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TRITERPENES AND QUINOVIC ACID GLYCOSIDES FROM *UNCARIA TOMENTOSA*

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Key Word Index—*Uncaria tomentosa*; Rubiaceae; polyoxygenated triterpenes; quinovic acid glycosides.

Abstract—Three new polyoxygenated triterpenes and six new quinovic acid glycosides have been isolated from *Uncaria tomentosa*. The triterpenes are based on ursolic or quinovic acid structures; the glycosides have a C-3, a C-3,27 or a C-27 glycosylation pattern, and the sugar moieties are made up of one to three hexopyranoses (rhamnose, glucose, quinovose, galactose). Their structures were determined by spectral methods. Copyright © 1997 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

The root bark of *Uncaria tomentosa* (Willd.) DC. has many traditional uses in South America including the treatment of gastritis, arthritis, cancer and inflammatory conditions. The first investigated constituents of the plant matter were oxindole alkaloids [1]. A more selective extraction procedure through a succession of solvents of increasing polarity gave a glucoindole alkaloid and six quinovic acid glycosides assigned to four groups having a C-3, a C-28, a C-3,28 or a C-3,27 glycosylation pattern [2–4]. These glycosides were characteristic of plants belonging to the family Rubiaceae [5–7]. Also, polyoxygenated triterpenes based on the ursolic acid skeleton [8] were found in the plant. In continuation of our work on *U. tomentosa*, we now report the results of a different and simplified extraction method which led to the isolation of nine minor constituents, i.e. three new polyoxygenated triterpenes (**1**–**3**) and six new quinovic acid glycosides with a C-3 (**4**–**7**), a C-3,27 (**8**) or a C-27 (**9**) substitution pattern.

RESULTS AND DISCUSSION

A methanolic extract of *U. tomentosa*, after separation, gave compounds **1**–**9**, the known triterpene **10** and the alkaloids pteropodine and isopteropodine [1], in addition to the major compounds previously reported [1–4, 8].

Compound **1** was assigned the molecular formula $C_{30}H_{46}O_5$. Mass spectrometry and ^{13}C and DEPT ^{13}C NMR analysis indicated its triterpenoid nature. The ^{13}C NMR spectrum showed the presence of a -COOH (δ 182.0), a keto (δ 220.5), a secondary alcohol (δ 69.3) and a tertiary alcohol (δ 73.6) group. In the EI mass spectrum significant fragments, resulting from the retro-Diels–Alder cleavage of ring C, were observed at *m/z* 264, 246 $[264-18]^+$ and 201 $[246-COOH]^+$; the carboxyl group was located at C-17 and the first hydroxyl group on ring D/E. A further fragment at *m/z* 222 indicated that the second hydroxyl group and the keto group were located on rings A or B of an urs-12-ene skeleton [8]. The ^1H NMR spectrum showed signals ascribable to six tertiary (between δ 1.16 and 1.56) and a secondary methyl (δ 0.95, $J = 6.0$ Hz) group; a methine on a carbon bearing a hydroxyl group (δ 4.45, *m*, $W_{1/2} = 6$ Hz, H-6); an olefinic hydrogen (δ 5.36, H-12) and signals at δ 2.59 (1H, *s*, H-18) and 1.34 (3H, *s*, Me-29) characteristic of an urs-12-en-28-oic acid which links a methyl and a hydroxyl groups at C-19 [8]. All these data suggested that **1** was an urs-12-en-28-oic acid possessing a 3-oxo and a 6β,19α-dihydroxy substitution pattern. Comparison of the ^{13}C NMR spectrum of **1** with that of 3β,6β,19α-trihydroxyurs-12-en-28-oic acid, the major triterpene isolated from the same plant [8], showed that most of the carbon resonances (from C-6 to C-22 and from Me-24 to Me-30) (Table 1) were almost superimposable except those due to C-2 (δ 35.2, CH_2 by DEPT), C-4 (δ 50.1, C), C-5 (δ 58.1, C) and Me-23 (δ 24.6) deshielded by the presence of the carbonyl group (δ 220.5) at C-3 [9]. In addition, the ^1H NMR spectrum

