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Dihydrochalcones from *Symplocos vacciniifolia*

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Abstract: A new dihydrochalcone glucoside, vacciniifolin, along with confusoside, trilobatin and sieboldin were isolated from the leaves of *Symplocos vacciniifolia*. By the method of spectral analysis, this new compound was elucidated as 2′,3,4,4′-tetrahydroxydihydrochalcone 4′-O-*β*-D-glucopyranoside.

Keywords: *Symplocos vacciniifolia*, Symplocacea, dihydrochalcones, vacciniifolin.

Three plants of the genus *Symplocos* (Symplocacea), *S. microcalyx*, *S. lancifolia* and *S. spicata*, have been known for their sweet property, and the sweeteners from them were reported as two dihydrochalcone glycosides, trilobatin and phlorizin[1]. Recently, a new species of the same genus, *S. vacciniifolia* H. S. Chen et H. G. Ye, has been found in the northern Guangdong Province of China and its leaves have long been used as sweet tea in the local area due to their sweet taste[2]. This prompted us to investigate sweeteners of this new plant. As a result of our investigation, we isolated confusoside **1**, trilobatin **3**, sieboldin **4** and a new dihydrochalcone glucoside named vacciniifolin **2**. Herein we report the structural elucidation of this new compound.

The MeOH percolate of the fresh leaves was extracted with water. The water extract was fractionated by Diaion HP-20 column chromatography (CC) to give a crude sweet fraction. This fraction was subjected to repeated silica gel CC, followed by polyamide CC, affording the only sweet principle of the plant trilobatin **3**[3, 4] and confusoside **1**[5], sieboldin **4**[6], and the new compound, vacciniifolin **2**.

Compound **2** was isolated as pale yellow needles (MeOH), mp 189-191°C (uncorrected), $[\alpha]_D^{25}$ −58.95 (*c* 0.285, MeOH). Its molecular formula $C_{21}H_{24}O_{10}$ was derived from the ESI-MS ions at *m/z* 437 $(M + H)^+$, 459 $(M + Na)^+$, and 475 $(M + K)^+$, together with the ^1H and ^{13}C NMR data. The IR band at 1633 cm^{-1} (C=O), UV absorptions in MeOH, λ_{max} (log ε): 217 (4.43), 271 (4.31) and 315 (3.92) nm, and ^1H NMR signals at δ 2.85 and 3.19 (each 2H, triplet, J = 7.6 Hz, phenyl-C$\mathbf{H}_2$-C$\mathbf{H}_2$-CO-phenyl) suggested that **2** was a dihydrochalcone derivative[5]. The proton signal at δ 4.99 (1H, d, J = 7.2 Hz), and the carbon signals at δ 101.2 (CH), 74.7 (CH), 78.2 (CH), 71.1 (CH), 77.8

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(CH), 62.3 (CH_2) indicated the presence of a *β*-D-glucopyranosyloxy in **2**. In the ^{1}H NMR spectrum of **2**, four doublets at *δ* 7.78 (*J* = 8.8 Hz), 6.66 (*J* = 2.0 Hz), 6.65 (*J* = 8.0 Hz) and 6.56 (*J* = 2.4 Hz), and two double doublets at *δ* 6.60 (*J* = 2.4, 8.8 Hz) and 6.53 (*J* = 2.0, 8.0 Hz) indicated the presence of two 1,2,4-trisubstituted phenyl groups. By comparison of the ^{1}H and ^{13}C NMR data of **2** with those of **1**[5] and **4**[6], **2** was deduced to be 2′,3,4,4′-tetrahydroxydihydrochalcone 4′-O-*β*-D-glucopyranoside. Detailed interpretation of ^{1}H-^{1}H COSY, ^{13}C-^{1}H COSY, and HMBC (**Figure 1**) spectra of **2** allowed the assignment of all ^{1}H and ^{13}C signals (**Table 1**) and confirmed the structure.

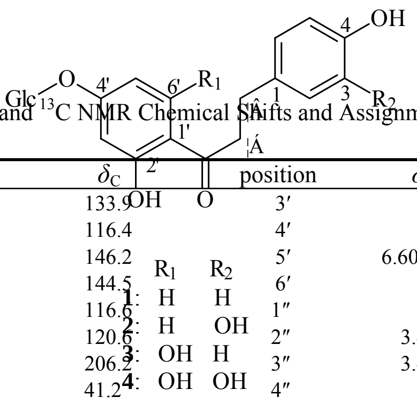
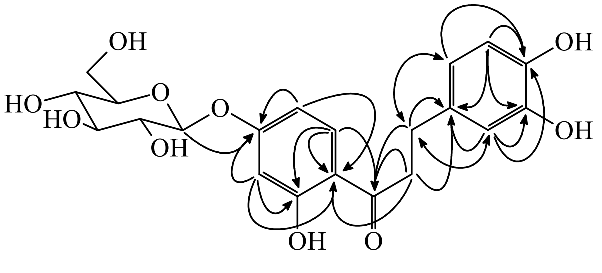


Table 1 ^{1}H and ^{13}C NMR Chemical Shifts and Assignments for **2**

position	δ_H (*J* in Hz)	δ_C	position	δ_H (*J* in Hz)	δ_C
1		133.9	3′	6.56 d (2.4)	105.0
2	6.66 d (2.0)	116.4	4′		165.7
3		146.2	5′	6.60 dd (2.4, 8.8)	109.3
4		144.5	6′	7.78 d (8.8)	133.4
5	6.65 d (8.0)	116.6	1″	4.99 d (7.2)	101.2
6	6.53 dd (2.0, 8.0)	120.6	2″	3.45 — 3.70 m	74.7
C=O		206.2	3″	3.45 — 3.70 m	78.2
α	3.19 t (7.6)	41.2	4″	3.39 m	71.1
β	2.85 t (7.6)	31.0	5″	3.45 — 3.70 m	71.8
1′		115.9	6″a	3.87 dd (1.6, 12.0)	62.3
2′		165.0	6″b	3.70 dd (4.2, 12.0)	

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in CD_3OD and used TMS as the internal standard.

Figure 1 Selected HMBC assignments of **2**



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References

1. T. Tanaka, K. Yamasaki, H. Kohda, O. Tanaka, S. B. Mahato, *Planta Med*., **1980,** *Suppl*, 81.
2. H. S. Chen, H. G. Ye, F. Y. Zeng, *J. Trop. Subtrop. Bot*., **2003,** *11*, 169.
3. R. L. Nie, T. Tanaka, J. Zhou, O. Tanaka, *Agric. Biol. Chem*., **1982**, *46*, 1933.
4. T. Tanaka, O. Tanaka, H. Kohda, W. H. Chou, F. H. Chen, *Agric. Biol. Chem.*, **1983,** *47*, 2403.
5. T. Tanaka, K. Kawamura, H. Kohda, K. Yamasaki, O. Tanaka, *Chem. Pharm. Bull*., **1982**, *30*, 2421.
6. I. Kazuo, I. Masataka, H. Mitsumasa, M. Hiroyuki, F. Hiroshi, *Phytochemistry*, **1980**, *19*, 476.

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