A New Cardenolide and Two New Pregnane Glycosides from the Root Barks of *Periploca sepium*

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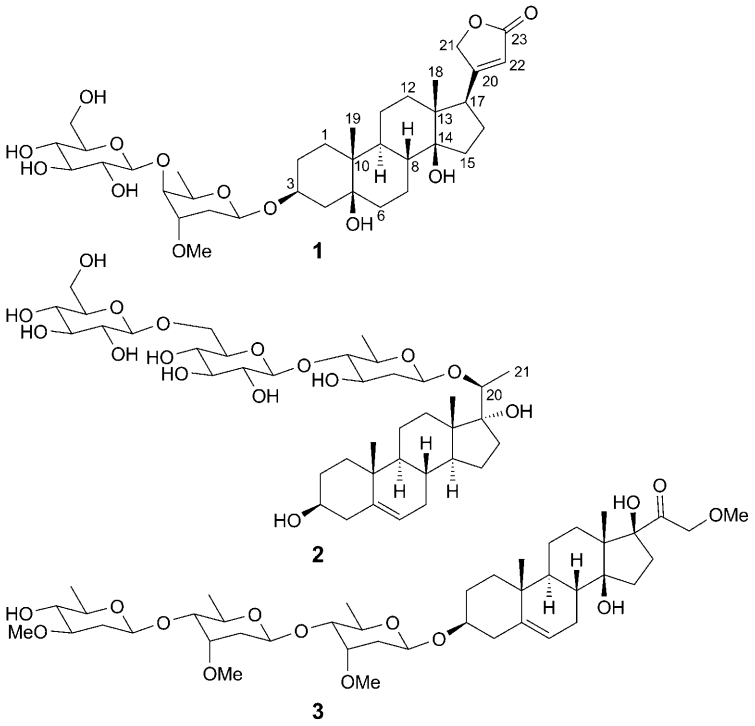
A new cardenolide and two new pregnane glycosides, periplogenin 3-[*O*-*β*-glucopyranosyl-(1→4)-*β*-sarmentopyranoside] (**1**), (3*β*,20*S*)-pregn-5-ene-3,17,20-triol 20-[*O*-*β*-glucopyranosyl-(1→6)-*O*-glucopyranosyl-(1→4)-*β*-canaropyranoside] (**2**), and (3*β*,14*β*,17*α*)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one 3-[*O*-*β*-oleandropyranosyl-(1→4)-*O*-*β*-cymaropyranosyl-(1→4)-*β*-cymaropyranoside] (**3**), were isolated from the root barks of *Periploca sepium* BGE, together with seven related known compounds, periplogenin, xysmalogenin, (3*β*,20*S*)-pregn-5-ene-3,17,20-triol, (3*β*,14*β*,17*α*)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one, (3*β*,20*S*)-pregn-5-ene-3,20-diol 3-*β*-glucopyranoside 20-*β*-glucopyranoside, (3*β*,20*S*)-pregn-5-ene-3,20-diol 3-[*O*-2-*O*-acetyl-*β*-digitalopyranosyl-(1→4)-*β*-cymaropyranoside] 20-[*O*-*β*-glucopyranosyl-(1→6)-*O*-*β*-glucopyranosyl-(1→2)-*β*-digitalopyranoside], and (3*β*,20*S*)-pregn-5-ene-3,20-diol 20-[*O*-*β*-glucopyranosyl-(1→6)-*β*-glucopyranoside]. Their structures were elucidated on the basis of spectroscopic analyses.

Introduction. – The root barks of *Periploca sepium* BGE (Asclepiadaceae), a traditional Chinese herb medicine called 'xiangjiapi', has been widely used for many years for relieving rheumatic conditions and slaking dropsy, and for strengthening the bone and the musculature [1]. More recently, the root barks of *Periploca sepium* has been used to suppress tumor and to treat chronic congestive heart failure [2–4]. Previous phytochemical studies on the *Periploca sepium* have led to the isolation of pregnane derivatives, cardenolides, oligosaccharides, coumarins, flavonoids, and triterpenoids, some of them being biologically active [5–6]. In the search of its bioactive constituents, a new cardenolide and two new pregnane glycosides were isolated from the root barks of *Periploca sepium* along with seven known compounds. In this article, we report the isolation and structure elucidation of these compounds.

