Triterpenes and Flavonol Glucuronides from *Oenothera cheiranthifolia*

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A new ursane-type triterpene, named as cheiranthic acid (1), was isolated from the MeOH extract of whole plants of *Oenothera cheiranthifolia* (Onagraceae) along with an isomeric pair of known oleanane- and ursane-type triterpenes (arjunolic acid and asiatic acid) and three flavonol glucuronide analogues (quercetin 3-*O*-glucuronide, its *n*-butyl ester, and myricetin 3-*O*-glucuronide). Their structures were elucidated based on spectroscopic evidence.

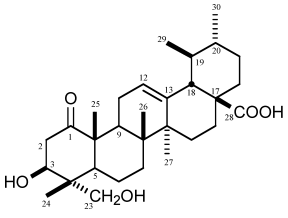
Key words *Oenothera cheiranthifolia*; Onagraceae; cheiranthic acid; ursane-type triterpene; oleanane-type triterpene; flavonol glucuronide

Oenothera cheiranthifolia (Onagraceae), called Beach-Primrose in English, is a perennial that has wiry and prostrate stems (radiating from a central rosette of leaves) and bright yellow flowers (in a small-flowered form with petals to one-third inch long) and grows flat on the sandy beach from Point Conception, Santa Barbara County, California to Coos Bay, Oregon.[1)]

As a part of a series of our phytochemical studies on western North American plants, chemical components of the MeOH extract obtained from whole plants of *O. cheiranthifolia* were investigated and as a result, a new ursane-type triterpene named as cheiranthic acid (**1**) was isolated together with an isomeric pair of known oleanane- and ursane-type triterpenes, arjunolic acid (**2**) and asiatic acid (**3**), and three known flavonols, 3-*O*-β-D-glucuronides of quercetin (**4**) and myricetin (**5**) and the *n*-butyl ester of **4** (**6**). This paper describes the isolation and structural elucidation of these components.

Each of the EtOAc- and *n*-BuOH soluble parts obtained from the MeOH extract was separated by a combination of silica gel, octadecyl silica gel (ODS), and Sephadex LH-20 column chromatography and HPLC separation to isolate each of a new (**1**) and two known (**2**, **3**) triterpenes and an abundant flavonol component (**4**) from the EtOAc soluble part and three flavonol glucuronide analogues (**4**—**6**) from the *n*-BuOH soluble part.

A new triterpene, cheiranthic acid (**1**), a colorless glassy solid, $[\alpha]_D$ +81.1° ($CHCl_3$), gave the molecular ion peak at *m*/*z* 486 (13%) along with abundant and significant fragment ions such as at *m*/*z* 248 (100%) and at *m*/*z* 203 (45%) in electron impact (EI)-MS. Furthermore, the molecular formula was determined as $C_{30}H_{46}O_5$ based on the high resolution (HR)-MS data (*m*/*z* 486.334) of the M^+ ion. The ^{1}H-NMR spectrum of **1** exhibited signals due to four tertiary methyls [δ 0.85 (26-Me), 1.08 (24-Me), 1.11 (27-Me), and 1.35 (25-Me)], two secondary methyls [δ 0.90 (d, J=6.6 Hz, 29-Me) and 0.95 (d, J=6.3 Hz, 30-Me)], a hydroxymethylene [δ 3.44 (1H, d, J=10.4 Hz) and 3.75 (1H, d, J=10.4 Hz), 23-CH_2OH], an oxygenated methine [δ 3.92 (dd, J=12.0, 5.0, 3α-ax. H)], and an olefinic proton [δ 5.27 (1H, t-like, J=3.5 Hz). The ^{13}C-NMR spectrum of **1** indicated that **1** was constituted by thirty carbon atoms including a cyclic ketone on a cyclohexane ring [δ_C 211.9 (C-1)],[2)] a carboxyl carbon [δ_C 181.4 (C-28)],[2)] and two olefinic carbons [δ_C 126.4 (C-12) and 137.2 (C-13)]. The above-mentioned spectral evidence suggested that **1** is a triterpenic acid having an ursolic acid framework and an urs-12-en-28-oic acid structure proposed for **1** was further corroborated by the following EI- and HR-EI-MS spectral evidence: the molecular ion underwent the retro-Diels-Alder fragmentation of the 12—13 double bond in the ring C to yield a typical fragment ion (*m*/*z* 248.177 observed for $C_{16}H_{24}O_2$; the base peak), arising from the D/E ring of **1**.[3)] Furthermore, the second abundant fragment ion observed at *m*/*z* 203 (45%) in the EI-MS and at *m*/*z* 203.179 (Calcd for $C_{15}H_{23}$: 203.180) in the HR-EI-MS seemed to arise from the base peak by the loss of a carboxyl unit, which also supports **1** having an ursolic acid skeleton. To determine the precise structure for **1**, ^{1}H- and ^{13}C-NMR analyses were performed with the aid of two dimensional (2D)-NMR [^{1}H–^{1}H shift-correlation spectroscopy (COSY),



