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## ON THE CONSTITUENTS OF THE LEAVES OF *WEIGELA CORAEENSIS*

Tetsuo IWAGAWA and Tsunao HASE\*

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### Abstract

From the leaves of *Weigela coraeensis* ursolic acid,  $\beta$ -sitosteryl  $\beta$ -D-glucoside, scopolin, secologanin dimethyl acetal and hyperin (quercetin-3-O- $\beta$ -D-galactoside) have been isolated.

### Introduction

*Weigela coraeensis* (Japanese name: hakoneutsugi) is an ornamental shrub and grows in the temperate zone of Japan. Although the family Caprifoliaceae is known as a rich source of iridoid glycosides[1], there seems to be no report on the constituents of *Weigela* species. We have now examined the methanolic extract of the leaves of *W. coraeensis*. Five compounds **1**, **2**, **3**, **4** and **5** have been isolated according to the isolation procedure shown Fig. 1.

### Results and Discussion

Compound (**1**) was crystallized as prisms, mp 251-252° with a molecular formula  $C_{30}H_{48}O_3 \cdot 1/4H_2O$ . It gave a positive Liebermann-Burchard's reaction. The IR spectrum showed absorption bands for a hydroxyl group at  $3400\text{ cm}^{-1}$  and a carboxyl group at  $1690\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum indicated signals of a proton attached to a carbon bearing hydroxyl group at  $\delta$  3.46 (1H, *t*-like,  $J=8\text{ Hz}$ ) and an olefinic proton at  $\delta$  5.50 (1H, *m*) besides those of typical triterpenoids at  $\delta$  0.8-2.4 (*m*). The characteristic fragmentations of the mass spectrum at  $m/z$  456  $[M]^+$ , 248, 203, 189 and 133, arising from a retro-Diels-Alder cleavage, suggested that compound **1** was either ursolic acid or oleanolic acid. The IR and  $^1\text{H}$  NMR spectra

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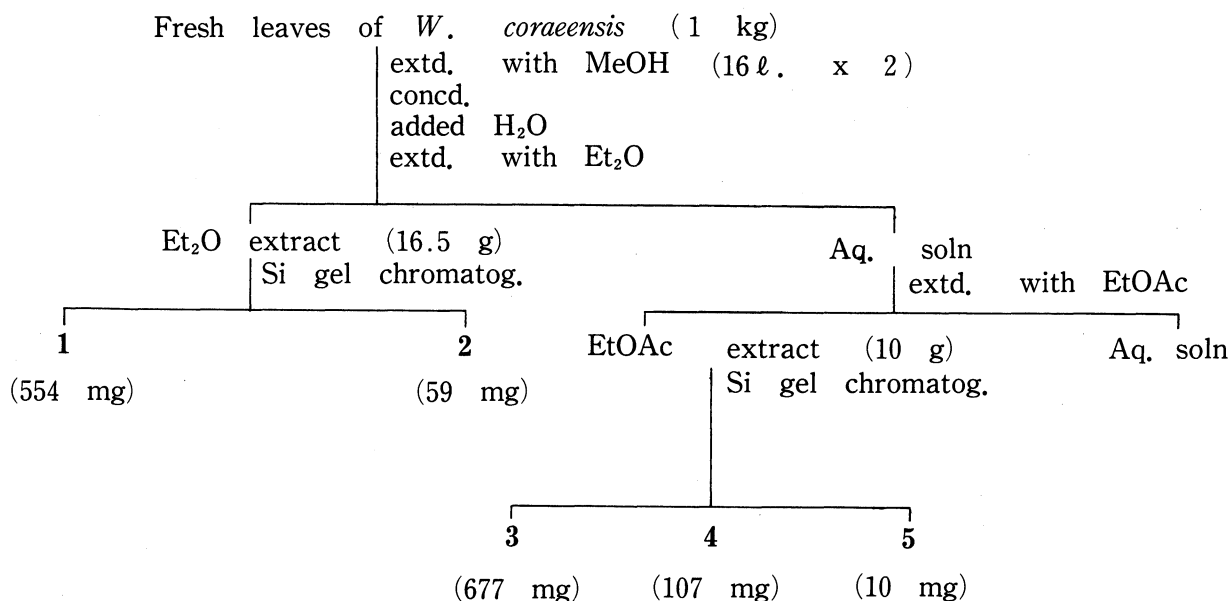


Fig. 1. Isolation procedure of the compounds

were identical with those of ursolic acid.

