Studies on the Constituents of *Catalpa* Species. VI.[1] Monoterpene Glycosides from the Fallen Leaves of *Catalpa ovata* G. Don

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Five new monoterpene glycosides, ovatolactone 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside, ovatic acid methyl ester 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside, 7-*O*-*p*-hydroxybenzoylovatol 1-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside, 6′-*O*-*p*-hydroxybenzoylcatalposide and (2*E*,6*R*)-2,6-dimethyl-8-hydroxy-2-octenoic acid 8-*O*-[6′-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside were isolated from the fallen leaves of *Catalpa ovata* G. Don. Their structures were determined by extensive spectroscopic studies and syntheses.

Key words *Catalpa ovata*; Bignoniaceae; fallen leaf; iridoid; monoterpene; glycoside

We recently reported the isolation and identification of 16 new iridoids from Catalpae Fructus ("kisasage" in Japanese, Bignoniaceae).[1,2] In the course of further studies on the constituents of this plant, we studied the fresh and fallen leaves of *Catalpa ovata* G. Don, of which only one constituent, *p*-hydroxybenzoic acid, has been identified, to the best of our knowledge.[3] We report here the isolation and structure determination of five new monoterpene glycosides from the fallen leaves of *C. ovata* G. Don.

Fallen leaves of *C. ovata* were collected in the Medicinal Plant Garden of our university. Compounds **1**—**5** were isolated from the AcOEt fraction of the MeOH extract by the procedures described in the Experimental section.

Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{25}$ −17.9°. The molecular formula was suggested to be $C_{22}H_{28}O_{10}$, based on high-resolution (HR)-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of **1** showed the characteristic signals of *p*-hydroxybenzoyl and β-glucopyranosyl units. The remaining NMR signals suggested the presence of an ester carbonyl [δ_C 176.6 (s)], a secondary methyl [δ_H 0.88 (3H, d, J=7.3 Hz, δ_C 15.7 (q)], an oxymethylene [δ_H 4.18 (1H, ddd, J=11.2, 10.0, 2.4 Hz), 4.29 (1H, ddd, J=11.2, 4.9, 3.4 Hz), δ_C 69.8 (t)] and an oxymethine [δ_H 3.92 (1H, br dd, J=4.4, 2.2 Hz, δ_C 87.0 (d)] moieties. The ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) correlations of the remaining signals revealed the presence of a tetra-substituted cyclopentane ring having the methyl and alkoxyl groups (Fig. 1, heavy line). The molecular formula of **1** required 9 degrees of unsaturation. The *p*-hydroxybenzoyl and β-glucopyranosyl units have 6 degrees of unsaturation, and therefore **1** must have a two-ring system of the cyclopentane and δ-lactone rings in the skeleton itself. The planar structure of **1** was established by the heteronuclear multiple bond correlation (HMBC) spectrum (Fig. 1). The stereochemistry of **1** was determined from the difference in nuclear Overhauser effect (NOE) spectra. An irradiation at δ 2.56 (5-H) produced NOE enhancements of one of the methylene protons at C-4 (δ 1.87) and one of the methylene protons at C-6 (δ 2.21) and 9-H (δ 3.32) suggesting that they were all on the same face (β) of the molecule. On the other hand, irradiation at δ 0.88 (10-H_3) caused NOE enhancements in the signals of 4-Hα (δ 1.36), 7-H (δ 3.92) and 6-Hα (δ 1.69) thereby establishing that these were on the same face (α), opposite the 5-H. Furthermore, the NOE was observed between 8-H/9-H. Thus, the aglycone moiety of **1** was revealed to be the epimer at the C-8 of boonein isolated from the bark of *Alstonia boonei*.[4] Consequently, the structure of **1** was elucidated as shown and termed ovatolactone 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside.

Compound **2** was obtained as its methyl ester (**2a**), and the molecular formula of **2a**, $C_{23}H_{32}O_{11}$, was established by HR-FAB-MS. In the ^{1}H- and ^{13}C-NMR spectra of **2a**, signal patterns were similar to those of **1**, except for the presence of a carbomethoxyl group [δ_H 3.60 (3H, s), δ_C 175.6 (s), 51.4 (q)]. The ^{13}C-NMR signal at C-3 of **2a** was shifted by −8.3 ppm in comparison with that of **1**. This shift was believed to be caused by the opening of the δ-lactone of **1**. This deduction was supported by the HMBC spectrum. The carbon resonance at δ 175.6 showed HMBC correlations with 5, 8 and 9-H, respectively (Fig. 1). The NOE correlations between 9-H/5-H and 8-H, and 10-H_3/1-COOC$\underline{H}_3$ and 7-H indicated that the relative configurations of **2a** were compatible with those of **1**. Consequently, the structure of **2a** was elucidated as shown and called ovatic acid methyl ester 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside. Compound **2a** may be an artifact formed from **2** during the extraction and isolation process.

