Triterpenoid Saponins from *Campsiandra guayanensis*[#]

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Thirteen new triterpenoid saponins (**1**−**13**) were isolated from the aerial parts of *Campsiandra guayanensis*. Their structures were elucidated by 1D and 2D NMR experiments including 1D-TOCSY, DQF-COSY, ROESY, HSQC, and HMBC spectroscopy, as well as ESIMS analysis. The aglycon moieties of **1**−**10** were assigned as oleanane derivatives and those of **11**−**13** as lupane derivatives.

In the course of our studies on South American medicinal plants, we have performed a phytochemical study on the aerial parts of *Campsiandra guayanensis* B. Stergios (Caesalpiniaceae), a tree growing in the Amazon forest of Venezuela.[1] *Campsiandra* species have been used in Venezuela as excitants, febrifuges, and tonics, and to treat ulcers.[2] In particular, *C. comosa* seeds are also used as a human food in the State of Apure and in the Territorio Federal Amazonas to prepare "chiga" flour.[3] Despite that this genus has had a long traditional use, a literature survey on the genus *Campsiandra* indicated that it has not been investigated previously phytochemically: only a few articles dealing with the nutritional value of "chiga" flour are reported.[3−5]

In the present investigation on *C. guayanensis* aerial parts, we report the isolation and structural characterization by spectroscopic and spectrometric analyses of 13 new triterpenoid saponins (**1**−**13**), based on the oleanane and lupane skeletons.

Results and Discussion

The methanol and chloroform−methanol extracts of the aerial parts of *C. guayanensis* were subjected separately to Sephadex LH-20 column chromatography, followed by CPC and then RP-HPLC, to afford 13 triterpenoid saponins (**1**−**13**).

Compound **1** was assigned the molecular formula $C_{77}H_{126}O_{41}$, as determined by ^{13}C, ^{13}C DEPT NMR, and positive ESIMS. The ESIMS of **1** showed a $[M + H]^+$ ion at *m/z* 1707 and prominent fragments at *m/z* 1545 $[M + H - 162]^+$ and 1383 $[M + H - 162 - 162]^+$, due to the subsequent loss of two hexose units, and *m/z* 927 $[M + H - 162 - 162 - 132 - 162 - 162]^+$, due to the sequential loss of a pentose and two hexose units. A peak at *m/z* 457 was attributed to the aglycon moiety. Data from the ^{13}C NMR spectrum (see Experimental Section and Table 1) suggested a triterpenoid glycoside structure. The ^{1}H NMR spectrum of the aglycon portion of **1** showed signals for seven tertiary methyl groups (δ 0.81, 0.86, 0.95, 0.97, 1.02, 1.08, 1.20), a typical signal of H-3ax at δ 3.19 (dd, J = 11.5, 4.0 Hz), and a characteristic olefinic proton at δ 5.38 (t, J = 3.5 Hz). The ^{13}C NMR spectrum showed for the aglycon moiety 30 signals that could be correlated unambiguously to the corresponding proton chemical shifts from the HSQC experiment, leading to the identification of the aglycon as oleanolic acid.[6] The sugar portion of **1** exhibited, in the ^{1}H NMR spectrum (Table 1), eight anomeric proton signals (δ 4.33, d, J = 8.0 Hz; 4.36, d, J = 8.5 Hz; 4.47, d, J = 7.6 Hz; 4.49, d, J = 8.0 Hz; 4.62, d, J = 8.0 Hz; 4.64, d, J = 8.0 Hz; 4.81, d, J = 7.5 Hz; 6.37, d, J = 1.5 Hz) and one methyl doublet (δ 1.25, d, J = 6.0 Hz), suggesting the occurrence of one deoxyhexose unit. The structures of the oligosaccharide moieties were deduced using 1D TOCSY and 2D NMR experiments, which indicated that six β-glucopyranoses, a β-xylopyranose, and a α-rhamnopyranose were present (Table 1). The configurations of the sugar units were assigned after hydrolysis of **1** with 1 N HCl. The hydrolysate was trimethylsilylated, and GC retention times of each sugar were compared with those of authentic sugar samples prepared in the same manner. The absence of any ^{13}C NMR glycosidation shift for two β-D-glucopyranosyl and the β-D-xylopyranosyl moieties suggested that these sugars were terminal units. Glycosidation shifts were observed for C-2_{glcI} (84.6 ppm), C-4_{glcI} (79.4 ppm), C-3_{glcII} (89.3 ppm), C-2_{glcIII} (81.7 ppm), C-2_{rha} (81.6 ppm), and C-6_{glcV} (69.0 ppm) (Table 1). The chemical shifts of H-1_{rha} (δ 6.37) and C-1_{rha} (93.7 ppm) indicated that this sugar unit is involved in an ester linkage with the C-28 carboxylic group.[7] Direct evidence for the sugar sequence and their linkage sites linked at C-3 was derived from the results of the HMBC experiment that showed unequivocal correlation peaks between resonances at δ 4.47 and 90.8 ppm (H-1_{glcI}−C-3), δ 4.62 and 84.6 ppm (H-1_{glcII}−C-2_{glcI}), δ 4.49 and 79.4 ppm (H-1_{glcIV}−C-4_{glcI}), δ 4.64 and 89.3 ppm (H-1_{glcIII}−C-3_{glcII}), and δ 4.81 and 81.7 ppm (H-1_{xyl}−C-2_{glcIII}). Similarly, the sequence of the trisaccharide chain at C-28 was indicated by the cross-peaks between δ 4.36 and 81.6 ppm (H-1_{glcV}−C-2_{rha}) and δ 4.33 and 69.0 ppm (H-1_{glcVI}−C-6_{glcV}). On the basis of this evidence, compound **1** was identified as 3β-*O*-{β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-glucopyranosyl}-olean-12-en-28-*O*-(β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl) ester.