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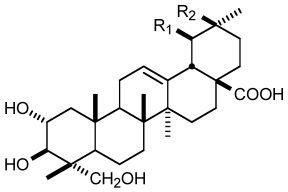
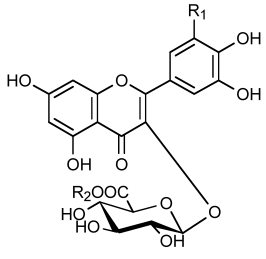


2 : R_1=H, R_2=Me
3 : R_1=Me, R_2=H



4 : R_1=H, R_2=H
5 : R_1=OH, R_2=H
6 : R_1=H, R_2=*n*-butyl

Chart 1

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Table 1. ^{1}H (600 MHz)- and ^{13}C (150 MHz)-NMR Data of **1** in $CDCl_3$[a)]

No.	^{1}H-NMR	^{13}C-NMR
C_1		211.9
C_2	2.40 (1H, dd, J=12.0, 5.0, α-eq.H), 3.05 (1H, dd, J=12.0, 12.0, β-ax.H)	43.3
C_3	3.92 (1H, dd, J=12.0, 5.0, α-ax.H)	75.6
C_4		42.4
C_5	1.12 (1H)[b)]	48.5
C_6	1.42 (1H)[b)], 1.54 (1H)[b)]	18.1
C_7	1.30 (1H)[b)], 1.43 (1H)[b)]	32.6
C_8		39.4
C_9	2.23 (1H, dd, J=11.4, 5.4, α-ax.H)	38.8
C_{10}		51.9
C_{11}	1.84 (1H)[b)], 2.40 (1H)[b)]	25.1
C_{12}	5.27 (1H, t-like, J=3.5)	126.4
C_{13}		137.2
C_{14}		42.2
C_{15}	1.06 (1H)[b)], 1.84 (1H)[b)]	28.0
C_{16}	1.68 (1H, β-eq.H)[b)], 2.02 (1H, ddd, J=13.8, 13.8, 4.8, α-ax.H)	24.1
C_{17}		48.0
C_{18}	2.20 (1H, d, J=11.4, β-H)	52.8
C_{19}	1.33 (1H)[b)]	39.0
C_{20}	1.01 (1H, m)	39.0
C_{21}	1.28 (1H)[b)], 1.51 (1H)[b)]	30.6
C_{22}	1.66 (1H)[b)], 1.72 (1H, ddd, J=13.0, 13.0, 3.5)	36.6
C_{23}	3.44 (1H, d, J=10.4 Hz), 3.75 (1H, d, J=10.4)	70.9
C_{24}	1.08 (3H, s)	12.1
C_{25}	1.35 (3H, s)	15.6
C_{26}	0.85 (3H, s)	17.9
C_{27}	1.11 (3H, s)	23.5
C_{28}		181.4
C_{29}	0.90 (3H, d, J=6.6)	17.0
C_{30}	0.95 (3H, d, J=6.3)	21.1

a) Chemical shifts are shown in ppm, coupling constants in Hz. *b*) Signals are overlapped by other signal(s) and therefore, their multiplicities could not be determined.

