A Tetrahydroisoquinoline-moneterpene Glucoside and an Iridoid Glucoside from Alangium kurzii

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From the leaves of Alangium kurzii, a new tetrahydroisoquinoline-moneterpene glucoside, 6-O-methyl-N-deacetylpiceosideic acid and a new iridoid glucoside, 10-O-benzoyladoxosidic acid, were isolated along with alangiside, demethylalangiside, 6′-O-β-D-glucoxylenosidose, uridine and four known flavonoid glycosides. The structures of new glucosides were determined on the basis of spectroscopic and chemical methods.

Key words Alangium kurzii; Alangiaceae; 6-O-methyl-N-deacetylpiceosideic acid; 10-O-benzoyladoxosidic acid

Alangium kurzii Craib. (Alangiaceae) is a deciduous shrub distributed in South China and Malaya. Previous phytochemical investigation demonstrated that the plant contained a pyridine alkaloid, anabasine, and a benzooquinolizine alkaloid, ankorine.1) The glycosidal fraction, in contrast, however, remained to be investigated. In the course of our chemical studies on the plants of Alangiaceae,2) we have investigated the constituents of the leaves of Alangium kurzii.3) We have isolated a new tetrahydroisoquinoline-monoterpene glucoside 1 and an iridoid glucoside 2 as well as eight known compounds, alangiside (3),4) demethylalangiside (4),5) kaempferol-3-O-[2,6-di-O-(α-L-rhamnopyranosyl)-β-D-galactopyranoside] (5),6) kaempferol-3-O-[2-O-(β-D-glucopyranosyl)-β-D-galactopyranoside] (6),7) kaempferol-3-O-[2-O-(β-D-xylpyranosyl)-β-D-galactopyranoside] (7),8) quercetin-3-O-[2-O-(β-D-xylpyranosyl)-β-D-galactopyranoside] (8),9) 6′-O-β-D-glucoxylenosidose (9) and uridine (10).3) Compounds 3—10 were isolated for the first time from this species. We report here the structural elucidation of two new glucosides, 1 and 2.

Compound 1 was isolated as a colorless crystalline solid, mp 203—205 °C. It showed UV maxima at 207, 228, 286 and 291sh nm, and IR bands at 3340, 1645 and 1539 cm−1.

The 1H-NMR spectrum of 1 showed a singlet for a methoxyl at δ 3.82, two singlets for aromatic protons at δ 6.68 and 6.71, a singlet for an olefinic proton at δ 7.27, signals for a terminal vinyl group at δ 5.47 (d, J = 8.0 Hz) and 4.75 (d, J = 8.0 Hz), and two acetal proton signals at δ 5.45 (dt, J = 10.5, 1.0 Hz) and 5.48 (dt, J = 18.0, 1.0 Hz) and 6.05 (dd, J = 18.0, 10.5, 7.5 Hz), and two acetal proton signals at δ 5.47 (d, J = 8.0 Hz) and 4.75 (d, J = 8.0 Hz). These spectral features as well as 13C-NMR spectral data of 1 demonstrated its structural similarity to alangiside (3), which was also isolated from this plant material. The high resolution secondary ion mass spectrum (HR-SI-MS) of 1, however, exhibited a strong peak at m/z 524.2125 ([M+H]+) indicating a molecular formula of C23H31NO11 for 1, H2O more than that of 3. All these results, together with its chromatographic behavior, suggested 1 to be a hydrolysate of alangiside, i.e. 6′-O-methyl-N-deacetylpiceosideic acid. The placement of the methoxyl group at C-6 was deduced from a nuclear Overhauser enhancement and exchange spectroscopy (NOESY) interaction between a methoxyl signal at δ 3.82 and an aromatic proton at δ 6.71, which was assignable to H-5 by a cross-peak with H-4.

Final structural confirmation was obtained from the chemical correlation of 1 with alangiside (3) and 6-O-methylpisidic acid (11).10) Conventional acetylation of 1 gave alangiside pentaacetate (12) and 13, the latter of which was methylated with CH32N2–Et3O to yield 6-O-methylpisidic pentaacetate (14).10) Accordingly, the structure of 1 was elucidated as 6′-O-methyl-N-deacetylpiceosideic acid.

