Eremosides A – C, New Iridoid Glucosides from *Eremostachys loasifolia*

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Eremosides A – C (**1** – **3**), three new iridoid glucosides, were isolated from the AcOEt-soluble fraction of the EtOH extract of the whole plant of *Eremostachys loasifolia*, along with buddlejoside B (**4**), 10-*O*-benzoylcatalpol (**5**), and pakiside A (**6**) reported for the first time from this species. The structures of these compounds were elucidated by spectroscopic data including 2D-NMR, FAB-MS, ESI-MS, as well as by acid and basic hydrolyses.

Introduction. – The genus *Eremostachys* (Lamiaceae) comprises 80 species as herbs which are mainly distributed in Russia and Afghanistan [1]. Out of these, eight species have so far been found in Pakistan [2]. The literature survey of the genus *Eremostachys* revealed that apart from essential oils [3], fatty acids [4], flavonoids [5–7], phenylethanoid glucosides [7], iridoids [8], and diterpenes [9] have so far been reported. Some of these showed antidepressant, antioxidant, and antibacterial activities [6–8]. One of the species of the genus *Eremostachys* is *E. loasifolia* BENTH which grows in S. E. Iran, Pakistan, and N. W. India [2]. Previously, two flavonoids and 6,7-dihydroxycoumarin have been reported by us from this species [5]. The fact that no systematic phytochemical or pharmacological studies have so far been carried out with *E. loasifolia* prompted us to carry out further phytochemical investigation of this species. As a result, we herein report the isolation and structural elucidation of three new iridoid glucosides, named eremosides A – C[1]) (**1** – **3**; *Fig.*), along with buddlejoside B (**4**), 10-*O*-benzoylcatalpol (**5**), and pakiside A (**6**), reported for the first time from the genus *Eremostachys*.

Results and Discussion. – The EtOH extract of the whole plant of *E. loasifolia* was suspended in H_2O and successively partitioned into hexane-, $CHCl_3$-, AcOEt-, and BuOH-soluble fractions. Separation of the AcOEt-soluble fraction by column-chromatographic techniques provided compounds **1** – **6**.

Eremoside A[1]) (**1**) was obtained as a colorless gummy solid. The molecular formula $C_{24}H_{33}O_{14}$ was deduced from the quasimolecular-ion peak in the HR-FAB-MS (*m*/*z* 545.1850 ($[M+H]^+$)). The IR spectrum revealed the absorption bands of OH (3402 – 3245 cm^{-1}), ester C=O (1709 cm^{-1}), C=C (1645 cm^{-1}), and aromatic moieties (1602,

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part*.

