New Cycloartane and Flavonol Glycosides from *Corchorus depressus*

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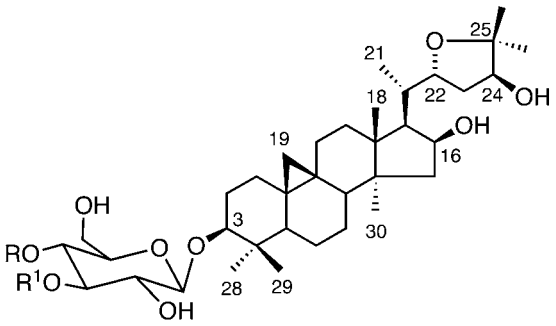
Two new monodesmosidic cycloartane triterpene glycosides, depressosides E and F, and two new flavonol glycosides, depressonol A and B, were isolated from the butanol-soluble part of the EtOH extract of *Corchorus depressus* L. The structures of the new compounds were elucidated as (22*R*,24*S*)-22,25-epoxy-9,19-cyclolanostane-3β,16β,24-triol 3-[α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranoside] (**1**), (22*R*,24*S*)-22,25-epoxy-9,19-cyclolanostane-3β,16β,24-triol 3-[α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside] (**2**), kaempferol 3-[β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranoside] 7-[α-L-arabinofuranoside] (**4**), and kaempferol 3-[β-D-glucopyranosyl-(1 → 6)-β-D-galactopyranoside] 7-[α-L-arabinofuranoside] (**5**) on the basis of chemical evidence and detailed spectroscopic studies.

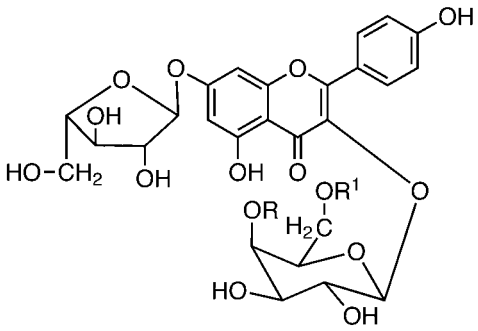
Introduction. – *Corchorus depressus* L., belonging to the family Tiliaceae, is a medicinal plant growing wild in sandy, clayey, and saline areas of Pakistan [1]. It is commonly known as 'bhauphali' and has been used in folk medicine in the subcontinent [2]. Previous phytochemical investigations of this species have led to the isolation of flavonoids, α-amyrin derivatives, and cycloartane-type glycosides [3–6]. Our re-investigation of the chemical constituents of *C. depressus* led to the isolation and structure elucidation of two new cycloartane triterpene saponins, depressosides E (**1**) and F (**2**), and two new kaempferol glycosides, depressonols A (**4**) and B (**5**), in addition to the already reported compounds from this species.

Results and Discussion. – The EtOH extract of the whole plants of *Corchorus depressus* was partitioned into hexane-, AcOEt-, BuOH-, and H_2O-soluble fractions. The BuOH extract was subjected to vacuum liquid chromatography (VLC; silica gel), column chromatography (*Sephadex LH-20*), and reversed-phase flash chromatography (FC) to yield two fractions, each containing two compounds. Further purification by HPLC afforded the two saponins, depressosides E (**1**) and F (**2**) and the two flavonol glycosides, depressonols A (**4**) and B (**5**) in pure form.

Depressoside E (**1**) was isolated as an amorphous powder. The positive-ion FAB-MS of **1** exhibited quasi-molecular ion peaks at *m*/*z* 805 ($[M+Na]^+$) and 783 ($[M+H]^+$), corresponding to the molecular formula $C_{42}H_{70}O_{13}$ for **1**. The fragment ions at *m*/*z* 659 and at 497 indicated the presence of two sugar units, one hexose and one deoxyhexose, in the molecule. The presence of two sugars in the molecule of **1** was also confirmed by the negative-ion FAB-MS. The assignments of all the ^{1}H- and ^{13}C-NMR signals of **1** were successfully carried out with ^{1}H,^{1}H COSY, HMQC, and HMBC experiments (*Table 1*). Thus, depressoside E (**1**) was identified as (22*R*,24*S*)-22,25-



1 R^1 = H, R = α-L-rhamnopyranosyl
2 R^1 = α-D-glucopyranosyl, R = H
3 R^1 = R^1 = H



4 R = β-D-glucopyranosyl, R^1 = H
5 R = H, R^1 = β-D-glucopyranosyl

epoxy-9,19-cyclolanostane-3β,16β,24-triol 3-[α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranoside].

