Four New Flavonol Glycosides from the Leaves of *Astragalus caprinus*

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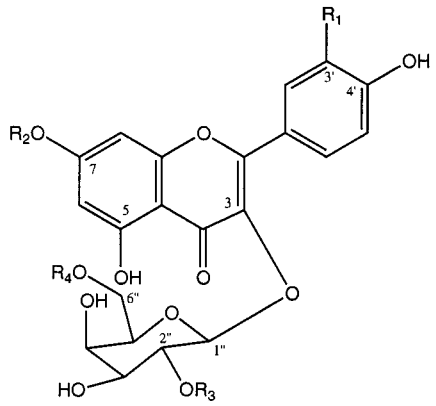
Received June 29, 2001

Four new flavonol 3-*O*-glycosides were isolated from the leaves of *Astragalus caprinus*. Their structures were elucidated by spectroscopic methods as rhamnocitrin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**1**), rhamnetin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)]-[β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**2**), kaempferol-3-*O*-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside (**3**), and quercetin-3-*O*-{[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**4**).

Astragalus caprinus Maire (Fabaceae) is an endemic species of North Africa, the leaves of which are used as an antihemorrhoidal agent in Tunisian folk medicine. Our previous paper describing the structure of a new 3-*O*-tetraglycoside of kaempferol from this plant was the first phytochemical report on this species.[1] Herein we report the isolation and structure elucidation of four new flavonol glycosides. Their structures were elucidated by spectroscopic methods as rhamnocitrin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**1**), rhamnetin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**2**), kaempferol-3-*O*-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside (**3**), and quercetin-3-*O*-{[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl-(1→6)][β-d-apiofuranosyl(1→2)]}-β-D-galactopyranoside (**4**). Compounds **1**−**4** are new according to the literature.[2−4]



	R_1	R_2	R_3	R_4
1	H	CH_3	api	3-OH-3-CH_3-glut
2	OH	CH_3	api	3-OH-3-CH_3-glut
3	H	H	H	-rha 3-xyl
4	OH	H	api	-rha 3-xyl

Compound **1** was isolated as an amorphous yellow powder. Its UV spectral properties indicated a 3,7-disubstituted kaempferol derivative.[5,6] Chromatography of the acid hydrolysis products allowed the identification of 7-methylkaempferol (rhamnocitrin) and apiose and galactose. The HRFABMS (positive-ion mode) of **1** exhibited a pseudomolecular ion peak at *m*/*z* 761.1908 $[M + Na]^+$ (calcd 761.1905), consistent with a molecular formula of $C_{33}H_{38}O_{19}$. Its ESIMS (positive-ion mode) displayed a pseudomolecular ion peak $[M + H]^+$ at *m*/*z* 739 and fragment ion peaks at *m*/*z* 607 $[M + H - 132]^+$, indicating the loss of apiose, and at *m*/*z* 301 $[M + H - 132 - 306]^+$, which was assigned to the additional loss of galactose (−162) linked to an unassigned moiety (−144). The peak at 1720 cm^{-1} in the IR spectrum was suggestive of a saturated acyl moiety. The ^1H NMR spectrum of **1** exhibited a signal at δ 3.95 (3H, s), which correlated in the HSQC spectrum to a ^{13}C NMR signal at δ 56.5 and corresponded to the methoxy group at C-7 of the aglycon (Table 1).[7] Four aromatic doublets corresponded to H-6 [δ 6.30 (1H, *J* = 1.9 Hz)], *meta*-coupled with H-8 [δ 6.59 (1H, *J* = 1.9 Hz)] on the A ring, and to H-2′, H-6′ [δ 8.13 (2H, *J* = 8.8 Hz)], *ortho*-coupled with H-3′, H-5′ [δ 6.90 (2H, *J* = 8.8 Hz)]. Full identification of the aglycon was finally achieved by 2D NMR spectroscopy, which led to the rhamnocitrin structure. Two anomeric protons at δ 5.44 (1H, d, *J* = 7.5 Hz) and at δ 5.45 (1H, d, *J* = 1.6 Hz) were assigned to a β-galactopyranosyl (Gal) and a β-apiofuranosyl (Api) unit, respectively, by a HSQC-TOCSY experiment and coupling constant measurements. HMBC experiments showed correlations between Gal H-1 and rhamnocitrin C-3 (δ 135.0) and between Api H-1 and Gal C-2 (δ 76.8). The downfield chemical shifts of the Gal methylene protons and Gal C-6 (Table 1) suggested acylation of the galactose unit at C-6.[8] These protons were correlated in the HMBC spectrum with a carboxylic carbon at δ 172.2. The HSQC and HMBC spectra showed this carboxyl to belong to an aliphatic acyl moiety, where it was successively linked to a methylene group [δ_C 46.0; δ_H 2.35 (d, *J* = 15.1 Hz); δ_H 2.42 (d, *J* = 15.1 Hz)], a central quaternary carbon (δ 70.6), another methylene group [δ_C 46.3; δ_H 2.36 (d, *J* = 14.9 Hz); δ_H 2.46 (d, *J* = 14.9 Hz)], and a terminal carboxyl (δ 175.6). Additionally, the central quaternary carbon (C-3) showed a HMBC correlation with a methyl group at δ_H 1.13 (3H, s) and δ_C 27.9. Consequently, the aliphatic acyl moiety was identified as a 3-hydroxy-3-methylglutaroyl substituent. On the basis of all these data, **1** was identified as rhamnocitrin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside. Esterification with 3-hydroxy-3-

