# Water-Soluble Constituents of Cumin: Monoterpenoid Glucosides

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**From the water-soluble portion of the methanol extract of cumin (fruit of *Cuminum cyminum* L.), which has been used as a spice and medicine since antiquity, sixteen monoterpenoid glucosides, including twelve new compounds, were isolated. Their structures were clarified by spectral investigation.**

**Key words** cumin; *Cuminum cyminum* fruit; *p*-menthane glucoside; hydroxycuminyl glucoside

Cumin [*Cuminum cyminum* L.; Umbelliferae] is known to have been cultivated since antiquity, and is now mainly cultivated in North Africa, Iran, India, Indonesia and China. Its fruit has been used as a popular aromatic herb and spice, such as a main constituent of curry powder. The fruit has also been used for medicinal purposes as a remedy for diarrhea, flatulence and indigestion.[1)] It contains an essential oil (3—4%) rich in cuminaldehyde (main; 35—60%), and $\alpha$- and $\beta$-pinene, $\delta$-3-carene, 1,8-cineole, $\alpha$- and $\beta$-phellandrene, *p*-cymene, limonene, $\alpha$- and $\gamma$-terpinene, $\alpha$-terpineol, terpinene-4-ol cuminyl alcohol, *trans*-dihydrocarvone (menthane type monoterpenoids), myrcene, linalool (acyclic monoterpenoids), $\beta$-caryophyllene, $\beta$-farnesene, $\beta$-elemene (sesquiterpenoids) *et al.* were reported as other constituents.[2,3)] However, only two flavonoid glycosides (7-*O*-$\beta$-D-glucopyranosides of apigenin and luteolin) have been published as constituents of the water-soluble portion of this fruit.[4)] In continuation of our studies on the water-soluble constituents of spices,[5)] and to show the relationship between the essential oil and the water-soluble constituents, we undertook a detailed investigation of this fruit. In this paper, we discuss the isolation and structural elucidation of monoterpenoid glucosides.

Commercial cumin was extracted with 70% methanol, and the methanolic extract was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. The methanol eluate fraction (glycoside fraction) was chromatographed on Sephadex LH-20, then subjected to a combination of silica gel, Lobar RP-8 column chromatography and HPLC to isolate sixteen monoterpenoid glucosides (**1**—**16**). Among them, twelve glucosides (**1**—**3**, **5**, **6**, **9**, **11**—**16**) are new compounds. All new glucosides described in this paper were $\beta$-D-glucopyranosides as shown by their $^1$H- and $^{13}$C-NMR data (Tables 1 and 2). This was confirmed by hydrolysis to yield D-glucose or by comparison of the $[\alpha]_D$ or $[M]_D$ values with those of their aglycones except **13**.[6,7)] Their molecular formulae were suggested from the accurate mass number of the $[M+H]^+$ or $[M+Na]^+$ or $[M+K]^+$ ion peak in the high-resolution positive FAB-MS.

Glucoside **1** ($C_{16}H_{24}O_7$, an amorphous powder, $[\alpha]_D^{24}$ $-44°$) was obtained as one of the main components of the glycoside fraction, and showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 329 and 149 in the positive FAB-MS. The $^1$H- and $^{13}$C-NMR spectral data of **1** (Tables 1, 2) revealed the presence of one 1,4-disubstituted benzene ring, two hydroxymethyls, one *sec*-methyl and one methine, in addition to the $\beta$-glucopyranosyl moiety. From analysis of the heteronuclear multiplet-bond correlation (HMBC) spectral data (correlations: H-2/C-4, C-6, C-7; H-3/C-1, C-2, C-4, C-5, C-8; H-5/C-1, C-3, C-6, C-8; H-6/C-2, C-4, C-7; $H_2$-7/C-1, C-2, C-6, Glc C-1; H-8/C-3, C-4, C-5, C-9, C-10; $H_2$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-7), the aglycone was clarified to be 9-hydroxycuminyl alcohol (*p*-mentha-1,3,5-triene-7,9-diol), and the location of the glucosyl group was indicated to be C-7. Enzymatic hydrolysis of **1** gave an aglycone (**1a**; $C_{10}H_{14}O_2$, an amorphous powder, $[\alpha]_D^{21}$ $+13°$), which showed a plus $[\alpha]_D$ value, and D-glucose. Since (8*S*)-*p*-mentha-1,3,5-trien-3-ol showed a minus optical rotation ($[\alpha]_D$ $-14.7°$),[8)] the configuration at C-8 of **1** should be *R*. Then, **1** was characterized as (8*R*)-9-hydroxycuminyl $\beta$-D-glucopyranoside.

Glucoside **2** ($C_{16}H_{24}O_8$, an amorphous powder, $[\alpha]_D^{22}$ $-31°$) showed $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at *m/z* 345 and 183 in the positive FAB-MS. Enzymatic hydrolysis with $\beta$-glucosidase gave an aglycone (**2a**; $C_{10}H_{14}O_3$, an amorphous powder, $[\alpha]_D^{22}$ $+12°$) and D-glucose. Glucoside **2** was considered to be an 8-hydroxylated derivative of **1** by comparison of its $^1$H- and $^{13}$C-NMR spectral data and glycosilaton shift values with those of **1**. The result of the HMBC experiment (see experimental) also supported this conclusion. As the optical rotation of (8*S*)-8,9-dihydroxycuminyl alcohol was reported be plus,[9)] the configuration at C-8 of **2** should be *S*. Therefore, **2** was characterized as (8*S*)-8,9-dihydroxycuminyl $\beta$-D-glucopyranoside.

Glucoside **3** ($C_{16}H_{24}O_7$, an amorphous powder, $[\alpha]_D^{24}$ $-40°$) revealed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 351 and 149 in the positive FAB-MS, and the $^1$H- and $^{13}$C-NMR spectral data (Tables 1, 2) showed the presence of one 1,4-disubstituted benzene ring, two *tert*-methyls, one hydroxymethyl and one hydroxylated quaternary carbon, in addition to the $\beta$-glucopyranosyl moiety. From the result of the HMBC experiment (see Experimental) of **3**, the aglycone was indicated to be 8-hydroxycuminyl alcohol, and the glucosyl group was located at C-7. Since the glucose was suggested to be D-form from its minus optical rotation,[6,7)] **3** was characterized as 8-hydroxycuminyl $\beta$-D-glucopyranoside.

Glucosides **4** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23}$ $-20°$), **5** ($C_{16}H_{28}O_7$, mp 215—217 °C, $[\alpha]_D^{23}$ $+89°$) and **6** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23}$ $+126°$) have the same molecular formulae, and their $^1$H- and $^{13}$C-NMR spectral data (Tables 1, 2) showed the presence of one $\beta$-glucopyranosyl group, and one tri-substituted double bond, one *tert*-