heteronuclear multiquantum coherence (HMQC), nuclear Overhauser enhancement spectroscopy (NOESY), and heteronuclear multiple bond connectivity (HMBC)] experiments and all protons and carbons were successfully assigned as shown in Table 1. Based on the established ^{1}H- and ^{13}C-assignments (Table 1), a whole structure for **1** was defined as shown by formula **1** and some important parts, *i.e.*, key points, in the structural elucidation are explained as follows. The COSY spectrum of **1** showed the presence of characteristic carbon linkages of $C_{(2)}H_2$–$C_{(3)}H(OH)$ and $C_{(18)}H$–$C_{(19)}H(CH_3)$–$C_{(20)}H(CH_3)$ in **1**. These COSY data, when considered with the HMBC correlations observed in **1** (Fig. 1), suggested that a plane structure of **1** is the same as that depicted in Fig. 1. Finally, the steric structure of **1** was clarified based on the following NMR evidence. The large coupling constant (12.0 Hz) observed between a proton (δ 3.05) of 2-H_2 and 3-H (δ 3.92) shows that these two protons are in a diaxial relationship, consistent with the 2β- and 3α-oriented protons. Needless to say, the 3-OH group has a β-equatorial configuration. The presence of a series of cross peaks in the NOESY between 24-Me and 25-Me, between 24-Me and 2β-H, between 25-Me and 2β-H, and between 24-Me and 23-CH_2OH suggested that the methyl attached at C-4 is oriented to β-axial (=24-Me) and the CH_2OH group is α-equatorial (=23-CH_2OH). In addition, two characteristic and significant NOESY cross peaks were observed between 9α-H and 27α-Me and between the olefinic proton (=12-H) and 18-H, indicative of the steric feature around the B-, C-, D-, and E-rings of **1**. Especially, based on the occurrence of the cross peak between 12-H and 18-H, the configuration of 18-H is considered β-equatorial on the D-ring (=β-axial on the E-ring). This result also shows that the D/E-ring juncture of **1** is *cis*. Furthermore, the large coupling constant between 18-H and 19-H ($J_{18,19}$=11.4 Hz) indicates that 18-H and 19-H are in a diaxial relation on the E-ring, that is, 19-H is oriented to α-axial whereas the methyl at C19 (C-29) is β-equatorial. The above-mentioned accumulated evidence revealed **1** to be shown by the structural formula **1** with an ursane (=α-amyrin) framework.

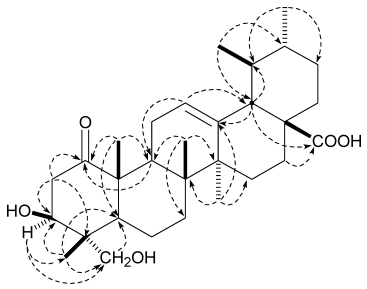

Fig. 1. The Key HMBC Correlations of **1**

The isolated arjunolic acid was defined as formula **2** based on our own structural elucidation by EI- and HR-EI-MS and ^{1}H- and ^{13}C-NMR (2D) spectral studies. Furthermore, it was identified by comparison of the ^{1}H- and ^{13}C-NMR data (in pyridine-d_5; 600 and 150 MHz, respectively) with those reported for arjunolic acid.[4,5)]

The isolated asiatic acid was decided as formula **3** in a similar manner as in the structural elucidation of **2** and further identified by direct comparison of ^{1}H- and ^{13}C-NMR spectra (in CD_3OD; 600 and 150 MHz, respectively) with authentic asiatic acid commercially obtained.

The isolated flavonol glucuronide (**4**) gave the quasi-molecular ion, $(M-H)^-$ at 477 and a significant fragment ion, (the aglycone$-$H)$^-$ at *m*/*z* 301 in the negative (=neg.) ion FAB-MS spectrum. Based on these MS data together with the ^{1}H- and ^{13}C-NMR (in DMSO-d_6; 600 and 150 MHz, respectively) and these 2D analyses the structure was assigned to formula **4**. Moreover, the identity with quercetin 3-*O*-β-D-glucuronide was confirmed by comparison of the ^{13}C-NMR data with the reported data.[6)]

The second flavonol glucuronide (**5**) isolated was identified with myricetin 3-*O*-β-D-glucuronide by comparison of its neg. ion FAB-MS, ^{1}H- and ^{13}C-NMR (in DMSO-d_6; 600 and 150 MHz, respectively) with those previously reported.[7)]

The last flavonol glucuronide analogue (**6**) isolated gave the $[M-H]^-$ ion peak at 533 in the neg. ion FAB-MS. The corresponding HR spectrum revealed the molecular formula to be $C_{25}H_{26}O_{13}$. In addition, the EI- and HR-EI-MS spectra of **6** exhibited a significant fragment ion at *m*/*z* 302 as the base peak, because of the aglycone of $C_{15}H_{10}O_7$. ^{1}H- and ^{13}C-NMR assignments (see Experimental) were carried out with the aid of the detailed 2D analyses (COSY, HMQC, NOESY, and HMBC) and the resulting NMR evidence revealed **6** to be defined as quercetin 3-*O*-(6″-*n*-butyl glucuronide). This flavonol derivative has been already isolated from leaves of *Parthenocissus tricuspidata* (Vitaceae).[8)] This report appears the second instance of its isolation from natural sources.