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10.1021/np010328l CCC: $22.00
Published on Web 03/01/2002

Table 1. ^{13}C and ^{1}H NMR Spectral Data of Compounds **1** and **2** in CD_3OD

	1		**2**	
position	δ_C	δ_H (J Hz)	δ_C	δ_H (J Hz)
aglycon				
2	158.8		158.8	
3	135.0		135.2	
4	179.6		179.5	
5	162.8		162.9	
6	99.0	6.30 d (1.9)	99.0	6.30 d (1.9)
7	167.2		167.2	
8	93.1	6.59 d (1.9)	93.0	6.58 d (1.9)
9	158.3		158.3	
10	106.7		106.7	
1′	122.8		123.1	
2′	132.4	8.13 d (8.8)	117.3	7.72 d (2.2)
3′	116.2	6.90 d (8.8)	149.9	
4′	161.6		146.0	
5′	116.2	6.90 d (8.8)	116.2	6.90 d (8.2)
6′	132.4	8.13 d (8.8)	123.4	7.68 dd (2.2, 8.2)
OMe-7	56.5	3.95 s	56.5	3.85 s
gal				
1	101.0	5.44 d (7.5)	101.4	5.42 d (7.6)
2	76.8	3.93 dd (7.9, 9.8)	76.6	3.96 dd (7.6, 9.5)
3	75.1	3.71[a]	75.1	3.72[a]
4	70.6	3.78 dd (0.6, 3.1)	70.7	3.81 dd (1.0, 3.1)
5	74.4	3.70[a]	74.3	3.70[a]
6	64.5	4.11 dd (7.6, 11.4)	64.2	4.09[a]
		4.13 dd (7.6, 11.4)		4.09[a]
api				
1	109.8	5.45 d (1.6)	110.8	5.46 d (1.3)
2	78.1	4.05 d (1.6)	78.1	4.05 d (1.3)
3	80.9		80.9	
4	75.5	3.72 d (9.8)	75.6	3.70 d (10.3)
		4.07 d (9.8)		4.06 d (10.3)
5	66.2	3.63 d (11.6)	66.3	3.64 d (11.4)
		3.72 d (11.6)		3.75 d (11.4)
glutaroyl				
1	172.2		172.2	
2	46.0	2.35 d (15.1)	46.8	2.35 d (13.9)
		2.42 d (15.1)		2.41 d (13.9)
3	70.6		70.7	
4	46.3	2.36 d (14.9)	46.8	2.25 d (15.4)
		2.46 d (14.9)		2.38 d (15.4)
5	175.6		176.0	
Me-3	27.9	1.13 s	27.7	1.10 s