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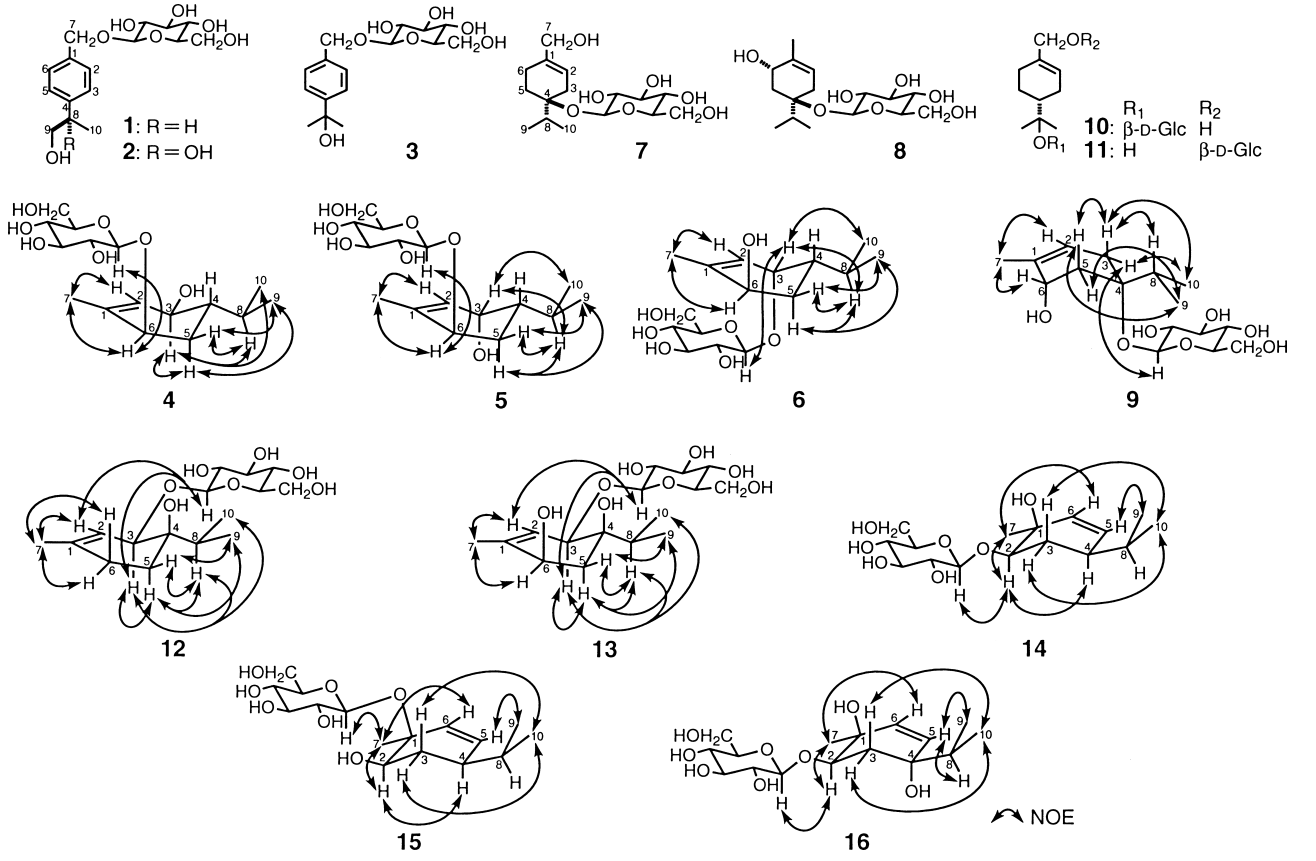


Fig. 1. Structures of **1**—**16**, and NOE Interactions Observed in the NOESY Spectra of **4**—**6**, **9** and **12**—**16**

methyl, two *sec*-methyls, one methylene, two methines and two hydroxylated methines in the aglycone moiety, respectively. From analysis of their HMBC correlations (see Experimental), the aglycones were confirmed to be *p*-menth-1-ene-3,6-diol, and the location of the glucosyl groups was indicated to be C-6 for **4** and **5**, and C-3 for **6**. The observed nuclear Overhauser effect (NOE) interaction between $H_3$-9/H-$5_{ax}$, H-$5_{eq}$ in their NOE spectroscopy (NOESY) spectra suggested that the configuration of their C-4 isopropyl was equatorial. The configuration of C-3 and C-6 hydroxyls of **4** was indicated to be equatorial and axial, respectively, by the NOE interaction between H-3/H-$5_{ax}$ in its NOESY spectrum (Fig. 1), and by the coupling constant of H-3 and H-6 signals (H-3; br d, $J$=10.0 Hz, H-6; dd, $J$=3.5, 3.5 Hz) in the $^1$H-NMR spectrum. Since the enzymatic hydrolysis of **4** gave an aglycone (**4a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{23}$ +8°) and D-glucose, **4** was revealed to be $4_{ax}$-H-*p*-menth-1-ene-$3_{eq}$,$6_{ax}$-diol 6-*O*-$\beta$-D-glucopyranoside. The absolute configuration at C-6 of **4** was indicated to be *R* by the values of the $^{13}$C glycosylation shift [$\Delta\delta$($\delta$ glycoside−$\delta$ aglycone)] of the $\alpha$- and $\beta$-carbon and the chemical shift of the glucosyl anomeric carbon [C-6 ($\alpha$-carbon): $\Delta\delta$+6.6, *R*-alcohols, about $\Delta\delta$+4 to +7, *S*-alcohols, about $\Delta\delta$+9 to +11; C-5 ($\beta$-carbon): $\Delta\delta$−4.8, $\beta$-pro-*S*-side carbon of *R*-alcohols, about $\Delta\delta$−4 to −5, $\beta$-pro-*S*-side carbon of *S*-alcohols, about $\Delta\delta$ 0 to −2; glucosyl C-1: $\delta$ 102.85, *R*-alcohols, about $\delta$ 102, *S*-alcohols, about $\delta$ 106; (Table 2)].[10—16] Thus, **4** was characterized as (3*S*,4*S*,6*R*)-*p*-menth-1-ene-3,6-diol 6-*O*-$\beta$-D-glucopyranoside. On the other hand, the configuration of the C-3 and C-6 hydroxyls of **5** was concluded to be axial by the narrow H-3 and H-6 signals found as a double doublet (H-3; $J$=3.0, 5.5 Hz, H-6; $J$=3.0, 3.0 Hz) in their $^1$H-NMR spectra. Enzymatic hydrolysis of **5** gave an aglycone (**5a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{23}$ +240°) and D-glucose, and the absolute configuration at C-6 was indicated to be *R* in the same way described for **4** (Table 2). So, **5** was characterized as (3*R*,4*S*,6*R*)-*p*-menth-1-ene-3,6-diol 6-*O*-$\beta$-D-glucopyranoside. Furthermore, **6** was hydrolyzed with $\beta$-glucosidase and, from the hydrolyzed mixtures, **5a** and D-glucose were obtained. As the position of the glucosyl unit was revealed to be C-3 from the HMBC experiment (see Experimental), **6** was characterized as (3*R*,4*S*,6*R*)-*p*-menth-1-ene-3,6-diol 3-*O*-$\beta$-D-glucopyranoside. Although **4** was reported as a constituent of *Eupatorium tinifolium*,[17] the absolute structure was defined in this paper.

Glucosides **7** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24}$ −16°) and **8** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24}$ −29°) were identified as (4*S*)-*p*-menth-1-ene-4,7-diol 4-*O*-$\beta$-D-glucopyranoside and (4*R*,6*S*)-*p*-menth-1-ene-4,6-diol 4-*O*-$\beta$-D-glucopyranoside, which were isolated from the fruit of ajowan.[18]

Glucoside **9** ($C_{16}H_{28}O_7$, mp 78—81 °C, $[\alpha]_D^{21}$ −2°) showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 355 and 153 in the positive FAB-MS, and enzymatic hydrolysis of **9** gave an aglycone (**9a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{21}$ +40°) and D-glucose. It showed $^1$H- and $^{13}$C-NMR spectral features similar to those of **8** (Tables 1, 2). From the analysis of HMBC spectral data (correlations: H-2/C-3, C-4, C-6, C-7; H-$3_{ax}$/C-1, C-2, C-5, C-8; H-$3_{eq}$/C-1, C-2, C-4, C-5, C-8; $H_2$-5/C-1, C-3, C-4, C-6, C-8; H-$6_{eq}$/C-1, C-2, C-4; $H_3$-7/C-1,

