 supported the assigned structure of **15Ac**. The H-3 β (equatorial) of **15Ac** occurred as a broad singlet at δ 3.91, whereas the axial H-3 α for **12Ac**–**14Ac** showed as multiplets at higher fields (δ 3.44–3.57). A resonance at

Table 1. Pertinent spectral data for compounds **3a**, **5a**, **7**, **13Ac** and **15Ac**

	<i>m/z</i> (rel. int.)	$\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$	δ_{H} (200 MHz)
3a	70 eV: 500 [M] ⁺ (7), 440 (5), 262 (100), 237 (12), 203 (65), 189 (17), 187 (10), 133 (31). HRMS, C ₃₂ H ₅₂ O ₄ requires 500.3867. Found: 500.3866.	3472, 2926, 1720.	CDCl ₃ : 0.72 (3H, s), 0.81 (3H, s), 0.82 (3H, <i>d</i> , <i>J</i> = 6.0 Hz), 0.91 (3H, <i>d</i> , <i>J</i> = 6.0 Hz), 0.95 (3H, s), 1.02 (3H, s), 1.05 (3H, s), 2.15 (1H, <i>d</i> , <i>J</i> = 11.2 Hz, H-18), 3.02 (1H, <i>d</i> , <i>J</i> = 9.4 Hz, H-3), 3.20 (1H, <i>ddd</i> , <i>J</i> = 9.7, 9.4, 4.2 Hz, H-2), 3.35 (3H, s, OMe), 3.58 (3H, s, CO ₂ Me), 5.23 (1H, <i>t</i> , <i>J</i> = 3.6, H-12)
5a	20 eV: 518 [M] ⁺ (8), 501 (17), 500 (15), 441 (20), 295 (3), 277 (4), 251 (100), 217 (3), 205 (15), 187 (15).	3416, 2936, 1707, 1151, 1049.	Pyridine- <i>d</i> ₅ : 0.93 (3H, s), 1.02 (3H, <i>d</i> , <i>J</i> = 6.3 Hz), 1.07 (3H, s), 1.15 (3H, s), 1.23 (3H, s), 1.58 (3H, s), 1.78 (3H, s), 2.25 (1H, <i>d</i> , <i>J</i> = 8.6 Hz, H-9), 2.94 (1H, s, H-18), 2.97 (1H, <i>dd</i> , H-1 β), 3.33 (1H, <i>d</i> , <i>J</i> = 9.3 Hz, H-3), 3.70 (3H, s, CO ₂ Me), 4.08 (1H, <i>m</i> , H-2), 4.84 (1H, <i>dd</i> , <i>J</i> = 8.6, 3.9 Hz, H-11), 6.18 (1H, <i>d</i> , <i>J</i> = 3.9 Hz, H-12).
7	FAB-NI: 663 [M–1] [–] , 487 (aglycone), 469.	3404, 2922, 1724, 1449, 1364, 1166, 1072, 1029.	Pyridine- <i>d</i> ₅ : 1.02 (3H, <i>d</i> , <i>J</i> = 6.0 Hz, Me-20), 1.06 (3H, s), 1.08 (3H, s), 1.17 (3H, s), 1.24 (3H, s), 1.36 (3H, s), 1.64 (3H, s), 2.91 (1H, s, H-18), 3.37 (1H, <i>d</i> , <i>J</i> = 9.0 Hz, H-3), 3.38 (3H, s, OMe), 3.95–4.28 (6H, <i>m</i>), 5.51 (1H, <i>br s</i> , H-12), 6.21 (1H, <i>d</i> , <i>J</i> = 7.8 Hz).
13Ac	20 eV: 758 [M] ⁺ (30), 426 (5), 412 (48), 410 (65), 394 (73), 331 (100), 271 (22), 168 (15).	2953, 1747, 1669, 1458, 1363, 1221, 1039, 906.	CDCl ₃ : 0.64 (3H, s, Me-18), 0.77 (3H, <i>d</i> , <i>J</i> = 6.6 Hz, Me-26)*, 0.79 (3H, <i>d</i> , <i>J</i> = 6.6 Hz, Me-27)*, 0.80 (3H, <i>t</i> , <i>J</i> = 7.3 Hz, Me-29), 0.88 (3H, <i>d</i> , <i>J</i> = 6.2 Hz, Me-21), 1.14 (3H, s, Me-19), 1.97 (3H, s, MeCO ₂), 1.99 (3H, s, MeCO ₂), 2.02 (3H, s, MeCO ₂), 2.04 (3H, s, MeCO ₂), 3.57 (1H, <i>m</i> , H-3), 3.65 (1H, <i>m</i> , H-5'), 4.08 (1H, <i>dd</i> , <i>J</i> = 12.2, 2.3 Hz, H-6'), 4.21 (1H, <i>dd</i> , <i>J</i> = 12.2, 4.7 Hz, H-6'), 4.56 (1H, <i>d</i> , <i>J</i> = 7.9 Hz, H-1'), 4.93 (1H, <i>dd</i> , <i>J</i> = 9.5, 8.0 Hz, H-2'), 5.04 (1H, <i>t</i> , <i>J</i> = 9.5 Hz, H-4'), 5.17 (1H, <i>t</i> , <i>J</i> = 9.5 Hz, H-3'), 5.64 (1H, s, H-6).
15Ac	20 eV: 762 [M] ⁺ (1), 761 (1), 743 (2), 413 (38), 396 (31), 331 (56), 271 (19), 253 (3), 169 (100), 109 (17).	3439, 2953, 1748, 1364, 1226, 1038.	CDCl ₃ : 0.65 (3H, s, Me-18), 0.78 (3H, <i>d</i> , <i>J</i> = 6.7 Hz, Me-26)*, 0.80 (3H, <i>d</i> , <i>J</i> = 6.7 Hz, Me-27)*, 0.81 (3H, <i>t</i> , <i>J</i> = 7.3 Hz, Me-29), 0.88 (3H, <i>d</i> , <i>J</i> = 6.2 Hz, Me-21), 1.22 (3H, s, Me-19), 1.98 (3H, s, MeCO ₂), 2.00 (3H, s, MeCO ₂), 2.02 (3H, s, MeCO ₂), 2.04 (3H, s, MeCO ₂), 3.67 (1H, <i>m</i> , H-5'), 3.91 (1H, <i>br s</i> , H-3), 4.10 (1H, <i>dd</i> , <i>J</i> = 12.2, 2.3 Hz, H-6'), 4.23 (1H, <i>dd</i> , <i>J</i> = 12.2, 4.9 Hz, H-6'), 4.57 (1H, <i>d</i> , <i>J</i> = 7.9 Hz, H-1'), 4.94 (1H, <i>dd</i> , <i>J</i> = 9.5, 8.0 Hz, H-2'), 5.05 (1H, <i>t</i> , <i>J</i> = 9.5 Hz, H-4'), 5.17 (1H, <i>t</i> , <i>J</i> = 9.5 Hz, H-3').