[a] Multiplicities were unclear due to overlapping with other signals.

methylglutaric acid is rarely found in the flavonoid literature. [9]

Compound **2** was isolated as an amorphous yellow powder. Its UV spectral properties and ESIMS showed that **2** differed from **1** only by an additional hydroxy group at C-3′ on the aglycon.[5,6] The HRFABMS (positive-ion mode) of **2** exhibited a pseudomolecular ion peak at m/z 777.1864 $[M + Na]^+$(calcd 777.1854), consistent with a molecular formula of $C_{33}H_{38}O_{20}$. Chromatography of the acid hydrolysis products allowed the identification of 7-methylquercetin (rhamnetin), and apiose and galactose. The occurrence in the ^{1}H NMR spectrum of an ABM spin system [δ 7.72 (d, $J = 2.2$ Hz), 6.90 (d, $J = 8.2$ Hz), and 7.68 (dd, $J = 2.2$, 8.2 Hz)] characterized an *ortho*-disubstituted B ring (Table 1). Thus, **2** was identified as rhamnetin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside. According to the literature, rhamnetin is rare in the genus *Astragalus*.[10]

Compound **3** was isolated as an amorphous yellow powder. Its chromatographic behavior and UV spectral properties suggested **3** to be a kaempferol 3-oligoglycoside.[5,6] The HRFABMS (positive-ion mode) of **3** exhibited a pseudomolecular ion peak at m/z 749.1907 $[M + Na]^+$ (calcd 749.1905), consistent with the molecular formula

Table 2. ^{13}C and ^{1}H NMR Spectral Data of Compounds **3** in CD_3OD and **4** in DMSO-d_6

	3		**4**	
position	δ_C	δ_H (J Hz)	δ_C	δ_H (J Hz)
aglycon				
2	159.4		156.7	
3	135.8		134.0	
4	179.6		178.1	
5	162.9		161.9	
6	100.0	6.20 d (1.9)	99.4	6.19 d (1.9)
7	166.0		164.8	
8	95.0	6.39 d (1.9)	94.3	6.39 d (1.9)
9	158.5		157.1	
10	105.6		104.7	
1′	122.6		122.0	
2′	132.6	8.10 d (8.8)	116.5	7.60 d (2.2)
3′	116.1	6.88 d (8.8)	145.6	
4′	161.6		149.1	
5′	116.1	6.88 d (8.8)	116.0	6.82 d (8.8)
6′	132.6	8.10 d (8.8)	123.1	7.74 dd (2.2, 8.8)
gal				
1	105.6	5.02 d (7.9)	100.0	5.52 d (7.9)
2	73.0	3.80 dd (7.9, 9.5)	75.5	3.78 dd (7.9, 10.1)
3	74.9	3.56 dd (3.5, 9.5)	74.1	3.62a
4	70.0	3.76[a]	69.1	3.60[a]
5	75.5	3.66[a]	74.0	3.58[a]
6	68.0	3.48[a]	65.9	3.28[a]
		3.70[a]		3.57[a]
rha				
1	101.9	4.52 d (1.9)	100.9	4.39 d (1.6)
2	71.7	3.77 dd (1.9, 3.2)	70.5	3.55[a]
3	82.4	3.55 dd (3.2, 9.5)	81.8	3.38[a]
4	72.7	3.44 t (9.5)	71.6	3.32[a]
5	69.5	3.54[a]	68.7	3.42[a]
6	18.1	1.16 d (6.0)	18.6	1.06 d (6.0)
xyl				
1	106.5	4.32 d (7.2)	106.0	4.27 d (7.3)
2	74.9	3.23 dd (7.2, 9.1)	74.6	3.05[a]
3	77.3	3.31[a]	76.7	3.12[a]
4	71.1	3.46 m	70.2	3.25 ddd (5.0, 9.1, 13.2)
5	66.9	3.09 dd (10.4, 11.4)	66.4	3.05[a]
		3.76[a]		3.66[a]
api				
1			109.6	5.31 d (1.6)
2			76.9	3.82[a]
3			80.0	
4			74.8	3.85[a]
				3.50[a]
5			65.1	3.39 d (8.9)
				3.47 d (8.9)

[a] Multiplicities were unclear due to overlapping with other signals.