The ^{1}H-NMR spectrum (500 MHz, CD_3OD) of **1** contained 6 *s* for tertiary Me groups at δ 0.88 (Me(29)), 0.98 (Me(30)), 1.09 (Me(28)), 1.18 (Me(18)), 1.23 (Me(27)), and 1.32 (Me(26)), 2 *d* for secondary Me groups at δ 0.93 (J = 6.8 Mz, Me(21)), 1.25 (J = 6.0 Hz, Me(6″)), and 2 *d* for a cyclopropyl CH_2 group at δ 0.35 and 0.55 (each J = 3.9 Hz, CH_2 (19)), indicating a cycloartane skeleton in the molecule. The two anomeric-proton signals at δ 4.58 (*d*, J = 8.5 Hz, H–C(1′)) and 5.20 (*d*, J = 1.6 Hz, H–C(1″)) suggested the presence of one β-D- and one α-L-linked sugar in **1**. The ^{13}C-NMR spectrum (125 MHz, CD_3OD) was compatible with a cycloartane-type triterpene for the aglycone of **1**. Of the total of 42 C-signals, 30 were attributed to the triterpenoid moiety and 12 to the saccharide part. The ^{13}C-NMR and DEPT spectra allowed the attribution of the 30 signals to 7 Me, 9 CH_2, 8 CH, and 6 quaternary C-atoms of the aglycone. Comparison of the ^{13}C-NMR data showed good general agreement with the previously reported saponin depressoside D [6], except for the signals in the sugar region.

Table 1. *^{13}C-* (125 MHz) *and ^{1}H-NMR* (500 MHz) *Data of Depressoside E* (**1**) *from 1D- and 2D-NMR Experiments in CD_3OD* (δ in ppm, J in Hz)

	δ(C)[a])	δ(H)
CH_2(1)	33.06	1.19, 1.53
CH_2(2)	30.35	1.73, 2.10
CH(3)	89.99	3.20 (*dd*, J = 4.1, 10.9)
C(4)	42.05	–
CH(5)	48.87	1.30 (*dd*, J = 3.0, 11.8)
CH_2(6)	22.08	0.81, 1.63
CH_2(7)	27.27	0.98, 1.28
CH(8)	49.50	1.62 (*dd*, J = 3.9, 12.2)
C(9)	21.05	–
C(10)	27.42	–
CH_2(11)	27.33	1.13, 2.03
CH_2(12)	34.38	1.36, 1.65
C(13)	48.20	–
C(14)	47.56	–
CH_2(15)	47.60	1.37, 1.95
CH(16)	73.10	4.51 (*ddd*, J = 5.3, 8.0, 8.2)
CH(17)	53.01	1.96 (*dd*, J = 6.8, 11.9)
Me(18)	19.42	1.18 (*s*)
CH_2(19)	31.01	0.35 (*d*, J = 3.9)
		0.55 (*d*, J = 3.9)
CH(20)	33.38	2.28 (*m*)
Me(21)	16.02	0.93 (*d*, J = 6.8)
CH(22)	81.12	4.02 (*ddd*, J = 3.0, 7.2, 8.3)
CH_2(23)	36.24	1.78 (*m*)
		2.21 (*m*)
CH(24)	78.35	4.03 (*dd*, J = 4.0, 6.9)
C(25)	84.21	–
Me(26)	26.01	1.32 (*s*)
Me(27)	23.15	1.23 (*s*)
Me(28)	26.17	1.09 (*s*)
Me(29)	15.50	0.88 (*s*)
Me(30)	20.54	0.98 (*s*)
Glc: CH(1′)	104.0	4.58 (*d*, J = 8.5)
CH(2′)	73.8	3.08 (*m*)
CH(3′)	77.00	3.45 (*m*)
CH(4′)	78.64	4.51 (*m*)
CH(5′)	77.40	3.37 (*m*)
CH_2(6′)	61.80	3.69 (*dd*, J = 5.2, 10.7)
		3.85 (*dd*, J = 2.8, 10.7)
Rha: CH(1″)	102.3	5.20 (*d*, J = 1.68)
CH(2″)	71.80	3.51 (*m*)
CH(3″)	72.20	3.43 (*m*)
CH(4″)	73.70	3.11 (*m*)
CH(5″)	68.80	3.01 (*m*)
Me(6″)	18.10	1.25 (*d*, J = 6.0)