Compound **3** was obtained as an amorphous powder, $[\alpha]_D^{25}$ +22.2°. The molecular formula of **3**, $C_{29}H_{34}O_{12}$, was established by HR-FAB-MS. Its NMR spectra were similar to those of **2a**, however, lacked signals from the C-1 carbomethoxyl and C-10 secondary methyl groups of **2a** and instead showed signals characteristic of the oxymethylene [δ_H 3.59, 3.91, δ_C 71.4 (t)] and exomethylene [δ_H 5.19, 5.30, δ_C 113.9 (t), 153.4 (s)] moieties. Furthermore, **3** possesses two *p*-hydroxybenzoyl groups. The location of an additional *p*-hydroxybenzoyl group at C-7 was suggested by downfield shift of the signal due to 7-H [δ 5.68 (+1.62 ppm)] on comparison of the ^{1}H-NMR spectrum of **2a**. On the other hand, the NMR chemical shifts at C-3 (δ_H 3.59, δ_C 61.8) and the signals owing to the β-glucopyranosy moieties in **3** were almost the same as those of **2a**. This finding suggested that β-glucopyranosyl moiety which possesses the other *p*-hydroxybenzoyl group at C-6′ was located at C-1 of **3**. The above deduction was supported by the HMBC correlations between 7-H/C-7‴, 1′-H/C-1 and 6′-H/C-7″ (Fig. 1). The NOE difference spectra of **3** showed that irradiation at 5-H resulted in NOE enhancements at 9-H and one of the methylene protons

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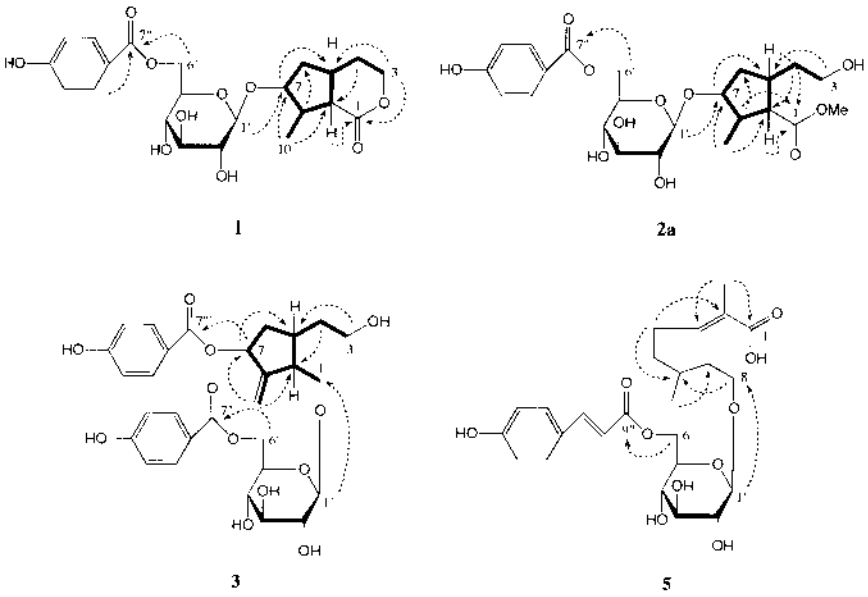

Fig. 1. Diagnostic HMBC Correlations

at C-6 (δ 1.83). Furthermore, an NOE interaction between 7-H/one of the other methylene protons at C-6 [δ 2.02] showed these protons to be on the same face, opposite the 5-H. The circular dichroism (CD) spectrum of **3** showed a positive Cotton effect at 252.5 nm ($\Delta\varepsilon$ +1.81). Considering that the UV absorption at 256 nm may be assigned to the transition due to the *p*-hydroxybenzoyl group, the observed Cotton effect at 252.5 nm was not caused by two *p*-hydroxybenzoyl groups attached at C-7 and C-6′, but was caused by the exciton interaction between the *p*-hydroxybenzoyl group attached at C-7 and the C-8, 10 double bond. Therefore, the absolute configuration at C-7 in **3** was determined as *S* by application of the allylic benzoate method.[5] Consequently, the structure of **3** was elucidated as shown and termed 7-*O*-*p*-hydroxybenzoylovatol 1-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D^{25}$ −123.5°. The molecular formula of **4**, $C_{29}H_{30}O_{14}$ was established by HR-FAB-MS. In the ^{1}H- and ^{13}C-NMR spectra of **4**, signal patterns were very similar to those of catalposide isolated from the Catalpae Fructus,[6] except for the appearance of signals assignable to an additional *p*-hydroxybenzoyl moiety and downfield shifts at the 6′-H_2 [δ 4.53 (1H, dd, J=11.7, 6.1 Hz), 4.64 (1H, dd, J=11.7, 2.4 Hz). catalposide; δ 3.65 (1H, dd, J=12.0, 6.3 Hz), 3.94 (1H, dd, J=12.0, 1.9 Hz)]. These indicated that the additional *p*-hydroxybenzoyl group in **4** is attached to 6′-OH in catalposide. This finding was supported by the HMBC correlation from 6′-H_2 to C-7″ (δ_C 167.8). Consequently, the structure of **4** was determined to be 6′-*O*-*p*-hydroxybenzoylcatalposide.