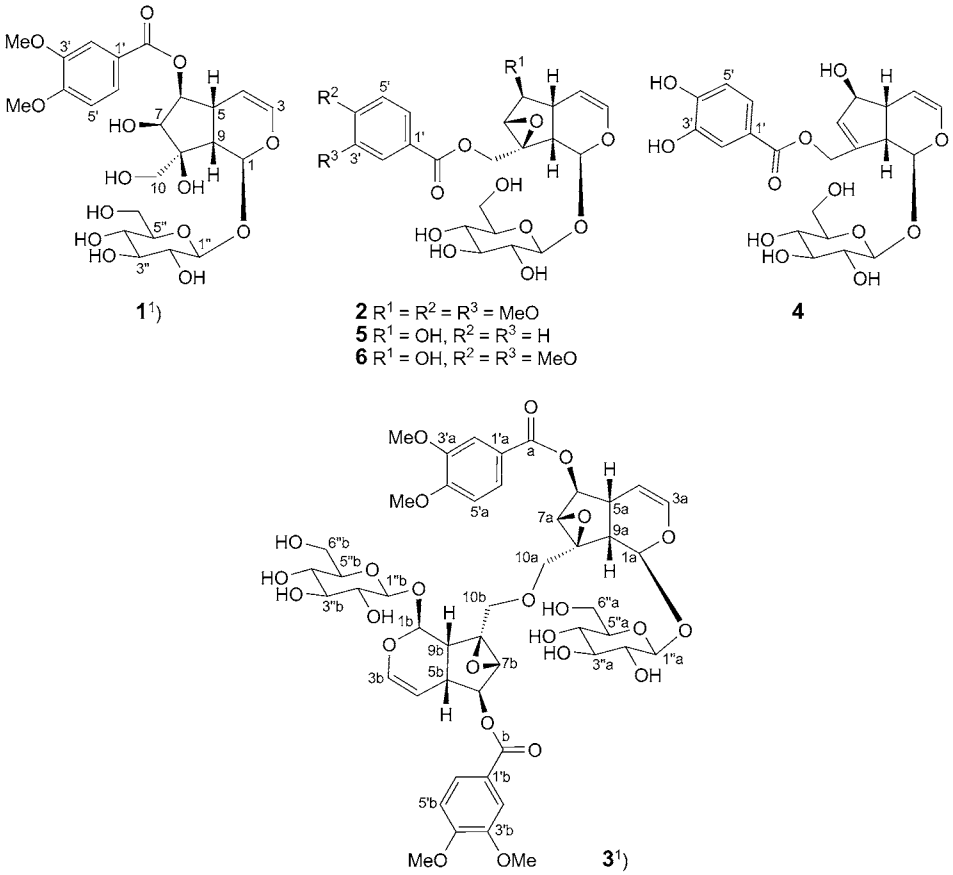

Figure. *Eremosides A* (**1**)*, B* (**2**)*, and C* (**3**) *and compounds* **4**–**6***; isolated from* Eremostachys loasifolia

1540, and 1500 cm^{-1}). The UV spectrum showed absorption bands at λ_{max} 204, 216, 229, 266, and 296 nm. In the EI-MS, the fragment peaks at *m*/*z* 382 and 379 resulted from the loss of a hexose and a dimethoxybenzoyl moiety, respectively, and the presence of a dimethoxybenzoyl moiety was also confirmed by the base peak at *m*/*z* 165. The ^{13}C-NMR and DEPT spectra (*Table 1*) showed 24 signals comprising two Me, two CH_2, and 15 CH groups, and five quaternary C-atoms. The olefinic C-atoms resonated at δ(C) 141.2 and 102.2, which are characteristic of an iridoid [10]. This was confirmed by the ^{1}H-NMR spectrum (*Table 1*) which showed characteristic signals of olefinic H-atoms at δ(H) 6.45 (*dd*, $J = 6.2, 1.6$ Hz, H–C(3)) and 5.37 (*dd*, $J = 6.2, 4.4$ Hz, H–C(4)). Further signals in the ^{1}H- and ^{13}C-NMR spectra confirmed the presence of an iridoid skeleton, along with hexose and veratroyl (= 3,4-dimethoxybenzoyl) moieties. The larger coupling constant ($J = 7.8$ Hz) of the anomeric H-atom allowed us to assign the β-configuration to the hexose moiety. Acid hydrolysis of **1** gave an aglycone which could not be worked up due to the paucity of material. The glycone could be identified as D-glucose by the sign of its optical rotation ($[\alpha]_D^{23} = +52$) and the comparison of the

Table 1. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.; C_5D_5N) *and Important HMBC Features of Compounds* **1** *and* **2**[1]). δ in ppm, J in Hz.