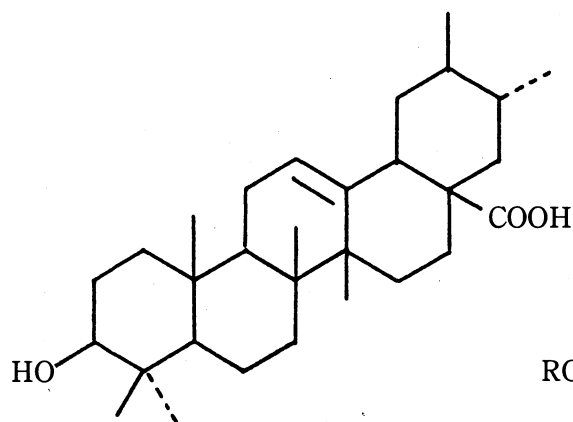
Compound (2) was isolated as a white mass, mp 263-264° with a molecular formula  $C_{35}H_{60}O_6 \cdot 2/3H_2O$ . The IR spectrum showed a strong hydroxyl absorption at  $3400\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed a typical phytosterol skeleton at  $\delta$  0.55-2.36. On acetylation with acetic anhydride and pyridine, compound 2 gave needles (6), mp 171-172° with a molecular formula  $C_{43}H_{60}O_{10}$ . The  $^1\text{H}$  NMR spectrum of the acetate indicated the presence of four acetoxy groups at  $\delta$  1.98-2.06 (3H x 4, s). The above results suggested that compound 2 was  $\beta$ -sitosteryl  $\beta$ -D-glucoside. The spectral and physical data of 2 were in agreement with those of  $\beta$ -sitosteryl  $\beta$ -D-glucoside.

Compound (3) was an amorphous powder with a molecular formula  $C_{19}H_{30}O_{11}$ . Acid hydrolysis yielded D-glucose and a brown polymerized product like other iridoids. The UV absorption maximum at 234 nm ( $\epsilon$ 8080) and the IR absorption bands at 1700 and  $1625\text{ cm}^{-1}$  were characteristic of a conjugated enol-ether system. The  $^1\text{H}$  NMR spectrum showed signals due to a C-3 proton at  $\delta$  7.60 (s), vinylic protons at  $\delta$  5.00-5.40 (3H, m) and carbomethoxy protons at  $\delta$  3.55 (3H, s) together with those of an anomeric proton at  $\delta$  5.27 (d,  $J=8\text{ Hz}$ ). The above results suggested that compound 3 was a secoiridoid glucoside. This was confirmed by a

