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5-*O*-glucosyldihydroflavones from the leaves of *Helicia cochinchinensis*

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Abstract

From the leaves of *Helicia cochinchinensis*, collected on Okinawa Island, seven phenolic glucosides and two terpenic glucosides were isolated. Five of the phenolic glucosides were previously known, being identified with *p*-coumaric and ferulic acids glucosyl esters, rhodioloside, helicidiol, and naringenin 5-*O*-β-D-glucopyranoside. The structures of two other phenolic glucosides, named heliciosides A and B, were elucidated to be 5-*O*-β-D-glucosides of 3-hydroxyflavanone, namely aromadendrin and taxifolin, by means of spectroscopic analyses. The two terpenic glucosides were identified with ampelopsisionoside and icariside C_1.

Keywords: *Helicia cochinchinensis*; Proteaceae; Flavanonol glucoside; Heliciosides A and B; Helicidol; Alloside

1. Introduction

As part of our ongoing studies of Okinawan plant resources, we investigated the constituents of *Helicia cochinchinensis* (Proteaceae) collected from Okinawa Island. *H. cochinchinensis* is an evergreen tree and grows up to 20 m in height. More than 1200 species in 55 genera belong to the Proteaceae and are distributed mainly in Australia and South Africa. Of these, 40 species in the *Helicia* genus are found both in Australia and in the tropical area of Asia. Only *H. cochinchinensis* has been found to grow wild in the subtropical area of Japan (Hatusima, 1975) and several species of Proteaceae are imported for ornamental or commercial purposes (Hatusima and Amano, 1994). An extract of a related plant, *H. nitida*, is known as "Bessiestroop" in the Cape Area of South Africa, and is used as a tonic and a cough treatment (Verotta et al., 1999). It is noteworthy that Proteaceous plants are characteristic in containing a relatively rare sugar, i.e., allopyranose in its glycosidic form (Beylis et al., 1971).

From the *n*-BuOH-soluble fraction of a MeOH extract of the leaves of *H. cochinchinensis*, nine compounds were isolated (**1**–**9**). Five were found to be known phenolic compounds, namely *p*-coumaric (Ina et al., 1987) and ferulic (Hashimoto et al., 1992) acid glucosyl esters (**3** and **4**, respectively), rhodioloside (**5**) (Miyase et al., 1987), helicidol (4-hydroxybenzyl alcohol 4-*O*-β-D-allopyranoside) (**6**) (Shide and Rücker, 1986), and naringenin 5-*O*-β-D-glucopyranoside (**7**) (Çubukçu and Yüksel, 1982). Two known terpene glucosides, such as ampelopsisionoside (**8**) (Inada et al., 1991; Otsuka et al., 2001), and icariside C_1 (**9**) (Miyase et al., 1987), were also isolated. Compounds **1** and **2** were new being 5-*O*-glucopyranosides of 3-hydroxyflavanone. This paper deals with the isolation and structural elucidation of the new compounds.

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2. Results and discussion

Air-dried leaves of *H. cochinchinensis* were extracted with MeOH three times with the concentrated MeOH extract partitioned with solvents of increasing polarity. The *n*-BuOH-soluble fraction from this was separated by sequential column chromatography (CC) on a highly porous synthetic resin (Diaion HP-20), normal silica gel and reversed-phase octadecyl silica gel (ODS) CC, as well as by droplet counter-current chromatography (DCCC) to afford seven known compounds and two new phenolic glucosides, to which the trivial names, heliciosides A (**1**) and B (**2**), are assigned. The details and yields are given in Section 4.