Table 1. $^1$H-NMR Chemical Shifts of **1**—**16**, **1a**, **2a**, **4a**, **5a**, **9a**, **11a**, **12a**, **14a** and **16a** (in Pyridine-$d_5$, 500 MHz)

| | **1** | **1a** | **2** | **2a** | **3** |
|---|---|---|---|---|---|
| H-2,6 | 7.50 d (8.0) | 7.40 d (8.0) | 7.57 d (8.0) | 7.67 d (8.0) | 7.57 d (8.0) |
| H-3,5 | 7.31 d (8.0) | 7.59 d (8.0) | 7.86 d (8.0) | 7.94 d (8.0) | 7.78 d (8.0) |
| $H_2$-7 | 4.84 d (11.5) | 4.97 s (2H) | 4.86 d (12.0) | 5.00 s (2H) | 4.87 d (12.0) |
| | 5.18 d (11.5) | — | 5.20 d (12.0) | — | 5.21 d (12.0) |
| H-8 | 3.12 sextet (7.0) | 3.15 sextet (7.0) | — | — | — |
| $H_2$-9 | 3.89 dd (7.0, 10.5) | 3.92 dd (7.0, 10.0) | 4.08 d (10.5) | 4.10 d (11.0) | — |
| | 4.00 dd (7.0, 10.5) | 4.03 dd (7.0, 10.0) | 4.13 d (10.5) | 4.15 d (11.0) | — |
| $H_3$-9 | — | — | — | — | 1.73 s |
| $H_3$-10 | 1.39 d (7.0) | 1.43 d (7.0) | 1.86 s | 1.89 s | 1.73 s |
| Glc H-1 | 5.00 d (7.5) | — | 5.02 d (7.5) | — | 5.02 d (8.0) |

| | **4** | **4a** | **5** | **5a** |
|---|---|---|---|---|
| H-2 | 5.95 br s | 5.93 br s | 6.04 d (5.5) | 6.02 d (5.5) |
| H-$3_{ax}$ | 4.22 br d (10.0) | 4.27 br d (9.5) | — | — |
| H-$3_{eq}$ | — | — | 4.31 dd (3.0, 5.5) | 4.29 dd (3.0, 5.5) |
| H-$4_{ax}$ | 2.28 dddd (3.0, 3.0, 10.0, 13.5) | 2.26 dddd (3.0, 3.0, 9.5, 13.0) | 1.79 dddd (3.0, 3.0, 8.0, 13.5) | 1.86 dddd (3.0, 3.0, 9.0, 13.0) |
| H-$5_{ax}$ | 1.31 ddd (3.5, 13.5, 13.5) | 1.55 ddd (3.0, 13.0, 13.0) | 1.89 ddd (3.0, 13.5, 13.5) | 2.12 ddd (4.5, 13.0, 13.0) |
| H-$5_{eq}$ | 2.26 ddd (3.0, 3.5, 13.5) | 2.05 ddd (3.0, 3.0, 13.0) | 2.40 ddd (3.0, 3.0, 13.5) | 2.19 ddd (3.0, 3.0, 13.0) |
| H-$6_{eq}$ | 4.37 dd (3.5, 3.5) | 4.28 dd (3.5, 3.5) | 4.40 dd (3.0, 3.0) | 4.43 dd (3.0, 4.5) |
| $H_3$-7 | 1.95 s | 1.99 s | 1.97 s | 2.01 s |
| H-8 | 2.50 dquintet (3.0, 7.0) | 2.54 dquintet (3.0, 7.0) | 2.05 dquintet (6.5, 8.0) | 2.09 dquintet (6.5, 9.0) |
| $H_3$-9 | 1.11 d (7.0) | 1.03 d (7.0) | 1.15 d (6.5) | 1.19 d (6.5) |
| $H_3$-10 | 0.91 d (7.0) | 0.91 d (7.0) | 1.09 d (6.5) | 1.08 d (6.5) |
| Glc H-1 | 4.94 d (7.5) | — | 4.96 d (8.0) | — |

| | **6** | **7** | **8** | **9** |
|---|---|---|---|---|
| H-2 | 6.32 d (5.5) | 5.88 br s | 5.51 br s | 5.49 br s |
| H-$3_{ax}$ | — | 2.36 br d (18.0) | 2.30 br d (18.0) | 2.32 dd (2.0, 18.0) |
| H-$3_{eq}$ | 4.38 dd (3.0, 5.5) | 2.61 br d (18.0) | 2.43 br d (18.0) | 2.60 dd (2.0, 18.0) |
| H-$4_{ax}$ | 1.89 dddd (3.0, 3.0, 7.0, 13.0) | — | — | — |
| H-$5_{ax}$ | 2.10 ddd (3.0, 13.0, 13.0) | 1.75 ddd (5.5, 8.5, 13.5) | 2.01 dd (9.0, 13.0) | 1.82 dd (5.0, 14.0) |
| H-$5_{eq}$ | 2.16 ddd (3.0, 3.0, 13.0) | 2.08 ddd (5.5, 5.5, 13.5) | 2.68 dd (5.0, 13.0) | 2.45 ddd (2.0, 2.0, 14.0) |
| H-$6_{ax}$ | — | 2.85 ddd (5.5, 8.5, 18.0) | 5.30 dd (5.0, 9.0) | — |
| H-$6_{eq}$ | 4.26 dd (3.0, 3.0) | 2.21 ddd (5.5, 5.5, 18.0) | — | 4.17 dd (2.0, 5.0) |
| $H_2$-7 | — | 4.30 br s | — | — |
| $H_3$-7 | 1.87 s | — | 2.02 s | 1.99 s |
| H-8 | 2.28 dquintet (7.0, 7.0) | 2.14 septet (7.0) | 2.24 septet (6.5) | 2.22 septet (7.0) |
| $H_3$-9 | 1.00 d (7.0) | 1.07 d (7.0) | 1.00 d (6.5) | 1.15 d (7.0) |
| $H_3$-10 | 1.16 d (7.0) | 1.05 d (7.0) | 1.08 d (6.5) | 0.89 d (7.0) |
| Glc H-1 | 4.99 d (7.5) | 5.03 d (7.5) | 5.06 d (7.5) | 4.94 d (7.5) |

| | **9a** | **10** | **11** | **11a** |
|---|---|---|---|---|
| H-2 | 5.50 br s | 5.90 br d (3.0) | 5.91 br d (3.0) | 5.97 br d (3.0) |
| H-$3_{ax}$ | 2.19 dd (2.0, 17.5) | 2.23 m | 2.04 br dd (13.0, 17.0) | 2.09 ddd (3.0, 13.0, 17.0) |
| H-$3_{eq}$ | 2.31 dd (2.0, 17.5) | 2.23 m | 2.27 ddd (3.0, 3.0, 17.0) | 2.38 br d (17.0) |
| H-$4_{ax}$ | — | 1.88 dddd (2.0, 2.0, 13.0, 13.0) | 1.69 dddd (3.0, 3.0, 13.0, 13.0) | 1.77 dddd (3.0, 3.0, 13.0, 13.0) |
| H-$5_{ax}$ | 1.83 dd (4.5, 14.0) | 1.32 br ddd (5.0, 13.0, 13.0) | 1.40 br ddd (4.0, 13.0, 13.0) | 1.44 br ddd (5.0, 13.0, 13.0) |
| H-$5_{eq}$ | 2.25 ddd (2.0, 3.0, 14.0) | 2.27 br d (13.0) | 2.12 br d (13.0) | 2.21 br d (13.0) |
| H-$6_{ax}$ | — | 1.95 br dd (13.0, 17.0) | 2.11 br dd (13.0, 16.0) | 2.23 br dd (13.0, 17.0) |
| H-$6_{eq}$ | 4.27 br s | 2.31 ddd (2.0, 5.0, 17.0) | 2.40 br dd (4.0, 16.0) | 2.34 ddd (3.0, 3.0, 17.0) |
| $H_2$-7 | — | 4.26 d (8.5) | 4.28 d (12.0) | 4.31 d (13.5) |
| | — | 4.28 d (8.5) | 4.50 d (12.0) | 4.34 d (13.5) |
| $H_3$-7 | 1.99 s | — | — | — |
| H-8 | 1.77 septet (7.0) | — | — | — |
| $H_3$-9 | 1.07 d (7.0) | 1.37[a] s | 1.30[a] s | 1.33[a] s |
| $H_3$-10 | 1.02 d (7.0) | 1.39[a] s | 1.31[a] s | 1.35[a] s |
| Glc H-1 | — | 5.03 d (8.0) | 4.92 d (8.0) | — |