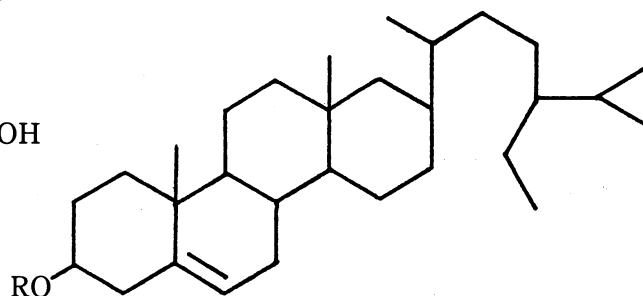
peak at  $m/z$  165 in the mass spectrum characteristic of secoiridoid glycosides[2] . In the  $^1\text{H}$  NMR spectrum, two singlets due to methoxyl protons at  $\delta$  3.26 (3H x 2) and signals assignable to a  $-\text{CHCH}_2\text{CH}-$  moiety at  $\delta$  1.79 (1H, *ddd*,  $J=6, 9$  and  $15$  Hz) , 2.39 (1H, *ddd*,  $J=7, 7$  and  $15$  Hz) and 4.62 (1H, *dd*,  $J=6$  and  $7$  Hz) were observed. Acetylation of **3** with acetic anhydride and pyridine afforded a tetra-acetate (**7**) with a molecular formula  $\text{C}_{27}\text{H}_{38}\text{O}_{15}$ . Compound **3** was therefore assumed to be secologanin dimethyl acetal on the basis of the data described above. The physical and chemical properties of **3** were identical with those of an authentic sample[3] . Compound **3** would be formed during extraction process.

Compound (**4**) was needles, mp  $216-220^\circ$  with a molecular formula  $\text{C}_{16}\text{H}_{18}\text{O}_9 \cdot 1\frac{1}{3}\text{H}_2\text{O}$ . Absorption bands at 1725, 1700, 1615 and 1565 and 1505  $\text{cm}^{-1}$  in the IR spectrum suggested that compound **4** was a coumarin. Additional evidence for the presence of this carbon skeleton came from the  $^1\text{H}$  NMR spectrum. The signals corresponding to C-3 and C-4 protons appeared as an AB system at  $\delta$  6.30 and 7.64 ( $J=9.5$  Hz) . Two singlets at  $\delta$  7.01 and 7.43 (1H each) were attributable to C-8 and C-5 protons, respectively. The  $^1\text{H}$  NMR spectrum also showed the presence of a methoxyl group at  $\delta$  3.74 (3H, *s*) and an anomeric proton at  $\delta$  5.64 (1H,  $W\frac{1}{2}$  12 Hz). Compound **4** was treated with acetic anhydride and pyridine to give a tetra-acetate (**8**), mp  $169-169.8^\circ$  with a molecular formula  $\text{C}_{24}\text{H}_{26}\text{O}_{13}$ . The above data suggested that compound **4** was scopolin. The spectral and physical data of **8** were identical with those of scoplin acetate[4] .

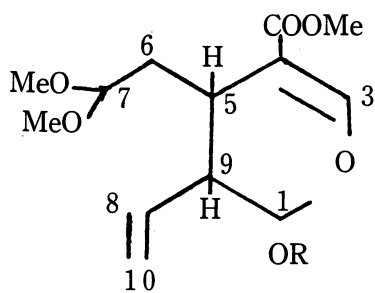
Compound (**5**) was yellow crystals, mp  $238-240^\circ$  and had a molecular formula  $\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot \text{H}_2\text{O}$ . The UV spectrum had absorption maxima at 257 nm ( $\epsilon$ 18000) and 359 nm ( $\epsilon$  15000). The IR spectrum showed absorption bands of a hydroxyl group at  $3400\text{ cm}^{-1}$ , a conjugated carbonyl at  $1655\text{ cm}^{-1}$  and a phenyl group at  $1605$  and  $1500\text{ cm}^{-1}$ . The above data suggested that compound **5** was a flavonoid glycoside. An AB system at  $\delta$  6.72 (1H,  $J=2$  Hz) and 6.77 (1H,  $J=2$  Hz) in the  $^1\text{H}$  NMR spectrum were due to C-6 and C-8 protons, respectively. Signals at  $\delta$  7.38 (1H, *d*,  $J=8$  Hz) , 8.22 (1H, *dd*,  $J=2$  and  $8$  Hz) and 8.58 (1H, *d*,  $J=2$  Hz) were characteristic for a 3,4-disubstituted B ring. Acetylation of **5** with acetic anhydride and pyridine yielded (**9**) an octa-acetate with a molecular formula  $\text{C}_{37}\text{H}_{36}\text{O}_{20}$ . The  $^1\text{H}$  NMR spectrum of the latter showed the presence of four alcoholic acetoxy groups at  $\delta$  1.86-2.11 (3H x 4, *s*) and four phenolic acetoxy groups at  $\delta$  2.28-2.41 (3H x 4, *s*) . Hydrolysis of **5** with 2N HCl afforded D-galactose and quercetin (**10**) , mp  $>300^\circ$ , whose IR spectrum were identical with that of an authentic sample. The UV spectrum of **5** in methanol and methanol-sodium acetate were similar to those of rutin[5] , which indicated that the glycosidic linkage in **5** was located at 3-position. Therefore compound **5** should be hyperin (quercetin-3-*O*- $\beta$ -D-galactoside) .