Compound **5** was obtained as an amorphous powder, $[\alpha]_D^{25}$ −15.0°. The molecular formula of **5**, $C_{25}H_{34}O_{10}$, was established by HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of **5** showed the presence of a (*E*)-*p*-coumaroyl and a β-glucopyranosyl moieties. The remaining signals revealed the presence of an α,β-unsaturated carbonyl [δ_H 6.72 (1H, br t, J=7.3 Hz), δ_C 173.1 (s), 143.6 (d), 127.2 (s)], an olefinic methyl [δ_H 1.78 (3H, s), δ_C 12.6 (q)], and a secondary methyl [δ_H 0.90 (3H, d, J=6.6 Hz), δ_C 19.8 (q)] moiety. Acid hydrolysis of **5** with 4% HCl gave the aglycone (**5a**). **5a** was identified as (2*E*)-2,6-dimethyl-8-hydroxy-2-octenoic acid by direct comparison with authentic sample.[7] Because the amount of **5a** was too small, the absolute configuration at C-6 of **5** could not be determined by the optical rotation of **5a**. So we applied the method described in the literature to this case (Chart 2).[8] That is, both enantiomers of (2*E*)-2,6-dimethyl-8-hydroxy-2-octenoic acid [(6*R*)-**6a** and (6*S*)-**7a**] were prepared from optically active β-citronellol, and natural **5a** derived from **5**, synthetic (6*R*)-**6a** and (6*S*)-**7a** was each converted to the corresponding methyl-(2*E*)-8-benzoyloxy-2,6-dimethyl-2-octenoate [**5c**, (6*R*)-**6c** and (6*S*)-**7c**]. The individual enantiomers of (6*R*)-**6c** and (6*S*)-**7c** could be separated with a chiral column by HPLC. The retention times of (6*R*)-**6c** and (6*S*)-**7c** were 12.2 and 14.6 min, respectively, whereas that of **5c** was 12.2 min. The absolute configuration at C-6 of aglycone moiety was deduced as *R*. The HMBC correlations of **5** suggested that the carbonyl carbon at C-9″ (δ_C 169.1) of (*E*)-*p*-coumaroyl moiety was esterified with the hydroxy group at C-6′ of the β-D-glucopyranosyl moiety, whose C-1′ β-hydroxy group was linked to the C-8 of the aglycone, (2*E*)-2,6-dimethyl-8-hydroxy-2-octenoic acid (Fig.1). From the combined evidence, the structure of **5** was determined to be (2*E*,6*R*)-2,6-dimethyl-8-hydroxy-2-octenoic acid 8-*O*-[6′-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside.

To the best of our knowledge, compound **1** is the first example of cyclopenta[c]pyrone type C-9 iridoid glycoside, and **3** is the second iridoid glycoside which is glycosylated at the C-1 hydroxymethyl.[9] From a biogenetic point of view, it is interesting to note that the configuration at C-6 of **5** is the same as C-8 of **1** and **2**. Though the absolute configurations at C-5, 7 and 9 of **1** and **2** have not been confirmed, they are presumably the same as those of **3** based on biogenetic considerations. Compounds **1** and **2** may arise from 10-hydroxygeranial, while compounds **3** and **5** may be generated from 10-oxogeraniol, respectively (Fig. 2).