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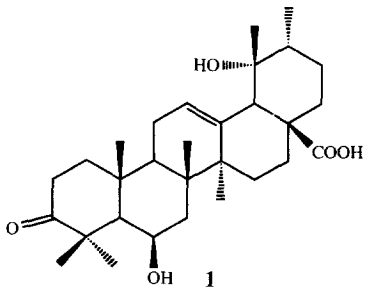

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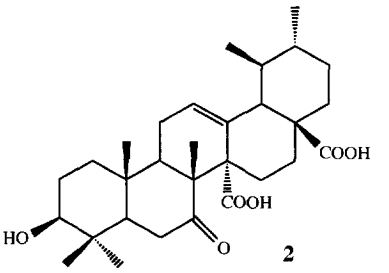

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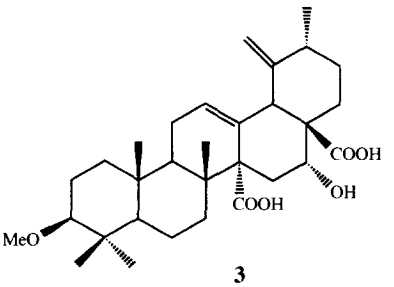

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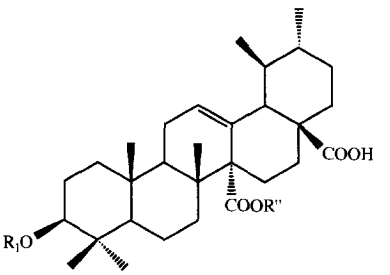

3

	R_1	R_2
4	Rha	H
5	Rha-(3—>1)-Glc	H
6	Qui-(3—>1)-Glc	H
7	Qui-(3—>1)-Gal	H
8	Rha-(3—>1)-Glc	Glc
9	H	Glc

Glc = β-D-Glucopyranosyl, Gal = β-D-galactopyranosyl, Qui = β-D-quinovopyranosyl, Rha = α-L-rhamnopyranosyl

of **1** was very similar to that of 3β,6β,19α-trihydroxyurs-12-en-28-oic acid [8], and differences were detected in the signals ascribable to H_2-1 (δ 2.10, *m*, and 1.40, *m*), H-2eq (δ 2.58, *m*), H-2ax (δ 2.87 *ddd*, J = 15.0, 11.0 and 4.1 Hz), Me-25 (δ 1.56, 3H, *s*) and Me-24 (δ 1.45, 3H, *s*), which appeared more downfield. Thus, **1** is 3-oxo-6β-19α-dihydroxyurs-12-en-28-oic acid.

Compounds **2** and **3** had molecular formula $C_{30}H_{44}O_6$ and $C_{31}H_{46}O_6$, respectively (mass spectrometry and ^{13}C and DEPT ^{13}C NMR). The presence of a quinovic (3β-ol-urs-12-en-27,28-dioic acid) acid skeleton and the substitution pattern followed from the NMR data (Table 1 and Experimental). The chemical shift values of the key carbons C-12 (δ 129.0), C-13 (*ca* δ 135.5), C-14 (*ca* δ 58.4) as well as of the C-27 and C-28 carboxyl groups and H-12 (δ 5.59, 1H, *m*) indicated that both compounds possessed a C-27 (δ 179.5) and a C-28 (δ 182.0) unsubstituted carboxyl group [2–4].

The ^{13}C NMR spectrum of **2** revealed the presence of a carbonyl group (δ 212.0), carbon signals due to the A, D and E rings typical of quinovic acid and strongly deshielded signals for C-6 (δ 34.9, CH_2) and C-8 (δ 55.9, C). Thus, the carbonyl group was located at C-7 [10, 11]. This was confirmed by the presence in

Table 1. ^{13}C NMR data for compounds **1**–**3** (500 MHz, CD_3OD)