Helicioside A (**1**), $[\alpha]_D + 31.0°$, was isolated as colorless needles and, by application of negative-ion high-resolution (HR)-FAB-MS, its elemental composition was determined to be $C_{21}H_{22}O_{11}$, with the degree of unsaturation being 11. The IR spectrum showed absorption bands attributable to a glycosidic feature (3305 and 1075 cm^{-1}), a carbonyl group (1677 cm^{-1}), and aromatic ring(s) (1620, 1583 and 1529 cm^{-1}). The UV spectrum also supported the presence of aromatic ring(s). Analysis of the ^1H and ^{13}C NMR (Table 1) spectra, including application of two-dimensional NMR spectroscopy showed six signals attributable to β-glucopyranose, together with *para*- and *tetra*-substituted aromatic rings [δ_H 6.79 and 7.31 (each 2H, *d*, $J = 9$ Hz), and δ_H 6.04 and 6.36 (each 1H, *d*, $J = 2$ Hz), respectively], and two oxygenated methines [δ_C 72.5 with δ_H 4.34 (d, $J = 11$ Hz), and δ_C 82.2 with δ_H 4.99 (d, $J = 11$ Hz)], and a carbonyl carbon atom (δ_C 191.1). This evidence led to the conclusion that compound **1** is a flavonoid derivative, namely 3,5,7,4′-tetrahydroxyflavanone with a β-glucopyranose moiety. In the ^1H NMR spectrum (DMSO-d_6), a highly-deshielded chelated signal, which is generally assigned as the 5-OH group of flavonoids, was not observed. Thus, the hydroxyl group at C-5 was presumed to be glucosylated. This assumption was made on inspection of the heteronuclear multiple bond coherence (HMBC) cross peaks (Fig. 2). First, H-2′ (6′) (δ_H 7.31) had cross-peaks with C-2 (δ_C 82.2), and its proton (δ_H 4.99) had cross-peaks with C-4 (δ_C 191.1) and 9 (δ_C 163.4). Second, since δ_H 6.04 (d, $J = 2$ Hz) had a cross-peak at C-9, this proton was assigned as H-8. Thus, δ_H 6.36 (d, $J = 2$ Hz) was assigned as H-6. Finally, the H-6 resonance had cross-peaks with C-7 and C-5 (δ_C 160.1), with the latter also having a cross-peak with the anomeric proton at δ_H 4.80. Therefore, the sugar moiety was confirmed to be linked to the hydroxyl group at the C-5 position. This was further supported by the difference nuclear Overhauser enhancement experiment, in which irradiation of the anomeric proton enhanced the signal strength of the H-6 proton. The large coupling constant ($J = 11$ Hz) between H-2 and H-3 suggested that they were in a *trans* geometry, and in the CD spectrum, negative and positive Cotton effects observed at 304 nm ($\Delta\varepsilon$ −10.9) and 335 nm ($\Delta\varepsilon$ +5.40), respectively, were diagnostically the same as those of astilbin ($\Delta\varepsilon$ −14.8 (293) and +4.24 (326)), which possesses a 2*R*,3*R* configuration (Kasai et al., 1988). Since hydrolysis liberated D-glucose, the structure of helicioside A was elucidated to be (2*R*,3*R*)-3,5,7,4′-tetrahydroxyflavanone 5-*O*-β-D-glucopyranoside (**1**), namely aromadendrin 5-*O*-β-D-glucopyranoside, as shown in Fig. 1.

Table 1
^{13}C NMR spectroscopic data for compounds **1** and **2**

C	1	2	
2	82.2	82.4	(84.4)[b]
3	72.5	72.7	(74.7)
4	191.1	190.9	(193.6)
5	160.1	161.1	(161.9)
6	97.9	98.0	(100.1)
7	164.8	164.9	(167.3)
8	97.1	97.1	(99.2)
9	163.4	163.4	(165.9)
10	103.4	103.3	(104.9)
1′	127.6	128.1	(130.0)
2′	129.2	115.0[a]	(115.9)[c]
3′	114.8	145.6	(147.1)
4′	157.6	144.8	(146.3)
5′	114.8	115.1[a]	(116.2)[c]
6′	129.2	119.1	(120.9)
1″	102.0	102.0	(104.1)
2″	73.3	73.3	(74.7)
3″	77.3	77.3	(78.6)
4″	69.5	69.5	(71.3)
5″	76.0	76.0	(77.4)
6″	60.6	60.6	(62.6)

[a,c] Maybe exchangeable;
[b] The figures in parentheses were obtained for a CD_3OD solution.

