Triterpenoid Saponins from *Elsholtzia bodinieri*

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A new oleanane-type triterpenoid estersaponin, bodinierin C (**1**), along with two known saponins, mazusaponin I (**2**) and ciwujianoside C (**3**), were isolated from the water-soluble part of the root barks of *Elsholtzia bodinieri*. The structure of bodinierin C was characterized by spectroscopic means and chemical hydrolysis as 3β-*O*-caffeoyl-23-hydroxylechinocystic acid 28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester. The known compounds were identified by comparing their spectral data with those of authentic samples or data reported in the literature. All compounds were firstly isolated from *Elsholtzia bodinieri* family.

Key Words : *Elsholtzia bodinieri*, Labiatae, 3β-*O*-Caffeoyl-23-hydroxylechinocystic acid 28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester, Bodinierin C

Introduction

The genus *Elsholtzia* belongs to the Labiatae family and has approximately 40 species worldwide, which are mainly distributed in East Asia. Thirty-three species, fifteen varieties and five forms of the genus *Elsholtzia* are found in China. Among these, some are used as medicines, some are taken as food and some are source of honey manufacture. The genus *E. wild* generally possesses plentiful volatile oil, which exerts strong inhibition of central nervous system and takes on definite analgesic effect. It shows antibiotic and anti-inflammatory effects as well. As a species of the genus *Elsholtzia*, *E. bodinieri* is an annual herbaceous plant, widely distributed in the mountainuous regions of the west and southwest district of China (Chinese name "Dongzisu").[1] which has been mainly used as a traditional Chinese folk drug for the treatment of eczema, enteritis, diarrhea, bacillary dysentery and cold, and are also known to have anticancer and antibacterial effects.[2] However, at the best of our knowledge, the active principles of this plant are unknown except for few constituents.[3-7] Therefore, as a continuation of our efforts to pursue the active natural products from *E. bodinieri*, three oleanane-type triterpenoid saponins were isolated by repeated column chromatography and preparative TLC from the *n*-BuOH fraction of the ethanolic extract of *E. bodinieri* gathered in Gansu province of China. Their structures were elucidated as bodinoside C (**1**) (3β-*O*-caffeoyl-23-hydroxylechinocystic acid 28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester), mazusaponin I (**2**)[8] and ciwujianoside C (**3**),[9] respectively. Among these compounds, **1** was a new one, and all compounds were firstly isolated from the genus *Elsholtzia*. We report herein the isolation and structural elucidation of bodinoside C using chemical and spectral evidence.

Results and Discussion

Compound **1** was obtained as a pale yellow amorphous powder from MeOH and responded positively to the Molisch and Liebermann-Burchard tests for triterpene glycoside. The molecular formula was established as $C_{57}H_{84}O_{22}$ from the HRFAB-MS (positive) ion peak at *m/z* 1143.5338 $[M+Na]^+$ ($C_{57}H_{84}O_{22}Na$, calcd. for 1143.5352), corresponding to 16 degrees of unsaturation. The positive-ion FAB-MS also displayed 975 $[M+H-146]^+$, 813 $[M+H-146-162]^+$ and 651 $[M+H-146-162-162]^+$, which showed the presence of one terminal 6-deoxysugar and two inter hexose units in a linear linkage. It exhibited UV maxima at 220, 237, 298 and 325 nm, suggesting the presence of strong conjugation in the molecule, a bathochromic shift of 47 nm by adding NaOH indicated the presence of free phenolic hydroxy, and a distinct bathochromic shift with $AlCl_3$ but again returning to normal value after adding HCl, indicated the presence of catechol group. Its IR spectrum (KBr) of **1** indicated the presence of hydroxyl groups (3450-3100 cm^{-1}), α,β-unsaturated ester moiety (1694 and 1270 cm^{-1}), trisubstituted double bond (1634 cm^{-1}), aromatic rings (1595 and 1514 cm^{-1}) and glucoside functionalities (1086, 1070, 1036 cm^{-1}). The broad band decoupled ^{13}C-NMR spectrum showed 57 carbon signals, of which 30 were assigned to the pentacyclic triterpene moiety, 9 to the caffeic acid moiety and 18 to the saccharide portion. The DEPT spectrum displayed the presence of twelve quaternary, twenty-six methine, twelve secondary methene and seven primary methyl carbons in the molecule. The analysis of NMR spectra by the aid of DEPT technique demonstrated the presence of a caffeoyl group [including two *trans*-conjugated olefinic protons at δ_H 6.32 (1H, d, J = 16.0 Hz) and 7.55 (1H, d, J = 16.0 Hz) were connected directly to carbons at δ_C 116.0 and 144.8, an ester carbonyl (δ_C 167.8), three aromatic methine protons of an typical ABX type at δ_H 7.08 (1H, d, J = 1.5 Hz), 6.88 (1H, d, J = 8.0 Hz) and 7.10 (1H, dd, J = 8.0, 1.5 Hz) were linked to three aromatic tertiary carbons at δ_C 115.4, 114.3 and 122.2, another three aromatic quanernary carbons at δ_C 127.1, 144.1, 146.6], a triaccharide chain [three anomeric proton signals at δ_H 6.18 (1H, d, J =