	1			**2**		
	δ(H)	δ(C)	HMBC	δ(H)	δ(C)	HMBC
Aglycone:						
H–C(1)	5.58 (*d*, *J* = 9.4)	95.2	C(3), C(9), C(1″)	5.52 (*d*, *J* = 9.5)	94.1	C(3), C(9), C(1″)
H–C(3)	6.45 (*dd*, *J* = 6.2, 1.6)	141.2	C(1), C(4), C(5)	6.40 (*dd*, *J* = 6.0, 1.6)	140.8	C(1), C(4), C(5)
H–C(4)	5.37 (*dd*, *J* = 6.2, 4.4)	102.2	C(3), C(5), C(9)	5.09 (*dd*, *J* = 6.0, 4.5)	102.0	C(3), C(5), C(9)
H–C(5)	2.95 – 2.98 (*m*)	35.9	C(1), C(3), C(4), C(6), C(9)	2.50 – 2.53 (*m*)	37.5	C(1), C(3), C(4), C(6), C(9)
H–C(6)	4.90 (*dd*, *J* = 5.9, 7.9)	81.3	C(4), C(5), C(7), C=O	4.75 (br. *d*, *J* = 7.9)	86.1	C(4), C(5), C(7), MeO
H–C(7)	4.32 (*d*, *J* = 5.9)	85.2	C(5), C(6), C(8), C (9), C(10)	4.03 (br. *s*)	63.5	C(5), C(6), C(8), C(9), C(10)
C(8)	–	81.1	–	–	65.1	–
H–C(9)	2.90 (*dd*, *J* = 9.4, 7.5)	43.2	C(1), C(4), C(5), C(7), C(8)	2.64 (*dd*, *J* = 9.5, 7.6)	42.7	C(1), C(4), C(5), C(7), C(8)
CH_2(10)	4.88 (*d*, *J* = 13.5),	66.7	C(7), C(8), C(9)	5.06 (*d*, *J* = 13.2),	63.5	C(7), C(8), C=O
	4.75 (*d*, *J* = 13.5)		C(7), C(8), C(9)	4.90 (*d*, *J* = 13.2)		C(7), C(8), C=O
*Me*O–C(6)	–	–	–	3.47 (*s*)	58.8	C(6)
Dimethoxybenzoyl (= *veratroyl*):						
C(1′)	–	122.2	–	–	122.5	–
H–C(2′)	7.77 (*d*, *J* = 2.0)	113.9	C(1′), C(3′), C(4′), C(6′), C=O	7.76 (*d*, *J* = 1.8)	112.9	C(1′), C(3′), C(4′), C(6′), C=O
C(3′)	–	149.7	–	–	149.1	–
C(4′)	–	153.8	–	–	153.8	–
H–C(5′)	6.96 (*d*, *J* = 8.7)	112.6	C(1′), C(3′), C(4′), C(6′)	6.96 (*d*, *J* = 8.5)	110.9	C(1′), C(3′), C(4′), C(6′)
H–C(6′)	7.89 (*dd*, *J* = 8.7, 2.0)	123.9	C(1′), C(2′), C(4′), C(5′), C=O	7.86 (*dd*, *J* = 8.5, 1.8)	123.9	C(1′), C(2′), C(4′), C(5′), C=O
C=O	–	166.1	–	–	166.0	–
*Me*O–C(3′)	3.75 (*s*)	55.7	C(3′)	3.70 (*s*)	56.0	C(3′)
*Me*O–C(4′)	3.71 (*s*)	55.4	C(4′)	3.67 (*s*)	55.6	C(4′)
β-D-*Glucose:*						
H–C(1″)	5.54 (*d*, *J* = 7.8)	99.8	C(1), C(2″)	5.51 (*d*, *J* = 7.9)	98.8	C(1), C(2″)
H–C(2″)	4.14 – 4.16 (*m*)	74.7	C(1″), C(3″)	4.10 – 4.13 (*m*)	74.0	C(1″), C(3″)
H–C(3″)	4.00 – 4.03 (*m*)	78.7	C(2″), C(4″)	3.98 – 4.00 (*m*)	78.2	C(2″), C(4″)
H–C(4″)	4.21 – 4.24 (*m*)	71.0	C(3″), C(5″)	4.13 – 4.16 (*m*)	70.1	C(3″), C(5″)
H–C(5″)	4.28 – 4.30 (*m*)	77.9	C(1″), C(4″), C(6″)	4.25 – 4.28 (*m*)	77.5	C(1″), C(4″), C(6″)
CH_2(6″)	4.51, 4.32 (2*d*, each *J* = 11.9)	62.2	C(4″), C(5″)	4.48, 4.30 (2*d*, each *J* = 12.0)	61.5	C(4″), C(5″)

