Two New Acylated Tridesmosidic Saponins from *Astragalus armatus*

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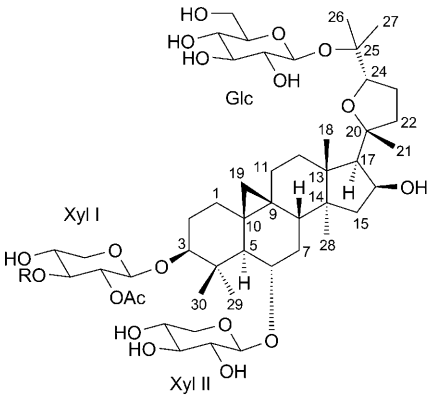
Two new tridesmosidic glycosides of (3*β*,6*α*,16*β*,20*R*,24*S*)-20,24-epoxycycloartane-3,6,16,25-tetrol (=cycloastragenol), armatosides I and II (**1** and **2**, resp.), were isolated from the roots of *Astragalus armatus* (Fabaceae) as well as the known bidesmosidic glycosides of cycloastragenol, trigonoside II (**3**) and trojanoside H (**4**). Their structures were elucidated as (3*β*,6*α*,16*β*,20*R*,24*S*)-3-*O*-(2,3-di-*O*-acetyl-*β*-D-xylopyranosyl)-20,24-epoxy-25-*O*-*β*-D-glucopyranosyl-6-*O*-*β*-D-xylopyranosylcycloartane-3,6,16,25-tetrol (**1**), and (3*β*,6*α*,16*β*,20*R*,24*S*)-3-*O*-(2-*O*-acetyl-*β*-D-xylopyranosyl)-20,24-epoxy-25-*O*-*β*-D-glucopyranosyl-6-*O*-*β*-D-xylopyranosylcycloartane-3,6,16,25-tetrol (**2**). These structures were established by extensive NMR and MS analyses and by comparison with literature data.

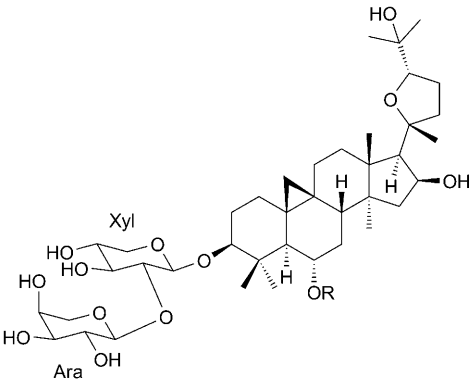
Introduction. – *Astragalus* is a great legume genus including more than 2200 species growing worldwide [1]. Saponins with aglycones of the cycloartane-, lanostane- and oleanane-type were isolated from many *Astragalus* species, but the cycloartane glycosides dominate the triterpenoids of this genus [2][3] (cycloartane = 9,19-cyclolanostane). Among the cycloartane-type skeletons, cycloastragenol (also known as cyclosiversigenin and astramembrangenin) is the most widely distributed genin of the glycosides in *Astragalus* genus [2]. The identified saponins were found to be diversified by their glycosylation types, degrees, and attachment points at the genin; moreover, several of them were acetylated. These different structural characteristics lead to specific chemical traits which could be used as fingerprints to distinguish different *Astragalus* species from each other. *Astragalus armatus* WILLD. (Fabaceae) is an endemic shrub species in the region of Maghreb. It mainly grows in arid regions where pastoral activity is important because of its low palatability [4][5]. To the best of our knowledge, there are no phytochemical studies on this species to date. In this article, we describe the isolation and structural elucidation of two new acylated tridesmosides of a 20,24-epoxycycloartane-type aglycone from the roots of *A. armatus*, named armatosides I (**1**) and II (**2**), together with two known cycloartane-type glycosides, trigonoside II (**3**) [6] and trojanoside H (**4**) [7]. The new compounds showed unique chemical substitutions which are not frequently found in the genus *Astragalus*.