8.0 Hz), 4.95 (1H, d, J = 8.0 Hz), 5.82 (1H, d, J = 1.5 Hz) and one doublet methyl at δ_H 1.66 (1H, d, J = 6.0 Hz), corresponding to three anomeric carbon and methyl signals at δ_C 95.7, 104.7, 102.8 and 18.8]. On alkaline hydrolysis, **1** yielded caffeic acid, *D*-glucose and *L*-rhamnose (in the molar ratio of 1:2:1), respectively, which was compared with authentic sample by *co*-TLC and *co*-PC. Moreover, The ^{1}H and ^{13}C-NMR of **1** exhibited six angular methyl groups [δ_H 1.32, 1.18, 1.10, 1.65, 0.98 and 1.08, corresponding to δ_C 15.6, 16.7, 17.7, 27.2, 33.3 and 24.8] and one double bond [δ_C 123.1 and 143.9, a broad triplet at δ_H 5.41(1H, br t)], characteristic of a typical Δ^{12}-oleanene skeleton.[10,11] The signals at δ_H 4.10 (1H, d, J = 11.0 Hz)/3.68 (1H, d, J = 11.0 Hz) and δ_C 66.1 were assigned to H_2-23 and C-23, respectively, suggesting that a hydroxyl group was linked at C-23 on the basis of the chemical shifts of C-23 and C-24.[12] This conclusion was also drawn from the correlations of H-23 with C-3/C-4/C-24 and H-24 with C-3/C-4/C-5/C-23 in the HMBC spectrum as well as the observed NOE interactions between H-23 and H-3/H-5, H-24 and H-25 in the ROESY spectrum. In addition, the signals at δ_H 5.06 (1H, m) and δ_C 74.2 were assigned to H-16 and C-16, which suggested that another hydroxyl group was linked at C-16[13] with α-configuration on account of the chemical shifts of C-16 and H-16, along with the correlations of H-16 with C-14/C-17/C-18/C-22/C-28 and H-16 with H-18 in the HMBC and ROESY spectrum. By comparison of the spectroscopic data of the aglycone of **1** with echinocystic acid[14] and 3β, 23, 28-trihydroxy-12-oleanene 3β-caffeate isolated previously from *Hibiscus syriacus*,[15] the aglycone of **1** was suggested to be 23-hydroxyechinocystic acid with a caffeoyl linkage at C-3, which was confirmed by the correlations of H-3 with C-2/C-4/C-23/C-24/C-9 in the HMBC spectrum, and also consistent with the observed downfield shifts of C-3 (δ_C 80.9) and H-3 (δ_H 5.02) with respect to the corresponding signal in hederagenin 28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranoside.[16] The β-configuration of 3-*O*-caffeoyl group was determined from the chemical shifts and coupling constants of H-3 (5.02, dd, J = 5.5, 11.0 Hz),[17,18] and further evidenced by the observed NOE interactions between H-3 and H-1/H-5/H-23 in the ROESY spectrum. These spectral features and physicochemical properties suggested **1** to be 3β-*O*-caffeoyl-23-hydroxylechinocystic acid with three sugar moieties.