retention time of its Me_3Si ether with a standard in the gas chromatogram (GC). The basic hydrolysis of **1** provided veratric acid and an iridoid glucoside which could be identified as paulownioside (=(1*S*4a*R*,5*S*,6*S*,7a*S*)-1,4a,5,6,7,7a-hexahydro-5,6,7-trihydroxy-7-(hydroxymethyl)cyclopenta[*c*]pyran-1-yl β-D-glucopyranoside) by comparison of its physical and NMR data with those reported in [11]. In the HMBC spectrum, the anomeric H-atom at δ(H) 5.54 showed ^3J correlation with C(1) (δ(C) 95.2) allowing us to assign the glucosyloxy moiety to C(1). The O–CH proton at δ(H) 4.90 showed ^3J correlations with C(4) (δ(C) 102.2), C(8) (δ(C) 81.1), as well as with the C=O C-atom at δ(C) 166.1, revealing the attachment of the (3,4-dimethoxybenzoyl)oxy moiety at C(6). Other HMBC, ^{1}H,^{1}H-COSY, and HMQC data were in complete agreement with the assigned structure of eremoside A (**1**) as 6-*O*-(3,4-dimethoxybenzoyl)paulownioside (*Fig.*).

Eremoside B[1]) (**2**) was obtained as a colorless gummy solid. The molecular formula was deduced as $C_{25}H_{33}O_{13}$ by HR-FAB-MS showing the quasimolecular-ion peak at *m*/*z* 541.1945 ($[M+H]^+$). The IR and UV spectra were similar to those of **1**. In the EI-MS, the key fragment peaks at *m*/*z* 378 and 375 resulted from the loss of a hexose moiety and dimethoxybenzoyl group, respectively. The presence of a dimethoxybenzoyl moiety was also revealed by a base peak at *m*/*z* 165.

The ^{13}C-NMR and DEPT spectra (*Table 1*) showed 25 signals comprising three Me, two CH_2, and 15 CH groups, and five quaternary C-atoms. The ^{13}C-NMR spectrum was similar to that of **1**, except for an additional signal of a MeO group at δ(C) 58.8, the slight downfield shift of an O–CH C-atom at δ(C) 86.1, and the upfield shift of the CH_2O at δ(C) 63.5, an O–CH at δ(C) 63.5, and the quaternary C-atom at δ(C) 65.1. The ^{1}H-NMR spectrum (*Table 1*) showed the iridoid olefinic H-atoms at δ(H) 6.40 (*dd*, $J=6.0$, 1.6 Hz, H–C(3)) and 5.09 (*dd*, $J=6.0$, 4.5 Hz, H–C(4)). Further signals in the NMR spectrum (*Table 1*) showed the presence of an iridoid skeleton with veratroyl and hexose moieties. The larger coupling constant ($J=7.9$ Hz) of the anomeric H-atom allowed us to assign the β-configuration to the hexose moiety. Acid hydrolysis of **2** gave a glycone which could be identified as D-glucose by the sign of its optical rotation ($[\alpha]_D^{23}=+53$) and by comparing the retention time of its Me_3Si ether with a standard in the GC. The basic hydrolysis of **2** provided veratric acid and an iridoid glucoside, the latter being identified as methyl catalpol (=(1a*S*,1b*S*,2*S*,5a*R*,6*S*,6a*S*)-1a,1b,2,5a,6,6a-hexahydro-1a-(hydroxymethyl)-6-methoxyoxireno[4,5]cyclopenta[1,2-*c*]pyran-2-yl β-D-glucopyranoside) by comparison of its physical and NMR data with those reported in [12]. In the HMBC experiment, the anomeric H-atom at δ(H) 5.51 showed ^3J correlation with C(1) (δ(C) 94.1) confirming the presence of the sugar moiety at C(1). The CH_2O protons at δ(H) 5.06 and 4.90 showed ^2J correlation with C(8) (δ(C) 65.1) and ^3J correlation with the C=O C-atom at δ(C) 166.0, revealing the attachment of the (3,4-dimethoxybenzoyl)oxy group at C(10). The MeO group at δ(H) 3.47 showed a HMBC cross-peak with C(6) (δ(C) 86.1), indicating the MeO group to be located at C(6). Other HMBC, ^{1}H,^{1}H-COSY, and HMQC data were in complete agreement with the assigned structure of eremoside B (**2**) as 10-*O*-(3,4-dimethoxybenzoyl)-6-*O*-methylcatalpol (*Fig.*).