Results and Discussion. – The MeOH/H_2O 7:3 extract of the roots of *Astragalus armatus* was partitioned between H_2O- and BuOH-soluble fractions. The BuOH fraction was subjected to vacuum liquid chromatography (VLC; *Lichroprep RP-8*) and

medium-pressure liquid chromatography (MPLC; silica gel) to yield compounds **1**–**4** as amorphous powders (see *Exper. Part*). Their structures were mainly determined by 1D- and 2D-NMR experiments (^{1}H, ^{13}C, DEPT, COSY, NOESY, TOCSY, HSQC, and HMBC), HR-ESI- and FAB-MS.



Armatoside I (**1**) R = Ac
Armatoside II (**2**) R = H



Trigonoside II (**3**) R = β-D-Xyl
Trojanoside H (**4**) R = β-D-Glc

The HR-ESI-MS (positive-ion mode) of armatoside I (**1**) exhibited a *quasi*-molecular-ion peak at *m*/*z* 1023.5150 ($[M+\mathrm{Na}]^+$), consistent with a molecular formula $C_{50}H_{80}NaO_{20}$. The negative-ion-mode FAB-MS displayed a *quasi*-molecular-ion peak at *m*/*z* 999 ($[M-\mathrm{H}]^-$). Other fragment-ion peaks at *m*/*z* 867 ($[M-\mathrm{H}-132]^-$), 837 ($[M-\mathrm{H}-162]^-$), 781 ($[M-\mathrm{H}-132-43-43]^-$), and 649 ($[M-\mathrm{H}-132-132-43-43]^-$) indicated the presence of three sugar units, one hexose and two pentoses, and two Ac groups. From the full assignment of all the ^{1}H- and ^{13}C-NMR signals (1D- and 2-D spectra), **1** was elucidated as a new saponin with the structure (3*β*,6*α*,16*β*,20*R*,24*S*)-3-*O*-(2,3-di-*O*-acetyl-*β*-D-xylopyranosyl)-20,24-epoxy-25-*O*-*β*-D-glucopyranosyl-6-*O*-*β*-D-xylopyranosylcycloartane-3,6,16,25-tetrol (*Tables 1* and *2*). The ^{1}H-NMR spectrum showed two signals for a cyclopropane CH_2 group at δ(H) 0.22 and 0.57 (each *d*, $J=4$ Hz, CH_2(19)), and seven signals for tertiary Me groups at δ(H) 1.10 (*s*, Me(28)), 1.30 (*s*, Me(26)), 1.31 (*s*, Me(21)), 1.35 (*s*, Me(30)), 1.42 (*s*, Me(18)), 1.58 (*s*, Me(27)), and 1.78 (*s*, Me(29)), indicating a cycloartane-type aglycone for **1** [2][3][8]. The assignments of the 20,24-epoxycycloartane structure were deduced from HMBCs between δ(H) 2.57 (H–C(17)) and 1.31 (*s*, Me(21)) and δ(C) 87.2 (C(20)), and between δ(H) 3.88 (H–C(24)), 1.30 (*s*, Me(26)), and 1.58 (*s*, Me(27)) and δ(C) 79.3 (C(25)). The following NOESY cross-peaks were observed: δ(H) 1.31 (*s*, Me(21))/3.88 (H–C(24)), δ(H) 3.12 (H_β–C(22))/1.42 (*s*, Me(18)) and 2.32 (H_β–C(23)), δ(H) 1.68 (H_α–C(22))/2.02–2.09 (H_α–C(23)) and 2.57 (H–C(17)), and δ(H) 3.88 (H–C(24))/1.58 (*s*, Me(27)); these allowed to deduce the configuration of the 20,24-epoxycycloartane. Also, the NOE correlations allowed to determine the *α* and *β* orientations of H-atoms of CH_2 groups in the aglycone part (*Table 1*). By analysis of all the 1D- and 2D- NMR spectra of **1**, the aglycone was identified as (3*β*,6*α*,16*β*,20*R*,24*S*)-20,24-epoxycycloartane-3,6,16,25-tetrol, *i.e.*, cycloastragenol, which is com-