$C_{32}H_{38}O_{19}$. The ESIMS gave a pseudomolecular ion peak $[M + H]^+$ at m/z 727 and three other ion peaks at m/z 595 $[M + H - 132]^+$, 449 $[M + H - 132 - 146]^+$, and 287 $[M + H - 132 - 146 - 162]^+$, indicating a terminal pentosyl, an intermediate rhamnosyl, and a primary hexosyl. Acid hydrolysis gave kaempferol and three sugars, identified by co-TLC as xylose, rhamnose, and galactose. On the basis of its ^{1}H and ^{13}C NMR data, the triglycoside **3** differed from a previously published kaempferol derivative from *A. caprinus* by the absence of apiose (Table 2).[1] Three anomeric ^{1}H NMR signals at δ 5.02 (d, $J = 7.9$ Hz), 4.52 (d, $J = 1.9$ Hz), and 4.32 (d, $J = 7.2$ Hz) were assigned to three corresponding ^{13}C NMR signals via HSQC correlations. A HSQC-TOCSY experiment and coupling constant measurements permitted the identification of the three sugar units as β-galactopyranosyl (Gal), α-rhamnopyranosyl (Rha), and β-xylopyranosyl (Xyl) (Table 2). HMBC experiments showed correlations between Gal H-1 (δ 5.02) and kaempferol C-3 (δ 135.8), Rha H-1/C-1 (δ 4.52/101.9) and Gal C-6/H-6 (δ 68.0/3.48), and Xyl H-1/C-1 (δ 4.32/106.5) and Rha C-3/H-3

(δ 82.4/3.55). Consequently, the structure of **3** was established as kaempferol-3-*O*-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside. According to the literature, flavonol tri- or higher glycosides are infrequent in the genus *Astragalus*.[11−13] The present work on *A. caprinus* has resulted in only the second report of a flavonol xyloside in this genus.[1,14]