C	1	2	3
1	40.2	40.3	40.3
2	35.2	27.2	26.7
3	220.5	79.3	90.9
4	50.1	39.8	39.0
5	58.1	56.4	56.7
6	69.3	34.9	19.0
7	41.6	212.0	31.5
8	39.1	55.9	39.9
9	47.9	48.0	47.8
10	36.2	37.1	38.2
11	24.2	23.7	23.7
12	129.5	129.0	129.0
13	139.0	135.5	135.3
14	42.9	58.4	58.0
15	29.5	26.6	36.9
16	25.9	25.8	78.8
17	47.8	47.9	48.8
18	55.2	55.7	50.0
19	73.6	39.6	153.3
20	42.9	38.6	37.8
21	26.8	31.2	32.5
22	37.5	36.8	37.9
23	24.6	16.2	16.8
24	27.3	27.8	28.9
25	16.5	16.4	16.8
26	18.7	18.1	18.1
27	24.2	179.5	179.5
28	182.0	182.0	181.7
29	27.0	16.6	107.6
30	16.5	21.4	21.4
-OMe	—	—	55.6

the ^1H NMR spectrum of signals assigned to H_2-6 at δ 2.59 (1H, *dd*, J = 14.0 and 14.8 Hz, H-6β) and 2.42 (1H, *dd*, J = 3.8 and 14.0 Hz, H-6α) and to H-5 (δ 2.01, *dd*, J = 3.8 and 14.8 Hz) by spin-decoupling experiments. Also, Me-26 resonating at δ 1.08 (δ 0.95 in the model) was deshielded by the presence of the keto group at C-7, as reported for analogous triterpenes [10, 11]. Thus, **2** was determined to be 7-oxo-3β-hydroxyurs-12-en-27,28-dioic acid.

The ^1H NMR spectrum of **3** compared with that of quinovic acid [2–4], lacked a doublet methyl signal (Me-29) and contained a complex signal at δ 4.63–4.72 ascribable to an *exo*-methylene group, two secondary hydroxyl (δ 3.89 and 3.20) and a hydroxymethyl (δ 3.38, 3H, *s*, -OMe) group. The ^{13}C NMR spectrum (31 signals) contained signals for an sp^2 quaternary carbon (δ 153.3), a CH_2= (δ 107.6), a CHOR (δ 90.9), a -OMe (δ 55.6) and a -CHOH (δ 78.8) group. The location of the exocyclic double bond at 19(29) was suggested by the absence of the Me-29 signal and confirmed by the chemical shifts (Table 1) of the vicinal carbons C-18 and C-20 (shielded by *ca* δ −5.7 and −0.8) and by the chemical shift of C-21 (deshielded by *ca* +δ 1.3 with respect to quinovic acid) [2–4]. Replacement of a methyl by an *exo*-methylene was reported to induce similar shifts in analogous compounds [8, 12]. The methoxyl was assigned to the C-3β position by analysis of the splitting pattern and coupling constants of H-3 (δ 3.20, 1H, *dd*, J = 11.0 and 4.0 Hz, -CHO-) in the ^1H NMR spectrum and by the chemical shifts of the A, B and C ring carbons being superimposable on those of a glycosylated quinovic acid models in the ^{13}C NMR spectrum [2–4]. In fact, C-3 was shifted downfield (β-effect) by *ca* +12 ppm, while C-2 and C-4 were shifted upfield (γ-effect) by *ca* −0.5 and −0.8 ppm with respect to the 3β-hydroxy-urs-12-en-27,28-dioic acid model, cf. **2**. Also, the proton resonances of Me-23 (δ 0.87 in **3** versus δ 0.79 in **2**) and Me-24 (δ 1.04 in **3** versus δ 0.98 in **2**) were consistent with a 3-*O*-methylation. The presence of the hydroxyl group at C-16 was indicated by the resonances at δ 78.8 (C-16) and 36.9 (C-15) and by small shifts observed for C-14 (upfield shift, γ-effect) and C-17 (downfield shift, β-effect) with respect to quinovic acid [2–4]. The orientation of the hydroxyl group at C-16 was axial (α) from the splitting pattern and values of coupling constants of its geminal proton (δ 3.89, *dd*, J = 3.6 and 6.6 Hz, H-16eq) and by comparison with 16α-hydroxytriterpene models [13]. It follows that **3** is 3β-methoxy-16α-hydroxyursa-12,19(29)-dien-27,28-dioic acid.

The molecular formula $C_{36}H_{56}O_9$ was assigned (FAB mass spectrometry and ^{13}C and DEPT ^{13}C NMR), to **4**, $C_{42}H_{66}O_{14}$ to **5**–**7**, $C_{48}H_{76}O_{19}$ to **8** and $C_{36}H_{56}O_{10}$ to **9**. The quinovic acid structure of the aglycones and the substitution pattern followed from the NMR and FAB mass spectral data (Table 2 and Experimental).