Eremoside C[1]) (**3**) was also obtained as a colorless gummy solid. The molecular formula was determined as $C_{48}H_{58}O_{25}$ by HR-ESI-MS showing a quasimolecular-ion peak at *m*/*z* 1057.3151 ($[M+Na]^+$). The IR and UV spectra were similar to that of **2**.

The broad-band and DEPT ^{13}C-NMR (*Table 2*) spectra showed 24 well-resolved signals comprising two Me, two CH_2, and 15 CH groups, and five quaternary C-atoms. The ^{13}C-NMR spectrum was similar to that of **2**, except for the absence of one of the three MeO groups and the downfield shift of C(10) to δ(C) 67.7. The ^{1}H-NMR spectrum (*Table 2*) was also similar to that of **2**, except for the absence of one of the three MeO groups. The NMR data showed close agreement, to that reported for 6-*O*-veratroyl-catalpol (= '6-*O*-veratroyl cataposide', (1a*S*,1b*S*,2*S*,5a*R*,6*S*,6a*S*)-6-[(3,4-dimethoxybenzoyl)oxy]-1a,1b,2,5a,6,6a-hexahydro-1a-(hydroxymethyl)oxireno[4,5]cyclopenta[1,2-*c*]-pyran-2-yl β-D-glucopyranoside) in [13], except for the downfield signal of C(10) (δ(C) 67.7) which suggested the attachment of two monomeric units through an ether linkage. The dimeric structure was corroborated by the HR-ESI-MS and the elemental analysis. The EI-MS showed a fragment at *m*/*z* 362 which was due to the loss of one of the monomer unit along with the remaining hexose moiety. Elimination of H_2O from this peak gave another fragment at *m*/*z* 344. The dimethoxybenzoyl moiety was also confirmed by the base peak at *m*/*z* 165. The downfield shift of both the C(10) signals indicated the attachment of the monomer units through an ether linkage. The absence of a free OH group at C(10) of the aglycone was finally confirmed by dissolving compound **3** in D_2O/C_5D_5N and repeating the ESI-MS which now gave an $[M + Na]^+$ peak at *m*/*z* 1065 due to deuterium exchange of eight OH groups of the glucose moieties. On the basis of these evidences, a dimeric structure was assigned to eremoside C (**3**) as shown in the *Figure*.

Table 2. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.; (D_6)DMSO) *of Compound* **3**. δ in ppm, *J* in Hz.