Helicioside B (**2**), $[\alpha]_D - 64.6°$, was isolated as an amorphous powder and, by negative-ion high-resolution (HR)-FAB-MS, its elemental composition was determined to be $C_{21}H_{22}O_{12}$. In the ^1H NMR spectrum, the AA′BB′-type coupling system in the B-ring of helicioside A was replaced by an ABX-type coupling system [δ_H 6.80 (1H, *d*, $J = 8$ Hz, H-5′), 6.84 (1H, *dd*, $J = 8$, 2 Hz, H-6′) and 6.96 (1H, *d*, $J = 8$ Hz, H-2′)]. Thus, the structure of heliocoside B was assumed to be the 3′-hydroxy derivative of helicioside A. This assumption was supported by the spectroscopic data reported in Section 4. Therefore, helicioside B was elucidated to be (2*R*,3*R*)-3,5,7,3′,4′-pentahydroxyflavanone 5-*O*-β-D-glucopyranoside (**2**), namely taxifolin 5-*O*-β-D-glucopyranoside, as shown in Fig. 1.

3. Conclusion

The occurrence of dihydroflavonols is relatively rare, when compared with that of flavones and flavonols, and furthermore these are not many 5-*O*-glucosides of dihydroflavonols found in nature (Harborne and Mabry, 1982). In this experiment, two new dihydroflavonol 5-*O*-β-D-glucopyranosides, named heliciosides A and B (**1** and **2**), and naringenin (flavanone) 5-*O*-β-D-glucopyranoside (**7**) were isolated.

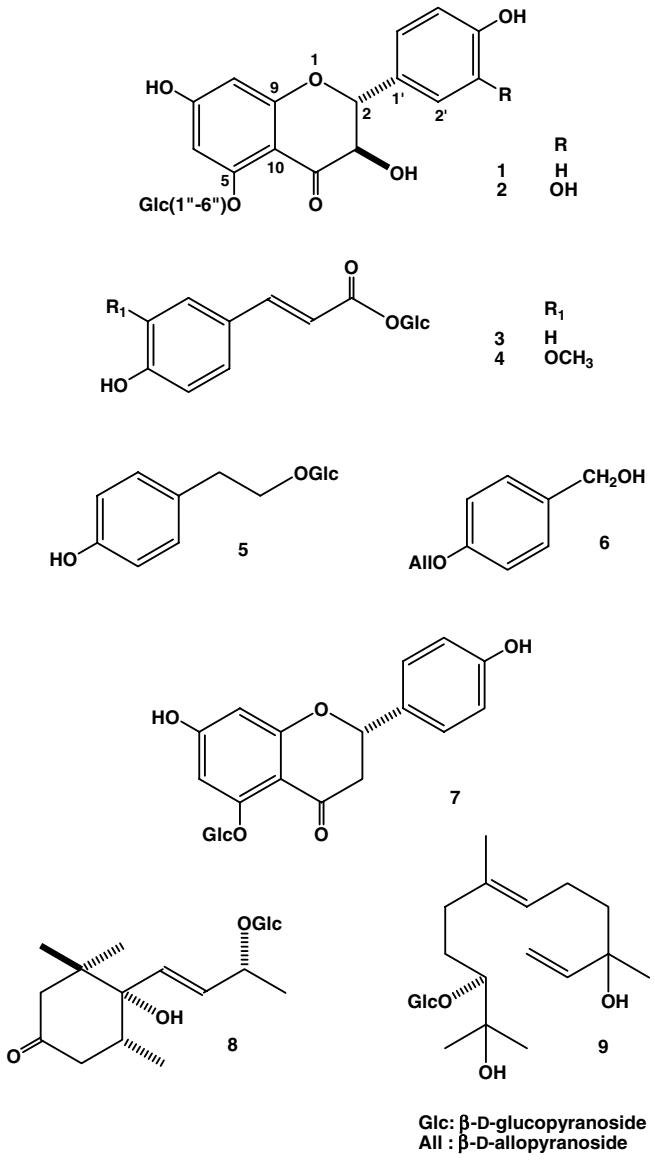

Fig. 1. Structures.