However, the question has been raised whether this butyl ester is a genuine naturally occurring product or an artificial compound derived from quercetin 3-*O*-glucuronide during the extraction procedure with *n*-butanol.

Experimental

General ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL JNM-ECA 600 spectrometer (^{1}H at 600 MHz and ^{13}C at 150 MHz). Chemical shifts are given in δ values (ppm) relative to tetramethylsilane (TMS) as internal standard. EI- and HR-EI-MS spectra (at 30 eV), along with FAB- and HR-FAB-MS spectra in negative mode (matrix: triethanolamine or glycerin), were obtained by JEOL JMS-700T spectrometer. Optical rotations were determined on a JASCO DIP-140 polarimeter. For column chromatography, silica gel 60 (230—400 mesh, Merck), Chromatorex ODS DM1020T (100—200 mesh, Fuji Silysia), and Sephadex LH-20 (Amersham Biosciences) were used. Kiesel gel 60 F_{254} (Merck) and RP-18 F_{254} (Merck) were used for analytical TLC. Preparative HPLC was performed on a JAI LC-918 instrument with an RI-50 differential refractometer and a JAIGEL-ODS column. An authentic asiatic acid used in this work was commercially obtained from Extrasynthese in France.

Plant Material Whole plants of *O. cheiranthifolia* were collected at a sandy beach in Oregon, U.S.A., in July 1997. A voucher specimen (Murata J. *et al.*, No. 97027) was deposited in the Herbarium, Botanical Gardens, The University of Tokyo (TI), Japan.

Extraction and Isolation The whole plants of *O. cheiranthifolia* were soaked in acetone (2.0 l) and the plant materials (118.0 g) after soaking were extracted three times with MeOH (each 2.0 l) at room temperature for 15, 9, and 9 d in turn. The resulting MeOH extract (22.2 g) was suspended in water (500 ml) and extracted four times with EtOAc (500 ml×1 then 250 ml×3) and subsequently, three times with *n*-BuOH (300 ml×3) to afford EtOAc (3.9 g) and *n*-BuOH (8.1 g) extracts, respectively. Most (3.8 g) of the EtOAc extract was subjected to column chromatography on silica gel (190.0 g) eluted successively with $CHCl_3$–MeOH (20 : 1; total 1050 ml) [giving 30 fractions of Nos. 1 to 30], (10 : 1; total 1320 ml) [giving 16 fractions of Nos. 31 to 46], the lower phase of $CHCl_3$–MeOH–H_2O (7 : 3 : 1; total 1.54 l) [giving 41 fractions of Nos. 47 to 87], the lower phase of $CHCl_3$–MeOH–H_2O (65 : 35 : 10; total 440 ml); [giving 6 fractions of Nos. 88 to 93], and a mixture solvent of $CHCl_3$–MeOH–H_2O (6 : 4 : 1; total 1.1 l); [giving 20 fractions of Nos. 94 to 113]. The fractions of Nos. 18 and 19 (20.6 mg) were collected and subjected to reversed-phase (ODS Chromatrex; 5.1 g) chromatography eluted with MeOH–H_2O (3 : 1) [giving 9 fractions (10 ml per fraction)] and the resulting third fraction gave compound **1** (2.2 mg). The fractions of Nos. 28—32 (85.6 mg) were collected and rechromatographed over ODS Chromatrex (8.2 g) eluted with MeOH–H_2O (3 : 1) [giving 10 fractions (10 ml per fraction)] and the resulting third fraction (15.7 mg) was subjected to preparative HPLC separation [JAIGEL-ODS column; an eluting agent, 80% aqueous (=aq.) MeOH; a rate of flow, 5 ml/min] to yield compounds **2** (4.3 mg) and **3** (5.6 mg). The fractions of Nos. 100—107 (146.8 mg) were collected and further column-chromatographed over ODS Chromatrex (15.6 g) [eluting with CH_3CN–H_2O (1 : 7) and giving 28 fractions (5 ml per fraction)] and the resulting fractions 9—11 gave compound **4** (38.2 mg) in pure form. An aliquot (3.8 g) of the *n*-BuOH extract (*vide ante*) was chromatographed over ODS (192 g), and eluted (100 ml per fraction) successively with CH_3CN : H_2O (1 : 4) [giving 15 fractions (Nos. 1 to 15)], CH_3CN : H_2O (1 : 2) [giving 13 fractions (Nos. 16 to 28)], CH_3CN : H_2O (1 : 1) [giving 4 fractions (Nos. 29 to 32)], and CH_3CN [giving 2 fractions (Nos. 33, 34)]. The fractions of Nos. 4—6 (937.7 mg) eluted with CH_3CN : H_2O (1 : 4) were combined and subjected to a Sephadex LH-20 column eluted with 30% aq. MeOH to afford 17 fractions (30 ml per fraction), the tenth fraction of which gave pure **5** (14.7 mg). The fractions of Nos. 9 and 10, eluted with CH_3CN : H_2O (1 : 4), corresponded to pure **4** (200.1 mg). The fractions of Nos. 22 and 23 (77.8 mg) eluted with CH_3CN : H_2O (1 : 2) were further separated on Sep-Pak C_{18} column (Waters; 10 g) eluted subsequently with CH_3CN : H_2O (2 : 3) [giving fractions of No. 1 to No. 7 (5 ml per fraction)] and with CH_3CN : H_2O (1 : 1) [giving fraction No. 8 (a 10 ml amount), fractions Nos. 9 and 10 (each 20 ml amount)] and the resulting fraction No. 9 yielded **6** (19.6 mg).