Comparison of NMR data of the sugar moieties with literature values[16] revealed that the glucoses and rhamnose were present in pyranoside form. The relative stereochemistry of each monosaccharide was determined as β-glucopyranose and α-rhamnopyranose based on the characteristic $^3J_{H\text{-}1,H\text{-}2}$ coupling constants (8.0 and 1.5 Hz)[20] and ^{13}C-NMR data. The HMBC correlations (Fig. 2) between H-1'''' of the terminal rhamnopyranosyl unit and C-4''' of the centre glucopyranosyl unit, H-4''' of the centre glucopyranosyl unit and C-1'''' of the terminal rhamnopyranosyl unit, H-1''' of the centre glucopyranosyl unit and C-6'' of the inner glucopyranosyl unit, together with H-6'' of the inner glucopyranosyl unit and C-1''' of the centre glucopyranosyl unit, suggested the linkage of α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl. Further supporting information came from the observed NOE interactions of H-6''/H-1''' and H-4'''/H-1'''' in ROESY experiment (Fig. 3), together with the FAB-MS ion peaks at *m/z* 975 $[M+H-146]^-$ (loss of a terminal rhamnose unit) and 813 $[M+H-146-162]^-$ and 651 $[M+H-146-162-162]^-$ (loss of two inner glucose units successively). Easy hydrolysis of the compound **1** with base comfirmed that sugar was attached by an ester linkage. The exact position of the trisaccharide chain at C-28 of the aglycone was established from the HMBC correlations between the H-1 (δ_H 6.18) of ester-linked β-glucopyranosyl unit and the C-28 (δ_C 176.3) of aglycone, this was also supported by the typical upfield (*ca* 4.4) *O*-glycosylation shift of C-28 compared to the shift of a free carboxylic acid[21] and the anomeric carbon signal (δ_C 95.7) of β-glucopyranosyl unit, indicating the presence of sugar ester. From the foregoing evidences, the structure of compound **1** was established as 3β-*O*-caffeoyl-23-hydroxyechinocystic acid 28-*O*-α-*L*-rhamnopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→6)-β-*D*-glucopyranosyl ester, named

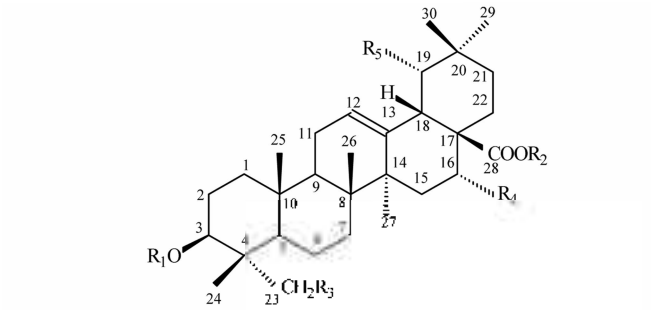

Figure 1. The structures of compound **1-3**.

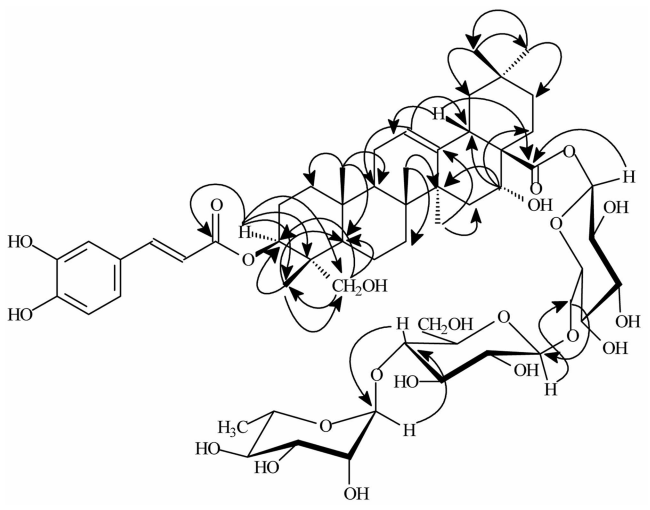

Figure 2. The key HMBC correlations of compound **1**.