monly found in the saponins of *Astragalus* [2][3]. The ^{1}H-NMR spectrum of **1** displayed signals for three anomeric H-atoms at δ(H) 4.82 (*d*, $J = 7.6$ Hz), 4.87 (*d*, $J = 7.0$ Hz), and 4.94 (*d*, $J = 7.2$ Hz) which were correlated in the HSQC spectrum with three anomeric C-atoms at δ(C) 104.0, 105.7, and 105.2, respectively, indicating the presence of three sugar units (*Table 2*). Furthermore, the ^{1}H-NMR spectrum showed two *s* at δ(H) 2.04 and 1.96 which gave HSQCs with two C-atoms at δ(C) 20.8 and 20.7, respectively, and HMBCs with two other C-atoms at δ(C) 169.9 and 170.5, respectively, indicating the presence of two Ac groups. The ring H-atoms of the monosaccharide residues were assigned starting from the anomeric H-atoms by means of TOCSY, COSY, HSQC, and HMBC experiments. Evaluation of spin–spin couplings and chemical shifts allowed the identification of one β-glucopyranosyl (Glc) and two β-xylopyranosyl (Xyl I and Xyl II) units. The common D-configurations for Glc and Xyl were assumed according to those encountered among the plant glycosides in each case. From the NOESY and HMBC experiments, the sites of attachment of the three sugars were determined to be at OH–C(3), OH–C(6), and OH–C(25) for Xyl I, Xyl II, and Glc, respectively (*Tables 1* and *2*): in the HMBC spectrum, the first anomeric H-atom at δ(H) 4.82 (H–C(1) of Xyl I) showed long-range correlation with C(3) of the aglycone at δ(H) 89.2. Also, the second anomeric H-atom at δ(H) 4.87 (H–C(1) of Xyl II) showed long-range correlation with C(6) at δ(C) 78.5. The third anomeric H-atom at δ(H) 4.94 (H–C(1) of Glc) had a HMBC with the quaternary C(25) at δ(C) 79.3. The linkage positions of Xyl I and Xyl II were confirmed by the reversed correlations δ(H) 3.40 (H–C(3) of Agly)/δ(C) 104.0 (C(1) of Xyl I) and δ(H) 3.85 (H–C(6) of Agly)/δ(C) 105.7 (C(1) of Xyl II). All these observations were supported by a NOESY experiment which showed the correlations δ(H) 3.40 (H–C(3) of Agly)/δ(H) 4.82 (H–C(1) of Xyl I) and δ(H) 3.85 (H–C(6) of Agly)/δ(H) 4.87 (H–C(1) of Xyl II). The positions of the two Ac groups were assigned at C(2) and C(3) of Xyl I according to the HMBCs δ(H) 5.44 (H–C(2) of Xyl I)/δ(C) 169.9 (C=O) and δ(H) 5.64 (H–C(3) of Xyl I)/δ(C) 170.5 (C=O).

The HR-ESI-MS (positive-ion mode) of armatoside II (**2**) exhibited a *quasi*-molecular-ion peak at *m*/*z* 981.5040 ($[M+Na]^+$), consistent with a molecular formula $C_{48}H_{78}NaO_{19}$. The negative-ion-mode FAB-MS of **2** displayed a *quasi*-molecular-ion peak at *m*/*z* 957 ($[M-H]^-$). Other fragment-ion peaks at *m*/*z* 914 ($[M-H-43]^-$), 782 ($[M-H-43-132]^-$), and 488 ($[M-H-43-132-132-162]^-$) indicated the presence of three sugar units, one hexose and two pentoses, with one Ac group. The full assignment of all the ^{1}H- and ^{13}C-NMR signals obtained from 2D-NMR analysis showed that **2** differed from **1** only by the absence of one Ac group at C(3) of Xyl I (*Tables 1* and *2*). Its structure was elucidated as (3β,6α,16β,20*R*,24*S*)-3-*O*-(2-*O*-acetyl-β-D-xylopyranosyl)-20,24-epoxy-25-*O*-β-D-glucopyranosyl-6-*O*-β-D-xylopyranosylcycloartane-3,6,16,25-tetrol. The NMR signals of **2** were similar to those of **1** with the difference that δ(H) 4.14 (H–C(3) of Xyl I) had no HMBC with a C=O signal. Only H–C(2) of Xyl I at δ(H) 5.55 showed a long-range correlation (HMBC) with δ(C) 170.0 (C=O) (*Table 2*). This last signal had a HMBC with δ(H) 2.05 (*s*) corresponding to a terminal Me group. The acetylation of C(2) of Xyl I was confirmed by a COSY cross-peak δ(H) 5.55 (H–C(2) of Xyl I)/δ(H) 4.77 (H–C(1) of Xyl I).