Compound **4** was isolated as an amorphous yellow powder. Its chromatographic behavior and UV spectral properties suggested this compound to be a quercetin 3-oligoglycoside.[5,6] The HRFABMS (positive-ion mode) of **4** exhibited a pseudomolecular ion peak at *m/z* 897.2293 $[M + Na]^+$ (calcd 897.2277), consistent with a molecular formula of $C_{37}H_{46}O_{24}$. The ESIMS (positive-ion mode) displayed a pseudomolecular ion peak $[M + H]^+$ at *m/z* 875 and showed that **4** differed from the previously published kaempferol tetraglycoside from this same plant only by an additional hydroxy group on the aglycon.[1] This was confirmed by acid hydrolysis, which yielded quercetin and the same sugars, namely, galactose, apiose, xylose, and rhamnose. The ^{1}H and ^{13}C NMR spectral data showed that **4** is a quercetin tetraglycoside with the same saccharide structure as an already known kaempferol tetraglycoside from this species (Table 2).[1] Four anomeric doublet signals corresponded to four sugar units at δ 4.27 (1H, J = 7.3 Hz), 4.39 (1H, J = 1.6 Hz), 5.31 (1H, J = 1.6 Hz), and 5.52 (1H, J = 7.9 Hz). A HMBC experiment allowed the glycosidic linkages to be determined between kaempferol C-3 (δ 134.0) and galactose H-1 (δ 5.52), Gal C-2 (δ 75.5) and Api H-1 (δ 5.31), Gal C-6 (δ 65.9) and Rha H-1 (δ 4.39), and Rha C-3 (δ 81.8) and Xyl H-1 (δ 4.27). Consequently, the structure of **4** was established as quercetin-3-*O*-{[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. UV and IR spectra were recorded on a Kontron Uvikon-860 and a Perkin-Elmer 681 spectrophotometer, respectively. The 1D and 2D NMR spectra (HSQC, HSQC-TOCSY, HMBC) were performed in CD_3OD for **1**−**3** and DMSO-d_6 for **4**, using a Bruker DRX 500 NMR spectrometer equipped to allow inverse detection (500 MHz for ^{1}H and 125 MHz for ^{13}C). ESIMS data were obtained on a Hewlett-Packard 1100 MSD spectrometer (100 and 150 eV) in the positive-ion mode. HRFABMS were obtained in the positive-ion mode (thioglycerol matrix) on a ZAB2-SEQ instrument. TLC were performed on polyamide [DC6, Macherey-Nagel; mobile phase, H_2O−MeOH−MeCOEt−2,4-pentanedione (13:3:3:1); system *p*] and cellulose [DC-microcrystalline, Merck, mobile phase, *n*-BuOH−AcOH−H_2O (4:1:5 upper phase); system *c*]. HPLC was conducted on a Kontron LC set (autosampler 360, pump 322) coupled to a Waters 991 diode array detector on a reversed-phase C_{18} Ultrabase (5 μm) column (200 × 4.6 mm i.d.), with a linear gradient from 10 to 45% of MeCN in H_2O with 2% AcOH for 118 min, a flow rate of 0.8 mL min^{-1}, and a detection range of 230−410 nm (system *hp*). MPLC separations were performed on a Büchi system equipped with a B-688 pump coupled to a B-687 gradient programmer, using 110 × 15 mm precolumns, 460 × 26 mm columns, filled with the stationary phase C_{18} [(40−63 μm, Merck), solvent, 50% MeOH in water, flow rate, 10 mL min^{-1}; system *rmp*], and 460 × 15 mm columns, filled with the stationary phase Lichroprep-diol [(40−63 μm, Merck) gradient of *i*-PrOH in $CHCl_3$ (linear 5 to 30% in 210 min, flow 6 mL min^{-1}; system *smp*]. Elution was monitored with a Knauer K-2501 UV detector set at 350 nm. Purification was carried out over Sephadex (LH-20, Pharmacia).

Plant Material. The leaves of *Astragalus caprinus* were collected during April−May 1998 at Monastir, Tunisia. A voucher specimen (No. 98/0039) is deposited at the Faculty of Pharmacy, University of Monastir, Tunisia.

Extraction and Isolation. Dried, powdered leaves (200 g) were macerated twice with 70% MeOH (500 mL) for 24 h. After partial evaporation the aqueous solution was extracted with *n*-BuOH (3 × 300 mL). The residue from the *n*-BuOH layer was prepurified on a cellulose column (5% EtOH), then separated on a polyamide column (5 to 40% EtOH). The fraction eluted with 5% EtOH was subjected to MPLC (system *rmp*), with the subfraction containing **4** (eluted with 50% MeOH) chromatographed on Sephadex with 50% MeOH to yield pure **4** (26 mg). The fraction eluted from polyamide with 25% EtOH was subjected to MPLC (system *smp*), with the subfraction containing **3** (eluted with 20% *i*-PrOH) purified by preparative TLC (system *p*), then by passage over Sephadex, eluted with MeOH, to yield **3** (13 mg). The fraction eluted from polyamide with 40% EtOH was subjected to MPLC (system *rmp*), with the subfractions containing **1** and **2**, respectively, then submitted to preparative TLC (system *p*, twice) followed by Sephadex eluted with MeOH to afford **1** (5 mg) and **2** (2 mg). Purity was monitored by HPLC (system *hp*). Compounds **1**−**4** were obtained as pale yellow amorphous powders.

