Iridoid glucoside, (3*R*)-oct-1-en-3-ol glycosides, and phenylethanoid from the aerial parts of *Caryopteris incana*

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Abstract From the aerial parts of *Caryopteris incana*, a new acyl derivative (**3**) of 8-*O*-acetylharpagide, two new (3*R*)-oct-1-en-3-ol glycosides (**5, 6**), and 6'''-*O*-caffeoylphlinoside A (**11**) along with seven known compounds, 8-*O*-acetylharpagide (**1**), 6'-*O*-*p*-coumaroyl-8-*O*-acetylharpagide (**2**), (3*R*)-oct-1-en-3-ol (matsutake alcohol) *O*-α-L-arabinopyranosyl(1→6)-*O*-β-D-glucopyranoside (**4**), apigenin 7-*O*-neohesperidinoside (**7**), 6'-*O*-caffeoylarbutin (**8**), and two phenylethanoids, leucosceptoside A (**9**) and phlinoside A (**10**), were isolated. This paper deals with structural elucidation of the new compounds.

Keywords *Caryopteris incana* · Verbenaceae · Iridoid · Matsutake alcohol · (3*R*)-Oct-1-en-3-ol · Phenylethanoid

Introduction

Caryopteris incana (Thunb.) Miq. (Verbenaceae) is a perennial herb that is found naturally in the north-west of Kyushu Island of Japan, the southern part of the Korean Peninsula, China and Taiwan. *C. incana* is sometimes cultivated for use in flower arrangement and for ornamental purposes. This plant is used as a Chinese folk medicine, i.e., as crude antibacterial and antitussive drugs [1]. Recently, phenylethanoids, isolated from *C. incana*, were reported to possess antioxidant and radical scavenging activities [2, 3].

From the 1-BuOH soluble-fraction of a MeOH extract of *C. incana*, three iridoid glucoside derivatives (**1**, **2** and **3**), three (3*R*)-oct-1-en-3-ol (matsutake alcohol) glycosides (**4**, **5** and **6**), and five phenolic glycosides (**7**–**11**) were isolated by means of various types of chromatographies. The structures of known compounds, 8-*O*-acetylharpagide (**1**) [4], 6'-*O*-*p*-Coumaroyl-8-*O*-acetylharpagide (**2**) [5], (3*R*)-oct-1-en-3-ol *O*-α-L-arabinopyranosyl(1"→6')-*O*-β-D-glucopyranoside (**4**) [6], apigenin 7-*O*-neohesperidinoside (**7**) [7], 6'-*O*-caffeoylarbutin (**8**) [8], leucosceptoside A (**9**) [9], and phlinoside A (**10**) [10], were determined by comparison of the physical data with those reported in the literature, and structural elucidation of the new compounds (**3**, **5**, **6** and **11**) was performed by spectroscopic analyses.

Results and Discussion

6'-*O*-Caffeoyl-8-*O*-acetylharpagide (**3**), $[\alpha]_D$ –62.6, was isolated as an amorphous powder and assigned the molecular formula of $C_{26}H_{32}O_{14}$, as deduced from its high-resolution (HR) negative-ion FAB-mass spectrometry. The IR spectrum showed signals assignable to hydroxyl groups (3403 cm^{-1}), a conjugated carbonyl group (1701 cm^{-1}), an aromatic ring (1515 cm^{-1}), and an enol ether (1237 cm^{-1}). The presence of an aromatic ring was also supported by the absorptions in the UV spectrum. In the ^{1}H-NMR spectrum, *trans* [δ_H 7.59 (d, J = 16 Hz) and 6.31 (d, J = 16 Hz)] and *cis* [δ_H 6.36 (d, J = 6 Hz) and 4.92 (d, J = 6 Hz)] double bonds, two hemiacetal protons [δ_H 6.01 (d, J = 1 Hz) and 4.61 (d, J = 8 Hz)], an acetyl methyl signal [δ_H 1.93 (3H, s)], and three aromatic protons coupled in an ABX system were observed. In the ^{13}C-NMR spectrum, nine and two signals were assignable to a caffeoyl moiety and an acetyl group, respectively (Table 1). Six signals were assigned for 6-*O*-acylated glucopyranose [11], the remaining nine signals together with the acetyl signals being expected for the aglycone of 8-*O*-acetylharpagide (**1**) [4] (Table 1). From this evidence, the structure of **3** was elucidated to be 6'-*O*-caffeoyl-8-*O*-acetylharpagide. A closely related compound,

6'-*O*-*p*-coumaroyl-8-*O*-acetylharpagide (**2**), was also isolated from this plant [5], and the connectivity of the acyl moiety was confirmed by the HMBC experiment, in which H_2-6' (δ_H 4.52 and 4.37) showed correlation cross peaks with the C-9" signal at δ_C 169.2 (Fig. 2). Other HMBC correlation cross peaks from H-2" (δ_H 7.04) to C-7"(δ_C 123.0) and H-7" (δ_H 7.59) to C-9" also supported the structure.

