PERGAMON

Phytochemistry 56 (2001) 377–381

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

Phenylbutanoids and stilbene derivatives of *Rheum maximowiczii*

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Received 25 June 1999; received in revised form 5 May 2000

Abstract

The methanol extract of the dried roots of *Rheum maximowiczii* afforded four phenylbutanoid and two stilbene derivatives. Their structures were established on the basis of chemical and spectroscopic studies.

Keywords: *Rheum maximowiczii*; Polygonaceae; Phenylbutanoid; Stilbene dimer

1. Introduction

Rheum maximowiczii Loinsk (Polygonaceae) grows in Central Asia, where it is a folk medicine used by the natives of Uzbekistan as a purgative, and for the treatment of stomach disorders. The genus *Rheum* is one of the world's important crude drugs, containing anthraquinones, glycosides, dianthrone glycosides and polyphenols, and the chemical constituents of this genus have been studied by many groups (Okabe, et al., 1973; Oshio, et al., 1974). However, the chemical constituents of *R. maximowiczii* have not been reported. As a part of our continuing study on the chemical constituents of medicinal plants of Uzbekistan, we have succeeded in the isolation and characterization of fifteen (**1**–**15**) compounds, including four new phenylbutanoids (**3–6**) and two dimeric stilbenes (**9** and **10**) from this plant. In this paper, we report the isolation and identification of these compounds.

2. Results and discussion

Repeated column chromatography of the ethyl acetate and *n*-BuOH soluble fractions from the methanol extract of the roots of *R. maximowiczii* yielded four new phenyl butanoids (**3–6**) and two new stilbene dimers (**9** and **10**), along with nine other known compounds (+)-rhododendrol (**1**), epirhododendrin (**2**) (Pan and Lundgren, 1994), lindleyin, (*S*)-4-(4-hydroxyphenyl)-2-butanone 4′-*O*-β-D-glucopyranoside (Kashiwada et al., 1986), torachrysone (Tsuboi et al., 1977), resveratrol, resveratrol 4′-*O*-β-D-glucopyranoside (Nonaka et al., 1977), emodin 8-*O*-β-D-glucopyranoside and physcion (Satake et al., 1990). The structures of the known compounds were identified by comparison with literature data.

Compound **3** showed the presence of hydroxyl (3271 cm^{-1}) and aromatic ring (1656, 1600 cm^{-1}) absorption bands in the IR spectrum. The ^{1}H and ^{13}C NMR spectral data of **3** were very close to those of (+)-rhododendrol (**1**), the evident difference between them being the chemical shift of C-2 (Table 1). 2D NMR spectral data also suggested that compounds **1** and **3** have the same skeleton. The negative ion FAB mass spectrum indicated that the molecular weight of **3** was 246 which was 80 mass units higher than that calculated for **1**. This increase in mass agreed with an esterification of one of the hydroxyl groups by $-PO(OH)_2$ (MW 81) or $-SO_2OH$ (MW 81). The acid moiety was presumed to be sulfate, because no couplings (J_{POC} and J_{POCC}) were observed in the ^{13}C NMR spectrum. From HR-FABMS analysis, the molecular formula of **3** was determined to be $C_{10}H_{13}O_5S$ (m/z:245.0473 $[M\text{-}H]^-$). The presence of a sulfur atom was confirmed further by elemental analysis (see Section 3). Furthermore, the acid hydrolysis of **3** gave **1** (identified by $[\alpha]_D$, ^{1}H and ^{13}C

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0031-9422/01/$ - see front matter
PII: S0031-9422(00)00370-8

NMR data). The absolute configuration of C-2 was determined to be *S* by comparison of its optical rotation $\{[\alpha]_D^{25} + 30.8^\circ$ (*c* 0.7 MeOH)$\}$ with that reported in the literature (Das and Padma Rao, 1993). From these facts, the structure of **3** was determined to be (*S*)-4-(4-hydroxyphenyl)-2-butanol 2-*O*-sulfate. The presence of a sulfate functionably is very rare in natural products.