Rhamnocitrin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)]-[β-D- apiofuranosyl(1→2)]}-β-D-galactopyranoside (1): $[\alpha]^{20}_D$ −81° (*c* 0.14, MeOH); UV λ_{max} (MeOH) 266 (log ϵ 4.39), 345 (log ϵ 4.29) nm; (MeOH + $AlCl_3$) 275, 293, 347, 397 nm; (MeOH + $AlCl_3$ + HCl) 274, 293, 346, 395 nm; (MeOH + NaOAc) 266, 351 nm; (MeOH + NaOAc + H_3BO_3) 266, 345 nm; (MeOH + NaOH) 266, 389 nm; (MeOH + NaOH, after 10 min) 266, 389 nm; IR ν_{max}(KBr) 3420, 2940, 1720, 1660, 1595, 1495, 1350, 1215, 1170, 1270, 1085, 1060 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 1; ESIMS *m/z* 739 $[M + H]^+$ (100), 607 $[M + H - 132]^+$ (60), 301 $[M + H - 132 - 306]^+$ (65); positive HRFABMS *m/z* 761.1908 $[M + Na]^+$ (calcd for $C_{33}H_{38}O_{19}Na$, 761.1905); TLC R_f 0.76 (system *c*), 0.20 (system *p*); HPLC R_t 78.2 min (system *hp*).

Rhamnetin-3-*O*-{[3-hydroxy-3-methylglutaroyl(1→6)]-[β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (2): $[\alpha]^{20}_D$ −67° (*c* 0.13, MeOH); UV λ_{max} (MeOH) 256 (log ϵ 4.40), 267, 354 (log ϵ 4.28) nm; (MeOH + $AlCl_3$) 275, 423 nm; (MeOH + $AlCl_3$ + HCl) 270, 358 (sh), 270 nm; (MeOH + NaOAc) 258, 357 nm; (MeOH + NaOAc + H_3BO_3) 260, 369 nm; (MeOH + NaOH) 264, 393 nm; (MeOH + NaOH, after 10 min) 264, 392 nm; IR ν_{max} (KBr) 3410, 2935, 1715, 1655, 1600, 1500, 1350, 1215, 1270, 1085, 1060 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 1; ESIMS *m/z* 755 $[M + H]^+$ (100), 623 $[M + H - 132]^+$ (20), 317 $[M + H - 132 - 306]^+$ (35); positive HRFABMS *m/z* 777.1864 $[M + Na]^+$ (calcd for $C_{33}H_{38}O_{20}Na$, 777.1854); TLC R_f 0.66 (system *c*), 0.18 (system *p*); HPLC R_t 70.2 min (system *hp*).

Kaempferol-3-*O*-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside (3): $[\alpha]^{20}_D$ −33.4° (*c* 0.46, MeOH); UV λ_{max} (MeOH) 266 (log ϵ 4.36), 349 (log ϵ 4.30) nm; (MeOH + $AlCl_3$) 274, 304, 348, 398 nm; (MeOH + $AlCl_3$ + HCl) 275, 304, 343, 396 nm; (MeOH + NaOAc) 272, 357 nm; (MeOH + NaOAc + H_3BO_3) 266, 339 nm; (MeOH + NaOH) 273, 324, 390 nm; (MeOH + NaOH, after 10 min) 273, 324, 390 nm; IR ν_{max} (KBr) 3400, 2915, 1655, 1605, 1495, 1355, 1205, 1280, 1085, 1060 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 2; ESIMS *m/z* 727 $[M + H]^+$ (100), 595 $[M + H - 132]^+$ (15), 449 $[M + H - 132 - 146]^+$ (10), 287 $[M + H - 132 - 146 - 162]^+$ (10); positive HRFABMS *m/z* 749.1907 $[M + Na]^+$ (calcd for $C_{32}H_{38}O_{19}$ Na, 749.1905); TLC R_f 0.50 (system *c*), 0.61 (system *p*); HPLC R_t 33.2 min (system *hp*).