Results and Discussion. – Compound **1** was isolated as a white amorphous powder and had a molecular formula $C_{36}H_{56}O_{13}$ on the basis of the HR-ESI-MS (*m*/*z* 719.3597 ($[M+Na]^+$)) and NMR analysis. The IR spectrum indicated the presence of OH (3448 cm^{-1}) and *α*,*β*-unsaturated *γ*-lactone groups (1779 and 1739 cm^{-1}). The ^{1}H- and ^{13}C-NMR and DEPT spectra revealed the presence of characteristic signals of a cardenolide. Further analysis of HSQC, HMBC, TOCSY, ^{1}H,^{1}H-COSY, and NOESY spectra defined the structure of **1** as periplogenin 3-[*O*-*β*-glucopyranosyl-(1→4)-*β*-sarmentopyranoside] (**1**), a new compound.

The ^{1}H-NMR spectrum of **1** displayed two angular Me groups at *δ*(H) 1.01 (*s*) and 1.03 (*s*), an O-bearing CH_2 moiety at *δ*(H) 5.02 and 5.29, and an olefinic H-atom at



δ(H) 6.13 (br. *s*) (*Table 1*). The ^{13}C-NMR and DEPT spectra of **1** revealed 36 C-atom signals, which consisted of four Me, twelve CH_2, fourteen CH, and six quaternary C-atoms (*Table 1*). A C=O signal resonated at δ(C) 174.5, and olefinic C-atom signals were observed at δ(C) 175.9 and 117.7. Interpretation of these results suggested the presence of a cardenolide skeleton. Comparing the ^{13}C-NMR data of the aglycone of **1** with those of the known compound periplogenin (=(3β,5β)-3,5,14-trihydroxycard-20(22)-enolide) [7], the significant differences were the downfield shift of C(3) ($\Delta\delta$ = +7.9 ppm), and the upfield shifts of C(2) and C(4) ($\Delta\delta$ = −2.1 and 2.5 ppm, resp.) owing to the glycosidation effect. Therefore, **1** was a 3-glycoside of periplogenin. In addition, the ^{1}H-NMR spectrum of **1** showed a secondary Me group and a MeO group of a deoxysugar, and two anomeric-H-atom signals at δ(H) 5.05 (*dd*, *J* = 9.2, 1.4 Hz) and 4.91 (*d*, *J* = 7.6 Hz), indicating the presence of two sugar moieties with two β-linkages. One sugar unit was assigned to a β-sarmentopyranose (=2,6-dideoxy-3-*O*-methyl-β-*arabino*-hexopyranose = Sar) unit on the basis of comparison of the ^{1}H- and ^{13}C-NMR data with those of [8][9], which was supported by the NOESY correlations H−C(1′)/H−C(5′) and H_α−C(2′), H−C(4′)/H−C(5′), and H−C(3′)/H_β−C(2′) (*Fig. 1*). Similarly, the other sugar unit was characterized as a β-glucopyranose (Glc). The HMBC spectrum of **1** showed ^{1}H,^{13}C long-range correlations between δ(H) 5.05 (H−C(1′) of Sar) and δ(C) 75.7 (C(3) of aglycone), and between δ(H) 4.91 (H−C(1″) of Glc) and δ(C) 73.6 (C(4′) of Sar), indicating the linkage of C(1′) of Sar to C(3) of the aglycone, and of C(1″) of Glc to C(4′) of Sar, respectively.