The ^{1}H and ^{13}C NMR (Table 1) spectral data for compounds **4** and **5** were very similar to those of **2** except for the appearance of signals due to galloyl and acetyl moieties, respectively, suggesting that **4** and **5** have the same phenylbutanoid glucoside moiety as for **2**. The positions of the galloyl and acetyl functions were established by COLOC correlations between the carbonyl carbon and H_2-6 of glucose, and acylation shifts (Table 1). Acid hydrolysis of **4** and **5** gave glucose and **1**. Thus, the structures of **4** and **5** were determined as (*S*)-4-(4-hydroxyphenyl)-2-butanol 2-*O*-(6-*O*-galloyl)-β-D-glucopyranoside and (*S*)-4-(4-hydroxyphenyl)-2-butanol 2-*O*-(6-*O*-acetyl)-β-D-glucopyranoside, respectively.

Compound **6** showed the molecular formula $C_{31}H_{42}O_{15}$ as determined by HR-FABMS. Its IR spectrum showed absorption bands due to hydroxyl (3402 cm^{-1}) and carbonyl (1709 cm^{-1}) groups. The ^{1}H and ^{13}C NMR (Table 1) spectral data of **6** were similar to those of **2** except for presence of the signals assignable to the galloyl and rhamnosyl moieties. In the COLOC spectrum of **6** (Fig. 1), the proton signals at δ 4.40 and 4.68 (H_2-6 of glucose) were correlated with the carbonyl carbon signal at δ_c 168.4, and the proton signal at δ 5.38 (H-1 of rhamnose) with the carbon signal at δ_c 139.7 (C-4 of galloyl). From these results, the connecting positions of the methoxyl, galloyl and rhamnose moieties were determined. Acid hydrolysis of **6** gave **1** which showed the optical rotation of $+20.0^\circ$ (*c* 0.08, MeOH). Hence, the structure of **6** was determined to be (*S*)-4-(4-hydroxyphenyl)-2-butanol 2-*O*-[6-*O*-(3,5-dimethoxy-4-*O*-α-L-rhamnopyranosylgalloyl)-β-D-glucopyranoside].

Maximol A (**9**) indicated the molecular formula $C_{28}H_{22}O_6$ by HR-FABMS. The IR spectrum indicated the existence of hydroxyl (3377 cm^{-1}) and aromatic groups (1601 cm^{-1}). The ^{1}H NMR spectrum of **9** (Table 2) exhibited 13 protons belonging to the aromatic rings, two *trans* olefinic protons [δ 6.78 and 6.97 (each 1H, *d*, $J = 16.2$ Hz)], and two methine protons [δ 4.40 and 5.39 (each 1H, *d*, $J = 8.3$ Hz)]. From the coupling pattern and integration in the ^{1}H NMR spectrum (Table 2), four aromatic rings (A, B, C and D) were recognized. On the basis of correlations in the COLOC spectrum, the aromatic rings of A and B were deduced to be connected with C-7 and C-8, respectively (Fig. 2). Long range correlations from the carbon signals at δ_c 94.9 (C-7), 107.7 (C-10, -14) to the proton signals at δ 7.17 (H-2, -6), 4.40 (H-8) were detected. Also, the carbon signals at δ_c 129.4 (C-7′) and 127.4 (C-8′) were correlated with the proton signals at δ 7.17 (H-2′) and 7.36 (H-6′) and 6.44 (H-10′, -14′) (Fig. 2). From these results, the connections between C-7′ and ring C, and between C-8′ and

Table 1
^{13}C NMR spectral data for compounds **1–6** (CD_3OD)[a]