(3*R*)-Oct-1-en-3-ol *O*-β-D-glucopyranosyl(1"→2')-*O*-β-D-glucopyranoside (**5**), $[\alpha]_D$ –23.0, was isolated as an amorphous powder. Its molecular formula was deduced to be $C_{20}H_{36}O_{11}$ from a $[M - H]^-$ peak observed at 451.2173 in the HR-FABMS. The IR spectrum exhibited a glycoside feature, as judged from the strong absorption at 3374 cm^{-1}. The ^{13}C-NMR spectral data showed eight signals for an aglycone and 12 signals for sugar moieties (Table 2). The signals for the aglycone moiety were also the same as those of (3*R*)-oct-1-en-3-ol *O*-β-D-arabinopyranosyl(1"→6')-*O*-β-D-glucopyranoside (**4**), which was also present in this plant and isolated from *Trifolium subterraneum* [6] and those of sugar portions were essentially the same as those of ebracteatoside C (**12**), which has been isolated from *Acanthus ebracteatus* [12]. Absolute configuration of the sugar moiety was analyzed by an optical rotation detector. The hydrolyzate of **5** gave a peak for D-glucose at the retention time of 14.5 min (positive optical rotation sign). Therefore, the structure of **5** was expected to be as shown in Fig. 1. The absolute

configuration of the 3-position of matsutake alcohol (**4a**), isolated from natural sources was generally found to be *R* [13, 14]. To confirm this, β-D-glucosylation-induced shift-trend rule in the ^{13}C-NMR spectrum was applied between **4a** and **5** [15]. However, differences of Δδ values of 2- and 4-positions on β-D-glucosylation were –2.0 ppm and –2.3 ppm, respectively, which were too close to draw a conclusion (Table 2). Therefore, 5 was catalytically reduced to **5a** and the rule was again applied between **5a** and octan-3-ol (**5b**). The upfield shift value for the 2-position was calculated to be –2.6 ppm and that of the 4-position –4.6 ppm (Table 2), which clearly demonstrated that the absolute configuration of the 3-position is *R*.

(3*R*)-Oct-1-en-3-ol

α-L-arabinopyranosyl(1'''→6'')β-D-glucopyranosyl(1''→2')-*O*-β-D-glucopyranoside (**6**), $[\alpha]_D$ –29.8, was isolated as an amorphous powder, and its molecular formula was determined to be $C_{25}H_{44}O_{15}$ by HR-ESI-MS (positive-ion mode). Spectroscopic evidence indicated that **6** was an analogous compound to **5** and ^{13}C-NMR signals for a terminal arabinopyranose were observed (Table 2) [6]. Absolute configurations of the sugar moiety were analyzed by the optical rotation detector. The hydrolyzate of **6** gave peaks for L-arabinose and D-glucose at the retention times of 10.3 min and 14.5 min (both positive optical rotation sign), respectively. The absolute configuration of

arabinose was determined to be of the L-series and thus the mode of linkage was determined to be the α-form from the coupling constant of anomeric proton (J = 7 Hz). The position of the glycosidic linkage of the arabinopyranose was substantiated by inspection of the HMBC spectrum, in which the protons (δ_H 4.03 and 3.69) of C-6" showed a correlation cross peak with the anomeric carbon signal (δ_C 104.8) of arabinopyranoside, and the anomeric proton (δ_H 4.33) of arabinopyranose also showed a cross peak with the C-6" carbon signal (δ_C 69.3) (Fig. 3). Other HMBC correlation peaks supported the structure of **6**, as shown in Fig. 3.

6"'-*O*-Caffeoylphlinoside A (**11**), $[\alpha]_D$ –19.9, was isolated as an amorphous powder, and its elemental composition was determined to be $C_{44}H_{52}O_{23}$ by observation of a quasi-molecular ion peak $[M + Na]^+$ at 971.2788 on HR-ESI-mass spectrometry. The IR spectrum revealed the presence of hydroxyl groups (3393 cm^{-1}), an ster linkage (1695 cm^{-1}), and benzene rings (1603 cm^{-1}), and the UV spectrum also supported the presence of benzene rings (329 nm). In the one- and two-dimensional NMR spectra, signals assignable for three anomeric signals [δ_H 5.43 (br s) on δ_C 102.3, 4.40 (d, J = 8 Hz) on δ_C 104.3 and 4.22 (d, J = 8 Hz) on δ_C 107.0], two sets of trans double bonds, three 1-substituted 3,4-dihydroxybenzene rings, one doublet methyl (δ_H 1.07, J = 6 Hz), and two carbonyl carbons were observed (Table 3). With a methylene (δ_C 36.6) and a

deshielded primary alcohol (δ_C 72.2), one of the benzene rings must be present in glycosylated 3,4-dihydroxyphenylethanol and two of them as caffeoyl esters. One of the sugar moieties was presumed to be rhamnopyranose from the coupling constant of the anomeric proton and the presence of a doublet methyl signal. This evidence suggests that **11** is a caffeoyl ester of phlinoside A (**10**), which co-occurs in this plant [10]. Based on the low field shifts of C-6 (δ_C 64.7) and H_2-6 (δ_H 4.61 and 4.35) of either glucopyranose, the hydroxyl group at this position was estimated to be esterified. In the H-H COSY spectrum, the correlation peaks of H_2-6 (δ_H 3.55 and 3.44) of glucopyranose to H-1, which showed a cross peak with C-8 in the HMBC spectrum, through the H-5, 4, 3 and 2 protons established the linkage of the second caffeoyl moiety to the outer glucopyranose unit. Therefore, the structure of **11** was elucidated to be 6'''-*O*-caffeoylphlinoside A, as shown in Fig. 1.