The two known compounds were identified as (3β,6α,16β,20*R*,24*S*)-3-*O*-[α-L-arabinopyranosyl-(1 → 2)-β-D-xylopyranosyl]-20,24-epoxy-6-*O*-β-D-xylopyranosylcy-

Table 1. *^{1}H-* (600 MHz) *and ^{13}C-NMR* (150 MHz) *Data of the Aglycone Parts of* **1** *and* **2** *from 1D- and 2D-NMR Experiments in (D_5)Pyridine.* δ in ppm, J in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1)	1.55–1.63 (*m*, H_α), 1.24–1.28 (*m*, H_β)	32.0	1.56 (*ddd*, *J* = 13.0, 12.1, 4.4, H_α), 1.26 (*ddd*, *J* = 13.0, 4.4, 3.0, H_β)	31.8
CH_2(2)	1.91–1.95 (*m*, H_α), 2.00–2.04 (*m*, H_β)	31.2	1.92–1.96 (*m*, H_α), 2.01–2.06 (*m*, H_β)	31.3
CH(3)	3.40 (*dd*, *J* = 4.4, 11.5)	89.2	3.35 (*dd*, *J* = 4.0, 11.4)	88.7
C(4)	–	42.3	–	42.2
CH(5)	1.89 (*d*, *J* = 8.4)	52.1	1.88 (*d*, *J* = 8.2)	52.1
CH(6)	3.85 (*ddd*, *J* = 8.4, 8.0, 4.2)	78.5	3.80 (*ddd*, *J* = 8.2, 7.9, 3.8)	77.9
CH_2(7)	1.94–1.97 (*m*, H_α), 2.17 (*ddd*, *J* = 4.2, 4.8, 12.3, H_β)	34.1	1.93–2.00 (*m*, H_α), 2.16 (*ddd*, *J* = 3.8, 4.7, 12.3, H_β)	33.8
CH(8)	1.85 (*dd*, *J* = 10.4, 4.8)	46.2	2.03 (*dd*, *J* = 10.5, 4.7)	44.2
C(9)	–	21.0	–	21.3
C(10)	–	28.7	–	29.9
CH_2(11)	1.86 (*ddd*, *J* = 13.5, 9.1, 4.9, H_α), 1.23–1.27 (*m*, H_β)	26.1	1.72 (*ddd*, *J* = 13.5, 9.1, 4.9, H_α), 1.37 (*ddd*, *J* = 13.5, 8.2, 6.5, H_β)	26.2