[a]) Attached protons by DEPT.

The presence of 3 downfield CH signals at δ 89.99, 73.10, and 78.35 and a far-downfield quaternary C-atom at δ 84.21 confirmed that the aglycone in **1** is the previously described genin depressogenin [5]. The presence of an additional Me group in **1** was attributed to the rhamnopyranosyl unit. The ^{13}C-NMR spectrum contained 2 anomeric C-signals at δ 102.3 and 104.0. The sugar moieties were identified as α-L-rhamnopyranose and β-D-glucopyranose. The ^{13}C-NMR glycosidation shift for C(3) and the HMBC signals observed between H–C(1′) (δ 4.58) of the glucose unit and C(3) (δ 89.99) of the aglycone confirmed that the oligosaccharide moiety is attached at C(3) of the aglycone. The anomeric proton of the rhamnose moiety at δ 5.20 (H–C(1″)) exhibited long-range correlations with C(4′) of the glucose moiety at δ 78.64. A strong inter-residual NOE between the anomeric proton of the rhamnose (δ 5.20) and H–C(4′) of the glucose (δ 4.51) unit was clearly observed, which further supported a $1 \rightarrow 4$ linkage between the rhamnose and glucose units [7].

Depressoside F (**2**) was isolated as white solid. The positive-ion FAB-MS of **2** exhibited a quasi-molecular-ion peak at *m*/*z* 821 ($[M+Na]^+$, $[C_{42}H_{71}O_{14}+Na]^+$). The fragment ions at *m*/*z* 659 and 497 and the negative-ion FAB-MS indicated the presence of two hexose units in the molecule. The enzymatic hydrolysis of saponin **2** with the enzyme α-glucosidase gave the previously reported glycoside depressoside A (**3**) [5], establishing that the terminal sugar in **2** is α-D-glucose. In accord with the ^{1}H- and ^{13}C-NMR data (*Table 2*), depressoside F (**2**) was identified as (22*R*,24*S*)-22,25-epoxy-9,19-cyclolanostane-3β,16β,24-triol 3-[α-D-glucopyranosyl-$(1 \rightarrow 3)$-β-D-glucopyranoside].

The ^{1}H-NMR spectrum (500 MHz, CD_3OD) of **2**, in addition to other signals, showed two anomeric signals at δ 4.32 (d, $J = 3.5$ Hz) and 4.58 (d, $J = 8.0$ Hz) also suggesting the presence of one α-D- and one β-D-linked sugar in the molecule. In the ^{13}C-NMR spectrum (CD_3OD, 125 MHz), the anomeric C-atoms were observed at δ 100.2 and 103.5. It has been reported earlier that the anomeric C-atom of methyl α-D-glucopyranoside appears at δ 100.0 and of methyl β-D-glucopyranoside at δ 103.9 [8]. As the anomeric proton corresponding to δ(C) 100.2 of **2** showed a small coupling constant (3.5 Hz), the presence of one α-D-glucose unit was confirmed. The position of the sugar residues was unambiguously assigned by comparison of the ^{13}C-NMR data with that of the aglycone, depressogenin, and was further confirmed by a HMBC experiment. The cross peak due to long-range correlations between C(3) (δ 90.01) of the aglycone and H–C(1′) of β-Glc (δ 4.58) confirmed that the glucose residue was linked to C(3) of the aglycone. The cross peaks between C(3′) of β-Glc (δ 83.9) and H–C(1″) of α-Glc (δ 4.32) confirmed the location of the second glucose unit at C(3′) of β-Glc.