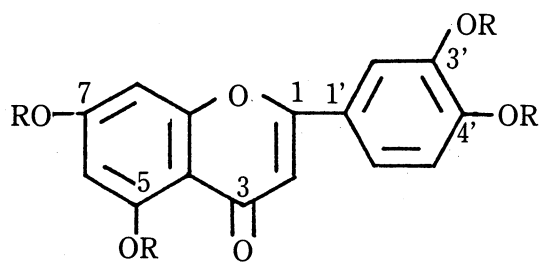
1



2 R=Glc

6 R=GlcAc<sub>4</sub>

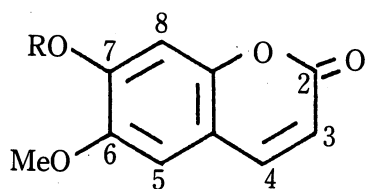
3 R=Glc

7 R=GluAc<sub>4</sub>

5 R=H R'=Glc

9 R=Ac R'=GlcAc<sub>4</sub>

10 R=R'=H



4 R=Glc

8 R=GlcAc<sub>4</sub>

## Experimental

*Extraction and Isolation.* Plant material was collected in the campus of Kagoshima University and identified by Drs. S. Higashi and M. Abe. The fresh leaves of *W. coraeensis* (2 kg) were extracted with MeOH (16 l. x 2). After concentration of the combined MeOH solns, H<sub>2</sub>O was added and the insoluble material was removed by filtration. The filtrate was extracted with Et<sub>2</sub>O and then EtOAc. The Et<sub>2</sub>O extract (16.5g) was chromatographed on a column of Si gel with CHCl<sub>3</sub>-MeOH with increasing proportions of MeOH. Elution with CHCl<sub>3</sub> gave **1** (554mg). From the fractions eluted with CHCl<sub>3</sub>-MeOH (9:1) **2** (39mg) was obtained. The EtOAc extract (10g) was subjected to CC on Si gel with CHCl<sub>3</sub>-MeOH with increasing proportions of MeOH. Elution with CHCl<sub>3</sub>-MeOH (92:8) afforded **3** (677mg). Compound **4** was obtained from the fractions eluted with CHCl<sub>3</sub>-MeOH (9:1). The fractions eluted with CHCl<sub>3</sub>-MeOH (17:3) gave **5** (10mg).

*Ursolic acid 1.* Prisms from EtOH-H<sub>2</sub>O, mp 251-252° (lit. [6] mp 285-288°); IR  $\nu_{\max}^{\text{Nujol}}$  cm<sup>-1</sup>: 3400, 1690; <sup>1</sup>H NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.8-2.4 (*m*), 3.46 (1H, *t*-like, *J* = 8 Hz), 5.50 (1H, *m*); MS *m/z*: 456 [M]<sup>+</sup>, 248, 203, 189, 133. (Found: C, 78.05; H, 10.75%. Calc. for C<sub>30</sub>H<sub>48</sub>O<sub>3</sub> · 1/4 H<sub>2</sub>O: C, 78.12; H, 10.60%.)