Experimental

General experimental procedures

Optical rotations were measured on a JASCO P-1030 polarimeter. IR and UV spectra were measured on Horiba FT-710 and JASCO V-520 UV/VIS spectrophotometers, respectively. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM α-400 spectrometer

at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal standard. Negative-ion HR-MS was performed with a JEOL SX-102 spectrometer in the FAB mode, and positive-ion HR-MS with an Applied Biosystems QSTAR® XL NanoSpray™ System.

A highly porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku (Tokyo, Japan). Silica gel column chromatography (CC) was performed on silica gel 60 (E. Merck, Darmstadt, Germany), and reversed-phase [octadecyl silica gel (ODS)] open CC on Cosmosil 75C_{18}-OPN (Nacalai Tesque, Kyoto) [Φ = 50 mm, L = 25 cm, linear gradient: MeOH-H_2O (1:9, 2 l) $\rightarrow$ (9:1, 2 l), fractions of 10 g being collected]. The DCCC (Tokyo Rikakikai, Tokyo, Japan) was equipped with 500 glass columns (Φ = 2 mm, L = 40 cm), and the lower and upper layers of a solvent mixture of $CHCl_3$-MeOH-H_2O-*n*-PrOH (9:12:8:2) were used as the stationary and mobile phases, respectively. Five-gram fractions were collected and numbered according to their order of elution with the mobile phase. HPLC was performed on an ODS column (Inertsil; GL Science, Tokyo, Japan; Φ = 20 mm, L = 250 mm, 6 ml/ min), and the eluate was monitored with a UV detector at 254 nm and a reflective index monitor.

Octan-3-ol (**4a**) and Oct-1-en-3-ol (matsutake alcohol) (**5b**) were purchased from Tokyo Chemical Industry Co., Lid. (Tokyo).

Plant material

Aerial parts of *C. incana* were collected in Nagasaki, Japan, in September 1998, and a voucher specimen was deposited in the Herbarium of Pharmaceutical Sciences, Graduate School of Biomedical Sciences, Hiroshima University (98-CI-Nagasaki-0915).

Extraction and isolation

Air-dried aerial parts of *C. incana* (7.08 kg) were extracted three times with MeOH (45 l) at room temperature for one week and then concentrated to 6 l *in vacuo*. The extract was washed with *n*-hexane (6 l, 192 g) and then the MeOH layer was concentrated to a gummy mass. The latter was suspended in water (6 l) and then extracted with EtOAc (6 l) to give 273 g of an EtOAc-soluble fraction. The aqueous layer was extracted with 1-BuOH (6 l) to give a 1-BuOH-soluble fraction (545 g), and the remaining water-layer was concentrated to furnish 765 g of a water-soluble fraction.

The 1-BuOH-soluble fraction (540 g) was subjected to Diaion HP-20 CC (Φ = 70 mm, L = 70 cm), using H_2O-MeOH (4 : 1, 10 1), (2 : 3, 12 1), (3 : 2, 12 1), and (1 : 4, 12 l), and MeOH (6 l), 2 1 fractions being collected. An aliquot (40.0 g) of the 40% MeOH

eluate (85.3 g in fractions 7–12) obtained on Diaion HP-20 CC was subjected to silica gel (790 g) CC, with elution with $CHCl_3$ (3 l), $CHCl_3$–MeOH [(99:1, 3 l), (97:3, 6 l), (19:1, 6 l), (37:3, 6 l), (9:1, 6 l), (7:1, 6 l), (17:3, 6 l), (33:7, 6 l), (4:1, 6 l), (3:1, 6 l), and (7:3, 6 l)], and $CHCl_3$-MeOH-H_2O (35:12:2, 6 l), 1 l fractions being collected. Combined fractions 30–37 (1.86 g) were separated by ODS CC and the residue (305 mg) in fractions 170–190 was further purified by DCCC to give **3** (153 mg), **5** (34 mg) and **4** (90 mg) in fractions 22–29, 60–70 and 74–79, respectively. The residue (22 mg) in DCCC fractions 94–103 was purified by HPLC to give 13 mg of **2** from the peak at 17.5 min.

