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# On the Constituents of the Leaves of Weigela coraeensis

IWAGAWA Tetsuo, HASE Tsunao

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ON THE CONSTITUENTS OF THE LEAVES OF
WEIGELA CORAEENSIS

Tetsuo IWAGAWA and Tsunao HASE*

(Received Sep. 10, 1988)

Abstract

From the leaves of Weigela coraeensis ursolic acid, β-sitosteryl β-D-glucoside, scopolin, secologanin dimethyl acetal and hyperin (quercetin-3-O-β-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} · 1/4H_{2}O. It gave a positive Liebermann-Burchard's reaction. The IR spectrum showed absorption bands for a hydroxyl group at 3400 cm⁻¹ and a carboxyl group at 1690 cm⁻¹. The ¹H NMR spectrum indicated signals of a proton attached to a carbon bearing hydroxyl group at δ 3.46 (1H, t-like, J=8 Hz) and an olefinic proton at δ 5.50 (1H, m) besides those of typical triterpenoids at δ 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 ¹H NMR spectra

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Fresh leaves of *W. coraeensis* (1 kg) extd. with MeOH (16 ℓ, x 2) concd. added H₂O extd. with Et₂O

Et₂O extract (16.5 g) Si gel chromatog.

1 (554 mg)

Aq. soln extd. with EtOAc

2 (59 mg)

EtOAc extract (10 g) Si gel chromatog.

3 (677 mg) 4 (107 mg) 5 (10 mg)

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 C₃₅H₆₀O₆·2/3H₂O. The IR spectrum showed a strong hydroxyl absorption at 3400 cm⁻¹. The ¹H NMR spectrum showed a typical phytosterol skeleton at δ 0.55-2.36. On acetylation with acetic anhydride and pyridine, compound 2 gave needles (6), mp 171-172° with a molecular formula C₄₃H₆₀O₁₉. The ¹H NMR spectrum of the acetate indicated the presence of four acetoxyl groups at δ 1.98-2.06 (3H x 4, s). The above results suggested that compound 2 was β-sitosteryl β-D-glucoside. The spectral and physical data of 2 were in agreement with those of β-sitosteryl β-D-glucoside.

Compound (3) was an amorphous powder with a molecular formula C₁₉H₃₀O₁₁. Acid hydrolysis yielded D-glucose and a brown polymerized product like other iridoids. The UV absorption maximum at 234 nm (ε 8080) and the IR absorption bands at 1700 and 1625 cm⁻¹ were characteristic of a conjugated enol-ether system. The ¹H NMR spectrum showed signals due to a C-3 proton at δ 7.60 (s), vinylic protons at δ 5.00-5.40 (3H, m) and carbomethoxyl protons at δ 3.55 (3H, s) together with those of an anomeric proton at δ 5.27 (d, J = 8 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 1H NMR spectrum, two singlets due to methoxyl protons at δ 3.26 (3H x 2) and signals assignable to a -CHCH₂CH- moiety at δ 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 C₂₇H₃₈O₁₅. 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° with a molecular formula C₁₆H₁₈O₅ • 1 1/3H₂O. Absorption bands at 1725, 1700, 1615 and 1565 and 1505 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 1H NMR spectrum. The signals corresponding to C-3 and C-4 protons appeared as an AB system at δ 6.30 and 7.64 (J = 9.5 Hz). Two singlets at δ 7.01 and 7.43 (1H each) were attributable to C-8 and C-5 protons, respectively. The 1H NMR spectrum also showed the presence of a methoxyl group at δ 3.74 (3H, s) and an anomeric proton at δ 5.64 (1H, W ½ 12 Hz). Compound 4 was treated with acetic anhydride and pyridine to give a tetra-acetate (8), mp 169-169.8° with a molecular formula C₂₄H₂₆O₁₃. The above date suggested that compound 4 was scopolin. The spectral and physical data of 8 were identical with those of scopolin acetate[4].

Compound (5) was yellow crystals, mp 238-240° and had a molecular formula C₂₁H₂₀O₁₂ • H₂O. The UV spectrum had absorption maxima at 257 nm (ε 18000) and 359 nm (ε 15000). The IR spectrum showed absorption bands of a hydroxyl group at 3400 cm⁻¹, a conjugated carbonyl at 1655 cm⁻¹ and a phenyl group at 1605 and 1500 cm⁻¹. The above data suggested that compound 5 was a flavonoid glycoside. An AB system at δ 6.72 (1H, J = 2 Hz) and 6.77 (1H, J = 2 Hz) in the 1H NMR spectrum were due to C-6 and C-8 protons, respectively. Signals at δ 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 C₃₇H₃₈O₂₀. The 1H NMR spectrum of the latter showed the presence of four alcoholic acetoxy groups at δ 1.86-2.11 (3H x 4, s) and four phenolic acetoxy groups at δ 2.28-2.41 (3H x 4, s). Hydrolysis of 5 with 2N HCl afforded D-galactose and quercetin (10), mp >300°, 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-β-D-galactoside).
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1. [Chemical structure 1]

2. $R = \text{Glc}$

3. $R = \text{Glc}$

4. $R = \text{Glc}$

6. $R = \text{GlcAc}_4$

7. $R = \text{GluAc}_4$

8. $R = \text{GlcAc}_4$

9. $R = \text{Ac} \quad R' = \text{GlcAc}_4$

10. $R = R' = \text{H}$
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 ℥ x 2). After concentration of the combined MeOH solns, H₂O was added and the insoluble material was removed by filtration. The filtrate was extracted with Et₂O and then EtOAc. The Et₂O extract (16.5g) was chromatographed on a column of Si gel with CHCl₃-MeOH with increasing proportions of MeOH. Elution with CHCl₃ gave 1 (554mg). From the fractions eluted with CHCl₃-MeOH (9:1) 2 (39mg) was obtained. The EtOAc extract (10g) was subjected to CC on Si gel with CHCl₃-MeOH with increasing proportions of MeOH. Elution with CHCl₃-MeOH (92 : 8) afforded 3 (677mg). Compound 4 was obtained from the fractions eluted with CHCl₃-MeOH (9 : 1). The fractions eluted with CHCl₃-MeOH (17 : 3) gave 5 (10mg).