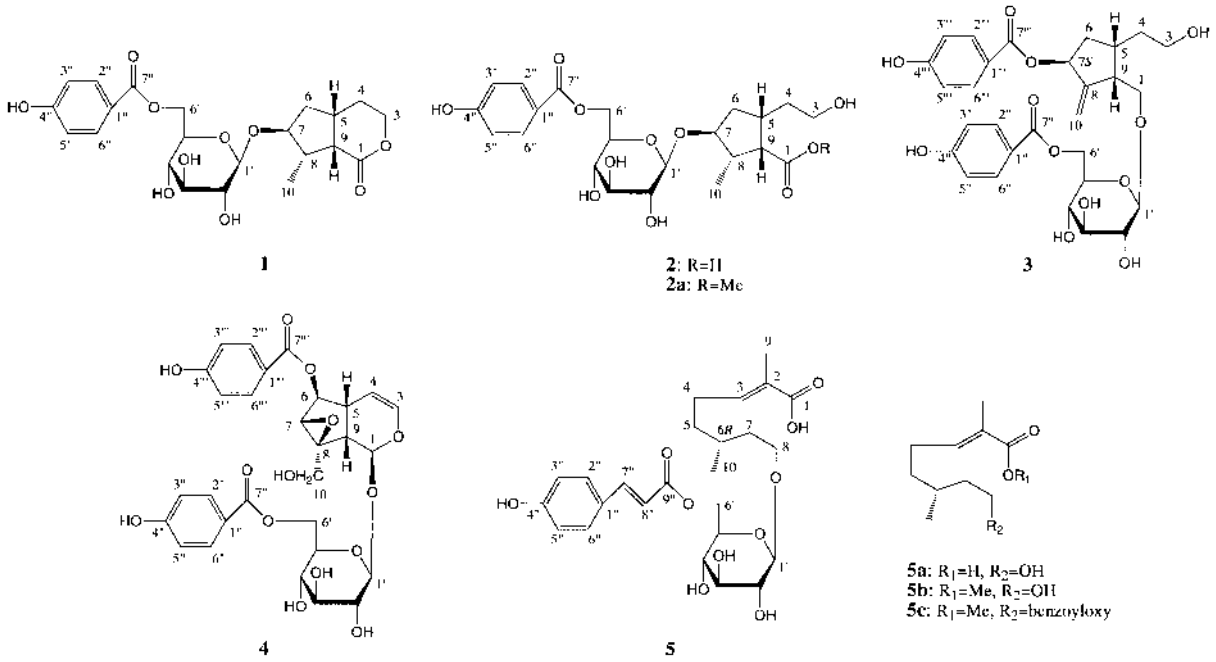

Chart 1

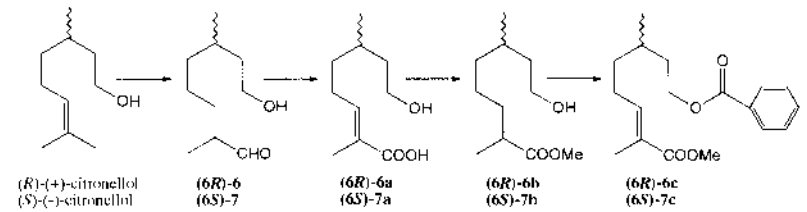

Chart 2

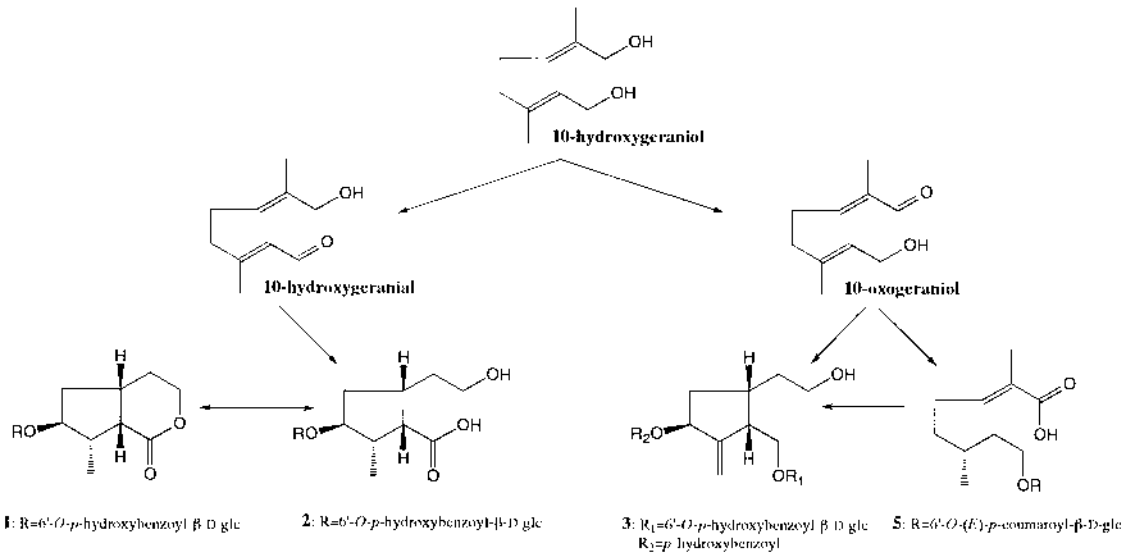

Fig. 2. Possible Biosynthetic Pathways

Experimental

Optical rotations were taken with a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrometer. The CD spectra were obtained with a JASCO J-720 spectropolarimeter. The ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-GSX 400 (400 and 100 MHz, respectively) spectrometer. Chemical shifts are given on a δ (ppm) scale with TMS as an internal standard. Electron impact (EI)-MS and FAB-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 70—230 mesh). Preparative HPLC was carried out on a Tosoh HPLC system [pump, CCPS; detector, UV-8020; column, Cosmosil 5C$_{18}$-AR (10 mm i.d.×25 cm, Nacalai Tesque), Cosmosil 5SL (10 mm i.d.×25 cm, Nacalai Tesque)]. GLC was carried out on a Shimadzu GC-7A equipped with FID. Analytical TLC was performed on precoated silica gel plates (Merck, 0.25 mm thickness)

and detection was achieved by spraying with 5% H_2SO_4 followed by heating.

Plant Material Fallen leaves of *C. ovata* G. Don were collected in the Medicinal Plant Garden of Tohoku Pharmaceutical University in November, 1999. They were identified by a botanist, Prof. F. Yoshizaki, and a voucher specimen (No. 10) is deposited in the laboratory of Prof. M. Kikuchi.