From fractions 38-47 obtained on silica gel CC, 1.28 g of **7** was obtained as a crystalline state and the residue (1.85 g) in fractions 48–57 was separated by ODS CC to afford 12.4 mg of **1** in fractions 111–115. The ODS residues in fractions120–131 and 132–144 were separated by DCCC to furnish 34 mg of **8** and 181 mg of **9** in fractions 45–51 and 46–53, respectively. The ODS residue (261 mg) in fractions 167–172 was also separated by DCCC to give 195 mg of **11** in fractions 10–15. From the ODS residue (243 mg) in fractions 173–187, 30 mg of **6** was obtained by DCCC in fractions 48–55.

An aliquot (1.55 g) of the residue (6.54 g) in fractions 67–71 obtained on silica gel CC was subjected to ODS CC (537 mg in fractions 146–165), followed by DCCC to give

23 mg of **10** in fractions 13–27.

6'-*O*-Caffeoyl-8-*O*-acetylharpagide (**3**)

Amorphous powder, $[\alpha]_D$ –62.6 (*c* 0.23, MeOH). IR ν_{max} (film) cm^{-1}: 3403, 2925, 1701, 1515, 1373, 1237, 1072, 852. UV λ_{max} (MeOH) nm (log ε): 327 (4.32), 244 (4.10). ^{1}H-NMR (CD_3OD, 400 MHz) δ:7.59 (1H, d, *J* = 16 Hz, H-7''), 7.04 (1H, d, *J* = 2 Hz, H-2''), 6.93 (1H, dd, *J* = 8, 2 Hz, H-6''), 6.77 (1H, d, *J* = 8 Hz, H-5''), 6.36 (1H, d, *J* = 6 Hz, H-3), 6.31 (1H, d, *J* = 16 Hz, H-8''), 6.01 (1H, d, *J* = 1 Hz, H-1), 4.92 (1H, d, *J* = 6 Hz, H-4), 4.61 (1H, d, *J* = 8 Hz, H-1'), 4.52 (1H, dd, *J* = 12, 2 Hz, H-6'a), 4.37 (1H, dd, *J* = 12, 6 Hz, H-6'b), 3.70 (1H, dd, *J* = 5, 2 Hz, H-6), 3.58 (1H, ddd, *J* = 9, 6, 2 Hz, H-5'), 3.43 (1H, dd, *J* = 9, 9 Hz, H-3'), 3.37 (1H, dd, *J* = 9, 9 Hz, H-4'), 3.26 (1H, dd, *J* = 9, 8 Hz, H-2'), 2.84 (1H, br s, H-9), 2.15 (1H, dd, *J* = 15, 2 Hz, H-7a), 1.96 (1H, dd, *J* = 15, 5 Hz, H-7b), 1.93 (3H, s, C*H*$_3$CO-), 1.40 (3H, s, H_3-10). ^{13}C-NMR (CD_3OD, 100 MHz): Table 1. HR-FAB-MS (negative-ion mode) *m*/*z*: 567.1715 $[M - H]^-$ (Calcd for $C_{26}H_{31}O_{14}$: 567.1714).

(3*R*)-Oct-1-en-3-ol *O*-β-D-glucopyranosyl(1''→2')-*O*-β-D-glucopyranoside (**5**)

Amorphous powder, $[\alpha]_D$ –23.0 (*c* 1.13, MeOH). IR ν_{max} (film) cm^{-1}: 3374, 2928, 1649,

1419, 1166, 1076, 926, 894. ^{1}H-NMR (CD_3OD, 400 MHz) δ:5.83 (1H, ddd, *J* = 17, 10, 6 Hz, H-2), 5.17 (1H, ddd, *J* = 10, 2, 1 Hz, H-1a), 5.04 (1H, ddd, *J* = 17, 2, 1 Hz, H-1b), 4.63 (1H, d, *J* = 8 Hz, H-1"), 4.44 (1H, d, *J* = 8 Hz, H-1'), 4.14 (1H, ddd, *J* = 7, 7, 6 Hz, H-3), 3.84 (1H, dd, *J* = 12, 2 Hz, H-6'a), 3.80 (1H, dd, *J* = 12, 2 Hz, H-6"a), 3.68 (1H, dd, *J* = 12, 6 Hz, H-6"b), 3.64 (1H, dd, *J* = 12, 6 Hz, H-6'b), 3.55 (1H, dd, *J* = 9, 9 Hz, H-3'), 3.48 (1H, dd, *J* = 9, 8 Hz, H-2'), 3.38 (1H, dd, *J* = 9, 9 Hz, H-3"), 3.33 (1H, dd, *J* = 9, 9 Hz, H-4'), 3.30 (1H, m, H-4"), 3.28 (1H, m, H-5"), 3.24 (1H, dd, *J* = 9, 8 Hz, H-2"), 3.20 (1H, ddd, *J* = 9, 6, 2 Hz, H-5'), 1.69 (1H, m, H-4a), 1.49 (1H, m, H-4b), 1.39 (2H, m, H_2-5), 1.34 (2H, m, H_2-6), 1.31 (2H, m, H_2-7), 0.90 (3H, t, *J* = 7 Hz, H_3-8). ^{13}C-NMR (CD_3OD, 100 MHz): Table 2. HR-FAB-MS (negative-ion mode) *m*/*z*: 451.2173 $[M - H]^-$ (Calcd for $C_{20}H_{35}O_{11}$: 451.2179).