The nature and the ratio of the sugars in **4**–**9** were established by acid methanolysis and GLC analysis of the persylilated methylsugars.

In the ^{13}C NMR spectra the aglycone signals between δ 90.7 and 90.5 (CH) showed that C-3 is the ether glycosylation site in **4**–**8** whereas the signal resonating at δ 78.9 (CH-3) in **9** suggested the location of a free hydroxyl group at its C-3 position. The chemical shifts of C-12, C-13 and C-14 and of C-27 and C-28 carboxyl groups (Table 2) were typical of a quinovic acid derivative with unsubstituted 27- and 28-COOH groups in **4**–**7** and of a C-27 ester derivatives in **8** and **9** [2–7]. The presence of a glucose attached by a β-linkage through an ester group (C-27) was indicated by anomeric signals at δ_H 5.41 (1H, *d*, J = 7.5 Hz) and δ_C 95.8 (CH) in the spectra of **8** and **9**. Inspection of the ^1H NMR spectra confirmed these findings through the characteristic resonances of Me-26 and H-12 in **4**–**8** [2–7]. The Me-23 (δ 0.78) and Me-24 (δ 1.00) signals were shifted upfield by *ca* 0.05 ppm in **9** with respect to **4**–**8** due to the presence of an unglycosylated hydroxyl group at C-3.

The configurations at the anomeric centres of the sugars were derived from the δ values, the form of the signals and the values of the coupling constants of the anomeric protons as well as by the resonances of the

Table 2. ^{13}C NMR data for sugar moieties of compounds **4** and **6–9** (500 MHz, CD_3OD)

C	4	6	7	8	9
Rha-1′	102.6			102.9	
Rha-2′	72.6			72.2	
Rha-3′	73.0			83.1	
Rha-4′	74.1			73.5	
Rha-5′	70.0			69.8	
Rha-6′	17.9			18.1	
Qui-1′		106.4	106.3		
		74.8	74.7		
		85.0	85.1		
		71.4	71.7		
		77.6	77.6		
		18.1	18.1		
Glc-1″		105.8		105.8	
Glc-2″		75.3		75.4	
Glc-3″		78.6		78.4	
Glc-4″		71.9		71.9	
Glc-5″		77.9		77.8	
Glc-6″		62.9		63.0	
Gal-1″			103.3		
Gal-2″			72.5		
Gal-3″			73.4		
Gal-4″			68.2		
Gal-5″			74.6		
Gal-6″			60.0		
Glc at C-27-1				95.8	95.8
Glc-2				74.4	74.5
Glc-3				78.6	78.6
Glc-4				71.8	71.8
Glc-5				78.4	78.4
Glc-6				62.9	63.0

Glc = β-D-glucopyranose; Rha = α-L-rhamnopyranose; Gal = β-D-galactopyranose; Qui = β-D-quinovopyranose.

anomeric carbons (Experimental). Spin-decoupling experiments allowed the identification of all proton signals in **4** (quinovic acid-3-β-*o*-α-L-rhamnopyranoside). The presence of $1 \rightarrow 3$ interglycosidic linkages in **5–9** were derived by ^{13}C NMR (Table 2) in which C-3 showed a *ca* 7.0 ppm downfield shift in comparison with the corresponding carbons of terminal sugar models [14, 15]. Thus, the structures of **5–9** are those shown in the formulae. Compound **5** was previously obtained by alkaline hydrolysis of a native C-28 glucosyl ether derivative from *Guettarda platypoda* [7]. Compound **10** was identified as 3β,6β, 19α,23-tetrahydroxyurs-12-en-28-oic acid by spectral data comparison [16].

EXPERIMENTAL

Plant material. Root bark of *U. tomentosa* was collected in Peru in October 1990 and identified by Prof. E. Cerrate. A voucher sample is deposited at the Herbarium of the Museo de Historia Natural 'J. Prado' in Lima, Peru.