CH_2(12)	1.66 (*ddd*, *J* = 12.9, 9.1, 6.5, , 1.55–1.61 (*m*, H_β)	33.5	1.66 (H_α)[a]), 1.54 (*ddd*, *J* = 12.9, 8.2, 4.9, H_β)	33.5
C(13)	–	45.2	–	42.2
C(14)	–	46.3	–	45.2
CH_2(15)	2.33 (*dd*, *J* = 12.6, 6.7, H_α), 1.85 (*dd*, *J* = 12.7, 7.9, H_β)	46.1	2.31 (*dd*, *J* = 12.5, 6.7), H_α), 1.84 (*dd*, *J* = 12.5, 7.9, H_β)	46.0
CH(16)	4.98 (*ddd*, *J* = 7.9, 7.6, 6.7)	73.5	5.04 (*ddd*, *J* = 7.9, 7.6, 6.7)	73.4
CH(17)	2.57 (*d*, *J* = 7.6)	58.1	2.57 (*d*, *J* = 7.6)	58.0
Me(18)	1.42 (*s*)	21.1	1.39 (*s*)	20.6
CH_2(19)	0.22 (*d*, *J* = 4.0, H_α), 0.57 (*d*, *J* = 4.0, H_β)	29.1	0.14 (*d*, *J* = 4.0, H_α), 0.57 (*d*, *J* = 4.0, H_β)	27.1
C(20)	–	87.2	–	87.3
Me(21)	1.31 (*s*)	28.5	1.31 (*s*)	28.6
CH_2(22)	1.68 (*ddd*, *J* = 12.3, 9.6, 3.2, H_α), 3.12 (*ddd*, *J* = 12.3, 11.3, 9.2, H_β)	34.9	1.66 (*ddd*, *J* = 12.3, 9.6, 3.2, H_α), 3.12 (*ddd*, *J* = 12.3, 11.4, 9.2, H_β)	34.9
CH_2(23)	2.02–2.09 (*m*, H_α), 2.32 (*dddd*, *J* = 12.7, 11.3, 7.2, 3.2, H_β)	26.4	2.05 (H_α)[a]), 2.31 (*dddd*, *J* = 12.5, 11.4, 7.2, 3.2, H_β)	26.5
CH(24)	3.88 (*dd*, *J* = 8.6, 7.2)	81.7	3.89 (*dd*, *J* = 8.6, 7.2)	81.7
C(25)	–	79.3	–	79.8
Me(26)	1.30 (*s*)	27.0	1.30 (*s*)	27.1
Me(27)	1.58 (*s*)	28.2	1.58 (*s*)	28.1
Me(28)	1.10 (*s*)	19.8	1.09 (*s*)	19.7
Me(29)	1.78 (*s*)	28.3	1.96 (*s*)	29.1
Me(30)	1.35 (*s*)	16.1	1.23 (*s*)	16.6