(3*R*)-Oct-1-en-3-ol *O*-α-L-arabinopyranosyl(1'''→6")-*O*-β-D-glucopyranosyl(1"→2')-*O*-β-D-glucopyranoside (**6**)

Amorphous powder, $[\alpha]_D^{29}$ –29.8 (*c* 2.10, MeOH). IR ν_{max} (film) cm^{-1}: 3367, 2929, 1073, 1043, 1013. ^{1}H-NMR (CD_3OD, 400 MHz) δ:5.86 (1H, ddd, *J* = 17, 10, 6 Hz, H-2), 5.21 (1H, ddd, *J* = 10, 2, 1 Hz, H-1a), 5.13 (1H, ddd, *J* = 17, 2, 1 Hz, H-1b), 4.63 (1H, d, *J* = 8 Hz, H-1"), 4.44 (1H, d, *J* = 8 Hz, H-1'), 4.33 (1H, d, *J* = 7 Hz, H-1'''), 4.03

(1H, dd, *J* = 12, 2 Hz, H-6"a), 3.87 (1H, dd, *J* = 10, 6 Hz, H-5'"a), 3.83 (1H, dd, *J* = 12, 2 Hz, H-6'a), 3.81 (1H, m, H-4'"), 3.69 (1H, dd, *J* = 12, 6 Hz, H-6"b), 3.67 (1H, dd, *J* = 12, 6 Hz, H-6'b), 3.60 (1H, dd, *J* = 9, 9 Hz, H-4"), 3.58 (1H, dd, *J* = 8, 7 Hz, H-2'"), 3.56 (2H, m, H-3" and 3'"), 3.55 (1H, m, H-3'), 3.53 (1H, m, H-5'"b), 3.49 (1H, dd, *J* = 9, 8 Hz, H-2'), 3.38 (1H, m, H-5"), 3.29 (1H, m, H-4'), 3.25 (1H, m, H-5'), 3.24 (1H, dd, *J* = 9, 8 Hz, H-2"), 1.63 (1H, m, H-4a), 1.51 (1H, m, H-4b), 1.37 (2H, m, H_2-5), 1.31 (4H, m, H_2-6 and 7), 0.90 (3H, t, *J* = 7 Hz, H_3-8). ^{13}C-NMR (CD_3OD, 100 MHz): Table 2. HR-FAB-MS (negative-ion mode) *m/z*: 607.2578 $[M + Na]^+$ (Calcd for $C_{25}H_{44}O_{15}Na$: 607.2572).

6'"-*O*-Caffeoylphlinoside A (**11**)

Amorphous powder, $[\alpha]_D^{28}$ –19.9 (*c* 11.1, MeOH). IR ν_{max} (film) cm^{-1}: 3393, 2937, 1695, 1630, 1603, 1522, 1446, 1367, 1281, 1163, 1115, 1068, 1039, 814. UV λ_{max} (MeOH) nm (log ε): 329 (3.98), 297sh (3.88), 241sh (3.80), 216 (3.99). ^{1}H-NMR (CD_3OD, 400 MHz) δ:7.63 (1H, d, *J* = 16 Hz, H-7''''), 7.58 (1H, d, *J* = 16 Hz, H-7''''), 7.10 (1H, d, *J* = 2 Hz, H-2''''), 7.06 (1H, d, *J* = 2 Hz, H-2''''), 6.98 (1H, dd, *J* = 8, 2 Hz, H-6''''), 6.95 (1H, dd, J = 8, 2 Hz, H-6''''), 6.79 (1H, dd, *J* = 8 Hz, H-5''''), 6.78 (1H, d, *J* = 8 Hz, H-5''''), 6.70 (1H, d, *J* = 2 Hz, H-2), 6.69 (1H, d, *J* = 8 Hz, H-5), 6.56 (1H, dd, *J*

= 8, 2 Hz, H-6), 6.36 (1H, d, *J* = 16 Hz, H-8''''), 6.26 (1H, d, *J* = 16 Hz, H-8''''), 5.43 (1H, br s, H-1''), 4.88 (1H, dd, *J* = 9, 9 Hz, H-4'), 4.61 (1H, dd, *J* = 12, 2 Hz, H-6'''a), 4.40 (1H, d, *J* = 8 Hz, H-1'), 4.35 (1H, dd, *J* = 12, 6 Hz, H-6'''b), 4.22 (1H, d, *J* = 8 Hz, H-1'''), 3.97 (1H, dt, *J* = 10, 7 Hz, H-8a), 3.68 (1H, dd, *J* = 9, 9 Hz, H-3'), 3.67 (1H, dt, *J* = 10, 7 Hz, H-8b), 3.55 (1H, dd, *J* = 12, 2 Hz, H-6'a), 3.54 (1H, m, H-5''), 3.53 (1H, m, H-5'''), 3.44 (1H, dd, *J* = 12, 5 Hz, H-6'b), 3.38 (1H, dd, *J* = 9, 9 Hz, H-3'''), (1H, dd, *J* = 9, 8 Hz, H-2'), 3.21 (1H, ddd, *J* = 9, 5, 2 Hz, H-5'), 3.30 (1H, m, H-2'''), 2.76 (2H, t, *J* = 7 Hz, H_2-7), 1.07 (3H, d, *J* = 6 Hz, H-6''), H-3'', 4'' and 4''' could not be assigned, due to overlapping. ^{13}C-NMR: Table 3. HR-ESI-MS (positive-ion mode) *m*/*z*: 971.2788 $[M + Na]^+$ (Calcd for $C_{44}H_{52}O_{23}Na$: 971.2791).