Extraction and Isolation One kilogram of the leaves was extracted with MeOH at room temperature for 10 d. The MeOH extract was concentrated under reduced pressure and the residue (140 g) was suspended in water (400 ml). This suspension was successively extracted with $CHCl_3$ and AcOEt. The AcOEt-soluble fraction was concentrated under reduced pressure to produce a residue (6.0 g). This residue was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (30 : 10 : 1) and the eluate was separated into 6 fractions (Frs. 1—6). Fraction 4 was rechromatographed on a Sephadex LH-20 column using 50% MeOH and the eluate was separated into 9 fractions (Frs. 4-1—4-9). Fraction 4-2 was subjected to prep. HPLC [column, Cosmosil 5C_{18}-AR; mobile phase, MeOH–H_2O (1 : 1); flow rate, 1.0 ml/min, 256 nm] to give the mixture of **1** and **2a**. This mixture was further purified by prep. HPLC [column, Cosmosil 5SL; mobile phase, $CHCl_3$–MeOH (5 : 1), flow rate, 1.5 ml/min; 256 nm] to give **1** (10.0 mg) and **2a** (5.2 mg). Fraction 4-4 was subjected to prep. HPLC [column, Cosmosil 5C_{18}-AR; mobile phase, MeOH–H_2O (2 : 1); flow rate, 1.5 ml/min, 312 nm] to give **5** (8.0 mg). Fraction 4-5 was subjected to prep. HPLC [column, Cosmosil 5C_{18}-AR; mobile phase, MeOH–H_2O (1 : 1); flow rate, 1.5 ml/min, 258 nm] to give **3** (12.0 mg) and **4** (11.0 mg).

Ovatolactone 7-*O*-(6′-*O*-*p*-Hydroxybenzoyl)-β-D-glucopyranoside (1) An amorphous powder. $[\alpha]_D^{25}$ −17.9° (c=0.6, MeOH). UV λ_{max}^{MeOH} nm (log ε): 256 (4.13), 206 (4.02). FAB-MS m/z: 453 $[M+H]^+$, 475 $[M+Na]^+$. HR-FAB-MS m/z: 453.1786 $[M+H]^+$ ($C_{22}H_{29}O_{10}$, Calcd for 453.1761). ^{1}H-NMR (CD_3OD) δ: 0.88 (3H, d, J=7.3 Hz, 10-H_3), 1.36 (1H, dddd, J=13.4, 10.0, 10.0, 3.4 Hz, 4-Hα), 1.69 (1H, ddd, J=14.1, 8.3, 4.4 Hz, 6-Hα), 1.87 (1H, dddd, J=13.4, 5.8, 4.9, 2.4 Hz, 4-Hβ), 2.21 (1H, ddd, J=14.1, 8.5, 1.5 Hz, 6-Hβ), 2.56 (1H, m, 5-H), 2.63 (1H, m, 8-H), 3.16 (1H, dd, J=8.7, 7.8 Hz, 2′-H), 3.32 (1H, m, 9-H), 3.36 (2H, m, 3′, 4′-H), 3.60 (1H, m, 5′-H), 3.92 (1H, br dd, J=4.4, 2.2 Hz, 7-H), 4.18 (1H, ddd, J=11.2, 10.0, 2.4 Hz, 3-Hβ), 4.29 (1H, ddd, J=11.2, 4.9, 3.4 Hz, 3-Hα), 4.35 (1H, d, J=7.8 Hz, 1′-H), 4.45 (1H, dd, J=11.7, 6.8 Hz, 6′-H_A), 4.56 (1H, dd, J=11.7, 2.3 Hz, 6′-H_B), 6.83 (2H, d, J=8.8 Hz, 3″, 5″-H), 7.90 (2H, d, J=8.8 Hz, 2″, 6″-H). ^{13}C-NMR (CD_3OD) δ: 176.6 (C-1), 69.8 (C-3), 31.0 (C-4), 34.3 (C-5), 38.1 (C-6), 87.0 (C-7), 43.9 (C-8), 46.5 (C-9), 15.7 (C-10), 103.3 (C-1′), 75.5 (C-2′), 78.0 (C-3′), 72.1 (C-4′), 75.1 (C-5′), 65.0 (C-6′), 122.3 (C-1″), 132.9 (C-2″, 6″), 116.2 (C-3″, 5″), 163.7 (C-4″), 168.0 (C-7″).