Extraction and isolation. Dried root bark (1 kg) was extracted at room temp. with MeOH to give 28.0 g of residue, which was partitioned between *n*-BuOH and H_2O. Part (14.0 g) of the dried BuOH extract was subjected to CC on Sephadex LH-20 (100 × 4 cm) using MeOH as eluent and collecting frs of 10 ml. All frs were combined according to TLC [*n*-BuOH–HOAc–H_2O (12:3:5) and $CHCl_3$–MeOH–H_2O (40:9:1)] composition to give 4 main frs (A, B, C and D). Spots corresponding to a mixt. of quinovic acid glycosides with major M_r were detected in fr. A, and with minor M_r in fr. B; spots corresponding to oxindole and glucoindole alkaloids were detected in fr. C and to triterpenes in fr. D. Final sepns were achieved by RP-HPLC using MeOH–H_2O (7:3) as eluent to give, in addition to the major constituents reported in refs [2–4, 8], **1** (R_t = 48.5 min, 15 mg), **2** (R_t = 37.3 min, 5 mg), **3** (R_t = 56.0 min, 8 mg) and **10** (R_t = 34.5 min, 12 mg) from fr. D; **7** (R_t = 28.0 min, 7.0 mg), **5** (R_t = 13.5 min, 17.5 mg), **6** (R_t = 16.0 min, 7 mg) and **8** (R_t = 4.2 min, 10 mg) from fr. A; **4** (R_t = 10.3 min, 17.1 mg) and **9** (R_t = 6.5 min, 8.7 mg) from fr. B. Pteropodine and isopteropodine [1] were isolated from fr. C. Compounds **5** and **10** were identified by comparison with lit. data [7, 15]. The ^{13}C NMR data for **1–3** and for the sugar moieties of **4–9**: Tables 1 and 2, respectively. All NMR data are in CD_3OD at 500 MHz.

Compound **1**. $[\alpha]_D^{25} = +28$ (MeOH, *c* 1); EIMS: *m/z* 486 $[M]^+$, 468 $[M-H_2O]^+$, 450 $[M-2\times H_2O]^+$, 440 $[M-HCO_2H]^+$, 422 $[M-HCO_2H-H_2O]^+$, $[450-15]^+$ 435, $[422-15]^+$ 407, 264, $[264-18]^+$ 246, $[246-15]^+$ 231, 222, 219 $[264-CO_2H]^+$, 218 $[264-HCO_2H]^+$, 201 $[246-CO_2H]^+$, 187 $[201-14]^+$; ^{1}H NMR: δ 0.95 (3H, *d*, $J = 6.0$ Hz, Me-30), 1.16 (3H, *s*, Me-26), 1.19 (3H, *s*, Me-27), 1.22 (3H, *s*, Me-23), 1.34 (3H, *s*, Me-29), 1.45 (3H, *s*, Me-24), 1.56 (3H, *s*, Me-25), 1.58 (1H, *ddd*, $J = 13.5, 4.5, 2.0$ Hz, H-16 eq), 1.40, 2.10 (each 1H, *m*, H_2-1), 2.20 (1H, *m*, H-2 eq), 2.53 (2H, *ddd*, $J = 13.5, 13.5, 4.5$ Hz, H-16 ax), 2.59 (1H, *s*, H-18), 2.87 (1H, *ddd*, $J = 15.0, 11.0, 4.1$ Hz, H-2 ax), 4.45 (1H, *m*, $W_{1/2} = 6.0$ Hz, H-6), 5.36 (1H, *br m*, H-12); ^{13}C NMR: Table 1.

Compound **2**. $[\alpha]_D^{25} = +14$ (MeOH, *c*, 1); FABMS: *m/z* 499 $[M-H]^-$, 455 $[M-H-44]^-$, 411 $[M-H-2\times44]^-$; ^{1}H NMR: δ 0.79 (3H, *s*, Me-23), 0.95 (6H, *d* sharp, Me-29, Me-30), 0.98 (3H, *s*, Me-24 or 25), 0.99 (3H, *s*, Me-25 or Me-24), 1.08 (3H, *s*, Me-26), 2.01 (1H, *dd*, $J = 3.8, 14.8$ Hz, H-5), 2.42 (1H, *dd*, $J = 3.8, 14.0$ Hz, H-6 eq), 2.59 (1H, *dd*, $J = 14.8, 14.0$ Hz, H-6 ax), 3.15 (1H, *dd*, $J = 11.0, 4.0$ Hz, H-3), 5.59 (1H, *br m*, H-12); ^{13}C NMR: Table 1.