The flavonol glycosides **4** and **5** were obtained as dark yellow amorphous powders, which appeared violet on TLC under UV light (366 nm) and turned yellow with NH_3. Acid hydrolysis of **4** and **5** with 2N HCl yielded kaempferol (= 3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one) (co-elution with standard on TLC (co-TLC), UV, EI-MS, and ^{1}H-NMR), glucose, galactose, and arabinose. The sugars were identified by co-TLC and also by GC analysis after trimethylsilylation [9]. The conclusions drawn from FAB-MS, ^{1}H-NMR, NOE difference measurement, and ^{13}C-NMR of **4** were also confirmed by ^{1}H,^{1}H COSY, HMQC, and HMBC experiments (see *Table 3*) and by comparison with published data (see below). Therefore, compound **4** is identified as kaempferol 3-[β-D-glucopyranosyl-$(1 \rightarrow 4)$-β-D-galactopyranoside] 7-(α-L-arabinofuranoside).

On the basis of spectroscopic data (*Table 3*) and comparison with **4**, the structure of compound **5** is established as kaempferol 3-[β-D-glucopyranosyl-$(1 \rightarrow 6)$-β-D-galactopyranoside] 7-(α-L-arabinofuranoside).

The UV spectrum of **4** in MeOH had absortion maxima at 263 and 347 nm, which is typical for a flavonol glycoside [10]. The bathochromic shift (47 nm) of band-I in $AlCl_3$/HCl solution/MeOH and the absence of a shift on band-II in NaOAc/MeOH solution suggested that **4** is a 3,7-disubstituted flavonol glycoside [11][12]. The EI-MS of **4** showed a base peak at *m*/*z* 286 along with other diagnostic fragments, which confirmed

Table 2. *^{13}C-* (125 MHz) *and ^{1}H-NMR* (500 MHz) *Data of Depressoside F* (**2**) *from 1D and 2D-NMR Experiments in CD_3OD* (δ in ppm, J in Hz)

	δ(C)[a])	δ(H)
CH_2(1)	33.08	1.20, 1.55
CH_2(2)	30.30	1.72, 2.13
CH(3)	90.01	3.22 (*dd*, J = 4.0, 10.5)
C(4)	42.15	–
CH(5)	49.0	1.35 (*dd*, J = 3.4, 11.7)
CH_2(6)	22.12	0.80, 1.64
CH_2(7)	27.55	0.97, 1.29
CH(8)	49.79	1.60 (*dd*, J = 3.8, 12.0)
C(9)	21.10	–
C(10)	27.32	–
CH_2(11)	27.23	1.15, 2.01
CH_2(12)	34.40	1.30, 1.63
C(13)	48.54	–
C(14)	47.59	–
CH_2(15)	47.91	1.38, 1.92
CH(16)	73.0	4.55 (*ddd*, J = 5.4, 8.1, 8.5)
CH(17)	52.72	1.98 (*dd*, J = 7.0, 12.1)
Me(18)	19.22	1.18 (*s*)
CH_2(19)	29.89	0.37 (*d*, J = 4.2)
		0.58 (*d*, J = 4.2)
CH(20)	33.35	2.25 (*m*)
Me(21)	16.05	0.95 (*d*, J = 6.9)
CH(22)	81.12	4.00 (*ddd*, J = 2.9, 7.1, 8.0)
CH_2(23)	36.27	1.77 (*m*)
		2.20 (*m*)
CH(24)	78.49	4.02 (*dd*, J = 4.1, 7.1)
C(25)	84.18	–
Me(26)	26.05	1.33 (*s*)
Me(27)	23.32	1.25 (*s*)
Me(28)	26.29	1.10 (*s*)
Me(29)	15.45	0.89 (*s*)
Me(30)	20.62	0.96 (*s*)
β-Glc: CH(1′)	103.5	4.58 (*d*, J = 8.0)
CH(2′)	73.8	3.06 (*m*)
CH(3′)	83.9	4.02 (*m*)
CH(4′)	68.9	3.26 (*m*)
CH(5′)	77.4	3.19 (*m*)
CH_2(6′)	61.8	3.72 (*m*)
		3.40 (*m*)
αGlc: CH(1″)	100.2	4.32 (*d*, J = 3.5)
CH(2″)	72.3	3.09 (*m*)
CH(3″)	75.9	3.14 (*m*)
CH(4″)	70.2	3.09 (*m*)
CH(5″)	76.5	3.15 (*m*)
CH_2(6″)	60.8	3.65, 3.45 (2*m*)