[a]) Overlapped signals.

cloartane-3,6,16,25-tetrol (= trigonoside II, **3**) [6] and (3β,6α,16β,20*R*,24*S*)-3-*O*-[α-L-arabinopyranosyl-(1 → 2)-β-D-xylopyranosyl]-20,24-epoxy-6-*O*-β-D-glucopyranosylcycloartane-3,6,16,25-tetrol (= trojanoside H; **4**) [7], on the basis of their NMR and MS data, and by comparison with literature data.

Table 2. *^{1}H-* (600 MHz) *and ^{13}C-NMR* (150 MHz) *Data of the Saccharide Moities of* **1** *and* **2** *from 1D- and 2D-NMR Experiments in (D_5)Pyridine.* δ in ppm, J in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
Xyl I				
CH(1)	4.82 (*d*, *J* = 7.6)	104.0	4.77 (*d*, *J* = 7.6)	104.7
CH(2)	5.44 (*dd*, *J* = 9.2, 7.6)	73.4	5.55 (*dd*, *J* = 8.5, 7.6)	75.4
CH(3)	5.64 (*dd*, *J* = 9.2, 8.8)	76.8	4.14[a])	76.3
CH(4)	4.23[a])	68.8	4.18[a])	71.3
CH_2(5)	3.66 (*dd*, *J* = 9.8, 10.2), 4.30 (*dd*, *J* = 5.5, 10.2)	66.8	3.67 (*dd*, *J* = 9.8, 10.2), 4.28 (*dd*, *J* = 5.5, 10.2)	67.0
*Ac*O–C(2)	2.04 (*s*)	169.9, 20.8	2.05 (*s*)	170.0, 21.1
*Ac*O–C(3)	1.96 (*s*)	170.5, 20.7	–	–
Xyl II				
CH(1)	4.87 (*d*, *J* = 7.0)	105.7	4.87 (*d*, *J* = 7.0)	105.7
CH(2)	4.00 (*dd*, *J* = 7.0, 8.5)	75.3	4.00 (*dd*, *J* = 7.0, 8.5)	75.4
CH(3)	4.13 (*t*, *J* = 8.5)	78.6	4.13 (*t*, *J* = 8.5)	78.6
CH(4)	4.17[a])	71.3	4.18[a])	71.1
CH_2(5)	3.71 (*dd*, *J* = 9.5, 10.2), 4.28 (*dd*, *J* = 5.5, 10.2)	67.0	3.70 (*dd*, *J* = 9.5, 10.2), 4.28 (*dd*, *J* = 5.5, 10.2)	67.2
Glc				
CH(1)	4.94 (*d*, *J* = 7.2)	105.2	4.94 (*d*, *J* = 7.4)	105.2
CH(2)	4.04 (*dd*, *J* = 7.2, 9.3)	75.6	4.04 (*dd*, *J* = 7.4, 9.1)	75.6
CH(3)	4.20[a])	79.2	4.22 (*t*, *J* = 9.1)	79.2
CH(4)	4.18[a])	71.9	4.20 (*t*, *J* = 9.1)	71.2
CH(5)	3.90 (*ddd*, *J* = 9.3, 5.7, 2.9)	78.1	3.91 (*ddd*, *J* = 9.1, 5.7, 2.9)	78.1
CH_2(6)	4.32 (*dd*, *J* = 5.7, 12.1), 4.28 (*dd*, *J* = 2.9, 12.1)	63.1	4.32 (*dd*, *J* = 5.7, 12.1), 4.49 (*dd*, *J* = 2.9, 12.1)	63.1

[a]) Overlapped signals.

The isolation from the roots of *A. membranaceus* of compounds closely related to **1** and **2** with a β-D-glucopyranosyloxy instead of a β-D-xylopyranosyloxy group at position 6 of the aglycone has been reported [9]. From the roots of *A. trojanus*, a not acetylated tridesmoside of cycloastragenol having the same sugars than **1** and **2** (Xyl I, Xyl II, Glc) has been obtained [10]. Thus, *A. armatus* appears to be differentiated from the two other species by a 6-*O*-Xyl moiety combined with an acetylated 3-*O*-Xyl moiety. In the genus *Astragalus*, only a few tridesmosides of cycloastragenol have been described compared with bi- and monodesmosides [9–11]. Also, cycloastragenol substituted by a 6-*O*-Xyl moiety was detected in few cases, viz. in *A. trojanus*, *A. gilvus* (Turkey), *A. trigonus* (Egypt), *A. adsurgens*, and *A. sieversianus* (China) [6][10–15]. When it was not free, the position 6 was generally substituted by a GlcO unit [7][9–11][13][15–27]. The position 25 was generally described as being free (OH–C(25)), but in the few substitution cases, it was attached to a GlcO unit [9][10][17][22][26][28–32]. Thus, the presence of tridesmosides with a 6-*O*-Xyl unit and a 25-*O*-Glc unit appears to be characteristic of *A. armatus* and *A. trojanus*. Finally in most cases, the position 3-*O* was described to be glycosylated by Glc or Xyl [2][13–

15][23–25][27], and the Xyl was often *O*-acetylated at positions 2, 3, and/or 4. Such a general chemical trait highlights a common metabolic backbone in the genus *Astragalus*.