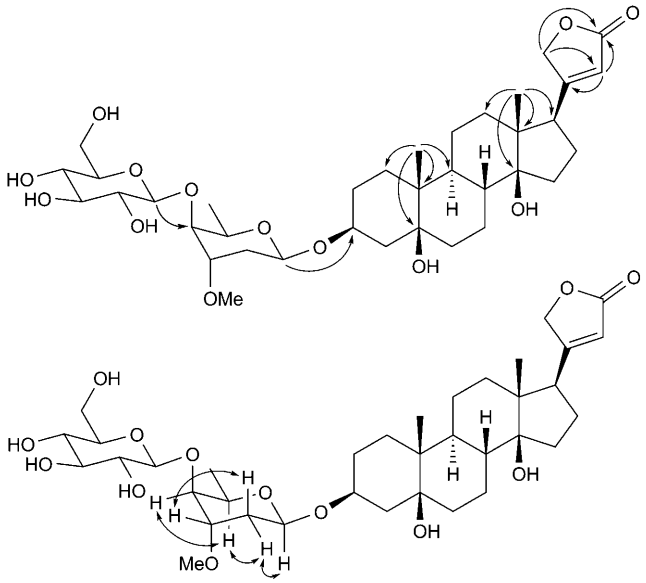


Fig. 1. *Key HMBC* (H → C) *and key NOESY* (H ↔ H) *correlations of* **1**

Table 1. *^{1}H- and ^{13}C-NMR Data of Compound* **1**. δ in ppm, J in Hz.

	δ(C)[a])	δ(H)[b])		δ(C)[a])	δ(H)[b])
CH_2(1)	26.1	1.33–1.36 (*m*), 1.40–1.41 (*m*)	H–C(17)	51.0	2.78–2.80 (*m*)
			Me(18)	16.2	1.01 (*s*)
CH_2(2)	26.5	1.63–1.67 (*m*), 2.05–2.07 (*m*)	Me(19)	17.2	1.03 (*s*)
			C(20)	175.9	–
H–C(3)	75.7	4.34–4.37 (*m*)	CH_2(21)	73.7	5.02 (br. *d*, *J* = 17.5), 5.29 (br. *d*, *J* = 17.5)
CH_2(4)	35.4	1.48–1.50 (*m*), 1.91–1.94 (*m*)	H–C(22)	117.7	6.13 (br. *s*)
C(5)	73.6	–	C(23)	174.5	–
CH_2(6)	35.4	1.48–1.50 (*m*), 1.84–1.87 (*m*)	Sar		
			H–C(1′)	97.8	5.05 (*dd*, *J* = 9.2, 1.4)
CH_2(7)	24.4	1.27–1.30 (*m*), 2.21–2.24 (*m*)	CH_2(2′)	31.6	2.30–2.32 (*m*, H_α), 2.02–2.04 (*m*, H_β)
H–C(8)	41.0	1.80–1.84 (*m*)	H–C(3′)	76.4	3.99 (*q*, *J* = 2.8)
H–C(9)	39.2	1.58–1.63 (*m*)	H–C(4′)	73.6	3.84 (br. *s*)
C(10)	41.2	–	H–C(5′)	69.5	4.12 (*q*, *J* = 6.5)
CH_2(11)	22.0	1.25–1.27 (*m*), 1.40–1.41 (*m*)	Me(6′)	17.5	1.48 (*d*, *J* = 6.5)
			*Me*O–C(3′)	56.6	3.25 (*s*)
CH_2(12)	39.9	1.36–1.38 (*m*), 1.41–1.45 (*m*)	Glc		
			H–C(1″)	103.5	4.91 (*d*, *J* = 7.6)
C(13)	50.0	–	H–C(2″)	74.7	3.96–3.98 (*m*)
C(14)	84.7	–	H–C(3″)	78.6	4.26–4.23 (*m*)
CH_2(15)	33.2	1.82–1.85 (*m*), 2.02–2.05 (*m*)	H–C(4″)	71.9	4.15–4.17 (*m*)
			H–C(5″)	78.5	3.94–3.97 (*m*)
CH_2(16)	27.3	1.90–1.94 (*m*), 2.05–2.07 (*m*)	CH_2(6″)	63.1	4.33–4.34 (*m*), 4.52–4.55 (*m*)

[a]) Measured at 100 MHz in C_5D_5N. [b]) Measured at 400 MHz in C_5D_5N.