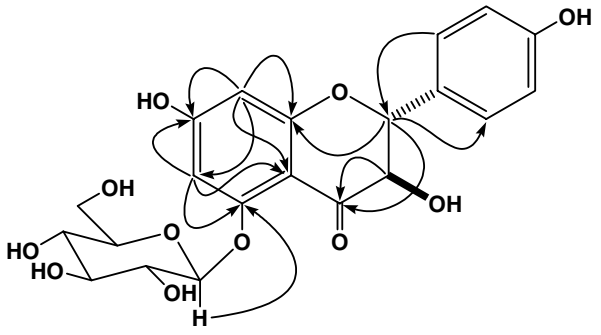

Fig. 2. Diagnostic HMBC correlations for helicioside A (**1**). Arrowheads denote carbon atoms tails proton atoms.

Allopyranose is an uncommon hexopyranose and the third glucopyranose epimer, found in nature, from *Protea rubropilosa* (Proteaceae) (Beylis et al., 1971). Isolation of its glycosidic form, helicidol (**6**) was first reported from *Helicia erratica* (Shide and Rücker, 1986). Therefore, the presence of allopyranose and its glycosides is expected to be a characteristic of Proteaceous plants. Isolation of helicidol from *H. cochinchinensis* is thus of interest from the chemotaxonomic point of view.

4. Experimental

4.1. General experimental procedures

A highly porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku (Tokyo, Japan). Silica gel CC was performed on silica gel 60 (E. Merck, Darmstadt, Germany) and reversed-phase [octadecyl silica gel (ODS)] open CC (RPCC) on Cosmosil 75C_{18}-OPN (Nacalai Tesque, Kyoto) [$\Phi = 50$ mm, $L = 25$ cm, linear gradient: MeOH–H_2O (1:9, 1 l) → (7:3, 1 l), fractions of 10 g being collected]. The DCCC (Tokyo Rikakikai, Tokyo, Japan) was equipped with 500 glass columns ($\Phi = 2$ mm, $L = 40$ cm), and lower and upper layers of a solvent mixture of $CHCl_3$–MeOH–H_2O–*n*-PrOH (9:12:8:2) were used as the stationary and mobile phases, respectively. Five gram fractions were collected and numbered according to their order of elution with the mobile phase. HPLC was performed on ODS (Inertsil; GL Science, Tokyo, Japan; $\Phi = 6$ mm, $L = 250$ mm), and the eluate (MeOH–H_2O, 1.6 ml/min) was monitored with a UV detector at 254 nm and a reflective index monitor.

Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured on a Union Giken PM-101 digital polarimeter with a 1 cm cell. IR spectra were measured on a Horiba FT-710 Fourier transform infrared spectrophotometer and UV spectra on a JASCO V-520 UV/Vis spectrophotometer. CD spectra were recorded on a JASCO J-720 spectropolarimeter. ^1H and ^{13}C NMR spectra were taken on a JEOL JNM α-400 spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane (TMS) as an internal standard. Negative-ion HR-FAB-MS spectra were taken on a JEOL JMS SX-102 spectrometer.

4.2. Plant material

Leaves of *H. cochinchinensis* Lour. (Porteaceae) were collected in Kunigami-son, Kunigami-gun, Okinawa, Japan, in July 1997, and a voucher specimen was deposited in the Herbarium of the Department of Pharmacognosy, Graduate School of Biomedical Sciences, Hiroshima University (97-HC-Okinawa-0716).

4.3. Extraction and fractionation

Air-dried leaves of *H. cochinchinensis* (3.12 kg) were extracted three times with MeOH. The MeOH extract was concentrated down to ~1.5 l with H_2O (75 ml) then