	δ(H)	δ(C)		δ(H)	δ(C)
Aglycone:			*β-D-Glucose:*		
H–C(1a,1b)	5.14 (*d*, *J* = 9.8)	92.9	H–C(1″a,1″b)	4.72 (*d*, *J* = 8.0)	98.8
H–C(3a,3b)	6.45 (*dd*, *J* = 6.3, 1.7)	141.0	H–C(2″a,2″b)	3.12–3.17 (*m*)	74.5
H–C(4a,4b)	4.93 (*dd*, *J* = 6.3, 4.6)	101.2	H–C(3″a,3″b)	3.00–3.05 (*m*)	76.2
H–C(5a,5b)	2.57–2.60 (*m*)	36.9	H–C(4″a,4″b)	3.17–3.21 (*m*)	71.3
H–C(6a,6b)	5.10 (br. *d*, *J* = 8.0)	85.0	H–C(5″a,5″b)	3.04–3.08 (*m*)	78.0
H–C(7a,7b)	3.70 (br. *s*)	63.4	CH_2(6″a,6″b)	3.75 (*dd*, *J* = 12.1, 5.0),	62.8
C(8a,8b)	–	65.3		3.41 (*dd*, *J* = 12.1, 2.5)	
H–C(9a,9b)	2.47–2.50 (*dd*, *J* = 9.8, 7.8)	42.4			
CH_2(10a,10b)	5.00 (*d*, *J* = 13.5),	67.7			
	3.92 (*d*, *J* = 13.5)				
Dimethoxybenzoyl (= *veratroyl*):					
C(1′a,1′b)	–	121.8			
H–C(2′a,2′b)	7.46 (*d*, *J* = 1.8)	111.5			
C(3′a,3′b)	–	149.1			
C(4′a,4′b)	–	153.0			
H–C(5′a,5′b)	7.10 (*d*, *J* = 8.4)	111.0			
H–C(6′a,6′b)	7.64 (*dd*, *J* = 8.4, 1.8)	123.9			
^{a}C=O, ^{b}C=O	–	165.5			
*Me*O–C(2′a,2′b)	3.84 (*s*)	55.9			
*Me*O–C(3′a,3′b)	3.86 (*s*)	55.6			

The known compounds were identified as buddlejoside B (**4**) [14], 10-*O*-benzoylcatalpol (**5**) [15], and pakiside A (**6**) [16] by comparison of their physical and spectral data with those reported in the literature.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 230–400 mesh; *E. Merck*, Darmstadt, Germany). TLC: SiO_2 *60-F$_{254}$* plates (*E. Merck*, Darmstadt, Germany). GC: *Schimadzu* gas chromatograph (*GC-9A*); *3% OV-1* silanized *Chromosorb-W* column; column temp. 180°; injection port and detector temp. 275–300°; flow rate 35 ml/min; flame-ionization detector. Optical rotations: *Jasco-P-2000* polarimeter. UV Spectra: *Hitachi-UV-3200* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Jasco-302-A* spectrometer; in KBr; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-AMX-500* instrument; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *Finnigan-MAT-312* mass spectrometer. HR-FAB-MS: *Jeol-JMS-HX-110* mass spectrometer, glycerol as matrix. HR-ESI-MS: *QSTAR-XL* spectrometer; in *m*/*z* (rel. %). Elemental analysis: *Perkin–Elmer 2400* series *II CHN/S.*

Plant Material. The whole plant material of *Eremostachys loasifolia* BENTH (Lamiaceae) (20 kg) was collected from the Ziarat Valley of the Balochistan Province, Pakistan, in April 2005, and identified by *R. B. Tareen*, plant taxonomist, Department of Botany, University of Balochistan, Quetta, where a voucher specimen has been deposited with the herbarium (voucher No. el. Rbt. 01. 2005).