Agylcone	1	2	3	4	5	6
C-1	24.2	21.8	20.5	22.0	22.1	22.3
C-2	66.3	76.7	77.2	78.8(a)	77.5	77.6
C-3	42.2	39.2	40.8	40.0	40.1	40.2
C-4	31.8	31.2	32.1	31.5	31.6	31.6
C-5	133.3	134.1	134.7	134.5	134.4	134.4
C-6,10	129.7	129.9	130.7	130.0	130.3	130.3
C-7,9	115.9	115.7	116.5	116.0	116.0	116.1
C-8	156.6	155.3	156.7	155.9	156.2	156.2
β-D-Glucose						
C-1		103.2		104.1	104.2	104.3
C-2		74.5		75.0	75.2	75.1
C-3		77.2		78.8(a)	77.9	78.0
C-4		70.8		71.7	71.7	72.1
C-5		76.9		75.3	75.5	75.3
C-6		62.2		64.9	64.8	65.6
Galloyl moiety						
C-1				121.4		127.1
C-2,6				110.2		107.8
C-3,5				146.3		154.5
C-4				139.7		140.0
−COO−				168.4		167.3
α-L-Rhamnose						
C-1						103.4
C-2						72.2
C-3						72.0
C-4						73.6
C-5						71.3
C-6						17.0
−COO−					172.8	
$-CH_3$					20.7	
$-OCH_3$						56.6

[a] Spectra were measured in CD_3OD at 100 MHz (δ values). Assignment of carbon signals was achieved by analysis of ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectra. (a) Overlapping signals.

Table 2
^{1}H NMR spectral data for compounds **9** and **10** (CD_3OD)[a]

	9	10
2(6)	7.17, 2H, *d*, $J = 8.3$ Hz (a)	7.17, 2H, *d*, $J = 10.7$ Hz (a)
3(5)	6.78, 2H, *d*, $J = 8.3$ Hz (a)	6.78, 2H, *d*, $J = 10.7$ Hz
7	5.39, 1H, *d*, $J = 8.3$ Hz	5.31, 1H, *d*, $J = 8.8$ Hz
8	4.40, 1H, *d*, $J = 8.3$ Hz	4.32, 1H, *d*, $J = 8.8$ Hz
10(14)	6.13, 2H, *d*, $J = 2.4$ Hz	6.04, 2H, *t*, $J = 2.4$ Hz
12	6.21, 1H, *t*, $J = 2.4$ Hz	6.15, 1H, *t*, $J = 2.4$ Hz
2′	7.17, 1H, *s* (a)	6.88, 1H, *brs*
5′	6.84, 1H, *d*, $J = 8.3$ Hz	6.70, 1H, *d*, $J = 8.3$ Hz
6′	7.36, 1H, *d*, $J = 8.3$ Hz	7.17, 1H, *d*, $J = 8.3$ Hz (a)
7′	6.97, 1H, *d*, $J = 16.2$ Hz	6.44, 1H, *d*, $J = 12.7$ Hz
8′	6.78, 1H, *d*, $J = 16.2$ Hz (a)	6.33, 1H, *d*, $J = 12.7$ Hz
10′(14′)	6.44, 2H, *d*, $J = 2.4$ Hz	6.22, 2H, *d*, $J = 2.4$ Hz
12′	6.16, 1H, *t*, $J = 2.4$ Hz	6.11, 1H, *t*, $J = 2.4$ Hz

[a] Spectra were measured in CD_3OD at 400 MHz (δ values). Assignment of proton signals was achieved by analysis of ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectra. (a) Overlapping signals.

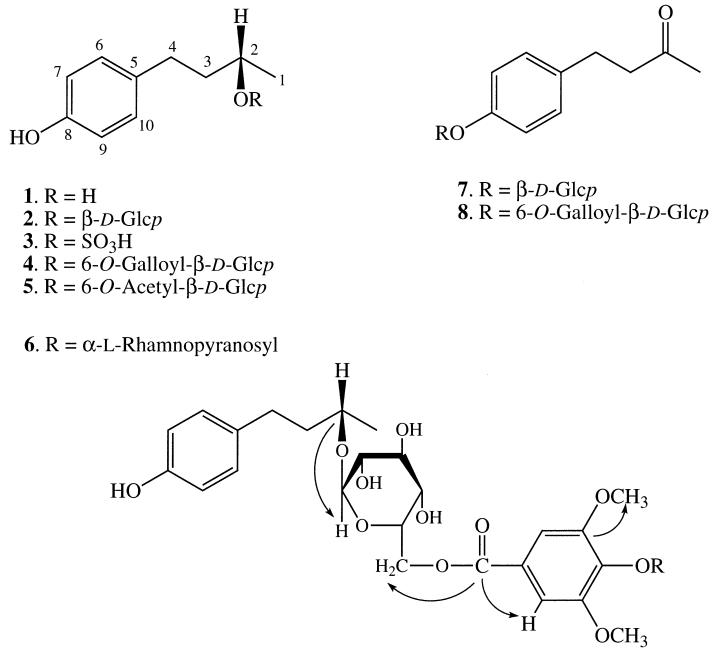

Fig. 1. ^{13}C-^{1}H long-range correlations.