added. This solution was next washed with 1.5 l of *n*-hexane (23.6 g) with the methanolic layer concentrated to a viscous gum. The gummy residue was suspended in H_2O (3.0 l), and then extracted successively with 3 l each of EtOAc and *n*-BuOH to afford 41.7 g and 96.2 g of EtOAc- and *n*-BuOH-soluble fractions, respectively. Evaporation of the H_2O solubles also gave 300 g of residue. The *n*-BuOH-soluble fraction was subjected to highly porous synthetic resin (Diaion HP-20) CC (Mitsubishi Chemical Co. Ltd.; $\Phi = 80$ mm, $L = 55$ cm), using H_2O–MeOH (4:1, 6 l), (2:3, 6 l), (3:2, 6 l), and (1:4, 6 l) and MeOH (6 l) as eluant, with 2-l fractions collected. The residue (9.28 g) of the MeOH–H_2O (1:4) eluate was subjected to silica gel (350 g) CC with increasing amounts of MeOH in $CHCl_3$ [$CHCl_3$ (1 l), $CHCl_3$–MeOH (99:1, 3 l), (39:1, 3 l), (19:1, 3 l), (37:3, 3 l), (9:1, 3 l), (17:3, 3 l), (4:1, 3 l), (3:1, 3 l), and (7:3, 3 l)], and then $CHCl_3$–MeOH–H_2O (70:30:4, 3 l), with 500-ml fractions were collected]. The residue (0.43 g) of the 5% MeOH–H_2O (5:95) eluate was subjected to RPCC and, from fractions 87–90, ferulic acid glucosyl ester (**4**) (17 mg) was obtained as an amorphous powder. The residue (1.91 g) of the 10%–15% MeOH in H_2O eluate was subjected to RPCC, with the residue of fractions 30–34 (106 mg) purified by DCCC to give crude hilicidol in fractions 16–24 (83 mg), which was finally purified by HPLC with MeOH-H_2O (3:37) to give hilicidol (**6**) (39 mg). The residues (151 mg) of fractions 54–63 obtained on RPCC was purified by DCCC to afford rhodioloside (= salidroside) (**5**) (66 mg in fractions 25–30). The residue (288 mg) of fractions 74–86 obtained on RPCC was subjected to DCCC and that of fractions 35–48 was recrystallized from MeOH to give *p*-coumaric acid glucosyl ester (**3**) (97 mg) as colorless cubes. The residue (1.29 g) of the MeOH–H_2O (1:4) eluate obtained on silica gel CC was subjected to RPCC, and then the residue of fractions 75–83 (106 mg) was purified by DCCC to give helicioside A (**1**) (34 mg) in fractions 16–21.

The residue (8.14 g) of the MeOH–H_2O (2:3) eluate obtained on Diaion HP-20 CC was subjected to silica gel (350 g) CC with the same solvent system as that used for the residue of the MeOH–H_2O (1:4) eluate. The residue (1.29 g) of the 7.5%–10% MeOH in H_2O eluate was subjected to RPCC, with the residue of fractions 88–101 (421 mg) purified by DCCC to give ampelopsisionoside (**8**) (270 mg) in fractions 72–87. The residue (1.19 g) of the 15–20% MeOH in H_2O eluate obtained on silica gel CC was subjected to RPCC, with the residue of fractions 91–95 recrystallized from MeOH to give helicioside B (**2**) (118 mg) as colorless needles.

The residue (16.9 g) of the MeOH–H_2O (6:4) eluate obtained on Diaion HP-20 CC was subjected to silica gel (330 g) CC with increasing amounts of MeOH in $CHCl_3$ ($CHCl_3$ (2 l), $CHCl_3$–MeOH (99:1, 3 l), (49:1, 3 l), (24:1, 3 l), (47:3, 3 l), (23:1, 3 l), (9:1, 3 l), (7:1, 3 l), (17:3, 3 l), (4:1, 3 l), (3:1, 3 l), and (7:3, 3 l)), and then $CHCl_3$–MeOH–H_2O (70:30:4, 3 l), and 500-ml fractions were collected. The residue (2.04 g) of the 6–8% MeOH in H_2O eluate was subjected to RPCC. The residue of fractions 116–123 was recrystallized from MeOH gave naringenin 5-*O*-β-D-glucopyranoside (helichrysin A) (**7**) (99 mg) as colorless needles. The residue (111 mg) of fractions 197–205 was purified by DCCC to give icariside C_1 (**9**) (40 mg) in fractions 116–140.