*These assignments are made according to ref. [20] but are not conclusive.

Table 2. ^{13}C NMR spectral data of compounds **3a**–**8a** (75 MHz, δ)

C	3a	4a	5a	6	7	8a
1	42.0	47.7	48.9	47.8	47.8	41.4
2	78.7	68.4	68.8	68.6	68.6	77.2
3	81.5	83.2	83.7	83.8	83.8	78.6
4	39.0	39.1	40.0	38.4	38.5	39.9
5	55.0	55.0	56.0	55.9	55.9	53.0
6	18.1	18.3	19.2	18.9	19.0	17.9
7	32.8	32.4	33.8	33.3	33.5	32.3
8	39.5	39.7	41.4	39.8	39.8	41.0
9	47.5	47.7	47.4	47.8	47.8	47.7
10	38.0	37.9	39.5	38.4	38.5	37.3
11	23.4	23.5	80.9	24.0	24.1	23.5
12	125.2	128.5	129.7	128.3	128.2	128.8
13	138.3	138.0	144.3	139.2	139.3	138.0
14	41.2	41.0	44.0	40.6	40.6	41.0
15	27.9	25.8	26.0	26.5	26.7	28.0
16	24.1	25.2	25.7	26.0	26.1	25.3
17	48.0	46.3	48.3	48.6	48.6	47.8
18	52.8	53.0	54.0	54.4	54.4	51.5
19	38.8	72.8	72.8	72.6	72.6	72.9
20	38.7	41.0	42.4	42.1	42.1	46.7
21	30.6	28.0	29.1	29.3	29.1	25.3
22	36.6	37.2	38.3	37.6	37.8	37.3
23	28.7	28.5	29.5	29.3	29.3	28.5
24	17.0	16.7	18.9	17.4	17.5	21.8
25	16.9	16.4	18.1	16.9	17.0	16.1
26	17.0	16.7	19.0	17.6	17.7	17.9
27	23.6	24.3	23.6	24.5	24.6	24.6
28	178.0	178.2	178.6	177.0	177.0	178.4
29	17.0	28.0	27.1	27.0	27.0	27.2
30	21.2	15.9	16.8	16.7	16.6	16.5
CO ₂ Me	51.4	51.4	51.8			66.2