*$\beta$ -Sitosteryl  $\beta$ -D-glucoside 2.* A white mass from MeOH, mp 263-264° (lit. [7] mp 250-255°, 280-298°); IR  $\nu_{\max}^{\text{Nujol}}$  cm<sup>-1</sup>: 3400, 1070, 1020; <sup>1</sup>H NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.55-2.36 (*m*), 3.66-4.58 (*m*, sugar H), 5.06 (1H, *d*, *J* = 8 Hz, H-1'), *ca* 5.6 (*m*). (Found: C, 71.35; H, 10.37%. Calc. for C<sub>35</sub>H<sub>60</sub>O · 2/3 H<sub>2</sub>O: C, 71.39; H, 10.50%.) Acetylation of **2** (19 mg) with Ac<sub>2</sub>O and pyridine gave **6** (13 mg), needles from EtOH, mp 171-172° (lit. [7] mp 168-169°): IR  $\nu_{\max}^{\text{Nujol}}$  cm<sup>-1</sup>: 1750, 1220; <sup>1</sup>NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  1.98, 2.00, 2.03, 2.06 (3H each, *s*). (Found: C, 69.05; H, 9.11%. Calc. for C<sub>43</sub>H<sub>60</sub>O<sub>10</sub>: C, 69.32; H, 9.20%.)

*Secologanin dimethyl acetal 3.* An amorphous powder, [ $\alpha$ ]<sub>D</sub>-58.8° (MeOH; *c* 0.2); UV  $\lambda_{\max}^{\text{MeOH}}$  nm: 234 ( $\epsilon$  8080); IR  $\nu_{\max}^{\text{film}}$  cm<sup>-1</sup>: 3400, 1700, 1625; <sup>1</sup>H NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  1.79 (1H, *ddd*, *J* = 6, 9 and 15 Hz, H-6), 2.39 (1H, *ddd*, *J* = 7, 7 and 15 Hz, H-6), 2.83 (1H, *ddd*, *J* = 6, 6 and 8 Hz, H-9), 3.26 (3H x 2, *s*, OMe), 3.55 (3H, *s*, COOMe), 4.62 (1H, *dd*, *J* = 6 and 7 Hz, H-7), 5.00-5.40 (3H, *m*), 5.27 (1H, *d*, *J* = 8 Hz, H'-1), 5.79 (1H, *d*, *J* = 6 Hz, H-1), 7.60 (1H, *d*-like, *J* = 1 Hz, H-3); MS *m/z*: 403 [M-MeO]<sup>+</sup>, 372, 171, 165, 139, 75. (Found: *m/z* 403.1609. Calc. for C<sub>19</sub>H<sub>30</sub>O<sub>11</sub>-MeO: *m/z* 403.1604.) Compound **3** (7 mg) was treated with 2N HCl to give D-glucose which was confirmed by co-paper chromatography (solvent system: EtOAc-pyridine-H<sub>2</sub>O-HOAc, 5:5:3:1). Acetylation of **3** (20 mg) with Ac<sub>2</sub>O and pyridine yielded **7** (8 mg), an amorphous powder; IR  $\nu_{\max}^{\text{Nujol}}$  cm<sup>-1</sup>: 1755, 1710, 1630, 1220; <sup>1</sup>H

NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.84, 1.95, 1.97, 2.04 (3H x 4, s). (Found:  $m/z$  571.1994. Calc. for  $\text{C}_{27}\text{H}_{38}\text{O}_{15}\text{-MeO}$ :  $m/z$  571.2025.)