Compound **2** was obtained as a white amorphous powder. Its molecular formula was determined to be $C_{39}H_{64}O_{16}$ by HR-ESI-MS (*m/z* 811.4062 ($[M+Na]^+$)) and ^{13}C-NMR data. The IR spectrum showed absorptions of OH (3426 cm^{-1}) and CH_2 groups (2936 cm^{-1}). The ^{13}C-NMR spectrum of **2** exhibited 39 C-atom signals, 21 of them corresponding to a pregnane skeleton and 18 corresponding to a sugar portion (*Table 2*). The ^{1}H-NMR spectrum of the aglycone portion showed signals for two angular Me groups at δ(H) 0.76 (*s*) and 1.07 (*s*), a secondary Me signal at δ(H) 1.61 (*d*, $J = 6.4$ Hz), and one olefinic H-atom at δ(H) 5.41 (br. *s*) (*Table 2*). The ^{13}C-NMR and DEPT spectra showed four Me, eleven CH_2, twenty CH, and four quaternary C-atoms (*Table 2*). In a detailed comparison of the ^{1}H- and ^{13}C-NMR data of the aglycone of **2** with those of (3β,20*S*)-pregn-5-ene-3,17,20-triol, all signals due to the aglycone of **2** were very similar to those of (3β,20*S*)-pregn-5-ene-3,17,20-triol [10]. Additionally, the ^{1}H- and ^{13}C-NMR spectra of **2** displayed signals for three anomeric H-atoms at δ(H) 4.87 (*d*, $J = 7.6$ Hz), 4.84 (*d*, $J = 7.6$ Hz), and 4.82 (br. *d*, $J = 9.6$ Hz), and the corresponding C-atoms at δ(C) 105.6, 104.5, and 102.0, respectively. The β-configuration of the anomeric H-atoms was evident from their large coupling constants ($^3J = 7.6-9.6$ Hz). The assignments of all the C- and H-atom signals of the sugar moieties were determined from HMBC, HSQC, ^{1}H,^{1}H-COSY, NOESY, and TOCSY experiments, and the three sugar units were identified as one β-canaropyranose (=2,6-dideoxy-β-*xylo*-hexopyranose = Can) unit and two β-glucopyranose units, by comparison of their ^{1}H- and ^{13}C-NMR data with those in [11]. In the TOCSY plot of **2**, the anomeric H-atom that was ascribed to the β-canaropyranose unit at δ(H) 4.82 (H–C(1′) of Can) showed connectivity with two CH_2 H-atoms at δ(H) 2.36–2.41 (H_α–C(2′)) and 1.82–1.84 (H_β–C(2′)) of Can, and with three CH at δ(H) 4.00 (H–C(3′)), 3.39 (H–C(4′)), and 3.71 (H–C(5′)) of Can. The NOESY plot also showed the NOE correlations H–C(1′)/H–C(2′) and H–C(5′), and H–C(3′)/H–C(5′) of Can (*Fig. 2*). The linkage sites of each sugar residue were determined from the following HMBC correlations: H–C(1′) of Can (δ(H) 4.82)/C(20) of the aglycone (δ(C) 83.2), H–C(1″) of Glc(I) (δ(H) 4.87/C(4′) of Can (δ(C) 89.4), and H–C(1‴) of Glc(II) (δ(H) 4.84)/C(6″) of Glc(I) (δ(C) 69.9). Therefore, compound **2**

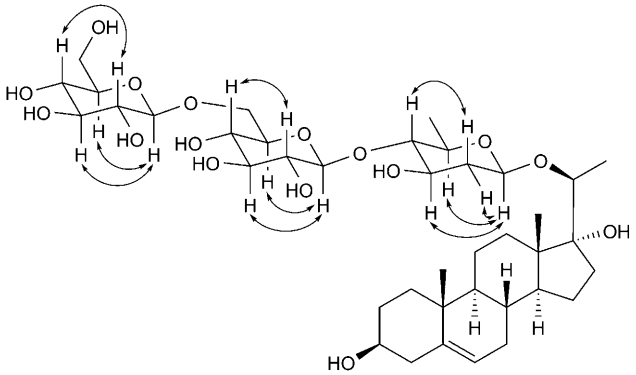


Fig. 2. *Main NOESY* (H↔H) *correlations of* **2**

Table 2. *^{1}H- and ^{13}C-NMR Data of Compounds* **2** *and* **3**. δ in ppm, J in Hz.