Experimental Part

General. TLC: silica gel *60* F_{254} (SiO_2; *Merck*); eluent $CHCl_3$/MeOH/HCOOH/H_2O 80:20:4:2; detection with *Komarowsky* reagent, a 5:1 mixture of 2% 4-hydroxybenzaldehyde in MeOH and 50% H_2SO_4 soln. Vacuum liquid chromatography (VLC): *Lichroprep RP-8* (25–40 μm; *Merck*). Medium-pressure liquid chromatography (MPLC): SiO_2 *60* (15–40 μm; *Merck*), *Gilson* pump *M 305*; *Büchi* columns (460 × 25 mm and 460 × 15 mm); *Büchi* precolumn (110 × 15 mm). IR Spectra: *Perkin-Elmer 281* IR spectrophotometer; KBr disc; $\tilde{\nu}$ in cm^{-1}. Optical rotation: *Perkin-Elmer-241* polarimeter. 1D- and 2D-NMR Spectra (^{1}H,^{1}H-COSY, TOCSY, NOESY, HSQC, and HMBC): *Varian-Unity-Nova-600* instrument equipped with a *SUN-4-L-X* computer system; at 600 (^{1}H) and 150 MHz (^{13}C) and 20°; conventional pulse sequences for COSY, HSQC, and HMBC; standard MLEV17 spin-locking sequence and 90 ms mixing time for TOCSY; 500 ms mixing time for NOESY; C-type (Me, CH_2, CH) by DEPT experiments; chemical shifts δ in ppm, J in Hz; (D_5)pyridine solns. (δ(C) 150.3, 155.9, and 123.9). HR-ESI-MS: *Q-TOF-1-Micromass* spectrometer; in *m*/*z* (rel. %). FAB-MS: *Jeol-SX-102* spectrometer (neg.-ion mode; glycerol matrix); in *m*/*z* (rel. %).

Plant Material. The roots of *Astragalus armatus* were collected in Medenine, Tunisia, in June 2007, and provided by *Y. M.* A voucher specimen (No. 19072007) was deposited with the Herbarium of the Laboratory of Pharmacognosy, Faculty of Pharmacy, Dijon, France.

Extraction and Isolation Procedures. Air-dried powdered roots of *A. armatus* (320 g) were extracted twice under reflux for 1 h with 70% MeOH (3.5 l). After evaporation of the solvent, the extract (43.4 g) was dissolved in H_2O (400 ml) and partitioned with H_2O-sat. BuOH (3 × 400 ml). The BuOH-soluble part (39 g) was subjected to VLC (*Lichroprep RP-8*, H_2O/MeOH 1:0, 1:1, and 0:1). An aliquot (1 g) of the fraction eluted with MeOH (6.2 g) was subjected to successive MPLC (SiO_2 *60*, $CHCl_3$/MeOH/H_2O 80:20:2): **1** (5 mg), **2** (5 mg), **3** (10 mg), and **4** (5 mg).

Armatoside I (=*(3β,6α,16β,20*R,*24*S*)-3-[(2,3-Di*-O*-acetyl-β-*D*-xylopyranosyl)oxy]-20,24-epoxy-16-hydroxy-6-(β-*D*-xylopyranosyloxy)-9,19-cyclolanostan-25-yl β-*D*-Glucopyranoside*; **1**): White amorphous powder. TLC: R_f 0.42. $[\alpha]_D^{25} = +5.5$ ($c = 2.74$, MeOH). IR: 3425, 1750, 1250, 1035. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 999 ($[M-H]^-$), 867 ($[M-H-132]^-$), 837 ($[M-H-162]^-$), 781 ($[M-H-132-43-43]^-$), 649 ($[M-H-132-132-43-43]^-$). HR-ESI-MS (pos.): 1023.5150 ($[M+Na]^+$, $C_{50}H_{80}NaO_{20}^+$; calc. 1023.5141).

Armatoside II (=*(3β,6α,16β,20*R,*24*S*)-3-[(2-O-acetyl-β-*D*-xylopyranosyl)oxy]-20,24-epoxy-16-hydroxy-6-(β-*D*-xylopyranosyloxy)-9,19-cyclolanostan-25-yl β-*D*-Glucopyranoside*; **2**): White amorphous powder. TLC: R_f 0.32. $[\alpha]_D^{25} = +13.7$ ($c = 0.75$, MeOH); IR: 3430, 1755, 1250, 1038. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 957 ($[M-H]^-$), 914 ($[M-H-43]^-$), 782 ($[M-H-43-132]^-$), 488 ($[M-H-43-132-132-162]^-$). HR-ESI-MS (pos.): 981.5040 ($[M+Na]^+$, $C_{48}H_{78}NaO_{19}^+$; calc. 981.5035).

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