[a]) Attached protons by DEPT.

Table 3. *^{13}C-Data* (125 MHz) *of Depressonols A* (**4**) *and B* (**5**) *from 1D and 2D-NMR Experiments in CD_3OD* (δ in ppm)

	δ(C)[a]) of **4**	δ(C)[a]) of **5**
C(2)	158.3	158.1
C(3)	135.5	135.2
C(4)	178.9	180.1
C(5)	163.9	162.8
CH(6)	99.8	99.9
C(7)	163.8	163.1
CH(8)	95.9	95.5
C(9)	158.5	158.3
C(10)	104.2	103.5
C(1′)	121.5	122.1
CH(2′)	132.5	132.3
CH(3′)	117.5	116.9
C(4′)	160.2	159.5
CH(5′)	117.5	116.9
CH(6′)	132.5	132.3
Gal: CH(1″)	101.1	99.9
CH(2″)	71.4	71.3
CH(3″)	73.9	74.3
CH(4″)	75.6	69.8
CH(5″)	77.4	77.5
CH_2(6″)	62.5	67.2
Glc: CH(1‴)	103.4	103.5
CH(2‴)	74.3	74.2
CH(3‴)	76.5	76.0
CH(4‴)	69.7	69.5
CH(5‴)	76.7	76.4
CH_2(6‴)	61.9	62.8
Ara: CH(1⁗)	108.4	108.9
CH(2⁗)	81.4	81.5
CH(3⁗)	77.3	77.6
CH(4⁗)	85.2	87.5
CH_2(5⁗)	61.1	62.5

[a]) Attached protons by DEPT.

kaempferol as the aglycone. The positive-ion FAB-MS of **4** displayed a quasi-molecular-ion peak at *m/z* 765 ($[M+Na]^+$, $[C_{32}H_{38}O_{20}+Na]^+$). In addition, two fragment-ion peaks were observed at *m/z* 471 ($[M+Na-132-162]^+$) and 309 ($[M+Na-132-2\times162]^+$), indicating the attachment of either two interlinked hexoses at position C(3) and a pentose at C(7) or of one hexose interlinked to a pentose at position C(3) and a hexose at position C(7) of the aglycone or *vice versa.* In the ^{1}H-NMR spectrum of **4**, three one-proton *d* at δ 5.54 ($J=6.9$ Hz), 5.30 ($J=7.2$ Hz), and 5.68 ($J=1.0$ Hz), typical for β-D- and α-L-sugar configurations, were assigned to the anomeric protons of a galactose, glucose, and arabinose moiety, respectively. The remaining sugar protons resonated at δ 3.30–4.58 ppm. In the NOE experiments, irradiation of H–C(8) of the aglycone enhanced the anomeric-proton signal of arabinose, indicating its attachment at C(7). Similarly, irradiation of H–C(2′) and H–C(6′) produced an NOE at the anomeric protons of galactose, indicating its attachment at C(3) of the aglycone. A strong inter-residual NOE connecting the anomeric proton of glucose to H–C(4″) of galactose at δ 3.68 was clearly detected, which supported a $1\rightarrow4$ type linkage [7]. The ^{13}C-NMR chemical shifts of compound **4** were similar to those reported for kaempferol 3-(sophorside) 7-(α-L-arabinofuranoside) [13], except for the signals arising from the sugars at position C(3), which were consistent with those already published for lilyn (kaempferol 3-(glucosyl galactoside)) [14]. The α-D-anomeric linkage between the arabinofuranose and the flavone is supported by the small coupling constant (*ca.* 1.0 Hz) of the anomeric proton