	2		**3**	
	δ(C)[a])	δ(H)[b])	δ(C)[a])	δ(H)[b])
CH_2(1)	37.8	1.03–1.07 (*m*), 1.82–1.84 (*m*)	37.2	1.05–1.07 (*m*), 1.79–1.82 (*m*)
CH_2(2)	32.4	1.50–1.53 (*m*), 1.79–1.82 (*m*)	30.3	1.66–1.69 (*m*), 2.08–2.11 (*m*)
H–C(3)	71.2	3.77–3.81 (*m*)	77.3	3.78–3.83 (*m*)
CH_2(4)	43.5	2.60–2.61 (*m*)	39.2	2.29–2.32 (*m*), 2.50–2.53 (*m*)
C(5)	141.9	–	140.0	–
H–C(6)	121.2	5.41 (br. *s*)	121.9	5.45 (br. *s*)
CH_2(7)	32.6	2.01–2.07 (*m*)	26.8	2.50–2.53 (*m*)
H–C(8)	32.3	1.60–1.65 (*m*)	37.8	1.97–1.99 (*m*)
H–C(9)	50.3	1.03–1.07 (*m*)	46.2	1.11–1.16 (*m*)
C(10)	36.9	–	37.8	–
CH_2(11)	21.0	1.41–1.45 (*m*), 1.54–1.60 (*m*)	20.7	1.21–1.24 (*m*), 1.40–1.41 (*m*)
CH_2(12)	37.8	1.90–1.94 (*m*), 2.00–2.07 (*m*)	31.7	1.21–1.24 (*m*), 1.30–1.31 (*m*)
C(13)	45.9	–	51.5	–
H–C(14) or C(14)	51.4	2.12–2.20 (*m*)	88.3	–
CH_2(15)	23.9	1.19–1.22 (*m*), 1.79–1.86 (*m*)	32.3	1.40–1.42 (*m*), 2.02–2.06 (*m*)
CH_2(16)	31.5	2.13–2.15 (*m*), 2.16–2.19 (*m*)	34.1	2.91–2.95 (*m*), 2.95–2.97 (*m*)
C(17)	85.2	–	93.5	–
Me(18)	14.5	0.76 (*s*)	13.6	1.36 (*s*)
Me(19)	19.6	1.07 (*s*)	19.6	0.94 (*s*)
H–C(20) or C(20)	83.2	3.90–3.93 (*m*)	208.5	–
Me(21) or CH_2(21)	18.1	1.61 (*d*, J = 6.4)	77.0	4.65 (*d*, J = 18.8), 4.92 (*d*, J = 18.8)
*Me*O–C(21)			58.9	3.52 (*s*)
Can			Cym(I)	
H–C(1′)	102.0	4.82 (br. *d*, J = 9.6)	96.3	5.28 (br. *d*, J = 9.2)
CH_2(2′)	39.5	1.82–1.84 (*m*), 2.36–2.41 (*m*)	37.0	1.73–1.78 (*m*), 2.29–2.31 (*m*)
H–C(3′)	70.3	4.00–4.05 (*m*)	78.0	4.07 (br. *s*)
H–C(4′)	89.4	3.39 (*t*, J = 8.8)	83.2	3.52 (*m*)
H–C(5′)	70.9	3.71 (*dq*, J = 8.8, 6.4)	68.0	4.15 (*dq*, J = 8.8, 6.4)
Me(6′)	18.4	1.69 (*d*, J = 6.4)	18.6	1.37 (*d*, J = 6.4)
*Me*O–C(3′)			58.8	3.47 (*s*)
Glc(I)			Cym(II)	
H–C(1″)	105.6	4.87 (*d*, J = 7.6)	100.4	5.11 (br. *d*, J = 9.2)
H–C(2″) or CH_2(2″)	74.7	4.01–4.03 (*m*)	37.6	1.75–1.80 (*m*), 2.31–2.32 (*m*)
H–C(3″)	77.9	4.23–2.26 (*m*)	77.7	3.98 (br. *s*)
H–C(4″)	71.8	4.01–4.03 (*m*)	83.4	3.46 (*m*)
H–C(5″)	78.2	4.20–4.23 (*m*)	69.0	4.23 (*dq*, J = 8.8, 6.2)
CH_2(6″) or Me(6″)	69.9	4.00–4.04 (*m*), 4.96 (br. *d*, J = 8.4)	19.0	1.38 (*d*, J = 6.2)
*Me*O–C(3″)			58.9	3.47 (*s*)
Glc(II)			Ole	
H–C(1‴)	104.5	4.84 (*d*, J = 7.6)	101.3	4.75 (br. *d*, J = 9.6)
H–C(2‴) or CH_2(2‴)	75.4	4.02–4.05 (*m*)	37.3	2.08–2.11 (*m*), 2.50–2.53 (*m*)
H–C(3‴)	76.2	4.15–4.17 (*m*)	79.0	3.72 (*m*)
H–C(4‴)	71.3	4.23–4.26 (*m*)	82.0	4.70 (br. *d*, J = 9.2)
H–C(5‴)	78.4	4.15–4.17 (*m*)	71.6	3.71 (*m*)
CH_2(6‴) or Me(6‴)	62.4	4.38 (*dq*, J = 12, 5.2), 4.50 (*dq*, J = 12, 2.4)	18.6	1.79 (*d*, J = 6.00)
*Me*O–C(3‴)			57.1	3.61 (*s*)