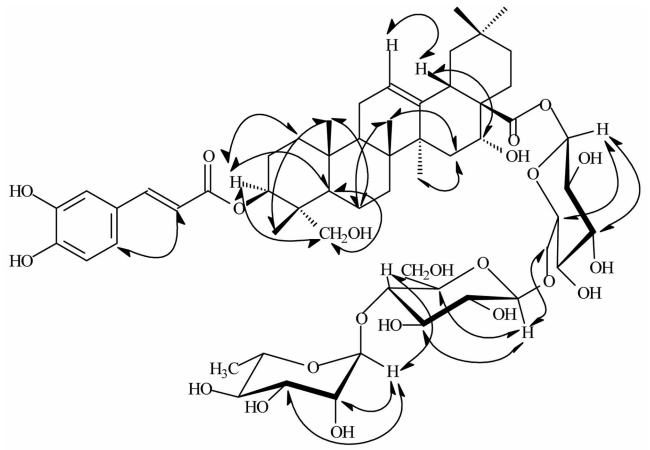

Figure 3. The key ROESY correlations of compound **1**.

bodinierin C. To our knowledge, **1** has not been reported previously from any plant source.

The known compounds **2** and **3** were identified by analysis and comparison of their spectral data obtained with literature values.

Experimental Section

General procedures. Melting points were measured on a Chinese X-4 melting point apparatus (uncorrected); Optical rotation was determined on a Perkin-Elmer 341 automatic polarimeter; IR spectra (KBr disks) were obtained on Alpha-Centari FT-IR spectrometer; UV spectra were run on a Shimadzu UV-300 spectrophotometer (double beam); NMR spectra were scanned on Bruker AM-500 spectrometer (chemical shifts in δ downfield from TMS internal standard) operating 500 and 125 MHz for ^{1}H and ^{13}C respectively, and FAB-MS spectra on VG Autospect 3000 spectrometer; TLC was performed on silica gel GF_{254} plates (0.50 mm thickness); Spots were visualized under UV light or by exposure to I_2 vapours and/or by spraying (analyt. TLC) with 10% H_2SO_4 in EtOH, followed by heating for a few minute; Separation and purification were performed by column chromatography on silica gel (100-200, 200-300 mesh). All solvents were distilled before use.

Plant materials. The root barks of *E. bodinier* were collected in August 2004 from Ziwuling mountainous area of Gansu Province in China, and identified by Fu-shun Liu (Department of Biology, Longdong University, China). A voucher specimen (No. 107083) of the plant is previously deposited at the Herbarium of the Botany Department, Longdong University, Qingyang, 745000, China.

Extraction and isolation. The air-dried root barks of *E. bodinier* (2.5 kg) were extracted in soxhlet successively with 75% EtOH for 3 days. The extracts were evaporated to dryness. The residue (155 g) was suspended in warm water

Table 1. ^{1}H and ^{13}C-NMR data of compound **1** (500/125 MHz, pyridine-d_5)[a]