Table 1. (Continued)

| | 12 | 12a | 13 |
|---|---|---|---|
| H-2 | 5.84 br s | 5.66 br s | 5.89 br s |
| H-$3_{ax}$ | 4.68 br s | 4.45 br s | 4.68 br s |
| H-$5_{ax}$ | 1.57 ddd (5.5, 8.0, 13.0) | 1.62 ddd (5.5, 8.0, 13.5) | 1.90 dd (4.5, 14.0) |
| H-$5_{eq}$ | 1.93 ddd (5.5, 5.5, 13.0) | 1.98 ddd (5.5, 5.5, 13.5) | 2.31 dd (4.5, 14.0) |
| H-$6_{ax}$ | 2.26 ddd (5.5, 8.0, 17.5) | 2.27 ddd (5.5, 8.0, 17.0) | — |
| H-$6_{eq}$ | 1.83 ddd (5.5, 5.5, 17.5) | 1.86 ddd (5.5, 5.5, 17.0) | 4.15 dd (4.5, 4.5) |
| $H_3$-7 | 1.62 s | 1.66 s | 1.94 s |
| H-8 | 2.31 septet (7.0) | 2.22 septet (7.0) | 2.33 septet (7.0) |
| $H_3$-9 | 1.09 d (7.0) | 1.15 d (7.0) | 1.09 d (7.0) |
| $H_3$-10 | 1.06 d (7.0) | 1.05 d (7.0) | 1.07 d (7.0) |
| Glc H-1 | 5.17 d (8.0) | — | 5.16 d (8.0) |

| | 14 | 14a | 15 |
|---|---|---|---|
| H-$2_{ax}$ | 4.45 dd (3.0, 7.5) | 4.37 dd (3.0, 7.5) | 4.41 dd (3.5, 8.0) |
| H-$3_{ax}$ | 2.08 ddd (7.0, 7.5, 13.5) | 2.03 ddd (6.5, 7.5, 13.5) | 1.92 ddd (7.0, 8.0, 13.5) |
| H-$3_{eq}$ | 2.16 ddd (3.0, 5.0, 13.5) | 2.25 ddd (3.0, 7.0, 13.5) | 2.25 ddd (3.5, 5.0, 13.5) |
| H-$4_{ax}$ | 2.40 dddd (3.0, 5.0, 7.0, 7.0) | 2.42 dddd (2.5, 6.5, 7.0, 7.0) | 2.30 dddd (3.0, 5.0, 7.0, 7.0) |
| H-5 | 5.66 dd (3.0, 10.0) | 5.78 dd (2.5, 10.0) | 5.86 dd (3.0, 10.0) |
| H-6 | 5.92 d (10.0) | 6.00 d (10.0) | 6.15 d (10.0) |
| $H_3$-7 | 1.67 s | 1.75 s | 1.75 s |
| H-8 | 1.58 octet (7.0) | 1.64 octet (7.0) | 1.64 octet (7.0) |
| $H_3$-9 | 0.86 d (7.0) | 0.89 d (7.0) | 0.88 d (7.0) |
| $H_3$-10 | 0.85 d (7.0) | 0.88 d (7.0) | 0.88 d (7.0) |
| Glc H-1 | 5.04 d (7.5) | — | 5.17 d (8.0) |

| | 16 | 16a |
|---|---|---|
| H-$2_{ax}$ | 4.57 dd (2.5, 6.0) | 4.45 dd (3.0, 7.0) |
| H-$3_{ax}$ | 2.30 dd (6.0, 14.5) | 2.20 dd (7.0, 13.5) |
| H-$3_{eq}$ | 2.69 dd (2.5, 14.5) | 2.72 dd (3.0, 13.5) |
| H-5 | 5.94 d (10.0) | 5.99 d (10.0) |
| H-6 | 5.96 d (10.0) | 6.02 d (10.0) |
| $H_3$-7 | 1.71 s | 1.75 s |
| H-8 | 1.95 septet (7.0) | 1.96 septet (7.0) |
| $H_3$-9 | 1.09 d (7.0) | 1.07 d (7.0) |
| $H_3$-10 | 1.16 d (7.0) | 1.15 d (7.0) |
| Glc H-1 | 5.16 d (8.0) | — |

$\delta$ in ppm from TMS [coupling constants ($J$) in Hz are given in parentheses]. *a*) Assignments may be interchanged in each column.

C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-4), **9** was clarified to be a $\beta$-D-glucopyranoside of *p*-menth-1-ene-4,6-diol, and the position of the glucosyl unit was C-4. The observed NOE interaction between $H_3$-9/H-$5_{ax}$, H-$5_{eq}$ and between $H_3$-10/H-$3_{ax}$, H-$3_{eq}$ in the NOESY spectrum suggested that the configuration of the C-4 isopropyl was equatorial, and the H-6 signal which was found to be a narrow double doublet ($J$=2.0, 5.5 Hz) in the $^1$H-NMR spectrum suggested that the configuration of the C-6 hydroxyl was axial. The absolute structure of the aglycone moiety of **9** was examined by comparison of its glycosylation shift values (C-3, C-4, C-5 and C-8) with those of **7** and **8**.[18] As the glycosylation shift values of **9** showed an obvious difference between the values of **7** and **8**, which have a 4*R* configuration [C-3 (**7** and **8**; −4.0 and −4.5, **9**; −5.4), C-4 (**7** and **8**; +8.4 and +8.6, **9**; +7.6), C-5 (**7** and **8**; −2.4 and −1.8, **9**; −2.8), C-8 (**7** and **8**; −3.4 and −3.9, **9**; −1.1)], the absolute configuration at C-4 of **9** was concluded to be *S*. So, **9** was characterized as (4*S*,6*S*)-*p*-menth-1-ene-4,6-diol 4-*O*-$\beta$-D-glucopyranoside.

Glucoside **10** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{22}$ +8°) was identified as (4*R*)-*p*-menth-1-ene-7,8-diol 8-*O*-$\beta$-D-glucopyranoside, which was isolated from fennel.[19]

Glucoside **11** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24}$ −6°) revealed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 333 and 153 in the positive FAB-MS, and showed similar $^1$H- and $^{13}$C-NMR spectral data with those of **10** (Tables 1, 2). Enzymatic hydrolysis of **11** gave an aglycone (**11a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{24}$ +66°), which was identical with the aglycone of **10**, as well as D-glucose. So, **11** was indicated to be a $\beta$-D-glucopyranoside of (4*R*)-*p*-menth-1-ene-7,8-diol. Since the position of the glucosyl unit was proved to be C-7 from the cross-peak between the glucosyl H-1/C-7 in the HMBC spectrum (see Experimental), **11** was characterized as (4*R*)-*p*-menth-1-ene-7,8-diol 7-*O*-$\beta$-D-glucopyranoside.

Glucoside **12** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{21}$ −86°) showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 333 and 153 in the positive FAB-MS, and was hydrolyzed with $\beta$-glucosidase to an aglycone (**12a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{21}$ −29°) and D-glucose. The $^1$H- and $^{13}$C-NMR spectral data of **12** (Tables 1, 2) showed the

Table 2. $^{13}$C-NMR Chemical Shifts of **1**—**16**, **1a**, **2a**, **4a**, **5a**, **9a**, **11a**, **12a**, **14a** and **16a** (in Pyridine-$d_5$, 125 MHz)

| | **1** | **1a** | **2** | **2a** | **3** | **4** | **4a** | **5** | **6** |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 136.64 (−4.7) | 141.38 | 136.80 (−4.8) | 141.63 | 136.54 | 134.15 (−2.7) | 136.83 | 135.97 (−2.5) | 138.61 |
| C-2 | 128.58 | 127.98 | 128.04 | 126.83 | 128.16 | 133.16 | 131.20 | 129.96 | 127.43 (−0.6) |
| C-3 | 128.02 | 127.26 | 126.20 | 126.24 | 125.20 | 68.88 | 69.05 | 64.30 | 74.94 (+10.5) |
| C-4 | 145.10 | 144.29 | 147.77 | 147.04 | 150.92 | 42.33 | 42.74 | 40.56 | 41.04 (+0.0) |
| C-5 | 128.02 | 127.26 | 126.20 | 126.24 | 125.20 | 26.36 (−4.8) | 31.13 | 26.45 (−5.0) | 31.87 |
| C-6 | 128.58 | 127.98 | 128.04 | 126.83 | 128.16 | 74.10 (+6.6) | 67.50 | 74.71 (+6.5) | 67.99 |
| C-7 | 71.02 (+6.7) | 64.28 | 70.93 (+6.7) | 64.28 | 70.89 | 20.79 | 21.06 | 21.24 | 21.35 |
| C-8 | 43.17 | 43.17 | 74.80 | 74.83 | 71.40 | 26.52 | 26.56 | 28.58 | 27.52 |
| C-9 | 68.50 | 68.54 | 71.74 | 72.07 | 32.61 | 21.31 | 21.37 | 21.19 | 21.24 |
| C-10 | 18.51 | 18.47 | 26.88 | 26.93 | 32.61 | 17.14 | 17.27 | 21.26 | 21.98 |
| Glc-1 | 104.03 | | 104.08 | | 104.03 | 102.85 | | 102.49 | 106.14 |
| Glc-2 | 75.32 | | 75.31 | | 75.31 | 75.03 | | 75.09 | 75.71 |
| Glc-3 | 78.60 | | 78.60 | | 78.60 | 78.73 | | 78.60 | 78.71 |
| Glc-4 | 71.79 | | 71.74 | | 71.74 | 71.99 | | 72.02 | 71.94 |
| Glc-5 | 78.63 | | 78.65 | | 78.65 | 78.46 | | 78.37 | 78.28 |
| Glc-6 | 62.89 | | 62.85 | | 62.84 | 63.09 | | 63.07 | 63.04 |