[a]) Measured at 100 MHz in C_5D_5N. [b]) Measured at 400 MHz in C_5D_5N.

could be identified as (3β,20*S*)-pregn-5-ene-3,17,20-triol 20-[*O*-β-glucopyranosyl-(1 → 6)-*O*-β-glucopyranosyl-(1 → 4)-β-canaropyranoside], a new compound.

Compound **3** was isolated as a white amorphous powder and had a molecular formula $C_{43}H_{70}O_{14}$ on the basis of the HR-ESI-MS (*m/z* 833.4612 ([M + Na]$^+$)), ^{13}C-NMR, and DEPT data. The IR spectrum revealed the presence of OH (3379 cm^{-1}), C=O (1725 cm^{-1}), and C=C groups (1648 cm^{-1}). The ^{1}H-NMR spectrum of **3** displayed two Me groups at δ(H) 0.94 (*s*) and 1.36 (*s*), a MeO group at δ(H) 3.52 (*s*), and one olefinic H-atom at δ(H) 5.45 (br. *s*) assigned to the aglycone of **3** (*Table 2*). In the ^{13}C-NMR spectrum, a total of 43 C-signals were observed, including one C=O group, five quaternary C-atoms, five Me, four MeO, twelve CH_2, and sixteen CH groups (*Table 2*).These data were characteristic of a C_{21} steroidal glycoside. Comparison of the ^{13}C-NMR data of **3** with those of the known compound (3β,14β,17α)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one, indicated that all the signals were very similar, except that C(3) (δ(C) 77.3) was shifted downfield by 5.9 ppm, while C(2) (δ(C) 30.3) and C(4) (δ(C) 39.2) were shifted upfield by 1.7 and 4.4 ppm, respectively [7][12]. The relative configuration of the aglycone of **3** was deduced from its NOESY plot as shown in *Fig. 3*. Therefore, this glycoside was a (3β,14β,17α)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one derivative with a sugar moiety linked at its HO−C(3) group. The ^{1}H-NMR spectrum of **3** displayed three secondary Me and three MeO signals of deoxysugars and three anomeric-H-atom signals at δ(H) 5.28 (1 H, br. *d*, J = 9.2 Hz), 5.11 (1 H, br. *d*, J = 9.2 Hz), and 4.75 (1 H, br. *d*, J = 9.6 Hz), indicating the presence of three sugar units with three β-linkages. Based on HMBC, HSQC, ^{1}H,^{1}H-COSY, NOESY, and TOCSY experiments, the three sugar residues were identified as two β-cymaropyranose (= 2,6-dideoxy-3-*O*-methyl-ribo-β-hexopyranose = Cym) units and one β-oleandropyranose (= 2,6-dideoxy-3-*O*-methyl-β-*xylo*-hexopyranose = Ole) unit by comparison of their ^{1}H- and ^{13}C-NMR data with those in the literature [12]. The sugar sequence and their linkage sites were confirmed by the HMBC experiment, which showed unequivocal correlations H−C(1′) of Cym(I) (δ(H) 5.28)/C(3) of the aglycone (δ(C) 77.3), H−C(1″) of Cym(II) (δ(H) 5.11)/C(4′) of Cym(I) (δ(C) 83.2), and H−C(1‴) of Ole (δ(H) 4.75)/C(4″) of Cym(II) (δ(C) 83.4). Therefore, the structure of **3** was determined to be (3β,14β,17α)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one 3-[*O*-β-oleandropyranosyl-(1 → 4)-*O*-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside], a new compound.