Analyses of the sugar moiety

Compounds **5** and **6** (about 500 μg, each) were hydrolyzed with 1N HCl (0.1 ml) at 100 °C for 2 h. The reaction mixtures were partitioned with an equal amount of EtOAc (0.1 ml), and the water layers were analyzed with a chiral detector (JASCO OR-2090*plus*) with an amino column [Asahipak NH_2P-50 4E, CH_3CN-H_2O (4:1), 1 ml/min]. The hydrolyzate of **5** gave a peak for D-glucose at the retention time of 14.5 min (positive optical rotation sign). Whereas that of **6** gave peaks for L-arabinose and

D-glucose at the retention times of 10.3 min and 14.5 min (positive optical rotation signs), respectively. The peaks were identified by co-chromatography with authentic L-arabinose and D-glucose.

Catalytic hydrogenation of **5**

(3*R*)-Oct-1-en-3-ol *O*-β-D-glucopyranosyl(1"→2')-*O*-β-D-glucopyranoside (**5**) (6 mg) in 1 ml of MeOH was reduced with 1 mg of PtO_2 under H_2 atmosphere for 1 hr at an ambient temperature. After removal of catalyst, the solvent was evaporated and the residue was purified by preparative TLC to give 1.1 mg of a reduced product (**5a**). Octan-3-ol *O*-β-D-glucopyranosyl(1"→2')-*O*-β-D-glucopyranoside (**5a**): amorphous powder, $[\alpha]_D$ –23.2 (*c* 0.11, MeOH). IR ν_{max} (film) cm^{-1}: 3365, 2927, 1073, 1034. ^{1}H-NMR (CD_3OD, 400 MHz) δ: 4.65 (1H, d, *J* = 8 Hz, H-1"), 4.43 (1H, d, *J* = 8 Hz, H-1'), 3.85 (1H, dd, *J* = 12, 2 Hz, H-6a'), 3.82 (1H, dd, *J* = 12, 2 Hz, H-6a"), 3.65 and 3.64 (1H each, each dd, *J* = 12, 6 Hz, H-6b' and 6b"), 3.64 (1H, m, H-3), 3.55 (1H, dd, *J* = 9, 9 Hz, H-3'), 3.46 (1H, dd, *J* = 9, 8 Hz, H-2'), 3.37 (1H, dd, *J* = 9, 9 Hz, H-3"), 3.32–3.23 (2H, m, H-4' and 4"), 3.25 (2H, m, H-5' and 5"), 1.60 (2H, m, H_2-2), 1.53 (2H, m, H_2-6), 1.35 (3H, m, H-4a, H_2-5 and H_2-7), 1.27 (1H, m, H-4b), 0.923 (3H, t, *J* = 7 Hz, H_3-8), 0.915 (3H, t, *J* = 7 Hz, H_3-8). ^{13}C-NMR (CD_3OD, 100 MHz): Table 2.

HR-ESI-MS (positive-ion mode) *m/z*: 453.2310 $[M + Na]^+$ (Calcd for $C_{20}H_{38}O_{11}Na$: 477.2306).

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Table 1. ^{13}C-NMR spectroscopic data for **1** and **3** (CD_3OD, 100 MHz)

C	**1**	**3**
1	94.4	94.4
3	143.9	143.5
4	107.0	107.4
5	73.3	73.0
6	77.7	77.7
7	46.1	46.0
8	88.7	87.9
9	55.6	55.9
10	22.5	22.5
1'	100.0	99.6
2'	74.6	74.6
3'	77.7	77.7
4'	71.8	72.1
5'	78.2	75.7
6'	63.0	64.8
CH_3CO-	22.2	22.1
CH_3*C*O-	173.2	172.5
1"		127.9
2"		115.3
3"		146.6
4"		149.6
5"		116.5
6"		123.0
7"		147.1
8"		115.2
9"		169.2

Table 2. ^{13}C-NMR spectroscopic data for **4a**, **5**, **5a**, **5b** and **6** (CD_3OD, 100 MHz)