Ovatic Acid Methyl Ester 7-*O*-(6′-*O*-*p*-Hydroxybenzoyl)-β-D-glucopyranoside (2a) An amorphous powder. $[\alpha]_D^{25}$ 0.0° (c=0.3, MeOH); UV λ_{max}^{MeOH} nm (log ε): 309 (3.12), 256 (3.86). FAB-MS m/z: 507 $[M+Na]^+$. HR-FAB-MS m/z: 507.2173 $[M+Na]^+$ ($C_{23}H_{32}O_{11}Na$, Calcd for 507.2140). ^{1}H-NMR (CD_3OD) δ: 1.05 (3H, d, J=6.8 Hz, 10-H_3), 1.31 (1H, m, 4-H_A), 1.46 (1H, m, 4-H_B), 1.88 (1H, ddd, J=13.7, 10.0, 9.0 Hz, 6-Hα), 1.97 (1H, ddd, J=13.7, 10.0, 3.4 Hz, 6-Hβ), 2.22 (1H, br q, J=6.8 Hz, 8-H), 2.36 (1H, br dd, J=10.0, 6.8 Hz, 5-H), 2.85 (1H, br t, J=6.8 Hz, 9-H), 3.19 (1H, dd, J=8.8, 7.8 Hz, 2′-H), 3.35 (2H, m, 3′, 4′-H), 3.43 (2H, m, 3-H_2), 3.59 (1H, m, 5′-H), 3.60 (3H, s, $COOCH_3$), 4.06 (1H, m, 7-H), 4.32 (1H, d, J=7.8 Hz, 1′-H), 4.38 (1H, dd, J=11.7, 7.4 Hz, 6′-H_A), 4.60 (1H, dd, J=11.7, 2.4 Hz, 6′-H_B), 6.83 (2H, d, J=9.0 Hz, 3″, 5″-H), 7.91 (2H, d, J=9.0 Hz, 2″, 6″-H). ^{13}C-NMR (CD_3OD) δ: 175.6 (C-1), 61.5 (C-3), 39.5 (C-4), 38.4 (C-5), 36.0 (C-6), 89.0 (C-7), 45.7 (C-8), 54.3 (C-9), 14.5 (C-10), 105.5 (C-1′), 75.35 (C-2′), 78.1 (C-3′), 72.3 (C-4′), 75.42 (C-5′), 65.1 (C-6′), 122.4 (C-1″), 133.0 (C-2″, 6″), 116.3 (C-3″, 5″), 163.6 (C-4″), 168.0 (C-7″), 51.4 ($COO\underline{C}H_3$).

7-*O*-*p*-Hydroxybenzoylovatol 1-*O*-(6′-*O*-*p*-Hydroxybenzoyl)-β-D-glucopyranoside (3) An amorphous powder. $[\alpha]_D^{25}$ +22.2° (c=0.3, MeOH). CD (c=1.10×10^{-4} M, MeOH) $\Delta\varepsilon$ (nm): +1.81 (252.5), +2.86 (214.5). UV λ_{max}^{MeOH} nm (log ε): 309 (2.57), 256 (4.44), 204 (4.44). FAB-MS m/z: 597 $[M+Na]^+$. HR-FAB-MS m/z: 597.1914 $[M+Na]^+$ ($C_{29}H_{34}O_{12}Na$, Calcd for 597.1948). ^{1}H-NMR (CD_3OD) δ: 1.45 (1H, m, 4-H_A), 1.80 (1H, m, 4-H_B), 1.83 (1H, m, 6-Hβ), 2.02 (1H, ddd, J=13.9, 8.5, 6.8 Hz, 6-Hα), 2.50 (1H, br dt, J=7.3, 6.8 Hz, 5-H), 3.00 (1H, m, 9-H), 3.22 (1H, dd, J=9.3, 7.8 Hz, 2′-H), 3.31 (2H, m, 3′, 4′-H), 3.59 (4H, m, 1-H_A, 3-H_2, 5′-H), 3.91 (1H, dd, J=9.8, 5.1 Hz, 1-H_B), 4.30 (1H, d, J=7.8 Hz, 1′-H), 4.43 (1H, dd, J=11.7, 6.6 Hz, 6′-H_A), 4.61 (1H, dd, J=11.7, 2.2 Hz, 6′-H_B), 5.19 (1H, s, 10-H_A), 5.30 (1H, s, 10-H_B), 5.68 (1H, m, 7-H), 6.80, 6.81 (each 2H, d, J=8.8 Hz, 3″, 5″-H, 3‴, 5‴-H), 7.83, 7.90 (each 2H, d, J=8.8 Hz, 2″, 6″-H, 2‴, 6‴-H). ^{13}C-NMR (CD_3OD) δ: 71.4 (C-1), 61.8 (C-3), 33.3 (C-4), 37.3 (C-5), 38.2 (C-6), 77.2 (C-7), 153.4 (C-8), 47.1 (C-9), 113.9 (C-10), 104.8 (C-1′), 75.2 (C-2′), 78.1 (C-3′), 72.1 (C-4′), 75.5 (C-5′), 64.9 (C-6′), 122.3, 122.7 (C-1″, C-1‴), 132.8, 132.9 (C-2″, 6″, C-2‴, 6‴), 116.2, 116.3 (C-3″, 5″, C-3‴, 5‴), 163.6, 163.7 (C-4″, C-4‴), 168.1 (C-7″, C-7‴).