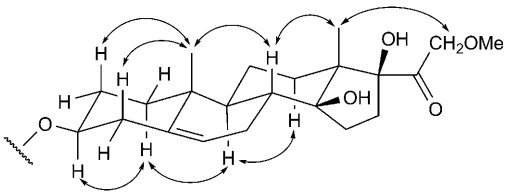


Fig. 3. *Main NOESY* (H ↔ H) *correlations of* **3**

The seven known compounds periplogenin, xysmalogenin (= (3β)-3,14-dihydroxycarda-5,20(22)-dienolide) [7], (3β,20*S*)-pregn-5-ene-3,17,20-triol, (3β,14β,17α)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one, (3β,20*S*)-pregn-5-ene-3,20-diol 3-β-glucopyranoside 20-β-glucopyranoside [13], (3β,20*S*)-pregn-5-ene-3,20-diol 3-[*O*-2-*O*-

acetyl-β-digitalopyranosyl-(1 → 4)-β-cymaropyranoside] 20-[*O*-β-glucopyranosyl-(1 → 6)-*O*-β-glucopyranosyl-(1 → 2)-β-digitalopyranoside] [14], and (3β,20*S*)-pregn-5-ene-3,20-diol 20-[*O*-β-glucopyranosyl-(1 → 6)-β-glucopyranoside] [15] were also isolated and identified by comparison of their spectroscopic data with those reported in the literature. Among them, compound (3β,20*S*)-pregn-5-ene-3,20-diol 3-β-glucopyranosid 20-β-glucopyranoside was isolated from this plant for the first time.

The research work was supported by the *Project in the National Science and Technology Pillar Program* (2006BAI14B01).

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 100–200 and 200–300 mesh; *Qingdao Haiyang Chemical Factory*, Qingdao, P. R. China). TLC: precoated plates (SiO_2 *G*; *Qingdao Haiyang Chemical Factory*, Qingdao, P. R. China), Column chromatography (CC): silica gel (SiO_2) or *RP-C*$_{18}$ SiO_2 (*Merck*). Optical rotation: *Perkin-Elmer-241MC* polarimeter. IR Spectra: *Bruker-Tensor-27* FT-IR spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-AM-400* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-ESI-MS: *Agilent-6520* LC/MS accurate-mass *Q-TOF* spectrometer; in *m*/*z* (rel. %).

Plant Material. The root barks of *Periploca sepium* were purchased from Anguo, Hebei Province, P. R. China, in Autumn 2007, and identified by Prof. *Jun-Hua Guo* (Tianjin University of Traditional Chinese Medicine). A voucher specimen (No. 20070912) was deposited with the Herbarium of Tianjin University of Traditional Chinese Medicine, Tianjin, P. R. China.