| | **5a** | **7** | **8** | **9** | **9a** | **10** | **11** | **11a** | **12** |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 138.50 | 139.32 | 139.14 | 137.66 | 135.86 | 139.26 | 135.14 (−4.0) | 139.15 | 138.57 |
| C-2 | 128.06 | 119.17 | 120.18 | 120.12 | 121.65 | 121.33 | 125.13 | 121.59 | 121.09 (−4.1) |
| C-3 | 64.46 | 31.30 (−4.0) | 31.02 | 30.70 (−5.4) | 36.14 | 27.14 | 27.24 | 27.24 | 76.04 (+8.1) |
| C-4 | 41.01 | 79.75 (+8.4) | 82.44 | 80.21 (+7.6) | 72.64 | 44.59 (−1.3) | 45.85 | 46.17 | 72.94 (−0.1) |
| C-5 | 31.40 | 29.41 (−2.4) | 40.70 | 36.64 (−2.8) | 39.40 | 23.96 | 24.16 | 24.34 | 26.89 |
| C-6 | 68.18 | 23.91 | 67.95 | 68.04 | 68.72 | 27.12 | 27.33 | 27.31 | 28.21 |
| C-7 | 21.35 | 66.23 | 19.90 | 21.14 | 21.19 | 66.55 | 73.15 (+6.6) | 66.59 | 23.21 |
| C-8 | 28.60 | 34.04 (−3.4) | 35.04 | 36.50 (−1.1) | 37.64 | 79.30 (+8.1) | 71.14 | 71.21 | 32.14 |
| C-9 | 21.20 | 17.72 | 18.15 | 18.57 | 17.14 | 23.71[a] (−3.3) | 27.03[a] | 27.01[a] | 16.84 |
| C-10 | 21.48 | 17.32 | 17.28 | 17.50 | 17.27 | 24.34[a] (−3.7) | 27.90[a] | 28.01[a] | 18.20 |
| Glc-1 | | 99.12 | 98.81 | 99.23 | | 98.63 | 103.54 | | 102.35 |
| Glc-2 | | 75.59 | 75.59 | 75.28 | | 75.43 | 75.30 | | 75.26 |
| Glc-3 | | 78.83 | 78.75 | 78.95 | | 78.96 | 78.67 | | 78.74 |
| Glc-4 | | 72.09 | 71.97 | 72.23 | | 71.94 | 71.80 | | 71.86 |
| Glc-5 | | 78.12 | 77.94 | 78.23 | | 78.15 | 78.54 | | 78.49 |
| Glc-6 | | 63.17 | 63.06 | 63.12 | | 63.05 | 62.89 | | 62.91 |

| | **12a** | **13** | **14** | **15** | **14a** | **16** | **16a** |
|---|---|---|---|---|---|---|---|
| C-1 | 136.46 | 140.29 | 70.05 (−0.5) | 79.28 (+8.7) | 70.57 | 69.21 (−1.4) | 70.63 |
| C-2 | 125.21 | 122.30 | 81.30 (+7.8) | 70.99 (−2.6) | 73.53 | 80.98 (+6.5) | 74.52 |
| C-3 | 67.97 | 76.63 | 27.15 (−3.2) | 29.71 | 30.35 | 32.87 (−3.1) | 35.92 |
| C-4 | 72.99 | 75.09 | 39.18 | 39.64 | 38.92 | 71.69 | 72.78 |
| C-5 | 26.91 | 34.82 | 130.45 | 133.94 | 130.62 | 134.61 | 133.77 |
| C-6 | 28.09 | 68.32 | 134.16 | 131.12 (−3.5) | 134.61 | 133.07 | 134.20 |
| C-7 | 23.18 | 20.47 | 25.85 | 23.25 (−2.1) | 25.36 | 26.42 | 25.63 |
| C-8 | 32.58 | 32.37 | 32.22 | 32.55 | 32.22 | 38.00 | 37.82 |
| C-9 | 17.11 | 16.74 | 20.14 | 20.28 | 20.04 | 17.92 | 17.83 |
| C-10 | 18.35 | 18.24 | 20.18 | 20.28 | 20.14 | 17.13 | 17.11 |
| Glc-1 | | 102.78 | 103.35 | 99.30 | | 102.28 | |
| Glc-2 | | 75.19 | 75.00 | 75.54 | | 75.05 | |
| Glc-3 | | 78.71 | 78.59 | 78.82 | | 78.69 | |
| Glc-4 | | 71.84 | 72.05 | 72.08 | | 72.12 | |
| Glc-5 | | 78.55 | 78.49 | 78.41 | | 78.69 | |
| Glc-6 | | 62.91 | 62.97 | 63.03 | | 62.98 | |

$\delta$ in ppm from TMS. $\Delta\delta$($\delta$ glucoside − $\delta$ aglycone) are given in parentheses. *a*) Assignments may be interchanged in each column.

presence of one *tert*-methyl, two *sec*-methyls, two methylenes, one methine, one hydroxylated methine, one hydroxylated quaternary carbon and one trisubstituted double bond, in addition to the $\beta$-glucopyranosyl moiety. From analysis of HMBC spectral data (correlations: H-2/C-4, C-6, C-7; H-3/C-1, C-2, Glc C-1; H-$5_{ax}$/C-1, C-3, C-4, C-6; H-$5_{eq}$/C-1, C-3, C-4, C-6, C-8; H-$6_{ax}$/C-1, C-2, C-4, C-5; H-$6_{eq}$/C-1, C-2, C-4, C-5, C-7; $H_2$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-3), the aglycone was suggested to be *p*-menth-1-ene-3,4-diol, and the location of the glucosyl group was indicated to be C-3. Since the NOE interactions between $H_3$-9/H-$5_{ax}$, H-$5_{eq}$, between $H_3$-10/H-$3_{ax}$, and between H-$3_{ax}$/H-$5_{ax}$ were observed in the NOESY spectrum of **12**, the configurations of C-3 and C-4 hydroxyls were concluded to be equatorial and axial, respectively. So, **12** was confirmed to be a 3-*O*-$\beta$-D-glucopyra-

noside of *p*-menth-1-ene-$3_{eq}$,$4_{ax}$-diol. As the glucosylation shift values of the $\alpha$- and $\beta$-carbon [C-2 ($\beta$-pro-*S*); −4.1, C-3 ($\alpha$); +8.1, C-4 ($\beta$-pro-*R*); −0.1] and the chemical shift of the anomeric carbon ($\delta$ 102.35) were in agreement with the *R* configuration,[10—16] the absolute configuration at C-3 was indicated to be *R*. Then, **12** was characterized as (3*R*,4*R*)-*p*-menth-1-ene-3,4-diol 3-*O*-$\beta$-D-glucopyranoside.

