Structure of Mimengosides A and B, New Triterpenoid Glycosides from Buddlejae Flos Produced in China

Ning Ding, Shoji Yahara and Toshihiro Nohara*

Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-hommachi 3-1, Kumamoto 862, Japan. Received September 7, 1991

Two new triterpenoid glycosides, named mimengosides A (1) and B (2), along with acteoside (3) were isolated from the Buddleja Flos (flower and bud of Buddleja officinalis). The structures of 1 and 2 were determined as 3-O-a-L-rhamnopyranosyl-(1→4)-a-D-glucopyranosyl-(1→3)-[a-D-glucopyranosyl(1→2)]-a-D-fucopyranoside of 16-dehydroxyxaikogenin G and that of 3,23,28-trihydroxy-11-methoxy-olean-12-ene, respectively, by spectral and chemical methods.

Keywords Buddleja Flos; Buddleja officinalis; Buddlejaceae; mimengoside A, B; 16-dehydroxyxaikogenin G

Buddleja Flos (Chinese name: Mi Meng Hua), the flower and bud of Buddleja officinalis Maxim. are a Chinese crude drug used for antiinflammation.1) With regard to the ingredient of this crude drug, the flavonoids such as larin and acacetin are known.2) We have now obtained two triterpenoid glycosides (1 and 2) together with acteoside (3). This paper deals with the structural characterization of these new triterpenic glycosides, named mimengosides A (1) and B (2).

A methanolic extract of the crude drug was defatted with benzene and then repeatedly chromatographed to give compounds 1, 2 and 3 in yields of 0.056, 0.051 and 1.03%, respectively.

Mimengoside A (1), a white powder, [x]D +32.0°, showed a quasi ion peak [M+H]+ at m/z 1073 in the positive ion fast atom bombardment mass spectrometry (FAB-MS) and absorption bands due to hydroxyl groups at 3428 cm⁻¹ in the infrared (IR) spectrum. The carbon-13 nuclear magnetic resonance (13C-NMR) spectrum (Table I) of 1 exhibited fifty four carbon signals constituted of one disubstituted double bond (δ 131.6, 131.9), two hydroxymethyls (δ 64.4, 76.9), one oxygenated methine (δ 82.4), one oxygenated quaternary carbon (δ 84.7), six methyls, nine methylenes, three methines and six quarternary carbons in the aglycone moiety, and four anomeric carbons and two methyls in the sugar moiety. These signals due to the aglycone moiety were in good coincident with those of saikosaponin a2) except for those due to C-14—17 carbons. Signals at δ 43.9 (s), 30.9 (t), 25.7 (t), and 41.5 (s) could be reasonably assigned to C-14—17, respectively, on the D-ring of the aglycone by comparing with those of 16-dehydroxyxaikogenin G.3) Acid hydrolysis with 1 N

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HCl of I yielded d-glucose, d-fucose and L-rhamnose as sugar components and compounds 4 and 5 as aglycone. Compound 4 showed a molecular ion peak at m/z 456 in the electron impact mass spectrometry (EI-MS), and ultraviolet (UV) absorption bands at 245, 254 and 263 nm due to conjugated double bonds. In the 13C-NMR spectrum (Table I) exhibited thirty carbon signals due to six methyls, two hydroxymethyls, one oxygenated methine, two double bonds, six quaternary carbons, nine methylenes and two methines. Compound 4 was therefore identified with 2,3,28-trihydroxyolean-11,13(18)-diene, isolated from Scrophularia smithii W. On the other hand, compound 5 showed a molecular ion peak at m/z 426 in the EI-MS and UV absorption band at 242 nm. The 13C-NMR spectrum (Table I) exhibited twenty nine carbon signals due to six methyls, one hydroxymethyl, one oxygenated methine, two double bonds, five quaternary carbons, ten methylenes and two methines. Compound 5 was therefore identified to 2,3-dihydroxy-28-nor-oleane-12,17-diene. Compounds 4 and 5 were recognized as artifact compounds from I. Partial acid hydrolysis with 2% trifluoroacetic acid (TFA) of I yielded L-rhamnose and a prosapogenin (6), [a]D -13.4°, which exhibited a [M+H]+ at m/z 927, and on acid hydrolysis provided 4 and 5 as aglycone part, and glucose as sugar component. The prosapogenin (6) showed signals due to two terminal β-glucopyranosyl residues and one β-fucopyranosyl residue shifted at C-2 (+5.4 ppm) and C-3 (+9.3 ppm) by comparing with those of β-D-fucopyranoside as listed in Table I. Therefore, the structure of 6 was elucidated as 3-O-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→2)-β-D-fucopyranosyl 3,23,28-trihydroxyoleane-11,13(18)-diene. The location of the glycosyl bond of rhamnose in I was determined by the 13C-NMR and 1H-13C long range (5 Hz) correlation spectroscopy (COSY) spectra. As listed in Table I, the shifts at glucosyl C-3, C-4 and C-5 in I were observed by -1.5, +5.3 and -1.3 ppm, respectively, in comparison with those of 6, and the cross peaks in the 1H-13C long range COSY were observed between δ 84.5 (fuc C-3) and δ 5.24 (glc H-1); and δ 78.1 (glc C-4) and δ 5.81 (rha H-1), indicating that the rhamnoso moiety attached to the C-4 of fuscosyl-3-O-glucosyl moiety. Consequently, the structure of mimengoside A (1) was elucidated as 3-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-fucopyranosyl 16-dehydroxy-saikogenin G.