Extraction and Isolation. The shade-dried whole plant material (20 kg) was chopped, ground, and extracted with EtOH (3 × 20 l, 10 d each) at r.t. The combined EtOH extract was concentrated to yield a residue (500 g), which was suspended in H_2O (1.0 l) and successively partitioned into hexane- (130 g), $CHCl_3$- (100 g), AcOEt- (60 g), and BuOH-soluble (80 g) fractions. The AcOEt-soluble subfraction (60 g) was subjected to CC (SiO_2, hexane, hexane/$CHCl_3$, $CHCl_3$, and $CHCl_3$/MeOH in increasing order of polarity). The fraction obtained with $CHCl_3$/MeOH 9.9 : 0.1 (1.2 g) was resubjected to CC (SiO_2, $CHCl_3$/MeOH). The fraction obtained with $CHCl_3$/MeOH 9.85 : 0.15 was further purified by prep. TLC ($CHCl_3$/MeOH 9.5 : 0.5): **5** (15.1 mg) and **4** (10.3 mg). The fraction obtained with $CHCl_3$/MeOH 9.8 : 0.2 (44.9 mg) was resubjected to CC (SiO_2, $CHCl_3$/MeO): **2** (8.0 mg). The fraction obtained with $CHCl_3$/MeOH 9.7 : 0.3 (2.6 g) was triturated with MeOH, and the residue was resubjected to CC (SiO_2; $CHCl_3$/MeOH 9.75 : 0.25): **1** (20.2 mg) and **6** (15.1 mg), from the head and tail fractions, resp. The fraction obtained with $CHCl_3$/MeOH 9.4 : 0.6 (2.6 g) was triturated with MeOH, and the residue was resubjected to CC (SiO_2; $CHCl_3$/MeOH 9.4 : 0.6): **3** (10.9 mg).

Eremoside A (*= 6-*O*-(3,4-Dimethoxybenzoyl)paulownioside = [(1*S*,4a*R*,5*S*,6*S*,7*S*,7a*S*)-1-(β-*D*-Glucopyranosyloxy)-1,4a,5,6,7,7a-hexahydro-6,7-dihydroxy-7-(hydroxymethyl)cyclopenta[*c*]pyran-5-yl 3,4-Dimethoxybenzoate = (1*S*,4a*R*,5*S*,6*S*,7*S*,7a*S*)-5-[(3,4-Dimethoxybenzoyl)oxy]-6,7-dihydroxy-7-(hydroxymethyl)cyclopenta[*c*]pyran-1-yl β-*D*-Glucopyranoside*; **1**): Colorless gummy solid. $[\alpha]_D^{23} = -12$ (*c* = 0.20, MeOH). IR (KBr): 3402–3245, 1709, 1645, 1602, 1540, 1500. UV (MeOH): 204 (2.1), 216 (2.0), 229 (3.4), 266 (2.9), 296 (4.1). ^{1}H- and ^{13}C-NMR: *Table 1.* EI-MS: 382 (10, $[M - Glc]^+$), 379 (9, $[M -$ dimethoxybenzoyl$]^+$), 364 (21, $[M - Glc - H_2O]^+$), 216 (22), 201 (25), 181 (65), 165 (100). HR-FAB-MS (pos.): 545.1850 ($[M + H]^+$, $C_{24}H_{33}O_{14}^+$; calc. 545.1870).

Eremoside B (*= 10-*O*-(3,4-Dimethoxybenzoyl)-6-*O*-methylcatalpol = [(1a*S*,1b*S*,2*S*,5a*R*,6*S*,6a*S*)-2-(β-*D*-Glucopyranosyloxy)-1b,5a,6,6a-tetrahydro-6-methoxyoxireno[4,5]cyclopenta[1,2-*c*]pyran-1a(2*H*)-yl]methyl 3,4-Dimethoxybenzoate = (1a*S*,1b*S*,5a*R*,6*S*,6a*S*)-1a-{[(3,4-Dimethoxybenzoyl)oxy]methyl}-1a,1b,2,5a,6,6a-hexahydro-6-methoxyoxireno[4,5]cyclopenta[1,2-*c*]pyran-2-yl β-*D*-Glucopyranoside*; **2**): Colorless gummy solid. $[\alpha]_D^{25} = -102$ (*c* = 0.18, MeOH). IR (KBr): 3437–3405, 1705, 1638, 1606, 1542, 1503. UV (MeOH): 207 (2.3), 217 (1.9), 232 (3.8), 263 (3.1), 298 (4.2). ^{1}H- and ^{13}C-NMR: *Table 1.* EI-MS: 378 (8, $[M - Glc]^+$), 375 (12, $[M -$ dimethoxybenzoyl$]^+$), 360 (17, $[M - Glc - H_2O]^+$), 345 (10), 212 (15), 197 (25), 181 (70), 165 (100). HR-FAB-MS (pos.): 541.1945 ($[M + H]^+$, $C_{25}H_{33}O_{13}^+$; calc. 541.1921).