Compound 2 was isolated as a colorless amorphous powder, and was analyzed for C23H29NO11 from its HR-SI-MS. This revealed UV absorptions at 229 and 279sh nm and IR bands at 3413, 1702, 1637 and 1508 cm−1. The 1H-NMR spectrum of 2 showed a doublet at δ 7.46 (J = 1.5 Hz) charac-
doxoside tetraacetate was chemically prepared from geniposide, which was acetylated to a tetraacetate, and benzoylated. Inspection of the chemical shifts of C-8 and C-9 (134.3, 134.4) and alangiside (130.1, 130.1) have so far been isolated only in species of the genera Alangiaceae and Cecropia (Rubiaceae). It is also well-known that 1 possesses amino and carboxy groups in its structure. This is the first instance of a tetrahydroallosoquinine-monoterpene glucoside with an amino group, implying the possibility of biogenetic condensation of secologanic acid (31) with dopamine.teristic of an olefinic proton of the enol ether system conjugated with a carbonyl group, and signals for two acetal protons at δ 5.18 (d, J=7.5 Hz) and 4.66 (d, J=8.0 Hz), implying an iridoidic skeleton for 2. Furthermore, it showed signals for H-6 and H-7 at δ 1.48—2.26, and acetyloxy methylene signals at δ 4.29 (dd, J=11.0, 6.5 Hz) and 4.37 (dd, J=11.0, 6.5 Hz), which were assigned to H-10 by a sequence of correlations of H-10, H-8 (δ 2.09) and H-1 (δ 5.18) in the 1H–1H chemical shift correlation spectroscopy (COSY) spectrum, and aromatic proton signals (5H) assignable to a benzoyl group. The 13C-NMR spectrum of 2 exhibited, besides the signals corresponding to a benzoyl group and a β-o-glucosyl unit, ten carbon signals including a carboxyl carbon (δ 171.5) and an oxymethylene (δ 69.1). In the 1H-detected heteronuclear multiple-bond connectivity (HMBC) spectrum, interactions from H-10 to a carbonyl carbon (δ 168.3) were observed. The presence of a carboxyl group was confirmed by the fact that the methylation of 2 with CH3N2Et2O gave a methyl ester, 15, which was further acetylated to a tetraacetate, 16. These findings suggest that compound 2 possesses adoxosidic acid (17)11) or its 8-epimer (18) as a basic skeleton, whose hydroxyl group at C-10 is benzoylated. Inspection of the chemical shifts of C-8 and C-9 in the 13C-NMR spectra of 15, adoxoside (19), and 20 implied the β-orientation of the oxymethylene group in 2.12) The configuration of C-8 was further supported by a NOESY interaction between H-8 and H-1. All these findings allowed us to formulate the structure of 2 as 10-O-benzoyloxidosidic acid.

In order to confirm the proposed structure, 10-O-benzoyloxidosidoic acid was chemically prepared from geniposide (21), as follows. Geniposide (21) was treated with 1 eq mol of trityl chloride (TrCl) in pyridine, giving two trityl ethers, 22 and 23, in the ratio of 3:1. The attachment of a trityl group to the hydroxyl at C-10 in 22 and at C-6' in 23 was determined by comparison of their 13C-NMR data, where a downfield shift was observed for C-10 in 22 and for C-6' in 23. This was further supported by downfield shifts due to the acetylation of H-10 in 24 (25: δ 3.63, 3.78; 25: δ 4.74, 4.88) and H-6' in 24 (24: δ 3.88, 4.12; 25: δ 3.10, 3.25), when 22 and 23 were acetylated to 24 and 25, respectively. Compound 24 was heated at 80°C in 80% AcOH to remove a trityl group, giving rise to 10-ol (26). Hydrogenation of 26 over Adams' catalyst afforded two stereoisomers, 27 and 28 (1:2). Comparative studies of their 13C-NMR spectra, in which carbon signals for C-9 and C-10 of 28 were observed in a higher region than those of 27, whereas the C-8 of 28 resonated at a lower field than that of 27, suggested that 27 has a β-oriented substituent at C-8.13) This assumption was supported by the fact that a NOESY correlation between H-1 and H-8 was observed in 27 but not in 28. The stereochemistry of 27 and 28 was further confirmed by acetylation of each compound to the two known acetates 29 and 30, respectively.13) Finally, compound 27 was benzoylated to give 10-O-benzoyloxidosidic acid, which was completely identical with 16 derived from 2. Thus, the new glucoside was unequivocally assigned as 10-O-benzoyloxidosidic acid (2).

Tetrahydroallosoquinine-monoterpene glucosides such as 6-O-methyl-N-deacetylpeicosidic acid (1) and alangiside (3), have so far been isolated only in species of the genera Alangium (Alangiaceae) and Cephalis (Rubiaceae). The present work gives an additional example of the isolation of this type of glucoside from the Alangium species. It is also noteworthy that 1 possesses amino and carboxy groups in its structure. This is the first instance of a tetrahydroallosoquinine-monoterpene glucoside with an amino group, implying the possibility of biogenetic condensation of secologanic acid (31) with dopamine.