Quercetin-3-*O*-{[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)][β-D-apiofuranosyl(1→2)]}-β-D-galactopyranoside (4): $[\alpha]^{20}_D$ −78.6° (*c* 0.17, MeOH); UV λ_{max} (MeOH) 255 (log ϵ 4.41), 267, 356 (log ϵ 4.32) nm; (MeOH + $AlCl_3$) 275, 435 nm; (MeOH + $AlCl_3$ + HCl) 269, 362, 401 nm; (MeOH + NaOAc) 272, 369 nm; (MeOH + NaOAc + H_3BO_3) 260, 374 nm; (MeOH + NaOH) 271, 405 nm; (MeOH + NaOH, after 10 min) 271, 405 nm; IR ν_{max} (KBr) 3380, 2920, 1652, 1605, 1500, 1355, 1205, 1180, 1280, 1130, 1080, 1045 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table 2; ESIMS *m/z* 875 $[M + H]^+$ (100), 743

$[M + H - 132]^+$ (15), 597 $[M + H - 132 - 146]^+$ (10), 465 $[M + H - 132 - 146 - 132]^+$ (10), 303 $[M + H - 132 - 146 - 132 - 162]^+$ (10); positive HRFABMS *m/z* 897.2293 $[M + Na]^+$ (calcd for $C_{37}H_{46}O_{24}$ Na, 897.2277); TLC R_f 0.35 (system *c*), 0.83 (system *p*); HPLC R_t 23.8 min (system *hp*).

Acid Hydrolysis of Compounds 1−4. Performed using a previously described procedure.[1]

Acknowledgment. This work was supported by a grant and a scholarship from the Rhone-Alpes (Fr)-Monastir (Tn) Research Convention.

References and Notes

(1) Semmar, N.; Fenet, B.; Lacaille-Dubois, M. A.; Gluchoff-Fiasson, K.; Chemli, R.; Jay, M. *J. Nat. Prod.* **2001**, *64*, 656−658.
(2) Markham, K. R.; Geiger, H. In *The Flavonoids: Advances in Research since 1986*; Harborne, J. B., Ed.; Chapman & Hall: London, 1994; pp 441−497.
(3) Bohm, B. A. S. *Introduction to Flavonoids: Chemistry and Biochemistry of Organic Natural Products*; Harwood Academic Publishers: Australia, 1998; Vol. 2.
(4) Harborne, J. B.; Baxter, H. *The Handbook of the Natural Flavonoids*; Harborne and Baxter, Eds.; Wiley & Son: Chichester, 1999; Vol. 1.
(5) Mabry, T. J.; Markham, K. R.; Thomas, M. B. *Systematic Identification of Flavonoids*; Springer-Verlag: New York, 1970.
(6) Markham, K. R. *Techniques of Flavonoid Identification*; Academic Press: London, 1982.
(7) Agrawal, P. K.; Thakur, R. S.; Bansal, M. C. In *Carbon-13 NMR of Flavonoids*; Agrawal P. K., Ed.; Elsevier: Amsterdam, 1989; pp 150−155.
(8) Bashir, A.; Hamburger, M.; Hiller, K.; Gupta, M. P.; Krause, E.; Solis, P. N.; Hostettmann, K. *Phytochemistry* **1991**, *30*, 3781−3784.
(9) Tschan, G. M.; König, G. M.; Wright, A. D.; Sticher, O. *Phytochemistry* **1996**, *41*, 643−646.
(10) Yasinov, R. K.; Syrovezho, N. V.; Yakovlev, G. P.; Ovcharenko, S. N. *Khim. Prir Soedin.* **1984**, *4*, 523−524.
(11) Bedir, E.; Calis, I.; Piacente, S.; Pizza, C.; Khan, I. A. *Chem. Pharm. Bull.* **2000**, *48*, 1994−1995.
(12) Yahara, S.; Kohhjyouma, M.; Kohoda, H. *Phytochemistry* **2000**, *53*, 469−471.
(13) Alaniya, M. D.; Chkadua, N. F. *Chem. Nat. Compd.* **2000**, *36*, 537.
(14) Alaniya, M. D.; Komissarenko, N. F.; Kemertelidze, E. P. *Izv. Akad. Nauk Gruz SSR, Ser. Khim.* **1976**, *2*, 31−38.

NP010328L