BRANDIOSIDE, A PHENYLPROPAANOYD GLYCOSIDE FROM BRANDISIA HANCEI

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Key Word Index—Brandisia hancei; Scrophulariaceae; phenylpropaanoic glycoside; brandioside.

Abstract—A new phenylpropanoid glycoside, brandioside, was isolated from Brandisia hancei. Its structure, [β-(3',4'-dihydroxyphenyl)-ethyl)-(2-O-acetyl)-(3,6-di-a-L-rhamnopyranosyl)-(4-O-cafeoyl)-β-D-glucopyranoside, was established by chemical and spectroscopic methods.

INTRODUCTION

As a continuation of our ethnobotanical and ethnopharmaceutical studies of the medicinal plants in Yunnan Province of China, we have investigated the chemical constituents of Brandisia hancei Hook. f. (Scrophulariaceae). Previously, we have isolated three known glycosides: acteioside (4), 2'-acetylaceoside (2) and polimisoside (3) from this plant [1]. This paper deals with the isolation and structural elucidation of a new phenylpropanoid glycoside, brandioside (1) from the whole plant.

RESULTS AND DISCUSSION

Brandioside (1) was isolated as an amorphous powder, [α]D 15 −91.5°, whose molecular formula C37H48O29 was established from its FAB mass spectrum (m/z 833 [M + Na]+, 898 [M + Li]−). The presence of glucose and rhamnose moieties in 1 was indicated by acid hydrolysis with 1 M HCl, followed by TLC. The 1H NMR spectrum exhibited two ABX systems downfield which belong to the caffeic acid moiety [δ6.833 (1H, d, J = 8.2 Hz), 6.990 (1H, dd, J = 2.0 Hz) and 7.114 (1H, d, J = 2.0 Hz)] and the aglycone moiety [δ6.549 (1H, dd, J = 8.0, 2.0 Hz), 6.680 (1H, d, J = 2.0 Hz) and 6.730 (1H, d, J = 8.0 Hz)].

two olefinic protons which appeared as an AB-system (the coupling constant, J = 15.9 Hz, indicated a trans geometry), two secondary methyl groups of rhamnose and three anionic protons at δ4.495 (J = 8.1 Hz), 4.655 (J = 1.4 Hz) and 4.675 (J = 1.4 Hz) which were consistent with the configurations for β-D-glucose and for α-L-rhamnose. The 13C NMR spectrum of 1 differed only from that of 2 by the addition of a terminal rhamnose moiety resonance and the signal of C-6 position of glucose which was downfield to δ67.1 [2]. Furthermore, the difference between 3 and 1 only the addition of an acetyl resonance and C-2, as well as C-1 and C-3 positions of glucose, showed acetylation shift effects in 1 [3]. These results were also confirmed by the acetylation of 1 with acetic anhydride and pyridine to yield a decaacetate (7) which was found to be identical with the nonacetate of 3 by direct TLC, IR and 13C NMR spectral comparison. Alkaline hydrolysis of 1 afforded 3, decaacetyl polimisoside (5) and methyl caffeate (6). Thus 1 is β-(3',4'-dihydroxyphenyl)-ethyl)-(2-O-acetyl)-(3,6-di-a-L-rhamnopyranosyl)-(4-O-cafeoyl)-β-D-glucopyranoside.

EXPERIMENTAL

Optical rotations were measured in MeOH. 1H and 13C NMR spectra were recorded at 400 MHz in CD3OD using TMS as int. standard. EIMS spectra were measured at 20 eV accelerating voltage after microscale acetylation.

EXTRACTION AND PURIFICATION. Dried whole herb (2.62 kg) of B. hancei collected in Da-Li, Yunnan province of China was extracted with hot MeOH. The combined extracts were evaporated in vacuo. The residue (282.5 g) was separated into frs by CC on Diaion HP-20 eluting with 50% EtOH. The fr. of first elution was repeatedly chromatographed over silica H with CHCl3-MeOH-H2O (14:6:1) as eluent to give a I (200 mg).

Brandioside (1). Amorphous powder, [α]D 15 −91.6° (MeOH; c 0.54); C37H48O29.C4H6O9; C 51.03, H 5.94; calc: C 51.24, H 5.54; FABMS m/z 833 [M + Na]+, 819 [M + Li]+; UV λmax (log ε); 202 (4.46), 220 (4.15), 248-249 (3.23), 288 (3.94), 335-337

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extract was chromatographed on a silica H column by eluting with CHCl₃–MeOH–H₂O (40:10:1) to afford 3 (20 mg) and 5 (70 mg).

**Polysimilum (3).** An amorphous powder, [δ]D +22 ≈ −77.95° (MeOH; c 0.526, FABMS m/z 793 [M + Na]+; 777 [M + Li]+; UV λmax (log ε): 202 (4.57), 220 (4.14), 248 (3.97), 288 (3.96), 335–337 (4.20) nm.)

**Descafeoylpolysimilum (5).** Amorphous powder; C₁₅H₂₀O₄ found: C 48.82, H 6.40; requires: C 48.72, H 6.32; UV λmax (log ε): 202 (4.30), 221 (3.80), 282–288 (3.50), 315 (3.06) nm; ¹H NMR data (δ): aglycone 6.713 (1H, d, J = 1.0 Hz, H-6), 6.734 (1H, d, J = 8.1 Hz, H-5), 6.531 (1H, dd, J = 8.1, 2.0 Hz, H-6), 2.765 (2H, dd, J = 11.0, 6.2 Hz, H-7), 3.664 (1H, dt, J = 11.0, 9.2 Hz, H-8a), 3.895 (1H, dt, J = 9.2, 6.2 Hz, H-8b), Glc 4.287 (1H, d, J = 8.3 Hz, H-1), 3.376 (1H, d, J = 8.3 Hz, H-2); Rha 5.153 (2H, d, J = 1.5 Hz, H-1 × 2); 13C NMR data (δ): aglycone 131.5 (1), 116.3 (2), 144.6 (3), 146.0 (4), 117.1 (5), 121.3 (6), 36.4 (7), 72.1 (8); Glc 104.1 (1), 75.5 (2), 84.7 (3), 70.8 (4), 77.8 (5), 67.5 (6); Rha 103.1 (1), 72.0 (2), 70.5 (3), 74.7 (4), 70.0 (5), 17.9 (6); Rha' 102.6 (1), 72.3 (2), 70.5 (3), 74.7 (4), 70.0 (5), 18.5 (6).

**Methyl caffeate (6).** C₁₅H₁₄O₄ found: C 62.07, H 5.45; requires: C 61.85, H 5.19, EIMS (20 eV) m/z 194 [M]+, 163 [M–OMe]+, 145 [M–OMe–H₂O]+, 135 [M–OMe–CO₂M]+; UV λmax (log ε): 204 (5.00), 218 (4.37), 233 (4.21), 245 (4.24), 298 (4.32), 330 (4.45) nm; ¹H NMR data (δ): 7.045 (1H, d, J = 1.2 Hz, H-2), 6.783 (1H, d, J = 8.0 Hz, H-5), 6.934 (1H, dd, J = 8.0, 1.2 Hz, H-6), 5.751 (1H, d, J = 16.0 Hz, H-7), 6.255 (1H, d, J = 16.0 Hz, H-8), 3.359 (3H, s, OMe); 13C NMR data (δ): 127.5 (1), 116.3 (2), 146.7 (3), 149.2 (4), 114.9 (5), 122.1 (6), 146.5 (7), 114.4 (8), 169.5 (CO), 51.7 (OMe).

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**REFERENCES**