C	**5**	**4a**	**5a**	**5b**	**6**
1	116.6	114.4	10.0	10.4	116.8
2	140.8	142.8 (–2.0)a	28.5 (–2.6)[b]	31.1	140.7
3	83.8	73.8 (+10.0)[a]	83.4 (+9.5)[b]	73.9	83.8
4	35.8	38.1 (–2.3)[a]	33.4 (–4.6)[b]	38.0	35.9
5	25.7	26.2	25.7	26.6	25.7
6	33.1	32.9	34.4	33.2	33.1
7	23.7	23.6	23.8	23.8	23.7
8	14.5	14.4	14.5	14.5	14.5
1'	101.8		102.5		101.9
2'	82.7		81.9		82.6
3'	78.2		78.4		78.2
4'	71.5		71.7		71.5
5'	77.8		77.9		77.8
6'	63.0		63.2		63.0
1"	105.0		104.7		105.1
2"	76.2		75.9		76.2
3"	77.8		77.8		78.0
4"	71.8		72.0		71.8
5"	78.2		78.4		76.7
6"	62.8		63.0		69.3
1"'					104.8
2"'					72.4
3"'					74.1
4"'					69.3
5"'					66.4

[a] $\Delta(\delta_5 - \delta_{4a})$.

[b] $\Delta(\delta_{5a} - \delta_{5b})$.

Table 3 ^{13}C-NMR spectroscopic data for **11** (CD_3OD, 100 MHz).

	C		
Aglycone			
1	131.7		
2	116.8		
3	146.1		
4	144.7		
5	117.2		
6	121.4		
7	36.6		
8	72.2		
Inner glucose		Outer glucose	
1'	104.3	1'''	107.0
2'	75.9	2'''	75.6[c]
3'	83.4[a]	3'''	77.8
4'	70.6[b]	4'''	71.8[d]
5'	75.7[c]	5'''	75.3
6'	62.2	6'''	64.7
Rhamnose			
1''	102.3		
2''	83.5[a]		
3''	71.7[d]		
4''	74.2		
5''	70.5[b]		
6''	18.3		
Caffeoyl to inner glucose		Caffeoyl to outer glucose	
1''''	127.9	1''''	127.8
2''''	115.5[e]	2''''	115.6[e]
3''''	147.1	3''''	147.1
4''''	149.7	4''''	149.7
5''''	116.6[f]	5''''	116.7[f]
6''''	123.2	6''''	123.2

7""	147.9	7"''	147.2
8""	115.5	8"''	115.5
9""	168.5	9"''	169.2

[a, b, c, d, e, f] The same superscripts may be interchangeable.