No.	δ_H	δ_C (DEPT)	No.	δ_H	δ_C (DEPT)
1	1.67(1H, m)/1.48(1H, m)	38.3(CH_2)	30	1.08(3H, s)	24.8(CH_3)
2	2.19/2.08(brd, 12.3)	24.2(CH_2)	1'	–	127.1(C)
3	5.02(1H, dd, 5.5, 11.0)	80.9(CH)	2'	7.08 (1H, d, 1.5)	115.4(CH)
4	–	43.7(C)	3'	–	144.1(C)
5	1.68(1H, m)	48.1(CH)	4'	–	146.6(C)
6	1.58(1H, m)/1.49(1H, m)	18.4(CH_2)	5'	6.88(1H, d, 8.0)	114.3(CH)
7	2.10(1H, m)/1.87(1H, m)	33.5(CH_2)	6'	7.10(1H, dd, 8.0, 1.5)	122.2(CH)
8	–	40.1(C)	7'	7.55(1H, d, 16.0)	144.8(CH)
9	1.68(1H, m)	47.4(CH)	8'	6.32(1H, d, 16.0)	116.0(CH)
10	–	37.1(C)	9'	–	167.8(C)
11	2.02(1H, m)/1.98(1H, m)	24.2(CH_2)	28-*O*-Glycosyl moieties		
12	5.41(1H, br t)	123.1(CH)	Glc-1''	6.18(1H, d, 8.0)	95.7(CH)
13	–	143.9(C)	2''	4.09(1H, t, 8.0)	74.1(CH)
14	–	42.3(C)	3''	4.17(1H, m)	78.6(CH)
15	1.74(1H, dd, 3.5, 14.9)/1.51(1H, dd, 2.6, 14.9)	36.4(CH_2)	4''	4.23(1H, m)	71.5(CH)
16	5.06(1H, m)	74.2(CH)	5''	4.08(1H, m)	78.0(CH)
17	–	49.4(C)	6''	4.66(1H, m)/4.30(1H, m)	69.2(CH_2)
18	3.41(1H, dd, 4.2, 13.5)	41.8(CH)	Glc-1'''	4.95(1H, d, 8.0)	104.7(CH)
19	1.27(1H, m)/2.33(1H, t, 13.7)	47.4(CH_2)	2'''	3.96(1H, t, 8.0)	75.5(CH)
20	–	30.8(C)	3'''	4.12(1H, m)	76.5(CH)
21	1.98(1H, m)/1.21(1H, m)	36.1(CH_2)	4'''	4.36(1H, t, 8.0)	78.5(CH)
22	1.95(1H, m)/1.82(1H, dd, 4.7, 13.4)	32.2(CH_2)	5'''	3.66(1H, m)	77.1(CH)
23	4.10(1H, d, 11.0)/3.68(1H, d, 11.0)	66.1(CH_2)	6'''	4.20(1H, m)/4.10(1H, m)	61.3(CH_2)
24	1.32(3H, s)	15.6(CH_3)	Rha-1''''	5.82(1H, d, 1.5)	102.8(CH)
25	1.18(3H, s)	16.7(CH_3)	2''''	4.64(1H, m)	72.5(CH)
26	1.10(3H, s)	17.7(CH_3)	3''''	4.53(1H, dd, 9.0, 2.0)	72.6(CH)
27	1.65(3H, s)	27.2(CH_3)	4''''	4.31(1H, m)	74.0(CH)
28	–	176.3(C)	5''''	4.91(1H, m)	70.5(CH)
29	0.98(3H, s)	33.3(CH_3)	6''''	1.66(1H, d, 6.0)	18.8(CH_3)

[a]Signals were assigned by ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, ROESY, HMBC, 90° and 135° DEPT.

and extracted with water-saturated *n*-BuOH. The organic layer was concentrated to obtain a residue (50 g) which was redissolved in MeOH (300 mL). Addition of Et_2O gave a flocculent precipitate which was washed with Et_2O (three time), yielded a crude saponin mixture (30 g) which was subjected to silica gel column chromatography (100-200 mesh) with EtOAc-MeOH-H_2O (10:5:1 → 100% MeOH, v/v/v) in increasing polarity and combined by monitoring with TLC to give ten fractions (A-J). Fraction G (2 g) was repeatedly subjected to silica gel column chromatography (200-300 mesh), then with MCI-gel CHP-20 to afford **2** (12 mg). Fraction I (560 mg) was separated successively over Sephadex LH-20 (MeOH-H_2O 8:2) and silica gel column ($CHCl_3$-MeOH-H_2O 6:4:1 → 10:5:1) to obtain **3** (11 mg). Fraction J (1.2 g) was further purified by preparative TLC and developed with Me_2CO-MeOH (1:8, v/v) as development to provide compound **1** (15 mg).

Bodinierin C (1): Pale yellow amorphous powder from MeOH, $C_{57}H_{84}O_{22}$, mp. 208-210 °C, $[\alpha]_D^{20}$ −19.2° (c 0.41, MeOH); UV λ_{max}^{MeOH}: 220, 237, 298 and 325 nm; (+NaOH): 372 nm; (+$AlCl_3$): 382 nm; IR ν_{max}^{KBr}: 3450-3100, 2921, 1723, 1694, 1634, 1595, 1514, 1464, 1270, 1086, 1070, 1036, 940 cm^{-1}; HRFAB-MS (positive-ion mode): *m/z* 1143.5338 $[M+Na]^-$; FAB-MS: m/z 975 $[M+H-146]^+$, 813 $[M+H-146-162]^+$ and 651 $[M+H-146-162-162]^+$; ^1H and ^{13}C-NMR see Table 1.