Compound **3**. $[\alpha]_D^{25} = +12$ (MeOH, *c* 1); FABMS: *m/z* 513 $[M-H]^-$, 499 $[M-H-14]^-$, 469 $[M-H-44]^-$, 425 $[M-H-2\times44]^-$, 411 $[M-H-25+14]^-$; ^{1}H NMR: δ 0.87 (3H, *s*, Me-23), 0.95 (6H, *d* sharp, Me-29, Me-30), 1.01 (3H, *s*, Me-25), 1.04 (3H, *s*, Me-24), 3.20 (1H, *dd*, $J = 11.0, 4.5$ Hz, H-3 ax), 3.38 (3H, *s*, -OMe), 3.89 (1H, *dd*, $J = 3.6, 6.6$ Hz, H-16 eq), 4.63–4.72 (2H, *br s*, H_2-29), 5.59 (1H, *br m*, H-12); ^{13}C NMR: Table 1.

Compound **4**. $[\alpha]_D^{25} = +10$ (MeOH, *c* 1); FABMS: *m/z* 631 $[M-H]^-$, 485 $[M-H-146]^-$, 587 $[M-H-44]^-$, 441 $[M-H-44-146]^-$, 425 $[M-H-44-162]^-$; ^{1}H NMR: δ 0.85 (3H, *s*, Me-23), 0.95 (3H, *s*, Me-26), 0.96 (6H, *d* sharp, Me-29, Me-30), 0.99 (3H, *s*, Me-25), 1.04 (3H, *s*, Me-24), 1.28 (3H, *d*, $J = 6.0$ Hz, Me-Rha), 3.20 (1H, *dd*, $J = 11.0, 4.5$ Hz, H-3 ax), 3.40 (1H, *t*, $J = 9.0$ Hz, H-4′), 3.65 (1H, *dd*, $J = 3.7, 9.0$ Hz, H-3′), 3.75 (1H, *dq*, $J = 6.0, 9.0$ Hz, H-5′), 3.89 (1H, *dd*, $J = 1.5, 3.7$ Hz, H-2′), 4.77 (1H, *d*, $J = 1.5$ Hz, H-1′), 5.59 (1H, *m*, H-12); ^{13}C NMR aglycone: δ 16.8 (C-25), 17.0 (C-29), 18.5 (C-26), 19.4 (C-23), 19.6 (C-6), 21.4 (C-30), 24.1 (C-11), 26.5 (C-16), 27.1 (C-15), 27.3 (C-2), 28.7 (C-24), 31.8 (C-21), 38.0 (C-7), 38.1 (C-10), 38.3 (C-22), 38.6 (C-20), 39.9 (C-1), 40.2 (C-4, C-19), 40.8 (C-8), 48.0 (C-9, C-17), 56.0 (C-18), 56.9 (C-5), 59.2 (C-14), 90.7 (C-3), 129.0 (C-12), 135.5 (C-13), 179.5 (C-27), 182.0 (C-28); for sugar moiety: Table 2.

Compound **6**. $[\alpha]_D^{25} = +36$ (MeOH, *c* 1); FABMS: *m/z* 793 $[M-H]^-$, 631 $[M-H-162]^-$, 615 $[M-H-178]^-$, 587 $[M-H-44-162]^-$, 571 $[M-H-44-178]^-$, 441 $[M-H-44^-162+146]^-$, 425 $[M-H-44-178+146]^-$; ^{1}H NMR: aglycone signals were superimposable on those of glycoside **4**, sugar signals: δ 1.33 (3H, *d*, $J = 6.0$ Hz, Me-Qui), 3.69 (1H, *dd*, $J = 12.0, 3.5$ Hz, H-6″b), 3.92 (1H, *dd*, $J = 12.0, 5.0$ Hz, H-6″a), 4.37 (1H, *d*, $J = 7.5$ Hz, H-1′), 4.68 (1H, *d*, $J = 7.0$ Hz, H-1″); ^{13}C NMR for aglycone superimposable on that of **4**; for sugar moiety: Table 2.