Compounds **3a**, **4a** and **8a** were measured in chloroform-*d*, compounds **5a**, **6** and **7** in pyridine-*d*₅. The OMe-2 group of compound **3a** showed a signal at δ 56.3. Signals for carbons of the glucosyl moiety in compound **6** occurred at δ 62.2 (C-6'), 71.1 (C-4'), 73.9 (C-2'), 78.8 (C-3'), 79.2 (C-5') and 95.7 (C-1'), while those of **7** showed at δ 57.0 (6'-OMe), 71.7 (C-4'), 72.6 (C-6'), 74.0 (C-2'), 77.9 (C-3'), 78.9 (C-5'), 95.7 (C-1').

δ 84.3 (s) was attributable to the tertiary carbon (C-5) with a substituent of the hydroxyl group. Changing the solvent from chloroform-*d* to pyridine-*d*₅ did not cause any apparent shift for either H-3 β or Me-10. This experiment indicated that the C-5 hydroxyl group was on the α -face, being away from the H-3 β and the Me-10 β group [17]. The sterols **12Ac**, **13Ac** and **15Ac** showed negative optical rotations. It is known that the sitosterols in most vascular plants possess the 24 α R-configuration [18]. Meticulous examination of the ^{13}C NMR spectra of **12Ac**–**15Ac** also revealed that they all have the 24R-configuration [19, 20].

EXPERIMENTAL

Plant material. Aerial parts of *R. laevigata* Michx (1.4 kg) were collected from the seaside area of Nanliaou. A specimen of this plant is deposited in the herbarium of our university. Aerial parts without fruits were extd with 3 \times 8 l Me₂CO. The Me₂CO extract was passed through a short column of activated charcoal. The filtrate was cond and the insol. oily solids collected. The semi-

solids (35 g) were subjected to CC on silica gel (340 g) and elution with gradients of EtOAc and *n*-hexane. The appropriate frs (monitored by TLC analyses) were combined to give 4 frs A (3 g), B (1.5 g), C (3 g) and D (3.2 g). The components of A were sepd by flash CC to give ursolic acid (**1**) (2 g) and oleanolic acid (**10**) (0.3 g) and hederagenin (**11**) (0.1 g). As the ^1H NMR spectrum of the portion B showed no signal for Me esters, portion B was treated with Et₂O–CH₂N₂ to convert the acids into their corresponding Me esters, which were then separated by flash CC to give Me esters **1a** (0.5 g), **10a** (0.1 g) and **11a** (30 mg). C was similarly treated with CH₂N₂ and the derivatives sepd to give 2 α -hydroxyursolic acid Me ester **2a** (150 mg), 2 α -methoxyursolic acid Me ester (**3a**) (34 mg), tormentic acid Me ester (**4a**) (300 mg), 11 α -hydroxy tormentic acid Me ester (**5a**) (20 mg) and euscaphic acid Me ester (**8a**) (134 mg). D was triturated with Et₂O and the ppts filtered. The mother liquor contained the glucosides **6** (58 mg), **7** (12 mg), **9** (42 mg) and **16** (0.8 g). The ppts, which showed no signal for acetates, were dissolved in pyridine and treated with excess Ac₂O to give the corresponding peracetates. After purification by HPLC on a LiChrosorb Si 60 column, the tetraacetates of sitosteryl glucosides **12Ac** (350 mg), **13Ac**

Table 3. ^{13}C NMR spectral data of compounds **12Ac**–**15Ac** (75 MHz, CDCl_3 , δ)