Glucoside **13** ($C_{16}H_{28}O_8$, an amorphous powder, $[\alpha]_D^{22}$ −97°) had one *tert*-methyl, two *sec*-methyls, one methylene, one methine, two hydroxylated methines, one hydroxylated quaternary carbon and one trisubstituted double bond, in addition to the $\beta$-glucopyranosyl moiety. By comparison of its $^1$H- and $^{13}$C-NMR spectral data with those of **12** (Tables 1, 2), and from the analysis of HMBC correlations (see Experimental), **13** was clarified to be $\beta$-glucopyranoside of *p*-menth-1-ene-3,4,6-triol, and the location of the glucosyl group was indicated to be C-3. The NOE interaction which was observed between $H_3$-9/H-$5_{ax}$, H-$5_{eq}$, and between H-$3_{ax}$/H-$5_{ax}$ in the NOESY spectrum of **13** suggested that the configurations of C-3 and C-4 hydroxyls were equatorial and axial, respectively. The configuration of C-6 hydroxyl was concluded to be axial by an H-6 narrow double doublet signal ($J$=4.5, 4.5 Hz) in its $^1$H-NMR spectrum. So, **13** was confirmed to be *p*-menth-1-ene-$3_{eq}$,$4_{ax}$,$6_{ax}$-triol 3-*O*-$\beta$-glucopyranoside. Since this glucose was considered to be the D-form, the same as the other glucoses, and the chemical shifts of C-3 and Glc C-1 revealed almost identical values to those of **12** [C-3 (**12**; $\delta$ 76.04, **13**; $\delta$ 76.63), glc C-1 (**12**; $\delta$ 102.35, **13**; $\delta$ 102.78)], the absolute configuration at C-3 was deduced to be *R*, the same as **12**. Consequently, **13** was concluded to be (3*R*,4*R*,6*R*)-*p*-menth-1-ene-3,4,6-triol 3-*O*-$\beta$-D-glucopyranoside.

Glucosides **14** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23}$ +8°) and **15** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{21}$ −23°) showed the presence of one disubstituted double bond, one *tert*-methyl, two *sec*-methyls, one methylene, two methines, one hydroxylated methine, one hydroxylated quaternary carbon and a $\beta$-glucopyranosyl group in their $^1$H- and $^{13}$C-NMR spectra (Tables 1, 2). From analysis of their HMBC correlations (see Experimental), the aglycone of these glucosides was indicated to be *p*-menth-5-ene-1,2-diol, and the location of the glucosyl group was concluded to be C-2 for **14**, and C-1 for **15**. The observed NOE interaction between $H_3$-9/H-$5_{ax}$, H-$5_{eq}$ in their NOESY spectra suggested that the configuration of their C-4 isopropyl was equatorial. The relative configurations of C-1 and C-2 hydroxyls of **14** and **15** were indicated to be axial and equatorial by the NOE interaction between H-2/H-4 and H-2/$H_3$-7 in their NOESY spectra (Fig. 1). Enzymatic hydrolysis of **14** and **15** gave the same aglycone (**14a**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{22}$ +24°) and D-glucose, thus they were suggested to be $\beta$-D-glucopyranosides of *p*-menth-5-ene-$1_{ax}$,$2_{eq}$-diol. The absolute configuration at the C-2 of **14** was indicated to be *R* by the values of the glycosylation shift of the $\alpha$- and $\beta$-carbon and the chemical shift of the glucosyl anomeric carbon, as shown in Table 2. Thus, **14** and **15** were characterized as (1*S*,2*R*,4*R*)-*p*-menth-5-ene-1,2-diol 2-*O*-$\beta$-D-glucopyranoside and (1*S*,2*R*,4*R*)-*p*-menth-5-ene-1,2-diol 1-*O*-$\beta$-D-glucopyranoside, respectively.

Glucoside **16** ($C_{16}H_{28}O_8$, an amorphous powder, $[\alpha]_D^{23}$ −60°) showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 349 and 169 in the positive FAB-MS, and was hydrolyzed with $\beta$-glucosidase to an aglycone (**16a**; $C_{10}H_{18}O_3$, an amorphous powder, $[\alpha]_D^{23}$ −50°) and D-glucose. By comparison of its $^1$H- and $^{13}$C-NMR spectral data with those of **14** and **15** (Tables 1, 2), **16** was suggested to be a mono-hydroxyl derivative of *p*-menth-5-ene-1,2-diol $\beta$-D-glucopyranoside. The locations of the additional hydroxyl group and the glucosyl group were indicated to be C-4 and C-2 from analysis of the HMBC spectral data (see Experimental). The NOE interaction observed between $H_3$-10/H-$3_{ax}$, H-$3_{eq}$ in the NOESY spectrum suggested that the configuration of the C-4 isopropyl was equatorial. From the coupling constant of H-2 of **16a** [**16a**; H-2: $\delta$ 4.45 ($J$=3.0, 7.0 Hz), **14a**; H-2: $\delta$ 4.37 ($J$=3.0, 7.5 Hz)] and the observed NOE interaction between H-2/$H_3$-7, **14** and **16** were estimated to have the same relative configurations at C-1 and C-2. The absolute configuration at C-2 of **16** was indicated to be *R* by the values of the glycosylation shift of the $\alpha$- and $\beta$-carbon and the chemical shift of the glucosyl anomeric carbon (Table 2). Consequently, **16** was considered to be (1*S*,2*R*,4*S*)-*p*-menth-5-ene-1,2,4-triol 2-*O*-$\beta$-D-glucopyranoside.

The ingredient relationship between the essential oil and the water-soluble constituent was confirmed by the isolation of these monoterpenoid glucosides (**1** to **3**), which showed a biosynthetic relation to cuminaldehyde.

## Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. FAB-MS were recorded with a JEOL HX-110 spectrometer using glycerol as a matrix. $^1$H- and $^{13}$C-NMR spectra were taken on a JEOL A-500 spectrometer with tetramethylsilane as an internal standard, and chemical shifts were recorded in $\delta$ values. $^1$H–$^{13}$C COSY, HMBC, NOESY and 1-D NOESY spectra were obtained with the usual pulse sequence, and data processing was performed with standard JEOL software. Column chromatography (C. C.) was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 $\mu$m, Pharmacia), Lobar RP-8 column (Merck) and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721) and spots were detected with *p*-anisaldehyde–$H_2SO_4$ reagent. HPLC separation was carried out with Symmetryprep $C_{18}$ 7 $\mu$m [Waters; column size, 7.8×300 mm; ODS], and carbohydrate analysis [Waters; column size, 3.9×300 mm; CHA] columns. Acetylation was done in the usual way using $Ac_2O$ and pyridine. No acetoxyl group had been detected by NMR spectral analysis of the materials prior to acetylation.

**Extraction and Separation** Commercial cumin (the fruit of *Cuminum Cyminums* L.; purchased from Asaoka Spices Ltd., Lot. No. 99012001; 2.0 kg) was extracted with 70% methanol (10 l×4), and the extract (281.1 g) was partitioned into ether–water and ethyl acetate–water, respectively. The aqueous portion (152.3 g) was chromatographed over Amberlite XAD-II ($H_2O$→MeOH) to give water eluate (87.1 g) and methanol eluate (65.2 g) fractions.