4.4. Characterization data

4.4.1. Helicioside A (*1*)

Colorless needles (MeOH), m.p. 252.5–254.0 °C, $[\alpha]_D^{28} + 31.0$ ($c = 0.71$, pyridine). IR ν_{max} (KBr): 3305, 2927, 1677, 1620, 1583, 1529, 1453, 1254, 1123, 1075, 1043, 992, 826 cm^{-1}. UV λ_{max} (MeOH): 226 (4.32), 284 (4.12) nm ($\log\varepsilon$). ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.20–3.37 (4H, *m*, H-2″, 3″, 4″ and 5″), 3.54 (1H, *dd*, $J = 12$, 6 Hz, H-6″a), 3.77 (1H, *dd*, $J = 12$, 2 Hz, H-6″b), 4.34 (1H, *d*, $J = 11$ Hz, H-3), 4.80 (1H, *d*, $J = 7$ Hz, H-1″), 4.99 (1H, *d*, $J = 11$ Hz, H-2), 6.04 (1H, *d*, $J = 2$ Hz, H-8), 6.36 (1 H, *d*, $J = 2$ Hz, H-6), 6.79 (2H, *d*, $J = 9$ Hz, H-3′ and 5′), 7.31 (2H, *d*, $J = 9$ Hz, H-2′ and 6′). For ^{13}C NMR (DMSO-d_6, 100 MHz) spectroscopic assignments, see Table 1. CD (MeOH): $\Delta\varepsilon$ (nm) −10.9 (304), +5.40 (335) ($c = 4.36 \times 10^{-5}$ M). HR-FAB-MS (negative-ion mode) *m/z*: 449.1050 $[M - H]^-$ (Calc. for $C_{21}H_{21}O_{11}$: 449.1084).

4.4.2. Helicioside B (*2*)

Amorphous powder, $[\alpha]_D^{22} - 64.6$ ($c = 1.35$, MeOH). IR ν_{max} (film): 3345, 2931, 1665, 1615, 1529, 1452, 1286, 1250, 1202, 1168 cm^{-1}. UV λ_{max} (MeOH): 226 (4.19), 285 (4.10) nm ($\log\varepsilon$). ^1H NMR (CD_3OD, 400 MHz) δ:3.30–3.50 (4H, *m*, H-2″, 3″ and 5″), 3.59 (1H, *dd*, $J = 8$, 8 Hz, H-4″), 3.75 (1H, *dd*, $J = 12$, 5 Hz, H-6″a), 3.94 (1H, *dd*, $J = 12$, 2 Hz, H-6″b), 4.34 (1H, *d*, $J = 11$ Hz, H-3), 4.82 (1H, *d*, $J = 7$ Hz, H-1″), 4.89 (1H, *d*, $J = 11$ Hz, H-2), 6.09 (1H, *d*, $J = 2$ Hz, H-8), 6.46 (1H, *d*, $J = 2$ Hz, H-6), 6.80 (1H, *d*, $J = 8$ Hz, H-5′), 6.84 (1H, *dd*, $J = 8$, 2 Hz, H-6′), 6.96 (1H, *d*, $J = 8$ Hz, H-2′). ^{13}C NMR (DMSO-d_6 and CD_3OD, 100 MHz): Table 1. CD (MeOH): $\Delta\varepsilon$ (nm) −8.14 (301), +3.45 (335) ($c = 7.23 \times 10^{-5}$ M). HR-FAB-MS (negative-ion mode) *m/z*: 465.1059 $[M - H]^-$ (Calc. for $C_{21}H_{21}O_{12}$: 465.1033).

4.4.3. Acid hydrolysis

Heliciosides A (**1**) and B (**2**) (5 mg each) were hydrolyzed with 1 ml of 2 N H_2SO_4 for 2 h on a water-bath. The hydrolyzates were neutralized with a mixed bed resin (M-3) and then dried. The residues were treated with cysteine methyl ester in pyridine to yield thiazolidine derivatives according to the reported procedure (Hara et al., 1987; Miyaichi et al., 1995), with the resulting derivatives analyzed by silica gel TLC ($CHCl_3$–MeOH–H_2O, 15:6:1) (R_f 0.54 and 0.46, and 0.52 and 0.45, respectively. Authentic thiazolidine derivatives obtained from D- and L-glucoses gave spots at R_f 0.52 and 0.47, and 0.49, respectively.

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