6′-*O*-*p*-Hydroxybenzoylcatalposide (4) An amorphous powder. $[\alpha]_D^{25}$ −123.5° (c=0.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 257 (4.40), 202 (4.43). FAB-MS m/z: 603 $[M+H]^+$. HR-FAB-MS m/z: 603.1725 $[M+H]^+$ ($C_{29}H_{31}O_{14}$, Calcd for 603.1714). ^{1}H-NMR (CD_3OD) δ: 2.62 (1H, m, 5-H), 2.64 (1H, m, 9-H), 3.30 (1H, m, 2′-H), 3.44 (2H, m, 3′, 4′-H), 3.59 (1H, d, J=13.2 Hz, 10-H_A), 3.60 (1H, m, 5′-H), 3.62 (1H, d, J=1.2 Hz, 7-H), 4.17 (1H, d, J=13.2 Hz, 10-H_B), 4.53 (1H, dd, J=11.7, 6.1 Hz, 6′-H_A), 4.64 (1H, dd, J=11.7, 2.4 Hz, 6′-H_B), 4.81 (1H, d, J=7.8 Hz, 1′-H), 4.84 (1H, m, 6-H), 4.85 (1H, m, 1-H), 4.95 (1H, m, 4-H), 6.31 (1H, dd, J=5.8, 1.7 Hz, 3-H), 6.838 (2H, d, J=8.8 Hz, 3″, 5″-H), 6.844 (2H, d, J=9.0 Hz, 3‴, 5‴-H), 7.91 (2H, d, J=8.8 Hz, 2″, 6″-H), 7.92 (2H, d, J=9.0 Hz, 2‴, 6-H). ^{13}C-NMR (CD_3OD) δ: 95.3 (C-1), 142.3 (C-3), 103.2 (C-4), 36.9 (C-5), 81.7 (C-6), 60.2 (C-7), 66.8 (C-8), 43.1 (C-9), 61.7 (C-10), 99.9 (C-1′), 74.9 (C-2′), 77.6 (C-3′), 71.9 (C-4′), 76.1 (C-5′), 64.2 (C-6′), 122.9 (C-1″), 133.1 (C-2″, 6″), 116.4 (C-3″, 5″), 163.7 (C-4″), 167.8 (C-7″), 121.9 (C-1‴), 132.9 (C-2‴, 6‴), 116.3 (C-3‴, 5‴), 163.9 (C-4‴), 168.1 (C-7‴).

(2*E*,6*R*)-2,6-Dimethyl-8-hydroxy-2-octenoic Acid 8-*O*-[6′-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside (5) An amorphous powder. $[\alpha]_D^{25}$ −15.0° (c=0.1, MeOH). UV λ_{max}^{MeOH} nm (log ε): 309 (4.15), 300 sh (4.11), 219 (4.16), 212 (4.16). FAB-MS m/z: 499 $[M+Na-H_2O]^+$. HR-FAB-MS m/z: 499.1995 $[M+Na-H_2O]^+$ ($C_{25}H_{32}O_9Na$, Calcd for 499.1944). ^{1}H-NMR (CD_3OD) δ: 0.90 (3H, d, J=6.6 Hz, 10-H_3), 1.25 (1H, m, 5-H_A), 1.44 (2H, m, 5-H_B, 7-H_A), 1.61 (1H, m, 6-H), 1.67 (1H, m, 7-H_B), 1.78 (3H, s, 9-H_3), 2.17 (2H, m, 4-H_2), 3.19 (1H, dd, J=9.0, 7.8 Hz, 2′-H), 3.31 (2H, m, 3′, 4′-H), 3.52 (1H, m, 5′-H), 3.62 (1H, m, 8-H_A), 3.86 (1H, m, 8-H_B), 4.27 (1H, d, J=7.8 Hz, 1′-H), 4.35 (1H, dd, J=11.7, 6.1 Hz, 6′-H_A), 4.48 (1H, dd, J=11.7, 2.2 Hz, 6′-H_B), 6.35 (1H, d, J=15.9 Hz, 8″-H), 6.72 (1H, br t, J=7.3 Hz, 3-H), 6.80 (2H, d, J=8.5 Hz, 3‴, 5‴-H), 7.45 (2H, d, J=8.5 Hz, 2″, 6″-H), 7.64 (1H, d, J=15.9 Hz, 7″-H). ^{13}C-NMR (CD_3OD) δ: 173.1 (C-1), 127.2 (C-2), 143.6 (C-3), 27.2 (C-4), 37.0 (C-5), 30.7 (C-6), 37.7 (C-7), 69.1 (C-8), 12.6 (C-9), 19.8 (C-10), 104.5 (C-1′), 75.1 (C-2′), 78.1 (C-3′), 71.9 (C-4′), 75.4 (C-5′), 64.7 (C-6′), 127.2 (C-1″), 131.2 (C-2″, 6″), 116.9 (C-3″, 5″), 161.4 (C-4″), 146.8 (C-7″), 115.1 (C-8″), 169.1 (C-9″).