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a—d Measured at a) 125 MHz or b) 75 MHz in c) CD3OD or d) CDCl3. e) Data taken from ref. 12. f) Compounds 16, 27 and 28 showed signals of acetyl groups at δ 20.6—20.7 (CH3) and 169.4—170.6 (CO). g) Compounds 22 and 23 showed signals of the trityl group at δ 113.3 (C), 143.4 (3×C) and 127.0—128.6 (15×CH) or close to those values.
Experimental

Melting points were measured on Yanagimoto microapparatus and are uncorrected. The UV spectra were recorded on a Shimadzu UV-240 spectrophotometer and the IR spectra on a Shimadzu FT-IR-8200 spectrophotometer. The optical rotations were measured on a Jasco DIP-370 digital polarimeter. SI-MS, electron impact (EI)-MS, HR-SI-MS and HR-EI-MS were obtained with a Hitachi M-4100 mass spectrometer. Glycerol or 3-nitrobenzyl alcohol (3-NBA) was used for SI-MS as the matrix. The NMR experiments were performed with Varian VXR-500, Varian Gemini-300 and Varian Gemini-200 spectrometers, with tetramethylsilane as an internal standard. HPLC was performed using a Waters system (510 HPLC pump, 486 Tunable absorbance detector). Thin-layer chromatography was performed on precoated Kieselgel 60F254 plates (Merck) and spots were visualized under UV light.

Isolation of Glucosides

Amanita caesia Cray. was collected in Xishuangbanna, Yunnan Province, People’s Republic of China. A voucher specimen (KPFY-942) was deposited in the laboratory of Kobe Pharmaceutical University. The dried leaves (173 g) were extracted with hot MeOH. The MeOH extract (34.5 g) was suspended in H2O and successively partitioned with increasing MeOH content (0—50%) giving 4 fractions, W-I (H2O), W-II (15% MeOH–H2O), W-III (20% MeOH–H2O), and W-IV (25% MeOH–H2O). The MeOH fraction (9.9 g) was further purified by a combination of prep. TLC (CHCl3–MeOH, 7 : 3) and prep. HPLC (μBondasphere 5 μC18-100 Å, MeOH–H2O, 1:9) giving 10 (9.2 mg). The following fractions were also purified by prep. HPLC (μBondasphere 5 μC18-100 Å, MeOH–H2O, 1:4; 3:1, 7:2, 2:3; 11:9; or MeCN–H2O, 13:87) and prep. TLC (CHCl3–MeOH, 7:3 or 6:4 or acetone–CHCl3–H2O, 8:2:1). Fraction B-IV (207 mg) yielded 9 (6.0 mg); fraction B-V (183 mg): 1 (3.7 mg); fraction B-VI (752 mg): 2 (45.9 mg). 3-NBA was used for SI-MS as the matrix.

Chart 2

[Chemical structure images are not rendered here.]

10-O-Benzoylglucosiloxic Acid (2): Colorless amorphous powder, [α]2°D −46° (c=1.11, MeOH). UV λmax nm (log ε): 229 (4.29), 279b (3.03). IR νmax cm−1: 3413, 1702, 1637, 1508. 1H-NMR (500 MHz, CD3OD, δ): 1.48 (2H, m, H-6), 7.95 (1H, m, H-7), 2.09 (1H, td, J = 7.5, 5.0 Hz, H-8), 2.26 (1H, m, H-6), 2.52 (1H, m, H-8), 2.90 (1H, br q, J = 7.5, H-5, H-6), 3.07 (1H, d, J = 9.0, 8.0 Hz, H-2), 3.25 (1H, dd, J = 9.5, 9.0 Hz, H-4), 3.28 (1H, d, J = 9.5, 5.5, 20.0 Hz, H-5), 3.35 (1H, t, J = 9.0 Hz, H-3), 3.65 (1H, d, J = 12.0, 5.5 Hz, H-6), 3.64 (1H, dd, J = 12.0, 20.0 Hz, H-6), 4.29 (1H, dd, J = 11.0, 6.5 Hz, H-10), 4.37 (1H, dd, J = 11.0, 6.5 Hz, H-10), 4.66 (1H, d, J = 8.0 Hz, H-1), 5.18 (1H, d, J = 7.5 Hz, H-5), 7.46 (1H, d, J = 1.5 Hz, H-3), 7.49 (2H, d, J = 7.5, 1.5 Hz, H-3'), 7.61 (1H, d, J = 7.5, 1.5 Hz, H-4'), 8.04 (2H, d, J = 7.5, 1.5 Hz, H-2').

