

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, rhodiolide, helicidol, 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 ampelopsinioside and icariside C₁.

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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), rhodiolide (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 ampelopsinioside (8) (Inada et al., 1991; Otsuka et al., 2001), and icariside C₁ (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, helicosides A (**1**) and B (**2**), are assigned. The details and yields are given in Section 4.

Helicoside A (**1**), $[\alpha]_D + 31.0^\circ$, 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*, $J = 9\text{ Hz}$), and δ_{H} 6.04 and 6.36 (each 1H, *d*, $J = 2\text{ Hz}$), respectively], and two oxygenated methines [δ_{C} 72.5 with δ_{H} 4.34 (*d*, $J = 11\text{ Hz}$), and δ_{C} 82.2 with δ_{H} 4.99 (*d*, $J = 11\text{ Hz}$)], 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-desielded 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*, $J = 2\text{ Hz}$) had a cross-peak at C-9, this proton was assigned as H-8. Thus, δ_{H} 6.36 (*d*, $J = 2\text{ Hz}$) 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 ($J = 11\text{ Hz}$) 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 ($\Delta\epsilon -10.9$) and 335 nm ($\Delta\epsilon +5.40$), respectively, were diagnostically the same as those of astilbin ($\Delta\epsilon -14.8$ (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 helicoside 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.

Helicoside B (**2**), $[\alpha]_D - 64.6^\circ$, 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 helicoside A was replaced by an ABX-type coupling system [δ_{H} 6.80 (1H, *d*, $J = 8\text{ Hz}$, H-5'), 6.84 (1H, *dd*, $J = 8, 2\text{ Hz}$, H-6') and 6.96 (1H, *d*, $J = 8\text{ Hz}$, H-2')]. Thus, the structure of helicoside B was assumed to be the 3'-hydroxy derivative of helicoside A. This assumption was supported by the spectroscopic data reported in Section 4. Therefore, helicoside 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 helicosides A and B (**1** and **2**), and naringenin (flavanone) 5-*O*- β -D-glucopyranoside (**7**) were isolated.

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 CD₃OD solution.

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