Extraction and Isolation. The air-dried root barks of *P. sepium* (15.0 kg) were extracted with 70% EtOH (3 × 30.0 l) for one week each time at r.t. The extract was concentrated, the residue suspended in H_2O (2.0 l) and then successively extracted with AcOEt (3 × 3.0 l) and BuOH (3 × 3.0 l), yielding an AcOEt extract (150 g) and a BuOH extract (600 g), resp. The AcOEt extract (150 g) was separated by CC (SiO_2; petroleum ether (PE)/AcOEt 50 : 1 → 1 : 1): *Fractions A – D*. *Fr. B* (5 g) was separated by CC (SiO_2; PE/AcOEt 6 : 1 → 1 : 2): (3β,14β,17α)-3,14,17-trihydroxy-21-methoxypregn-5-en-20-one (35 mg) and periplogenin (50 mg). *Fr. C* (6 g) was separated by CC (SiO_2; PE/AcOEt 4 : 1 → 1 : 4): (3β,20*S*)-pregn-5-ene-3,17,20-triol (28 mg) and xysmalogenin (15 mg). The BuOH extract (600 g) was subjected to dry CC (SiO_2; AcOEt/EtOH 25 : 1): *Fractions E – J*. *Fr. E* (5 g) was subjected to CC (*RP-C*$_{18}$, MeOH/H_2O 20 → 40%): **1** (18 mg), **2** (18 mg), and (3β,20*S*)-pregn-5-ene-3,20-diol 3-β-glucopyranoside 20-β-glucopyranoside (21 mg). *Fr. F* (3 g) was subjected to CC (*RP-C*$_{18}$, MeOH/H_2O 60 → 70%): (3β,20*S*)-pregn-5-ene-3,20-diol 3-[*O*-2-*O*-acetyl-β-digitalopyranosyl-(1 → 4)-β-cymaropyranoside] 20-[*O*-β-glucopyranosyl-(1 → 6)-*O*-β-glucopyranosyl-(1 → 2)-β-digitalopyranoside] (35 mg). *Fr. G* (4.5 g) was subjected to CC (*RP-C*$_{18}$, MeOH/H_2O 50 → 60%): **3** (22 mg) and (3β,20*S*)-pregn-5-ene-3,20-diol 20-[*O*-β-glucopyranosyl-(1 → 6)-β-glucopyranoside] (16 mg).

*Periplogenin 3-[*O*-β-Glucopyranosyl-(1 → 4)-β-sarmentopyranoside]* (= *(3β,5β)-3-[(2,6-Dideoxy-4-*O*-β-glucopyranosyl-3-*O*-methyl-β-*arabino*-hexopyranosyl)oxy]-5,14-dihydroxycard-20(22)-enolide*; **1**). White amorphous powder. $[\alpha]_D^{25} = -8.7$ (*c* = 0.28, MeOH). UV (MeOH): 218 (3.13). IR: 3448, 2938, 2879, 1779, 1739, 1627, 1449, 1093, 1037. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS: 719.3597 ($[M + Na]^+$, $C_{36}H_{56}NaO_{13}^+$; calc. 719.3619).

*(3β,20*S*)-Pregn-5-ene-3,17,20-triol 20-[*O*-β-Glucopyranosyl-(1 → 6)-*O*-β-glucopyranosyl-(1 → 4)-β-canaropyranoside]* (= *(3β,20*S*)-3,17-Dihydroxypregn-5-en-20-yl *O*-β-Glucopyranosyl-(1 → 4)-*O*-β-glucopyranosyl-(1 → 4)-2,6-dideoxy-β-*xylo*-hexopyranoside*; **2**). White amorphous powder. $[\alpha]_D^{25} = -58.2$ (*c* = 0.20, pyridine). IR: 3426, 2936, 2891, 1657, 1461, 1168, 1063, 1030. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS: 811.4062 ($[M + Na]^+$, $C_{39}H_{64}NaO_{16}^+$; calc. 811.4092).

*(3β,14β,17α)-3,14,17-Trihydroxy-21-methoxypregn-5-en-20-one 3-[*O*-β-oleandropyranosyl-(1 → 4)-*O*-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside]* (= *(3β,14β,17α)-3-{[*O*-2,6-Dideoxy-3-*O*-methyl-β-*xylo*-hexopyranosyl-(1 → 4)-*O*-2,6-dideoxy-3-*O*-methyl-*ribo*-β-hexopyranosyl-(1 → 4)-2,6-dideoxy-3-*O*-methyl-*ribo*-β-hexopyranosyl]oxy}-14,17-dihydroxy-21-methoxypregn-5-en-20-one*; **3**). White amor-

phous powder. $[\alpha]_D^{25} = -27.6$ ($c = 0.20$, MeOH). IR: 3379, 2965, 2895, 1725, 1648, 1447, 1365, 1161, 1100, 1061, 1004. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS: 833.4612 ($[M + Na]^+$, $C_{43}H_{70}NaO_{14}^+$; calc. 833.4663).

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