Ursolic acid 1. Prisms from EtOH-H₂O, mp 251-252° (lit. [6] mp 285-288°); IR ν₅₅₀ to cm⁻¹: 3400, 1690; ¹H NMR (100 MHz, C₅D₅N): δ 0.8-2.4 (m), 3.46 (1H, t-like, J = 8 Hz), 5.50 (1H, m); MS m/z: 456 [M]+, 248, 203, 189, 133. (Found: C, 78.05; H, 10.75%. Calc. for C₃₇H₅₈O₃: C, 78.12; H, 10.60%.)

β-Sitosteryl β-D-glucoside 2. A white mass from MeOH, mp 263-264° (lit. [7] mp 250-255°, 280-289°); IR ν₅₅₀ to cm⁻¹: 3400, 1070, 1020; ¹H NMR (100 MHz, C₅D₅N): δ 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 C₃₅H₆₁O₂: 2/3 H₂O: C, 71.39; H, 10.50%). Acetylation of 2 (19mg) with Ac₂O and pyridine gave 6 (13mg), needles from EtOH, mp 171-172° (lit. [7] mp 168-169°): IR ν₅₅₀ to cm⁻¹: 1750, 1220; ¹H NMR (100 MHz, CDCl₃): δ 1.98, 2.00, 2.03, 2.06 (3H each, s). (Found: C, 69.05; H, 9.11%. Calc. for C₄₅H₆₃O₁₁: C, 69.32; H, 9.20%).

Secologanin dimethyl acetal 3. An amorphous powder, [α]D-58.8° (MeOH; c 0.2); UV λₘₐₓ MeOH: 234 (ε 8080); IR ν₅₅₀ to cm⁻¹: 3400, 1700, 1625; ¹H NMR (100 MHz CDCl₃): δ 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]+, 372, 171, 165, 139, 75. (Found: m/z 403.1609. Calc. for C₁₉H₂₉O₁₁-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-H₂O-HOAc, 5 : 5 : 3 : 1). Acetylation of 3 (20mg) with Ac₂O and pyridine yielded 7 (8mg), an amorphous powder; IR ν₅₅₀ to cm⁻¹: 1755, 1710, 1630, 1220; ¹H
On the Constituents of the Leaves of *Weigela coreaeensis*

NMR (100 MHz, CDCl₃): δ 1.84, 1.95, 1.97, 2.04 (3H x 4, s). (Found: m/z 571.1994. Calc. for C₂₇H₃₈O₁₅-MeO: m/z 571.2025.)

**Scopolin 4.** Needles from MeOH, 216-220° (lit. [6] mp 218°); IR ν̇(ν̈max cm⁻¹): 3350, 1725, 1700, 1615, 1565, 1505; ¹H NMR (100 MHz, C₅D₅N): δ 3.74 (3H, s, OMe), 3.88-4.60 (6H, m, sugar H), 5.64 (1H, W½ 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 C₁₆H₁₈O₉·1/₂H₂O: C, 50.79; H, 5.51%). Acetylation of 4 (42 mg) with Ac₂O and pyridine gave 8 (30 mg), prisms from EtOH, mp 169-169.8° (lit. [6] mp 166° or mp 184-185°); IR ν̇(ν̈max cm⁻¹): 1760-1740, 1620, 1570, 1510, 915, 890, 825; ¹H NMR (100 MHz, CDCl₃): δ 2.05, 2.06, 2.08, 2.14 (3H each, s); MS m/z: 522 [M]⁺. (Found: C, 55.22; H, 5.08%. Calc. for C₂₄H₂₆O₁₃: C, 55.17; H, 5.02%.)

**Hyperin 5.** Yellow crystals from MeOH, mp 238-240° (lit. [8] mp 238°; UV λ̈ max nm: 257 (ε 18000), 359 (ε 15000); λ̈ max MeOH nm: 269, 368; IR ν̇(ν̈max cm⁻¹): 3400, 1655, 1605, 1550, 1500; ¹H NMR (100 MHz, C₅D₅N): δ 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 C₂₁H₂₁O₁₂·H₂O: C, 52.47; H, 4.58%). Acetylation of 5 (21 mg) with Ac₂O and pyridine gave 9 (20 mg), an amorphous powder; IR ν̇(ν̈max cm⁻¹): 1775, 1750, 1210; ¹H NMR (100 MHz, CDCl₃): δ 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 C₃₆H₃₆O₁₅: 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 recrystallized from MeOH to give quercetin 10 (0.8 mg), yellow needles, mp > 300°; IR ν̇(ν̈max 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-H₂O-HOAc, 5: 5: 3: 1).

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**References**


Tetsuo Iwagawa and Tsunao Hase