Mazusaponin I (2): White powder from MeOH, $C_{26}H_{44}O_{11}$, mp. 189-191 °C, $[\alpha]_D^{20}$ −32.5° (c 0.25, MeOH); UV λ_{max}^{MeOH}: 210 nm; ^{13}C-NMR (125 MHz, pyridine-d_5): δ_C 38.8 (C-1), 26.7 (C-2), 88.6 (C-3), 39.6 (C-4), 55.1 (C-5), 18.6 (C-6), 33.2 (C-7), 40.2 (C-8), 48.3 (C-9), 37.2 (C-10), 24.2 (C-11), 123.1 (C-12), 144.3 (C-13), 42.2 (C-14), 28.9 (C-15), 27.9 (C-16), 46.7 (C-17), 44.5 (C-18), 81.2 (C-19), 35.5 (C-20), 29.1 (C-21), 33.1 (C-22), 28.1 (C-23), 16.8 (C-24), 15.6 (C-25), 17.7 (C-26), 24.9 (C-27), 177.2 (C-28), 28.6 (C-29), 24.7 (C-30), α-Ara: 107.6 (C-1), 72.7 (C-2), 74.4 (C-3), 69.6 (C-4), 66.8 (C-5), β-Glc: 95.8 (C-1), 73.8 (C-2), 78.5 (C-3), 70.7 (C-4), 78.1 (C-5), 69.3 (C-6), β-Glc: 105.1 (C-1), 75.2 (C-2), 78.3 (C-3), 71.4 (C-4), 78.4 (C-5), 62.7 (C-6); FAB-MS (negative-ion mode): *m/z* 927 $[M-H]^-$, 603 $[M-H-2Glc]^-$, 471 $[M-H-2Glc-Ara]^-$. ^1H-NMR and IR data were consistent with those reported in the literature.[8]

Ciwujianoside C (3): White powder from MeOH, $C_{53}H_{86}O_{21}$, mp. 211-213 °C (decompose), UV λ_{max}^{MeOH} 210 nm; ^{13}C-NMR (125 MHz, pyridine-d_5): δ_C 38.7 (C-1), 26.5 (C-2), 87.9 (C-3), 39.5 (C-4), 55.8 (C-5), 18.1 (C-6), 33.6 (C-7), 39.6 (C-8), 47.8 (C-9), 36.5 (C-10), 23.1 (C-11), 122.5 (C-12), 143.8 (C-13), 41.8 (C-14), 26.6 (C-15), 23.6 (C-16), 46.9 (C-17), 41.6 (C-18), 45.9 (C-19), 30.7 (C-20), 33.5 (C-21), 32.3 (C-22), 28.2 (C-23), 16.9 (C-24), 15.5 (C-25), 17.6 (C-26), 25.6 (C-27), 176.2 (C-28), 32.8 (C-29), 23.1 (C-30), α-Ara: 106.9 (C-1), 72.5 (C-2), 74.2 (C-3), 69.1 (C-4), 66.3 (C-5), β-Glc: 95.9 (C-1), 73.6 (C-2), 78.1 (C-3), 70.4 (C-4), 76.5 (C-5), 69.1 (C-6), β-Glc: 104.9 (C-1), 75.1 (C-2), 76.3 (C-3), 78.4 (C-4), 77.8 (C-5), 61.1 (C-6), α-Rha: 102.2 (C-1), 72.3 (C-2), 72.7 (C-3), 73.6 (C-4), 70.1 (C-5), 18.2 (C-6); FAB-MS (negative-ion mode): *m/z* 1057 $[M-H]^-$, 587 $[M-H-2Glc-Rha]^-$, 455 $[M-H-2Glc-Rha-Ara]^-$. ^1H-NMR and IR data were identical with those of literature.[9]

Alkaline hydrolysis of compound 1: Compound **1** (5 mg) was treated with an aqueous solution of $Ba(OH)_2$ (0.30 mol/L) for 4 hr at 100 °C. The reaction mixture was cooled, then adjusted to PH = 7 with 10% H_2SO_4. The $BaSO_4$ was removed by filtration and the solution was extracted with Et_2O (twice), then the ether layer was concentrated under reduced pressure to give a light-yellow solution of caffeic acid, which was identified by *co*-TLC with authentic samples using bromphenol blue as chromogenic reagent. The aqueous layer was partitioned between *n*-BuOH/H_2O, and the aqueous layer was concentrated *in vacuo*. The sugar were identified by *co*-PC with authentic samples using [*n*-BuOH:HOAc:H_2O (4:1:5, v/v/v)] as developing solvent and 0.9% aniline-oxalate solution as color developing reagent (*D*-glucose R_f: 0.19, brown; *L*-rhamnose R_f: 0.37, brown).

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