of this sugar moiety [13]. The anomeric C-atoms of the galactose, glucose, and arabinose units of **4** appeared at δ 101.1, 103.4, and 108.4, respectively. A comparison of the ^{13}C-NMR sugar signals with the reported values for lilyn indicated a 5.8-ppm downfield shift for C(4″) of the galactose [14]. This downfield shift of C(4″) established the $1 \rightarrow 4$ linkage between the glucose and galactose units and confirmed the results obtained by NOE experiments. The ^{13}C-NMR signals additional to those of a kaempferol 3-(glucosylgalactoside) were observed at δ 108.7, 82.6, 78.5, 86.4, and 63.0 and were consistent with published data for an arabinofuranoside rather than an arabinopyranoside moiety [15–17].

The UV and EI- and FAB-MS data of compound **5** were similar to those of compound **4**. In the ^{1}H-NMR spectrum of **5**, the *d*s for three anomeric protons were observed at δ 5.28 ($J = 7.2$ Hz), 5.59 ($J = 6.9$ Hz), and 5.62 ($J = 1.3$ Hz). The ^{13}C-NMR, NOE difference measurements, and 2D NMR experiments showed that the only difference between compounds **4** and **5** is the $1 \rightarrow 6$ interglycosidic linkage between the glucose, and galactose units, which was also confirmed by a downfield shift (6.5 ppm) of C(6″) of the galactose unit. Anomeric C-atom signals of the galactose, glucose, and arabinose units appeared at δ 99.9, 103.5, and 108.9, respectively.

All new and known depressosides are currently being tested for different enzyme-inhibition activities. Depressoside A (**3**) has shown inhibitory activity against α-glucosidase enzyme type-VI (*Sigma*, No G6136) with an IC_{50} of 0.236 mM.

Experimental Part

General. VLC ($CHCl_3$/MeOH): silica gel *60* (35–70 mesh, *Merck*). Column chromatography (CC): *Sephadex LH-20* (*Pharmacia*). Flash chromatography (FC): *Eyela EF-10* flash-chromatography instrument; column packed with *RP-8* silica (*Merck*, No 16105). HPLC: *Shimadzu LC-6A* dual-pump system with *RID-6A* and *SPD-6A* UV detectors; *RP-18* reversed-phase semi-prep. column. TLC: pre-coated silica gel *60*, *F254* aluminum sheets (*Merck*). GC: sugar analysis was carried out by GC of trimethylsilyl derivatives on *SE-54* (25 × 0.25 mm) at a flow rate of 4.0 ml min^{-1} with N_2 as carrier gas. Optical rotations: *Jasco DIP-360* instrument. M.p.: uncorr.; *Gallenkamp* melting-point apparatus. UV: in nm. IR: *Jasco A-320* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR (125 MHz): at 500 and 125 MHz, resp.; *Bruker AM-500* spectrometer; chemical shifts δ in ppm, coupling constants *J* in Hz; 2D-NMR experiments included ^{1}H,^{1}H COSY, HMQC, NOESY, DEPT, and HMBC. EI-MS: *Finnigan MAT-312* double-focusing mass spectrometer. FAB-MS: *Jeol JMS-HX-110* spectrometer; in *m*/*z* (rel. int. %).

Plant Material. The plant material was collected in Karachi in August 2000. A voucher specimen of the plant is deposited at the herbarium of the Department of Botany, University of Karachi (voucher specimen #2300).