The methanol fraction was subjected to Sephadex LH-20 [MeOH–$H_2O$ (9 : 1)] to give four fractions (frs. A—D). Fraction B (17.95 g) was chromatographed over silica gel [$CHCl_3$–MeOH–$H_2O$ (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give thirteen fractions (frs. $B_1$—$B_{13}$). Fraction $B_3$ (0.50 g) was passed through a Lobar RP-8 column [MeCN–$H_2O$ (3 : 17—3 : 7)] to give fifteen fractions (frs. $B_{3\text{-}1}$—$B_{3\text{-}15}$), and fr. $B_{3\text{-}10}$ was subjected to Sephadex LH-20 (MeOH) and HPLC [ODS, MeOH–$H_2O$ (1 : 1)] to give **9** (17 mg). Fraction $B_4$ (2.00 g) was passed through a Lobar RP-8 column [MeCN–$H_2O$ (3 : 17)] to give eleven fractions (frs. $B_{4\text{-}1}$—$B_{4\text{-}11}$), and fr. $B_{4\text{-}3}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (3 : 37) and CHA (MeCN–$H_2O$ (19 : 1)] to give **5** (15 mg) and **6** (7 mg). Fraction $B_{4\text{-}4}$ was passed through Sephadex LH-20 (MeOH) and HPLC [ODS, MeCN–$H_2O$ (1 : 9) and CHA, MeCN–$H_2O$ (24 : 1)] to give **8** (13 mg). Fraction $B_{4\text{-}7}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (3 : 17)] to give **4** (20 mg). Fraction $B_{4\text{-}10}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (3 : 17)] to give **7** (151 mg) and **14** (58 mg), and fr. $B_{4\text{-}10}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (1 : 9) and CHA, MeCN–$H_2O$ (24 : 1)] to give **12** (14 mg). Fraction $B_5$ (2.00 g) was passed

through a Lobar RP-8 column [MeCN–$H_2O$ (3 : 17)] to give twelve fractions (frs. $B_{5\text{-}1}$—$B_{5\text{-}12}$), and fr. $B_{5\text{-}6}$ was subjected to HPLC [CHA, MeCN–$H_2O$ (19 : 1)] to give **3** (14 mg). Fraction $B_{5\text{-}7}$ was passed through Sephadex LH-20 (MeOH) to give fr. $B_{5\text{-}7a}$, $B_{5\text{-}7b}$ and **10** (15 mg). Fraction $B_{5\text{-}7a}$ was subjected to silica gel column chromatography [$CHCl_3$–MeOH–$H_2O$ (15 : 5 : 0.4→7 : 3 : 0.5)] to give **1** (293 mg). Fraction $B_{5\text{-}7b}$ was acetylated with $Ac_2O$ and pyridine, and the acetylated fraction was subjected to HPLC [ODS, MeCN–$H_2O$ (7 : 3)] to give three fractions. The first fraction was deacetylated by heating in a water bath with 5% $NH_4OH$–MeOH for 2 h, then passed through a Sephadex LH-20 (MeOH) to give **11** (18 mg). Fraction $B_{5\text{-}8}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (1 : 9) and CHA, MeCN–$H_2O$ (19 : 1)] to give **13** (3 mg). Fraction $B_{5\text{-}9}$ was subjected to HPLC [ODS, MeCN–$H_2O$ (3 : 17) and CHA, MeCN–$H_2O$ (19 : 1)] to give **15** (118 mg). Fraction $B_7$ (0.82 g) was passed through a Lobar RP-8 column [MeCN–$H_2O$ (3 : 17)] to give seven fractions (frs. $B_{7\text{-}1}$—$B_{7\text{-}7}$), and fr. $B_{7\text{-}3}$ was subjected to HPLC [CHA, MeCN–$H_2O$ (14 : 1)] to give **16** (39 mg). Fraction $B_9$ (2.40 g) was passed through a Lobar RP-8 column [MeCN–$H_2O$ (3 : 17)] to give nine fractions (frs. $B_{9\text{-}1}$—$B_{9\text{-}9}$), and fr. $B_{9\text{-}4}$ was subjected to HPLC [CHA, MeCN–$H_2O$ (19 : 1)] to give **2** (12 mg).

The following compounds were identified by comparison with authentic compounds: (4*S*)-*p*-menth-1-ene-4,7-diol 4-*O*-*β*-D-glucopyranoside (**7**), (4*R*,6*S*)-*p*-menth-1-ene-4,6-diol 4-*O*-*β*-D-glucopyranoside (**8**) and (4*R*)-*p*-menth-1-ene-7,8-diol 7-*O*-*β*-D-glucopyranoside (**10**).

**(8*R*)-9-Hydroxycuminyl *β*-D-Glucopyranoside (1)** An amorphous powder, $[\alpha]_D^{24}$ −44° (*c*=1.5, MeOH). Positive FAB-MS *m/z*: 657 $[2M+H]^+$, 367 $[M+K]^+$, 351.1428 $[M+Na]^+$ (Calcd for $C_{16}H_{24}NaO_7$; 351.1420), 329 $[M+H]^+$, 311 $[M-H_2O+H]^+$, 149 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**Enzymatic Hydrolysis of 1** A mixture of **1** (13 mg) and hesperidinase (5 mg, ICN Biomedicals, Inc., Lot 72635) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (9 : 1) and $CHCl_3$–MeOH–$H_2O$ (7 : 3 : 0.5)] to afford an aglycone **1a** (2 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector and JASCO OR-990 chiral detector, solv.; MeCN–$H_2O$ (17 : 3), 2 ml/min; $t_R$ 4.50 min (same location as that of D-glucose)] showed the presence of D-glucose.

**(8*R*)-9-Hydroxycuminyl Alcohol (1a)** An amorphous powder, $[\alpha]_D^{21}$ +13° (*c*=0.3, $CHCl_3$). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**(8*S*)-8,9-Dihydroxycuminyl *β*-D-Glucopyranoside (2)** An amorphous powder, $[\alpha]_D^{22}$ −31° (*c*=0.4, MeOH). Positive FAB-MS *m/z*: 345.1548 $[M+H]^+$ (Calcd for $C_{16}H_{25}O_6$; 345.1550), 327 $[M-H_2O+H]^+$, 183 $[M-C_6H_{10}O_5+H]^+$ (base), 165 $[M-C_6H_{12}O_6+H]^+$. $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-3, C-4, C-6, C-7; H-3/C-1, C-2, C-5, C-8; H-5/C-1, C-3, C-6, C-8; H-6/C-2, C-4, C-5, C-7; $H_2$-7/C-1, C-2, C-6, Glc C-1; $H_2$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-7.

**Enzymatic Hydrolysis of 2** A mixture of **2** (4 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **2a** (1 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(8*S*)-8,9-Dihydroxycuminyl Alcohol (2a)** An amorphous powder, $[\alpha]_D^{22}$ +12° (*c*=0.1, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**8-Hydroxycuminyl *β*-D-Glucopyranoside (3)** An amorphous powder, $[\alpha]_D^{24}$ −40° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 351.1418 $[M+Na]^+$ (Calcd for $C_{16}H_{24}NaO_7$; 351.1420), 311 $[M-H_2O+H]^+$, 149 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-3, C-4, C-6, C-7; H-3/C-1, C-2, C-5, C-8; H-5/C-1, C-3, C-6, C-8; H-6/C-2, C-4, C-5, C-7; $H_2$-7/C-1, C-2, C-6, Glc C-1; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-7.

**(3*S*,4*S*,6*R*)-*p*-Menth-1-ene-3,6-diol 6-*O*-*β*-D-Glucopyranoside (4)** An amorphous powder, $[\alpha]_D^{23}$ −20° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 665 $[2M+H]^+$, 371.1488 $[M+K]^+$ (base, Calcd for $C_{16}H_{28}KO_7$; 371.1472), 355.1717 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$. $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-4, C-6, C-7; H-4/C-3, C-5, C-6, C-8, C-9, C-10; H-$5_{ax}$/C-3, C-4; H-$5_{eq}$/C-1, C-2, C-3, C-4, C-8; H-6/C-1, C-2, C-4, Glc C-1; $H_3$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-6.

**Enzymatic Hydrolysis of 4** A mixture of **4** (7 mg) and *β*-glucosidase in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **4a** (3 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(3*S*,4*S*,6*R*)-*p*-Menth-1-ene-3,6-diol (4a)** An amorphous powder, $[\alpha]_D^{23}$ +8° (*c*=0.2, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**(3*R*,4*S*,6*R*)-*p*-Menth-1-ene-3,6-diol 6-*O*-*β*-D-Glucopyranoside (5)** Colorless needles (MeOH), mp 215—217 °C, $[\alpha]_D^{23}$ +89° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 665 $[2M+H]^+$, 371 $[M+K]^+$, 355 $[M+Na]^+$, 333.1897 $[M+H]^+$ (base, Calcd for $C_{16}H_{29}O_7$; 333.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$. $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-3, C-4, C-6, C-7; H-3/C-5; H-4/C-3, C-5, C-6, C-8, C-9, C-10; H-$5_{ax}$/C-3, C-4, C-8; H-$5_{eq}$/C-1, C-3, C-4, C-6; H-6/C-1, C-2, C-4, C-7, Glc C-1; $H_3$-7/C-1, C-2, C-6; H-8/C-4, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-6.