Eremoside C (*= Bis(6-*O*-veratroylcatalpol-10-yl) Ether = (1a*S*,1′a*S*,1b*S*,1′b*S*,2*S*,2′*S*,5a*R*,5′a*R*,6*S*,6′*S*,6a*S*,6′a*S*)-1a,1′a-[Oxybis(methylene)]bis[6-[(3,4-dimethoxybenzoyl)oxy]-1a,1b,2,5a,6,6a-hexahydrooxireno[4,5]cyclopenta[1,2-*c*]pyran-2-yl β-*D*-Glucopyranoside]*; **3**): Colorless gummy solid. $[\alpha]_D^{25} = -79$ (*c* = 0.08, MeOH). IR (KBr): 3425–3401, 1707, 1635, 1605, 1539, 1500. UV (MeOH): 205 (2.0), 218 (2.1),

231 (4.1), 262 (2.8), 296 (3.9). ^{1}H- and ^{13}C-NMR: *Table* 2. EI-MS: 362 (12, $[M - \text{monomer} - \text{Glc}]^+$), 344 (10, $[M - \text{monomer} - \text{Glc} - H_2O]^+$), 181 (85), 165 (100). HR-ESI-MS: 1057.3151 ($[M + Na]^+$, $C_{48}H_{58}O_{25}Na^+$; calc. 1057.3165). Anal. calc. for $C_{48}H_{58}O_{25}$ (1034.96): C 55.72, H 5.64, O 38.64; found C 55.70, H 5.65, O 38.65.

Acid Hydrolysis of **1** *and* **2**. A soln. of **1** (3.0 mg) in MeOH (5 ml) and 1N HCl (2 ml) was refluxed for 4 h and then concentrated. The residue was treated with H_2O and extracted with AcOEt. The aq. phase was concentrated to obtain the sugar residue which could be identified as D-glucose by the sign of its optical rotation ($[\alpha]_D^{23} = +52$, $c = 0.02$, MeOH). It was further confirmed by comparing the retention times t_R of its Me_3Si ethers (α-anomer t_R 3.7 min, β-anomer t_R 5.1 min) with a standard sample in GC. The preparation of the Me_3Si ethers and subsequent GC analysis was carried out according to [17]. The aglycone was a mixture of products which could not be worked up due to the paucity of material. The glycone obtained from compound **2** ($[\alpha]_D^{23} = +53$, $c = 0.03$, MeOH) could be identified as D-glucose by using the same procedure.

Alkaline Hydrolysis of **1** *and* **2**. A soln. of **1** (4 mg) in 0.5% NaOH soln. (2 ml) was heated at 60° for 50 min. Then, the mixture was neutralized with 0.2% HCl soln. and subjected to CC (polyamide, $CHCl_3$/MeOH). Elution with $CHCl_3$/MeOH 9.6:0.4 provided a pure compound which crystallized from EtOH, melted at 180–182°, and could be identified as *veratric acid* by comparison of physical and spectral data with those reported in the literature. Elution with $CHCl_3$/MeOH 9.7:0.3 provided the deacetylated iridoid glucoside ($[\alpha]_D^{25} = -65$ ($c = 2.5$, MeOH)), which was identified as *paulownioside* by comparison of physical and NMR spectral data with those reported in [11]. In the case of compound **2** (4 mg), a similar protocol provided *veratric acid* and an iridoid glucoside (m.p. 212–213°; $[\alpha]_D^{20} = -173$ ($c = 0.02$, EtOH)), which was indentified as *catalpol* by comparison of its physical and spectral data with those reported in [18].

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