Extraction and Isolation Procedures. Air-dried whole plants of *Corchorus depressus* (10 kg) were extracted with EtOH (7 days × 3). The EtOH extract was evaporated and the gummy residue (200 g) partitioned between hexane, AcOEt, and BuOH. The BuOH extract was evaporated and the solid residue (25 g) then subjected to VLC (gradient $CHCl_3$/MeOH). The VLC fraction eluted with $CHCl_3$/MeOH 75:25 gave a mixture of crude saponins that was subjected to CC (*Sephadex LH-20*, MeOH/H_2O 1:1). The fractions obtained were subjected to reversed-phase FC (*Lichrosphere RP-8* silica gel (20 g). The fractions eluted with MeOH/H_2O 60:40 revealed the presence of two partially overlapping spots on TLC (BuOH/AcOH/H_2O 12:3:5). These FC fractions were submitted to HPLC (semi-prep. *RP-18* (24.4 cm × 40 mm), isocratic MeOH/H_2O 70:30, flow rate 1 ml/min, refractive-index detector): **1** (15.7 mg; t_R 11.7 min) and **2** (12.3 mg; t_R 15.3 min).

The VLC fractions eluted with $CHCl_3$/MeOH 70:30 to 65:35 showed the presence of partially overlapping yellow spots on TLC (BuOH/AcOH/H_2O 12:3:5) along with impurities. These combined fractions were subjected to CC (*Sephadex LH-20*, MeOH/H_2O 60:40). The fractions obtained containing partially overlapped yellow spots free of impurities were purified by HPLC (semi-prep. *RP-18* (24.4 cm × 40 mm), isocratic MeOH/H_2O 60:40), flow rate 1.5 ml/min, UV detector): **4** (11.6 mg; t_R 7.5 min) and **5** (9.8 mg; t_R 9.4 min). The purity of **1**, **2**, **4**, and **5** was again checked on HP-TLC plates, and spots were visualized by spraying with ceric ammonium sulfate reagent followed by heating.

Depressoside E (=*(3β,16β,22*R,*24*S*)-22,25-Epoxy-3-[[4*-O-*(α*-L-*rhamnopyranosyl)-β*-D-*glucopyranosyl]-oxy]-1,19-cyclolanostane-16,24-diol* = *(3β,16β,22*R,*24*S*)-22,25-Epoxy-16,24-dihydroxy-1,19-cyclolanostan-3-yl 4*-O-*(α*-L-*Rhamnopyranosyl)-β*-D-*glucopyranoside*; **1**). Amorphous solid. M.p. 212–214°. $[\alpha]_D^{25} = -19.8$ (c = 0.18, MeOH). ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. FAB-MS (pos.): 805 ($[M + Na]^+$), 783 ($[M + H]^+$), 659

($[M+Na-146]^{+)}$, ^{641} ($[M+Na-146-H_2O]^{+)}$, ^{497} ($[M+Na-146-162]^{+)}$, ^{461} ($[M+Na-146-162-H_2O]^{+}$). FAB-MS (neg.): 781 ($[M-H]^-$), 635 ($[M-H-146]^-$), 473 ($[M-H-146-162]^-$), 455 ($[M-H-146-162-H_2O]^-$).

Depressoside F (*= (3β,16β,22*R,*24*S*)-22,25-Epoxy-3-[[3-*O*-(α-D-glucopyranosyl)-β-D-glucopyranosyl]oxy]-1,19-cyclolanostane-16,24-diol = (3β,16β,22*R,*24*S*)-22,25-Epoxy-16,24-dihydroxy-1,19-cyclolanostan-3-yl 3-O-(α-D-Glucopyranosyl)-β-D-glucopyranoside*; **2**) Amorphous solid. M.p. 202–204° (dec.). $[\alpha]_D^{25} = -10.9$ (*c* = 0.24, MeOH). ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 2*. FAB-MS (pos.): 821 ($[M+Na]^+$), 799 ($[M+H]^+$), 659 ($[M+Na-162]^+$), 641 ($[M+Na-162-H_2O]^+$), 497 ($[M+Na-2\times162]^+$), 479 ($[M+Na-2\times162-H_2O]^+$). FAB-MS (neg.): 797 ($[M-H]^-$), 635 ($[M-H-162]^-$), 599 ($[M-H-162-2H_2O]^-$), 473 ($[M-H-2\times162]^-$), 455 ($[M-H-2\times162-H_2O]^-$).