**Enzymatic Hydrolysis of 5** A mixture of **5** (7 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **5a** (2 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(3*R*,4*S*,6*R*)-*p*-Menth-1-ene-3,6-diol (5a)** An amorphous powder, $[\alpha]_D^{23}$ +240° (*c*=0.1, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**(3*R*,4*S*,6*R*)-*p*-Menth-1-ene-3,6-diol 3-*O*-*β*-D-Glucopyranoside (6)** Colorless needles (MeOH), mp 215—217 °C, $[\alpha]_D^{23}$ +126° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 371 $[M+K]^+$, 333.1930 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 333.1913), 153 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-3, C-4, C-6, C-7; H-3/C-1, C-2, Glc C-1; H-$5_{ax}$/C-3, C-4; H-$5_{eq}$/C-1, C-3, C-4, C-6; $H_3$-7/C-1, C-2, C-6; H-8/C-4; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-3.

**Enzymatic Hydrolysis of 6** A mixture of **6** (4 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **5a** (1 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(4*S*,6*S*)-*p*-Menth-1-ene-4,6-diol 4-*O*-*β*-D-Glucopyranoside (9)** Colorless needles (MeOH), mp 78—81 °C, $[\alpha]_D^{21}$ −2° (*c*=0.7, MeOH). Positive FAB-MS *m/z*: 355.1724 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**Enzymatic Hydrolysis of 9** A mixture of **9** (6 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **9a** (2.5 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(4*S*,6*S*)-*p*-Menth-1-ene-4,6-diol (9a)** An amorphous powder, $[\alpha]_D^{21}$ +40° (*c*=0.2, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**(4*R*)-*p*-Menth-1-ene-7,8-diol 7-*O*-*β*-D-Glucopyranoside (11)** An amorphous powder, $[\alpha]_D^{24}$ −6° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 371 $[M+K]^+$, 355.1735 $[M+Na]^+$ (base, Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 333 $[M+H]^+$, 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$. $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2. HMBC Correlations: H-2/C-4, C-6, C-7; H-$3_{ax}$/C-1, C-2; H-$3_{eq}$/C-1, C-2, C-4, C-5; H-4/C-3, C-5, C-6, C-8, C-9, C-10; H-$5_{ax}$/C-1, C-4, C-8; H-$5_{eq}$/C-1, C-3, C-4, C-6, C-8; H-$6_{ax}$/C-1, C-4, C-5; H-$6_{eq}$/C-1, C-2, C-4, C-5, C-7; $H_2$-7/C-1, C-2, C-6, Glc C-1; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-7.

**Enzymatic Hydrolysis of 11** A mixture of **11** (6 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford an aglycone **11a** (1.7 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(4*R*)-*p*-Menth-1-ene-7,8-diol (11a)** An amorphous powder, $[\alpha]_D^{24}$ +66° (*c*=0.1, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) *δ*: Table 2.

**(3*R*,4*R*)-*p*-Menth-1-ene-3,4-diol 3-*O*-*β*-D-Glucopyranoside (12)** An amorphous powder, $[\alpha]_D^{21}$ −86° (*c*=0.6, MeOH). Positive FAB-MS *m/z*: 665 $[2M+K]^+$, 371 $[M+K]^+$, 355.1729 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$;

355.1733), 333 $[M+H]^+$, 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2.

**Enzymatic Hydrolysis of 12** A mixture of **12** (5 mg) and $\beta$-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 5 d. The mixture was treated in the same way as described for **1** to afford an aglycone **12a** (2 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(3*R*,4*R*)-*p*-Menth-1-ene-3,4-diol (12a)** An amorphous powder, $[\alpha]_D^{21}$ −29° ($c$=0.2, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2.

**(3*R*,4*R*,6*R*)-*p*-Menth-1-ene-3,4,6-triol 3-*O*-$\beta$-D-Glucopyranoside (13)** An amorphous powder, $[\alpha]_D^{22}$ −97° ($c$=0.1, MeOH). Positive FAB-MS $m/z$: 697 $[2M+K]^+$, 387 $[M+K]^+$, 371 $[M+Na]^+$, 349.1867 $[M+H]^+$ (base, Calcd for $C_{16}H_{29}O_8$; 349.1863), 331 $[M-H_2O+H]^+$, 169 $[M-C_6H_{12}O_6+H]^+$. $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2. HMBC Correlations: H-2/C-4, C-6, C-7; H-3/C-1, C-2, Glc C-1; H-5$_{ax}$/C-3, C-4, C-6; H-5$_{eq}$/C-1, C-3, C-4, C-6, C-8; H-6$_{eq}$/C-1, C-2, C-4, C-7; $H_3$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-3.

**(1*S*,2*R*,4*R*)-*p*-Menth-5-ene-1,2-diol 2-*O*-$\beta$-D-Glucopyranoside (14)** An amorphous powder, $[\alpha]_D^{23}$ +8° ($c$=1.8, MeOH). Positive FAB-MS $m/z$: 665 $[2M+K]^+$, 371 $[M+K]^+$, 355.1738 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 333.1902 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 333.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2. HMBC Correlations: H-2/C-1, C-3, C-4, C-6, Glc C-1; $H_2$-3/C-1, C-2, C-4, C-5, C-8; H-4/C-5, C-6, C-8, C-9, C-10; H-5/C-1, C-3, C-4, C-8; H-6/C-1, C-2, C-4, C-7; $H_3$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-2.

**Enzymatic Hydrolysis of 14** A mixture of **14** (12 mg) and $\beta$-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **1** to afford an aglycone **14a** (5 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(1*S*,2*R*,4*R*)-*p*-Menth-5-ene-1,2-diol (14a)** An amorphous powder, $[\alpha]_D^{22}$ +24° ($c$=0.3, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2.

**(1*S*,2*R*,4*R*)-*p*-Menth-5-ene-1,2-diol 1-*O*-$\beta$-D-Glucopyranoside (15)** An amorphous powder, $[\alpha]_D^{21}$ −23° ($c$=0.6, MeOH). Positive FAB-MS $m/z$: 371 $[M+K]^+$, 355.1733 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 333 $[M+H]^+$, 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2. HMBC Correlations: H-2/C-1, C-3, C-4, C-6, C-7; $H_2$-3/C-1, C-2, C-4, C-5, C-8; H-4/C-2, C-3, C-5, C-6, C-8, C-9, C-10; H-5/C-1, C-3, C-4, C-8; H-6/C-2, C-4, C-7; $H_3$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-1.

**Enzymatic Hydrolysis of 15** A mixture of **15** (5 mg) and $\beta$-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **1** to afford an aglycone **14a** (5 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(1*S*,2*R*,4*S*)-*p*-Menth-5-ene-1,2,4-triol 2-*O*-$\beta$-D-Glucopyranoside (16)** An amorphous powder, $[\alpha]_D^{23}$ −60° ($c$=1.1, MeOH). Positive FAB-MS $m/z$: 387 $[M+K]^+$, 371.1693 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$; 371.1681), 349 $[M+H]^+$, 313 $[M-2H_2O+H]^+$, 169 $[M-C_6H_{12}O_6+H]^+$ (base). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2. HMBC Correlations: H-2/C-1, C-3, C-4, C-6, C-7, Glc C-1; $H_2$-3/C-1, C-2, C-4, C-5, C-8; H-5/C-1, C-3, C-4, C-6, C-8; H-6/C-1, C-2, C-4, C-5, C-7; $H_3$-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; $H_3$-9/C-4, C-8, C-10; $H_3$-10/C-4, C-8, C-9; Glc H-1/C-2.

**Enzymatic Hydrolysis of 16** A mixture of **16** (14 mg) and $\beta$-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was treated in the same way as described for **1** to afford an aglycone **16a** (6 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **1**.

**(1*S*,2*R*,4*S*)-*p*-Menth-5-ene-1,2,4-triol (16a)** An amorphous powder, $[\alpha]_D^{23}$ −50° ($c$=0.5, MeOH). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: Table 1. $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: Table 2.

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