Cheiranthic Acid (**1**): A colorless glassy solid, $[\alpha]_D$ +81.1° (c=0.5, $CHCl_3$). EI-MS (30 eV) *m/z* (%): 486 (13, M^+), 248 (100), 219 (10), 203 (45), 133 (23). HR-EI-MS *m/z*: 486.334 (Calcd for $C_{30}H_{46}O_5$, M^+: 486.335), 248.177 (Calcd for $C_{16}H_{24}O_2$: 248.178), 203.179 (Calcd for $C_{15}H_{23}$, $C_{16}H_{24}O_2$–COOH: 203.180). ^{1}H- and ^{13}C-NMR: Given in Table1.

2: EI-MS (30 eV) *m/z* (%): 488 (0.7, M^+), 248 (100), 219 (7.6), 203 (76.6), 191 (11.9), 133 (15.7). HR-EI-MS *m/z*: 488.349 (Calcd for $C_{30}H_{48}O_5$, M^+: 488.350), 248.178 (Calcd for $C_{16}H_{24}O_2$: 248.178), 203.180 (Calcd for $C_{15}H_{23}$, $C_{16}H_{24}O_2$–COOH: 203.180). The ^{1}H- and ^{13}C-NMR spectral data of **2** were in agreement with those reported for arjunolic acid.[4,5]

3: EI-MS (30 eV) *m/z* (%): 488 (1.3, M^+), 248 (100), 219 (12.5), 203 (52.8), 191 (15.2), 133 (26.8). HR-EI-MS *m/z*: 488.350 (Calcd for $C_{30}H_{48}O_5$, M^+: 488.350), 248.177 (Calcd for $C_{16}H_{24}O_2$: 248.178), 203.180 (Calcd for $C_{15}H_{23}$, $C_{16}H_{24}O_2$–COOH: 203.180). The structure of **3** was confirmed by direct comparison of ^{1}H- and ^{13}C-NMR spectra (in MeOH-d_4; 600 and 150 MHz, respectively) with an authentic sample of asiatic acid.