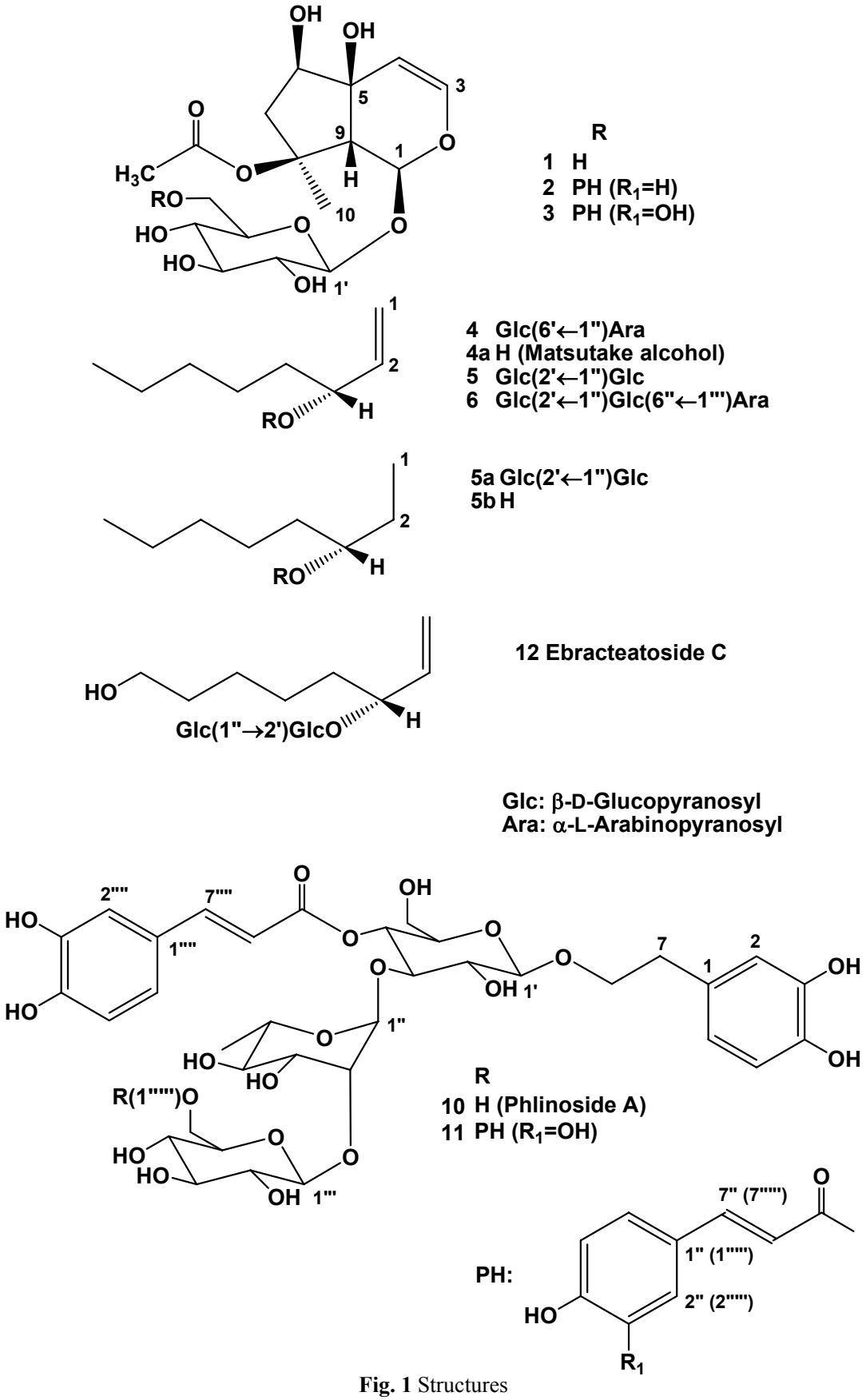

Fig. 1 Structures

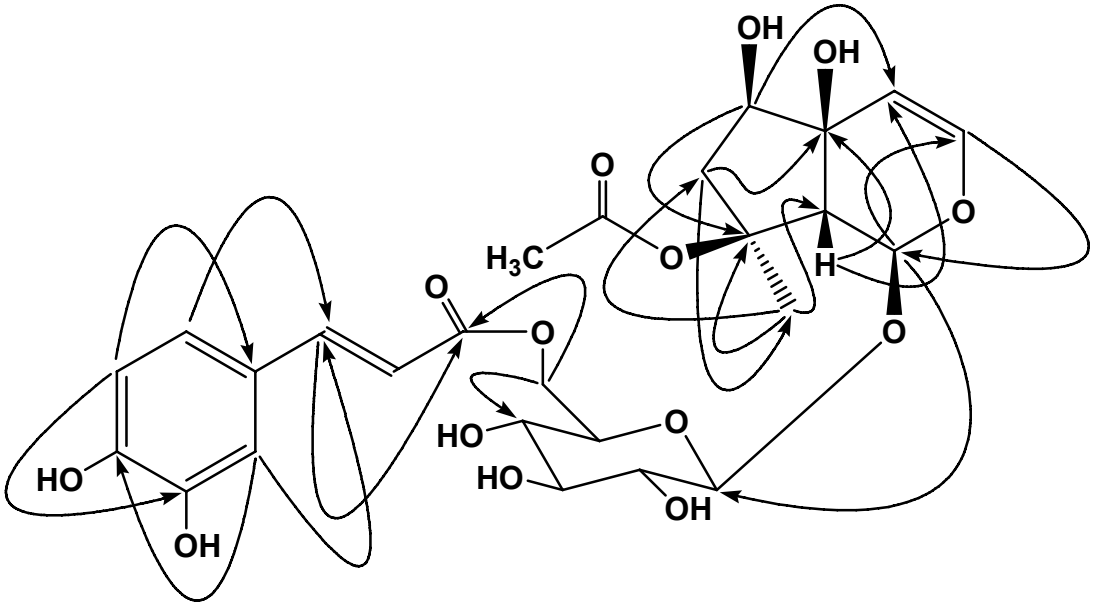

Fig. 2 Diagnostic HMBC (H → C) correlations of **3**

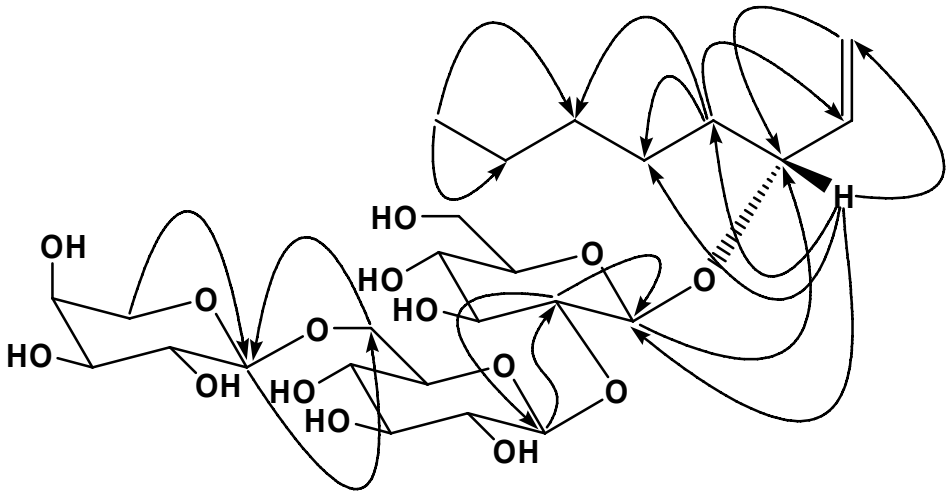

Fig. 3 Diagnostic HMBC (H→C) correlations of **6**