ring D were determined. The degree of unsaturation in **9** was 18; **9** was established to have dihydrobenzofuran moieties of a stilbene dimer biosynthesized from resveratrol. The relative structure of **9** was revealed by an NOE experiment, wherein the proton signal at δ 5.39 (H-7) was correlated with the proton signals at δ 7.17 (H-2, -6) and 6.13 (H-10, -14), and the proton signal at δ 4.40 (H-8) was correlated with proton signals at δ 7.17 (H-2, -6) and 6.13 (H-10, -14). These facts clearly showed that the configuration of rings A and B was *trans*. Thus, the structure of maximol A (**9**) was assigned as shown. According to a previous paper (Langcake and Pryce, 1977), **9** was synthesized from resveratrol by treatment with horseradish peroxidase and H_2O_2. This is the first time that **9** has been isolated from a natural source.

Maximol B (**10**) ($C_{28}H_{22}O_6$) showed very similar ^{1}H and ^{13}C NMR spectral data to those of **9** except for double bond signals [**10**:δ 6.78 and 6.97 (each 1H, *d*, $J=16.2$ Hz), **9**:δ 6.33 and 6.44 (each 1H, *d*, $J=12.7$ Hz)] and benzofuran proton signals [**10**:δ 4.40 and 5.39 (each 1H, *d*, $J=8.3$ Hz), **9**:δ 4.32 and 5.31 (each 1H, *d*, $J=8.8$ Hz)]. From the coupling constant of the double bond, its geometry of **10** was determined to be *cis*. That evidence was supported by the NOESY spectrum (Fig. 2). *Cis* orientation of the benzofuran ring was deduced from an NOE correlation between δ 5.31 (H-7) and 4.32 (H-8) (Fig. 2), and the coupling constant values at H-7/H-8 ($J=8.8$ Hz), (Kurihara et al., 1990). From these results, the structure of maximol B (**10**) was determined as shown.

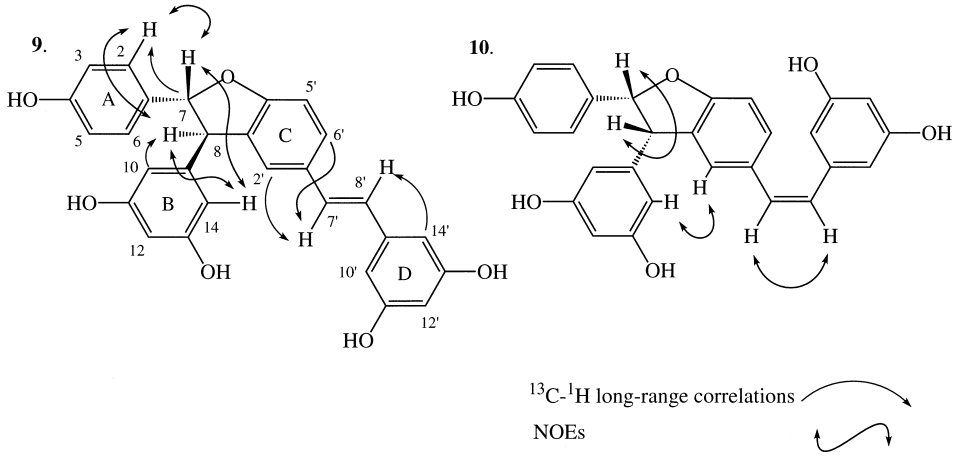

Fig. 2. ^{13}C-^{1}H long-range correlations of **9** and NOE correlations of **9** and **10**.