Compound **7**. $[\alpha]_D^{25} = +18°$ (MeOH, *c* 1); FABMS and ^{1}H NMR data for the aglycone were superimposable on those of glycoside **6**, sugar signals: δ 1.28 (3H, *d*, $J = 6.0$ Hz, Me-Qui), 3.39 (1H, *dd*, $J = 12.0, 3.5$ Hz, H-6″b), 3.52 (1H, *dd*, $J = 12.0, 5.0$ Hz, H-6″a), 4.31 (1H, *d*, $J = 7.5$ Hz, H-1′), 4.60 (1H, *d*, $J = 8.0$ Hz, H-1″); ^{13}C NMR for aglycone superimposable on that of **4**; for sugar moiety: Table 2.

Compound **8**. $[\alpha]_D^{25} = +25$ (MeOH, *c* 1); FABMS: *m/z* 955 $[M-H]^-$, 793 $[M-H-162]^-$, 777 $[M-H-178]^-$, 587 $[M-H-44-2\times162]^-$, 571 $[M-H-44-162+178]^-$, 425 $[587-146]^-$ 441, $[571-146]^-$; ^{1}H NMR: δ 0.86 (3H, *s*, Me-23), 0.92 (3H, *s*, Me-26), 0.95 (6H, *d* sharp, Me-29, Me-30), 0.99 (3H, *s*, Me-25), 1.04 (3H, *s*, Me-24), 1.27 (3H, *d*, $J = 6.0$ Hz, Me-Rha), 3.20 (1H, *dd*, $J = 11.0, 4.5$ Hz, H-3 ax), 4.58 (1H, *d*, $J = 7.0$ Hz, H-1″), 4.72 (1H, *d*, $J = 1.5$ Hz, H-1′), 5.41 (1H, *d*, $J = 8.0$ Hz, H-1‴), 5.64 (1H, *m*, H-12); ^{13}C NMR aglycone: δ 16.7 (C-25), 17.1 (C-29), 18.4 (C-26), 19.3 (C-23), 19.5 (C-6), 21.8 (C-30), 24.2 (C-11), 25.8 (C-16), 26.8 (C-15), 27.2 (C-2), 28.6 (C-24), 31.3 (C-21), 37.8 (C-7), 38.2 (C-10), 37.6 (C-22), 38.4 (C-20), 39.8 (C-1), 40.3 (C-4, C-19), 40.9 (C-8), 48.0 (C-9, C-17), 55.7 (C-18), 57.0 (C-5), 57.7 (C-14), 90.5 (C-3), 130.7 (C-12), 133.7 (C-13), 178.0 (C-27), 182.0 (C-28); for sugar moiety: Table 2.

Compound **9**. $[\alpha]_D^{25} = +55$ (MeOH, *c* 1); FABMS: *m/z* 647 $[M-H]^-$, 485 $[M-H-162]^-$, 469 $[M-H-178]^-$, 441 $[M-H-44-162]^-$, 425 $[M-H-44-178]^-$; ^{1}H NMR: δ 0.78 (3H, *s*, Me-23), 0.92 (3H, *s*, Me-26), 0.95 (6H, *d* sharp, Me-29, Me-30), 0.98 (3H, *s*, Me-25), 1.00 (3H, *s*, Me-24), 3.20 (1H, *dd*, $J = 11.0, 4.5$ Hz, H-3 ax), 3.62 (1H, *dd*, $J = 12.0, 3.5$ Hz, H-6″b), 3.85 (1H, *dd*, $J = 12.0, 5.0$ Hz, H-6″a), 5.41 (1H, *d*, $J = 8.0$ Hz, H-1‴), 5.64 (1H, *m*, H-12); ^{13}C NMR aglycone: δ 16.5 (C-23), 16.8 (C-25), 17.2 (C-29), 18.5 (C-26), 19.7 (C-6), 21.6 (C-30), 24.3 (C-11), 25.9 (C-16), 26.8 (C-15), 26.9 (C-2), 28.2 (C-24), 31.3 (C-21), 38.1 (C-7), 38.3 (C-10), 38.0 (C-22), 38.6 (C-20), 39.8 (C-4), 40.0 (C-1), 40.3 (C-19), 40.8 (C-8), 48.0 (C-9, C-17), 55.7 (C-18), 57.0 (C-5), 57.7 (C-14), 78.9 (C-3), 130.7 (C-12), 133.8 (C-13), 178.0 (C-27), 182.0 (C-28); for sugar moiety: Table 2.

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