**Scopolin 4.** Needles from MeOH, 216-220° (lit. [6] mp 218°); IR  $\nu_{\text{max}}^{\text{Nujol}}$   $\text{cm}^{-1}$ : 3350, 1725, 1700, 1615, 1565, 1505;  $^1\text{H}$  NMR (100 MHz,  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  3.74 (3H, s, OMe), 3.88-4.60 (6H, *m*, sugar H), 5.64 (1H, *W*  $\frac{1}{2}$  12 Hz, H-1'), 6.30 (1H, *d*,  $J=9.5$  Hz, H-3), 7.01 (1H, s, H-8), 7.43 (1H, s, H-5), 7.64 (1H, *d*,  $J=9.5$  Hz, H-4). (Found: C, 50.90; 5.07%. Calc. for  $\text{C}_{16}\text{H}_{18}\text{O}_9 \cdot 1\frac{1}{3}\text{H}_2\text{O}$ : C, 50.79; H, 5.51%.) Acetylation of 4 (42 mg) with  $\text{Ac}_2\text{O}$  and pyridine gave 8 (30 mg), prisms form EtOH, mp 169-169.8° (lit. [6] mp 166° or mp 184-185°); IR  $\nu_{\text{max}}^{\text{Nujol}}$   $\text{cm}^{-1}$ : 1760-1740, 1620, 1570, 1510, 915, 890, 825;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.05, 2.06, 2.08, 2.14 (3H each, s); MS  $m/z$ : 522  $[\text{M}]^+$ . (Found: C, 55.22; H, 5.08%. Calc. for  $\text{C}_{24}\text{H}_{26}\text{O}_{13}$ : C, 55.17; H, 5.02%.)

**Hyperin 5.** Yellow crystals from MeOH, mp 238-240° (lit. [8] mp 238°; UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm: 257 ( $\epsilon$  18000), 359 ( $\epsilon$  15000);  $\lambda_{\text{max}}^{\text{MeOH-AcONa}}$  nm: 269, 368; IR  $\nu_{\text{max}}^{\text{MeOH}}$   $\text{cm}^{-1}$ : 3400, 1655, 1605, 1550, 1500;  $^1\text{H}$  NMR (100 MHz,  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  4.18-4.98 (6H, *m*, sugar), 6.10 (1H, *d*,  $J=8$  Hz, H-1'), 6.72 and 6.77 (1H each, *d*,  $J=2$  Hz, H-6 and H-8), 7.38 (1H, *d*,  $J=8$  Hz, H-5), 8.22 (1H, *dd*,  $J=2$  and 8 Hz, H-6), 8.58 (1H, *d*,  $J=2$  Hz, H-2). (Found: C, 52.10; H, 4.44%. Calc. for  $\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot \text{H}_2\text{O}$ : C, 52.47; H, 4.58%.) Acetylation of 5 (21 mg) with  $\text{Ac}_2\text{O}$  and pyridine gave 9 (20 mg), an amorphous powder; IR  $\nu_{\text{max}}^{\text{Nujol}}$   $\text{cm}^{-1}$ : 1775, 1750, 1210;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.86 and 1.96 (3H each, s), 2.11 (3H x 2, s), 2.28 (3H, s), 2.32 (3H x 2, s), 2.41 (3H, s). (Found: C, 55.56; H, 4.56%. Calc. for  $\text{C}_{37}\text{H}_{36}\text{O}_{20}$ : C, 55.50; H, 4.53%.) To a soln of 5 (6.3 mg) in MeOH (1 ml), was added 2N HCl (0.5 ml) and the mixture was refluxed for 4 hr. The reaction mixture was diluted with  $\text{H}_2\text{O}$ . The resulting precipitate was recrystallized from MeOH to give quercetin 10 (0.8 mg), yellow needles, mp  $>300^\circ$ ; IR  $\nu_{\text{max}}^{\text{Nujol}}$   $\text{cm}^{-1}$ : 3350, 1660, 1620, 1560, 1520. The Aq. soln was neutralized with Amberlite IRA-45 (3g) to give a residue. Paper chromatography of the residue showed the presence of D-glucose (solvent system: EtOAc-pyridine- $\text{H}_2\text{O}$ -HOAc, 5: 5: 3: 1) .

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