Epirhododendrin (**2**) was obtained in high yield (23% of the dry weight of *n*-BuOH soluble layer). A previous paper (Fujita et al., 1990) reported that epirhododendrin is more stable than (+)-rhododendrol (1.3% of the dry weight of AcOEt soluble layer), and is useful for pharmaceuticals and skin-lightening cosmetics, and as a melanin inhibitor (Ikemoto and Nakatsugawa, 1998). Therefore, *R. maximowiczii* is an important source of phenylbutanoids.

3. Experimental

3.1. General

^{1}H NMR: 400 MHz with TMS as int. stand: ^{13}C NMR: 100 MHz: CC: silica gel 60 (Merck), Sephadex LH-20 (Pharmacia) and Toyo pearl HW-40 (TOSOH); HPLC: GPC H-2002 (SHODEX), ODS: D-ODS-5 (YMC).

3.2. Plant material

The roots of *R. maximowiczii* were collected in June 1998 from Uzbekistan. Herbarium specimens were deposited in the herbarium of Institute of Botany, Academy of Sciences, Uzbekistan. This plant was identified by Dr Olimjon K. Kodzhimatov.

3.3. Extraction and fractionation

The MeOH extracts (261 g) of the dried roots of *R. maximowiczii* (1.9 kg) were partitioned between EtOAc and H_2O. The EtOAc layer was concentrated to give a residue (46 g), which was subjected to silica gel column chromatography. The column was eluted with solvents of increasing polarity ($CHCl_3$–MeOH) to give 15 frs. (frs. 1–15). Fr. 11 (714 mg) was applied to a Toyo pearl column, eluted with $CHCl_3$–MeOH (2:1) to give 6 frs. (11.1–11.6). Fr. 11.2 (66 mg) was sepd. by HPLC (GPC) with MeOH to give **5** (18 mg). Fr. 12 (1.6 g) was subjected to Toyo pearl column chromatography eluted with $CHCl_3$–MeOH (2:1) to give 7 frs. (12.1–12.7). Fr. 12.6 (242 mg) was purified by HPLC (ODS) with CH_3CN–H_2O (7:3) to give **9** (30 mg) and **10** (5 mg). Fr. 15 (5 g) was applied to a Toyo pearl column eluted with $CHCl_3$–MeOH (2:1) to give 7 frs. (15.1–15.7). Fr. 15.2 (165 mg) was chromatographed on a silica gel column using $CHCl_3$–MeOH (8:2 to 1:1) to give **6** (21 mg). The water layer was partitioned between *n*-BuOH and H_2O to give the *n*-BuOH soluble part (128 g). Half (64 g) of the *n*-BuOH layer was separated by using silica gel chromatography to yield 12 frs. (1.1–1.12) and **2** (15 g). Fr. 1.8 (673 mg) was chromatographed on Sephadex LH-20 with MeOH to give 4 frs. (1.8.1–1.8.4). Fr. 1.8.2 (82 mg) was purified by HPLC (ODS) with MeOH–H_2O (7:3) to give **3** (33 mg). Fr. 1.9 (1.2 g) was chromatographed on Sephadex LH-20 with MeOH to give 9 frs. (1.9.1–1.9.9). Fr. 1.9.2 (220 mg) was purified by HPLC (ODS) with MeOH–H_2O (7:3) to give **4** (27 mg).

3.4.1. (*S*)-4-(4-Hydroxyphenyl)-2-butanol 2-*O*-sulfate (**3**)

Hygroscopic white amorphous powder, $[\alpha]_D^{25}$ +20.9° (*c* 1.3, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3271, 2951, 1656, 1600, 1518, 1451, 1381, 1220, 1042, 951; UVλ_{max}^{MeOH} nm (logε): 278 (3.2). 223 (3.8); HR-FABMS: *m*/*z* 245.0473 [M-H]$^-$, calcd. for $C_{10}H_{13}O_5S$, 245.0484; ^{1}H NMR spectral data (CD_3OD) δ: 7.02 (2H, *d, J* = 8.3 Hz, H-6, 10), 6.67 (2H, *d, J* = 8.3 Hz, H-7, 9), 4.47 (1H, *m*, H-2), 2.58 (2H, *m*, H-4), 1.89 (1H, *m*, H-3), 1.76 (1H, *m*, H-3), 1.33 (3H, *d, J* = 6.3 Hz, H-1); ^{13}C NMR spectral data: Table 1; Found: S, 7.62. $C_{10}H_{14}O_5S{\cdot}10\ H_2O$ requires: S, 7.52%.