C	12Ac	13Ac	14Ac	15Ac
1	37.2	36.7	38.4	34.2
2	29.7	28.5	29.4 ^a	28.2
3	80.0	78.6	79.7/79.5	75.7
4	38.9	38.4	39.5	39.7
5	140.3	164.3	143.0/145.0	84.3
6	122.1	126.3	124.2/125.9	28.2
7	31.9	202.2	73.3/64.5	33.5 ^a
8	31.8	29.0	29.1 ^a	36.1
9	50.1	49.9	48.3	46.1
10	36.7	36.2	36.6	39.8
11	21.0	21.1	21.0	21.2
12	39.7	38.6	40.9	39.7
13	42.3	42.8	42.2	42.9
14	56.7	55.9	55.9	56.1
15	24.3	25.9	24.3	24.1
16	28.2	28.5	28.5	29.1
17	56.0	54.6	55.4	55.7
18	11.8	11.8	11.8	12.0
19	19.3	19.0	19.1	19.0
20	36.1	36.0	36.1	36.1
21	18.8	17.2	18.8	18.2
22	33.9	33.9	34.0	33.9 ^a
23	26.0	26.2	26.1	26.1
24	45.8	45.8	45.8	45.8
25	29.5	29.1	29.2 ^a	30.3
26	19.0 ^{**}	18.9 ^{**}	19.0 ^{**}	18.7 ^{**}
27	19.8 ^{**}	19.7 ^{**}	19.8 ^{**}	19.8 ^{**}
28	23.0	23.0	23.1	23.0
29	11.9	11.9	12.0	12.1
1'	99.6	99.8	99.7	100.4
2'	71.7 ^a	71.8 ^a	71.7 ^a	71.7 ^a
3'	71.5 ^a	71.7 ^a	71.5 ^a	71.6 ^a
4'	68.5	68.4	68.5	68.5
5'	72.9	72.7	72.9	72.9
6'	62.1	61.9	62.1	62.1
MeCO ₂	20.6, 20.7, 169.2, 169.3, 170.3, 170.5	20.5, 20.6, 169.2, 169.3, 170.2, 170.6	20.6, 20.7, 169.2, 169.3, 169.4, 170.3	20.6, 20.7, 169.7, 169.8, 170.4, 170.7

^aThese assignments may be interchangeable.

^{*}These assignments are made according to ref. [20] but are not conclusive.

(51 mg), **14Ac** (20 mg) and a stigmastadiol derivative **15Ac** (40 mg) were obtained. All of these compounds are obtained as crystals from MeOH. Compound **1**. Mp 290–292°, $[\alpha]_D^{25} + 70.5^\circ$ (MeOH; *c* 1.4); **1a**, mp 110–111°. Compound **2a**, mp 202–204°, $[\alpha]_D^{25} + 39.8^\circ$ (CHCl_3 ; *c* 8.6). Compound **3a**, mp 84–86°, $[\alpha]_D^{25} + 16.5^\circ$ (CHCl_3 ; *c* 2.25). Compound **4a**, mp 146–148°, $[\alpha]_D^{25} + 30.2^\circ$ (CHCl_3 ; *c* 1.4). Compound **5a**, mp 141–143°, $[\alpha] - 11.6^\circ$ (CHCl_3 ; *c* 1.35). Compound **6**, mp 207–209°, $[\alpha]_D^{25} + 15^\circ$ (MeOH; *c* 1.1). Compound **7**, mp 195–198°, $[\alpha]_D^{25} + 1.5^\circ$ (MeOH; *c* 0.2). Compound **8a**, mp 122–124°, $[\alpha]_D^{25} + 23.8^\circ$ (CHCl_3 ; *c* 8.9). Compound **9**, mp 203–205°, $[\alpha]_D^{25} + 4.2^\circ$ (MeOH; *c* 0.3). Compound **10**, mp 302–304°, $[\alpha]_D^{25} + 79.2^\circ$ (CHCl_3 ; *c* 1.4). Compound **11**, mp 328–331°, $[\alpha]_D^{25} + 75.4^\circ$ (MeOH; *c* 1.6); **11a**, mp 218–220°. Compound **12Ac**, mp 165–167°, $[\alpha]_D^{25} - 29.1^\circ$ (CHCl_3 ; *c* 2.1). Compound **13Ac**, mp 114–116°, $[\alpha]_D^{25} - 34.9^\circ$ (CHCl_3 ; *c* 3.37). Compound **14Ac** (two epimers), mp 98–100°. Compound **15Ac**, mp 99–101°, $[\alpha]_D^{25} - 14.0^\circ$ (CHCl_3 ; *c* 0.6). Compound **16**, mp 106–109°, $[\alpha]_D^{25} - 30^\circ$ (Me_2CO ; *c* 1.2).

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