Mimengoside B (2), a white powder, [a]D +1.5°, showed a quasi ion peak due to [M+Na]+ at m/z 1127 and a fragment ion peak at m/z 1073 [M-MeOH]+. The 1H- and 13C-NMR spectra of 2 were similar to those of I, except for signals at 52.6 (q), 122.4 (d), 149.3 (s) and 68.6 (t) assignable to methoxy, trisubstituted double bond function and hydroxymethyl groups, instead of signal at 5131.9 (d), 131.6 (d), 84.7 (s) and 76.9 (t) originated from C-11—13 and C-28 in I. These signals could be reasonably assigned to C-11 methoxy, C-12, C-13, and C-28 on the C-ring of the aglycone, by comparison with those of saikosaponin b2. Treatment of I with p-toluenesulfonic acid (p-TSOH) in MeOH afforded a product identical with 2. The solution of 2 in acetate buffer (pH 4.2) was heated at 37°C for one day to yield 1. Therefore the structure of 2 was concluded to be as shown in the Chart. Compound 2 might be changed from I during extraction and chromatographic procedure.
Acid Hydrolysis of 2 A solution of 1 (100.0 mg) in 1 n HCl (10 ml) was heated at 80°C for 3 h on a hot plate, then it was poured into water and extracted with CHCl₃. Removal of the respective solvent furnished the water and CHCl₃ extracts. The water extraction was purified by silica gel column chromatography (CHCl₃ : MeOH : H₂O : 7:3:0.5) to furnish n-glucose (7.1 mg. [x]D₂⁰ +64.8° (c = 0.70, H₂O), Rf 0.35), d-fucose (1.2 mg. [x]D₂⁰ +69.3° (c = 0.03, H₂O), Rf 0.62) and l-rhamnose (3.0 mg. [x]D₂⁰ +6.7° (c = 0.30, H₂O), Rf 0.76) detected by TLC (impregnated 0.5 m NaH₂PO₄, 2-propanol: acetone = 1:4:2; 60) and the CHCl₃ extract was purified by silica gel column chromatography (benzene:acetone = 6:1) to give 4 (3.3 mg) and 5 (21.0 mg). 4: Colorless needles (from MeOH-CHCl₃), mp 286-289°C (dec.), [x]D₂⁰ +64.8° (c = 0.70, H₂O), Rf 0.35. UV λmax nm (log e): 245, 254, 248 (4.55), 254 (4.58), 263, 240 (4.41). 1H-NMR (pyridine-d₅): δ 1.05, 1.05, 0.96, 1.07, 0.89, 0.87 (3H, each, s), 2.05, 2.17, -29, -30, 2.13 (1H, brs), 2.30 (1H, brd, δ = 10.6 Hz), 2.38 (1H, brd, δ = 10.6 Hz), 2.54 (1H, dd, δ = 14.3 Hz), 3.75, 4.23 (each 1H, δ = 10.3 Hz, H-2), 3.75, 4.11 (each 1H, δ = 11.0 Hz, H-2), 4.29 (1H, δ = 10.3, 5.3 Hz, H-3), 5.74 (1H, dd, δ = 10.6 Hz, H-12), 5.60, 6.07, 6.03 (each 1H, brs, OH), 6.51 (1H, dd, δ = 10.6, 2.6 Hz, H-11). 5: Colorless needles (MeOH-CHCl₃), mp 246-249°C, [x]D₂⁰ +126.3° (c = 0.20, CHCl₃). UV λmax nm (log e): 242 (4.18). 1H-NMR (pyridine-d₅): δ 1.08, 1.02, 0.95, 0.99, 0.91 (each 3H, each 3H, s), 2.17-28, -29, -30, 3.74, 4.19 (each 1H, δ = 9.9 Hz, H-23), 2.12 (1H, m, H-3), 5.80, 6.36 (each 1H, brs, OH), 5.63 (1H, brs, H-12).

References and Notes