3.4.2. (*S*)-4-(4-Hydroxyphenyl)-2-butanol 2-*O*-(6-*O*-galloyl)-β-D-glucopyranoside (**4**)

Pale orange oil, $[\alpha]_D^{25}$−41.6° (*c* 1.0, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3393, 1702, 1614, 1515, 1448, 1348, 1040; UV λ_{max}^{MeOH} nm (log ε): 277 (4.2), 220 (4.7); HR-FABMS *m*/*z*:503.1455 $[M+Na]^+$, calcd. for $C_{23}H_{28}O_{11}Na$, 503.1529; ^{1}H NMR spectral data (CD_3OD) δ:7.31 (2H, *s*, H-2, 6 of gal), 7.06 (2H, *d, J* = 8.3 Hz, H-6, 10), 6.82 (2H, *d, J* = 8.3 Hz, H-7, 9), 4.67 (1H, *d, J* = 10.6 Hz, H-6 of glc), 4.54 (1H, *dd, J* = 5.8, 10.6 Hz, H-6 of glc), 4.48 (1H, *d, J* = 7.7 Hz, H-1 of glc), 3.70 (1H, *m*, H-2), 3.67–3.45 (4H, *m*, H-2–5 of glc), 2.69 (2H, *m*, H-4), 1.85 (1H, *m*, H-3), 1.67 (1H, *m*, H-3), 1.23 (3H, *d, J* = 6.2 Hz, H-1); ^{13}C NMR spectral data: Table 1.

3.4.3. (*S*)-4-(4-Hydroxyphenyl)-2-butanol 2-*O*-(6-*O*-acetyl)-β-D-glucopyranoside (**5**)

Colorless powder, $[\alpha]_D^{25}$−40.2° (*c* 0.8, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3400, 1722, 1620, 1516, 1376, 1036; UV λ_{max}^{MeOH} nm (log ε): 278 (3.0), 223 (3.6); HR-FABMS *m*/*z*: 369.1557 [M-H]$^-$, calcd. for $C_{18}H_{25}O_8$, 369.1549; ^{1}H NMR spectral data (CD_3OD) δ:7.02 (2H, *d, J* = 8.3 Hz, H-6, 10), 6.67 (2H, *d, J* = 8.3 Hz, H-7, 9), 4.45 (1H, *d, J* = 10.0 Hz, H-6 of glc), 4.30 (1H, *d, J* = 8.2 Hz, H-1 of glc), 4.18 (1H, *dd, J* = 5.8, 10.0 Hz, H-6 of glc), 3.70 (1H, *m*, H-2), 3.50–3.20 (4H, *m*, H-2–5 of glc), 2.65 (2H, *m*, H-4), 2.08 (3H, *s*, −$COOCH_3$), 1.84 (1H, *m*, H-3), 1.72 (1H, *m*, H-3), 1.28 (3H, *d, J* = 6.2 Hz, H-1); ^{13}C NMR spectral data: Table 1.

3.4.4. (*S*)-4-(4-Hydroxyphenyl)-2-butanol 2-*O*-[6-*O*-(3,5-dimethoxy-4-*O*-α-L-rhamnopyranosylgalloyl)-β-D-glucopyranoside] (**6**)

Pale yellow oil, $[\alpha]_D^{25}$−13.8° (*c* 1.3, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3402, 1709, 1596, 1516, 1338, 1132, 1073; UV λ_{max}^{MeOH} nm (log ε): 270 (4.2); HR-FABMS *m*/*z*:653.2427 [M-H]$^-$, calcd. for $C_{31}H_{41}O_{15}$, 653.2445; ^{1}H NMR spectral data (CD_3OD) δ:7.02 (2H, *d, J* = 8.3 Hz, H-6,