Acetylation of Compound 1

Compound 1 (10.8 mg) was acetylated with AcCl–pyridine, and the crude acetyl (14.6 mg) was purified by prep. TLC (CHCl3–MeOH, 19:1) to yield 12 (10.0 mg) and 13 (12.5 mg). Compound 12 was identified with authentic alangiside pentaacetate.

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Acetylation of Compound 2

Compound 2 (10.3 mg) was dissolved in MeOH and treated with CH3N2–Et2O in the usual way. Purification of the product (6.6 mg) by prep. TLC (CHCl3–MeOH, 19:1) gave 14 (5.9 mg) as a colorless amorphous powder. [c]25 D = −163° (c = 0.35, CHCl3).

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Positive ion HR-SI-MS Calcd for C$_{30}$H$_{35}$O$_{14}$: 559.2024. Found: 559.2028.

**Acetylation of 27** Compound 27 (7.7 mg) was acetylated in the usual way and the resulting crude product (8.2 mg) was purified by prep. TLC (EtOAc) to yield 29 (6.7 mg, 80%) as colorless needles, mp 141—142°C (EtOH). [α]$_D^{20}$ = -58° ($c=0.34$, CHCl$_3$). IR $v_{	ext{max}}$ cm$^{-1}$: 1751, 1705, 1636. $^1$H-NMR (500 MHz, CDCl$_3$) δ: 1.37 (1H, m, H-7), 1.61 (1H, m, H-6), 1.80 (1H, m, H-7), 1.94, 2.01, 2.03, 2.06, 2.09 (1H, each, s, 5×Ac), 2.06—2.09 (2H, m, H-6, 9), 2.19 (1H, m, H-8), 2.89 (1H, br q, J = 7.5 Hz, H-5), 3.71 (3H, s, COOAc), 3.73 (1H, ddd, J = 9.5, 4.5, 2.5 Hz, H-1), 4.02 (1H, dd, J = 11.5, 6.5 Hz, H-10), 4.06 (1H, dd, J = 11.5, 6.5 Hz, H-10), 4.16 (1H, dd, J = 12.0, 2.5 Hz, H-6'), 4.26 (1H, dd, J = 12.0, 4.5 Hz, H-6'), 4.86 (1H, d, J = 8.0 Hz, H-1'), 4.99 (1H, dd, J = 9.5, 8.0 Hz, H-2'), 5.10 (1H, t, J = 9.5 Hz, H-4'), 5.18 (1H, d, J = 4.0 Hz, H-1), 5.23 (1H, t, J = 9.5 Hz, H-3'), 7.37 (1H, d, J = 1.5 Hz, H-3), $^{13}$C-NMR (125 MHz, CDCl$_3$) δ: 20.3, 20.6 (×2), 20.7, 20.9 (5×COMe), 27.1 (C-7), 31.0 (C-6), 33.7 (C-5), 38.9 (C-8), 44.1 (C-9), 51.2 (OMe), 61.7 (C-6'), 67.1 (C-10), 68.3 (C-4'), 70.7 (C-2'), 72.2 (C-3'), 72.5 (C-5'), 95.6 (C-1), 96.2 (C-1'), 111.8 (C-4), 150.5 (C-3), 167.2 (C-11), 169.1, 169.4, 170.2, 170.6, 171.1 (5×COMe). Positive ion SI-MS m/z: 601 [M+H]+, 331. Positive ion HR-SI-MS Calcd for C$_{30}$H$_{35}$O$_{14}$: 601.22134. Found: 601.2134.

**Benzoylation of 27** A mixture of 27 (3.5 mg), benzyol chloride (0.1 ml) and pyridine (0.3 ml) was allowed to stand at room temperature overnight. The conventional workup of the reaction mixture afforded a crude residue, which was subjected to prep. TLC (EtOAc) to yield 16 (4.4 mg, 100%) as colorless needles, mp 180—182°C (MeOH). [α]$_D^{20}$ = -51° ($c=0.25$, CHCl$_3$). Positive ion HR-SI-MS Calcd for C$_{26}$H$_{32}$O$_{14}$: 663.2290. Found: 663.2297. The $^1$H-NMR, HR and SI-MS data for the compound were completely identical with those of 16 derived from 2.

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**References and Notes**