Hydrolysis of 5 Compound **5** (3.0 mg) was refluxed with 4% HCl (1.5 ml) for 3.5 h. The reaction solution was added to H_2O and extracted with Et_2O. The Et_2O extract was evaporated to dryness *in vacuo* and the residue was purified by prep. HPLC [column, Cosmosil 5C_{18}-AR; mobile phase, MeOH–H_2O (3 : 1); flow rate, 1.5 ml/min; UV detector, 215 nm] to give **5a** (0.8 mg). ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, d, J=6.6 Hz, 10-H_3), 1.32 (1H, m, 5-H_A), 1.46 (2H, m, 5-H_B, 7-H_A), 1.62 (2H, m, 6-H, 7-H_B), 1.84 (3H, d, J=1.2 Hz, 9-H_3), 2.22 (2H, m, 4-H_2), 3.70 (2H, m, 8-H_2), 6.88 (1H, dt, J=7.6, 1.2 Hz, 3-H). EI-MS m/z: 168 $[M-H_2O]^+$.

Preparation of (6*R*)-6c and (6*S*)-7c[2d] Both enantiomers of methyl-(2*E*)-8-benzoyloxy-2,6-dimethyl-2-octenoate [(6*R*)-**6c** and (6*S*)-**7c**] were prepared from optically active β-citronellol (each 200.0 mg) according to the method reported by Tsuji and his colleagues[8] (6*R*)-**6**: $[\alpha]_D^{25}$ +5.7° (c=2.3, $CHCl_3$). (6*S*)-**7**: $[\alpha]_D^{25}$ −5.9° (c=3.7, $CHCl_3$). (6*R*)-**6a**: $[\alpha]_D^{25}$ +12.8° (c=1.32, $CHCl_3$). (6*S*)-**7a**: $[\alpha]_D^{25}$ −10.8° (c=0.453, $CHCl_3$). (6*R*)-**6b**: $[\alpha]_D^{25}$ +7.5° (c=1.4, $CHCl_3$). (6*S*)-**7b**: $[\alpha]_D^{25}$ −8.1° (c=0.42, $CHCl_3$). (6*R*)-**6c**: $[\alpha]_D^{25}$ +7.7° (c=0.76, $CHCl_3$). (6*S*)-**7c**: $[\alpha]_D^{25}$ −7.9° (c=0.48, $CHCl_3$).

Identification of the Absolute Configuration at C-6 of 5 by HPLC Compounds **5b** and **5c** were prepared from **5a** (0.8 mg) in the same manner as (6*R*)-**6b** and (6*R*)-**6c**, respectively. **5b** (0.7 mg, 81.4%): ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, d, J=6.3 Hz, 10-H_3), 1.25—1.67 (5H, m, 5-H_2, 6-H and 7-H_2), 1.84 (3H, d, J=1.2 Hz, 9-H_3), 2.19 (2H, m, 4-H_2), 3.71 (2H, m, 8-H_2), 3.73 (3H, s, $COOCH_3$), 6.75 (1H, dt, J=7.6, 1.2 Hz, 3-H). EI-MS m/z: 200 $[M]^+$. **5c** (0.8 mg, 75.1%): ^{1}H-NMR ($CDCl_3$) δ: 1.00 (3H, d, J=6.6 Hz, 10-H_3), 1.33—1.72 (5H, m, 5-H_2, 6-H and 7-H_2), 1.84 (3H, d, J=1.5 Hz, 9-H_3), 2.22 (2H, m, 4-H_2), 3.72 (3H, s, $COOCH_3$), 4.37 (2H, m, 8-H_2), 6.75 (1H, dt, J=7.3, 1.5 Hz, 3-H), 7.44 (2H, m, 3′, 5′-H), 7.56 (1H, m, 4′-H), 8.03 (2H, m, 2′, 6′-H). EI-MS m/z: 304 $[M]^+$. **5c**, (6*R*)-**6c** and (6*S*)-**7c** were analyzed by HPLC [column, DAICEL CHIRALCEL OD (Daicel Chemical Co., 4.6 mm i.d.×25 cm); mobile phase, *n*-hexane–isopropanol (9 : 1); flow rate, 0.5 ml/min; UV detector, 227 nm]. **5c**, t_R 12.2 min; (6*R*)-**6c**, t_R 12.2 min; (6*S*)-**7c**, t_R 14.6 min.

Determination of Absolute Structures of Glucosyl Moieties in 1—5 Each of compounds **1**—**5** (*ca.* 1 mg) was refluxed with 4% HCl for 3.5 h. The reaction mixture was neutralized with Ag_2O, filtered and excess Ag^+ of the filtrate was removed with H_2S. The solution was concentrated *in vacuo* and dried to give a glucosyl residue which was subjected to the preparation of the corresponding thiazolidine derivative, followed by trimethylsilylation and GLC analysis, according to the reported procedure.[10] GLC conditions:

column, G-column (Kagakuhin Kensa Kyokai, 1.2 mm i.d.×40 m); column temperature, 240 °C; carrier gas, N_2 (25 ml/min). D-Glucose, t_R 54.6 min (ref.: L-glucose, t_R 55.4 min).

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References and Notes

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