10), 6.68 (2H, *d*, $J=8.3$ Hz, H-7, 9), 5.38 (1H, *br s*, H-1 of rham), 4.68 (1H, *d*, $J=10.6$ Hz, H-6 of glc), 4.40 (1H, *dd*, $J=5.8$, 10.6 Hz, H-6 of glc), 4.38 (1H, *d*, $J=7.7$ Hz, H-1 of glc), 4.25 (1H, *m*, H-5 of rham), 4.12 (1H, *br s*, H-2 of rham), 3.95 (1H, *m*, H-3 of rham), 3.89 (6H, *s*, $-OCH_3$), 3.72 (1H, *m*, H-2), 3.56 (1H, *m*, H-4 of rham), 3.46–3.17 (4H, *m*, H-2–5 of glc), 2.65 (2H, *m*, H-4), 1.84 (1H, *m*, H-3), 1.72 (1H, *m*, H-3), 1.19 (6H, *d*, $J=6.2$ Hz, H-1, H-1 of rham); ^{13}C NMR spectral data: Table 1.

3.4.5. Maximol A (**9**)

Brown amorphous powder, $[\alpha]_D^{25}-16.3^\circ$ (*c* 0.75, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3377, 1601, 1488, 1237, 1152, 997; UV λ_{max}^{MeOH} nm (logε): 310 (4.6), 211 (4.8); HR-FABMS *m*/*z*:455.1420 $[M+H]^+$, calcd. for $C_{28}H_{23}O_6$, 455.1485; ^{13}C NMR spectral data (CD_3OD) δ:132.3 (C-1), 128.7 (C-2, 6), 116.3 (C-3, 5), 158.7 (C-4), 94.9 (C-7), 58.7 (C-8), 145.3 (C-9), 107.7 (C-10, 14), 159.9 (C-11, 13), 102.5 (C-12), 132.8 (C-1′), 124.1 (C-2′), 132.4 (C-3′), 161.0 (C-4′), 110.3 (C-5′), 128.7 (C-6′), 129.4 (C-7′), 127.4 (C-8′), 141.1 (C-9′), 105.8 (C-10′, 14′), 159.6 (C-11′, 13′), 102.7 (C-14′); ^1H NMR spectral data: Table 2.

3.4.6. Maximol B (**10**)

Brown amorphous powder, $[\alpha]_D^{25}+99.4^\circ$ (*c* 0.34, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3371, 1631, 1469, 1286, 1144, 1047; UV λ_{max}^{MeOH} nm (logε): 298 (4.5), 205 (4.9); HR-FABMS *m*/*z*:453.1309 $[M-H]^-$, calcd. for $C_{28}H_{21}O_6$, 453.1338; ^{13}C NMR spectral data (CD_3OD) δ:132.8 (C-1), 128.6 (C-2, 6), 116.3 (C-3, 5), 158.7 (C-4), 94.7 (C-7), 58.7 (C-8), 145.1 (C-9), 107.7 (C-10, 14), 159.8 (C-11, 13), 102.5 (C-12), 131.7 (C-1′), 127.3 (C-2′), 131.4 (C-3′), 160.3 (C-4′), 109.8 (C-5′), 130.7 (C-6′), 131.0 (C-7′), 129.7 (C-8′), 140.9 (C-9′), 108.4 (C-10′, 14′), 159.2 (C-11′, 13′), 102.4 (C-14′); ^1H NMR spectral data: Table 2.

3.5. Hydrolysis of compounds **2–6**

A solution of **2** (10 mg) in MeOH (10 ml) was treated with 10% HCl (10 ml), and the mixture was refluxed for 6 h. After cooling, the reaction mixture was diluted with water (30 ml) and extracted with EtOAc (30 ml). The organic layer were combined and concentrated in vacuo. The residue was purified by GPC (MeOH) to give compound **2a** (4 mg), identified by ^1H NMR, ^{13}C NMR, TLC and $[\alpha]_D$ comparison to (+)-rhododendrol (Das et al., 1993). Compounds **3–6** were identified by the same method.

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