Enzymatic Hydrolysis of **2**. Saponin **2** (0.2 mM), mixed with sodium phosphate (50 mM) and sodium chloride (100 mM) (pH 6.8), was incubated with the enzyme α-glucosidase (from *Brewers* yeast; 0.032 U/ml, *Sigma* No. 6136) for 1 h at 37°, and the product was extracted with MeOH. The hydrolyzed product was identified as *depressoside A* (*= (22*R,*24*S*)-22,25-epoxy-9,19-cyclolanostane-3β,16β,24-triol 3-β-D-glucopyranoside] = (3β,16β,22*R,*24*S*)-22,25-epoxy-16,24-dihydroxy-1,19-cyclolanostan-3-yl β-D-glucopyranoside)*, by comparing its NMR data with the literature values [5], thus confirming that the second sugar unit of **2** has an α-D-glucosidic linkage.

Depressonol A (*= 7-[(α-L-Arabinofuranosyl)oxy]-3-[[4-O-(β-D-glucopyranosyl)-β-D-glucopyranosyl]-oxy]-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one*; **4**). Yellow amorphous powder. UV (MeOH): 261, 346. UV (MeOH + NaOMe): 266, 380. UV (MeOH + $AlCl_3$/HCl soln.): 270, 300, 345, 393. UV (MeOH + NaOAc/H_3BO_3): 266, 350. ^{1}H-NMR (CD_3OD, 500 MHz): 5.30 (*d*, *J* = 7.2, H–C(1) of Glc); 5.54 (*d*, *J* = 6.9, H–C(1) of Gal); 5.68 (*d*, *J* = 1.0, H–C(1) of Ara); 6.43 (*d*, *J* = 2.2, H–C(6)); 6.70 (*d*, *J* = 2.2, H–C(8)); 6.88 (*d*, *J* = 8.8 Hz, H–C(3′), H–C(5′)); 7.99 (*d*, *J* = 8.8, H–C(2′), and H–C(6′)). ^{13}C-NMR (CD_3OD): *Table 3*. EI-MS: 286 (100), 285 (17.0), 258 (8.1), 153 (5.8), 121 (30.5), 93 (10.8). FAB-MS (pos.): 765 ($[M+Na]^+$), 471 ($[M+Na-132-162]^+$), 309 ($[M+Na-132-2\times162]^+$).

Depressonol B (**5**). Yellow amorphous powder. UV (MeOH): 266, 347. UV (MeOH + NaOMe): 266, 386. UV (MeOH + $AlCl_3$): 262, 299, 346, 394. UV (MeOH + $AlCl_3$/HCl): 270, 274, 300, 393. UV (MeOH + NaOAc/H_3BO_3): 266, 348. ^{1}H-NMR (CD_3OD, 500 MHz): 5.28 (*d*, *J* = 7.2, H–C(1) of Glc); 5.59 (*d*, *J* = 6.9, H–C(1) of Gal); 5.62 (*d*, *J* = 1.3, H–C(1) of Ara); 6.42 (*d*, *J* = 2.0, H–C(6)); 6.73 (*d*, *J* = 2.0, H–C(8)); 6.89 (*d*, *J* = 8.1, H–C(3′), H–C(5′)); 8.05 (*d*, *J* = 8.1, H–C(2′), H–C(6′)). ^{13}C-NMR (CD_3OD): *Table 3*. EI-MS: 286 (100), 285 (17.0), 258 (8.1), 153 (5.8), 121 (30.5), 93 (10.8). FAB-MS (pos.): 765 ($[M+Na]^+$), 471 ($[M+Na-132-162]^+$), 309 ($[M+Na-132-2\times162]^+$).

Acid Hydrolysis of Depressonol A (**4**) *and B* (**5**). Each flavonol glycoside (6.0 mg) in 2N HCl (5 ml) was refluxed for 1 h. The aglycones were extracted with AcOEt and identified by co-TLC with an authentic sample of kaempferol, UV, and ^{1}H-NMR spectra. The sugars were isolated from the aq. layer in the usual way and identified by co-TLC (cellulose, BAW, BEW, EPAW, and BBPW) with authentic samples and by GC analysis of their Me_3Si derivatives [9].

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