4: FAB-MS (negative ion mode) *m/z*: 477 $(M-H)^-$, 301 $(aglycone-H)^-$. ^{1}H-NMR (in DMSO-d_6; 600 MHz): 3.26—3.41 (3H, m, 2″, 3″, 4″-Hs), 3.58 (1H, d, J=9.6 Hz, 5″-H), 5.51 (1H, d, J=7.2 Hz, 1″-H), 6.21 (1H, d, J=2.0 Hz, 6-H), 6.41 (1H, d, J=2.0 Hz, 8-H), 6.84 (1H, d, J=8.8 Hz, 5′-H), 7.53 (1H, d, J=2.0 Hz, 2′-H), 7.61 (1H, dd, J=8.8, 2.0 Hz, 6′-H), 12.57 (1H, s, 5-OH). The ^{13}C-NMR data (in DMSO-d_6; 150 MHz) of **4** was consistent with those (in DMSO-d_6; 75.47 MHz) reported for quercetin 3-*O*-β-D-glucuronide.[6]

5: FAB- and HR-FAB-MS (negative ion mode) *m/z*: 493.062 [Calcd for $C_{21}H_{17}O_{14}$, $(M-H)^-$: 493.062], 317 $(aglycone-H)^-$. EI- and HR-EI-MS (%): 318.037 (47) [Calcd for $C_{15}H_{10}O_8$, $(aglycone)^+$: 318.037], 170 (100). ^{1}H-NMR (in DMSO-d_6; 600 MHz): 3.27 (1H, dd, J=9.0, 8.4 Hz, 3″-H), 3.40 (1H, dd, J=8.4, 7.8 Hz, 2″-H), 3.42 (1H, dd, J=9.6, 9.0 Hz, 4″-H), 3.55 (1H, d, J=9.6 Hz, 5″-H), 5.50 (1H, d, J=7.8 Hz, 1″-H), 6.20 (1H, d, J=1.8 Hz, 6-H), 6.38 (1H, d, J=1.8 Hz, 8-H), 7.19 (2H, s, 2′-, 6′-Hs), 12.59 (1H, s, 5-OH). Finally, **5** was identified by comparing its FAB-MS (negative ion mode), ^{1}H- and ^{13}C-NMR (in DMSO-d_6; 600 and 150 MHz, respectively) spectral data with those reported for myricetin 3-*O*-β-D-glucuronide.[7]

Quercetin 3-*O*-(6″-*n*-Butyl Glucuronide) (**6**): HR-FAB-MS (negative ion mode) *m/z*: 533.129 [Calcd for $C_{25}H_{25}O_{13}$, $(M-H)^-$: 533.130]. EI- and HR-EI-MS *m/z* (%): 302.044 (100) [Calcd for $C_{15}H_{10}O_7$, $(aglycone)^+$: 302.043]. ^{1}H-NMR (in $CDCl_3$; 600 MHz): 0.83 [3H, t, J=7.8 Hz, $C\underline{H}_3(CH_2)_3O$–], 1.25 [2H, sextet, J=7.8 Hz, $CH_3C\underline{H}_2(CH_2)_2O$–], 1.50 (2H, m, $CH_3CH_2C\underline{H}_2CH_2O$–), 3.47 (1H, dd, J=9.0, 9.0 Hz, 3″-H), 3.54 (1H, dd, J=9.0, 7.8 Hz, 2″-H), 3.60 (1H, dd, J=9.6, 9.0 Hz, 4″-H), 3.74 (1H, d, J=9.6 Hz, 5″-H), 4.06 [2H, t, J=6.6 Hz, $CH_3(CH_2)_2C\underline{H}_2O$–], 5.28 (1H, d, J=7.8 Hz, 1″-H), 6.19 (1H, d, J=1.8 Hz, 6-H), 6.38 (1H, d, J=1.8 Hz, 8-H), 6.84 (1H, d, J=8.4 Hz, 5′-H), 7.60 (1H, d, J=1.8 Hz, 2′-H), 7.61 (1H, dd, J=8.4, 1.8 Hz, 6′-H). ^{13}C-NMR (in $CDCl_3$; 150 MHz): 159.2 (C-2), 135.4 (C-3), 179.3 (C-4), 163.1 (C-5), 100.0 (C-6), 166.0 (C-7), 94.8 (C-8), 158.5 (C-9), 105.6 (C-10), 122.9 (C-1′), 117.2 (C-2′), 146.0 (C-3′), 149.9 (C-4′), 116.0 (C-5′), 123.5 (C-6′), 104.5 (C-1″), 75.4 (C-2″), 77.5 (C-3″), 72.7 (C-4″), 77.3 (C-5″), 170.2 (C-6″), 66.3 (butyl C-1), 31.5 (butyl C-2), 20.0 (butyl C-3), 14.0 (butyl C-4). The compound having the same structure as **6** was recently isolated from leaves of *P. tricuspidata* (Vitaceae).[8]

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