The ESIMS of compound **2** ($C_{65}H_{106}O_{31}$) showed a prominent fragment at *m/z* 1383 ($[M + H]^+$) and a fragmentation pattern similar to that of **1**. The spectroscopic data of the aglycon moiety of **2** were identical to those of **1**. Comparison of NMR spectral data of the sugar moiety (Table 1) of **2** with those of **1** indicated that **2** differed from **1** only by the absence of the two glucopyranosyl units linked at C-28. Thus, compound **2** was determined to be 3β-*O*-{β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-glucopyranosyl}-olean-12-en-28-*O*-α-L-rhamnopyranosyl ester.

Compound **3** (molecular formula $C_{64}H_{104}O_{31}$) showed a quasi-molecular ion peak at *m/z* 1391 $[M + Na]^+$ in the positive ESIMS. Furthermore, fragment ion peaks at *m/z* 921 $[M + Na - 162 - 162 - 146]^+$ and 789 $[M + Na - 162 - 162 - 146 - 132]^+$ indicated the loss of two hexose units, one deoxyhexose unit, and one pentose unit. The ^{13}C NMR spectrum (Table 2 and Experi-

[#] Dedicated to the memory of Prof. Ivano Morelli, Università di Pisa.

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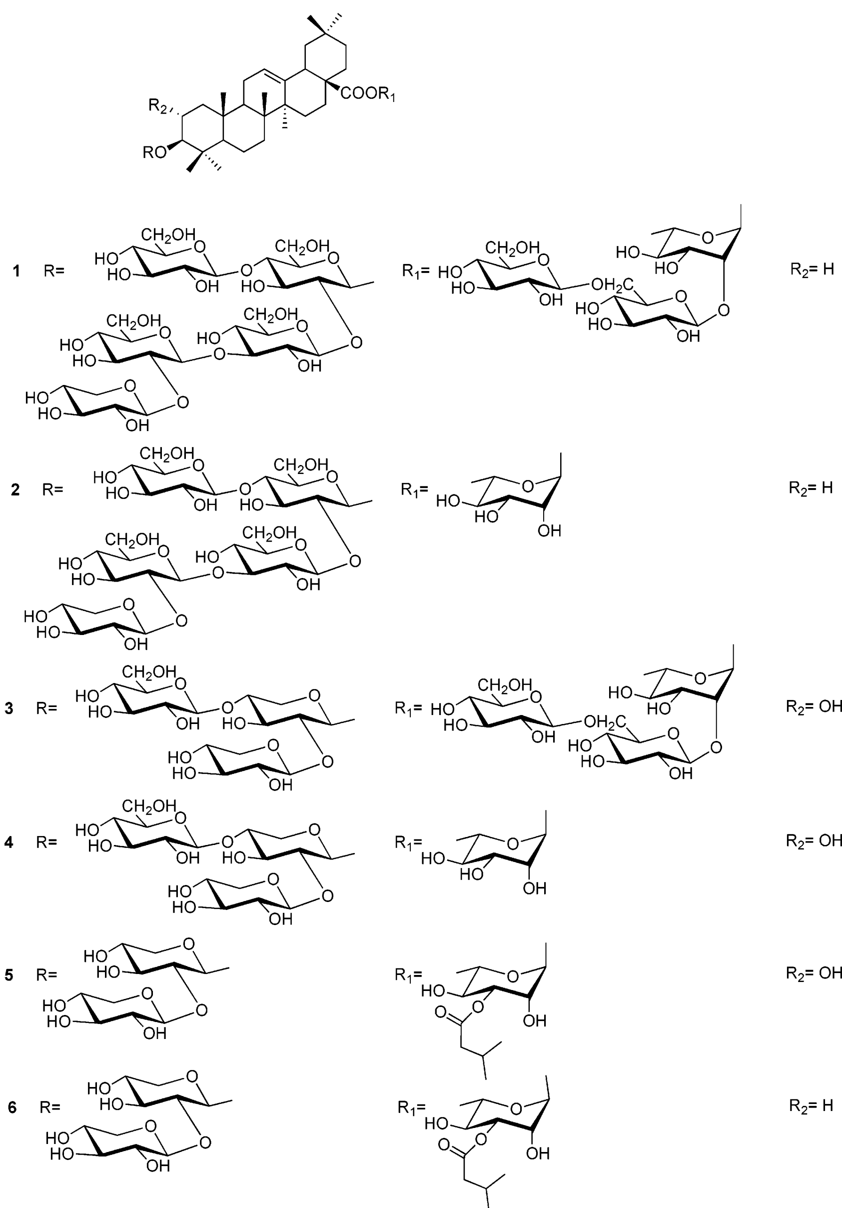
Chart 1

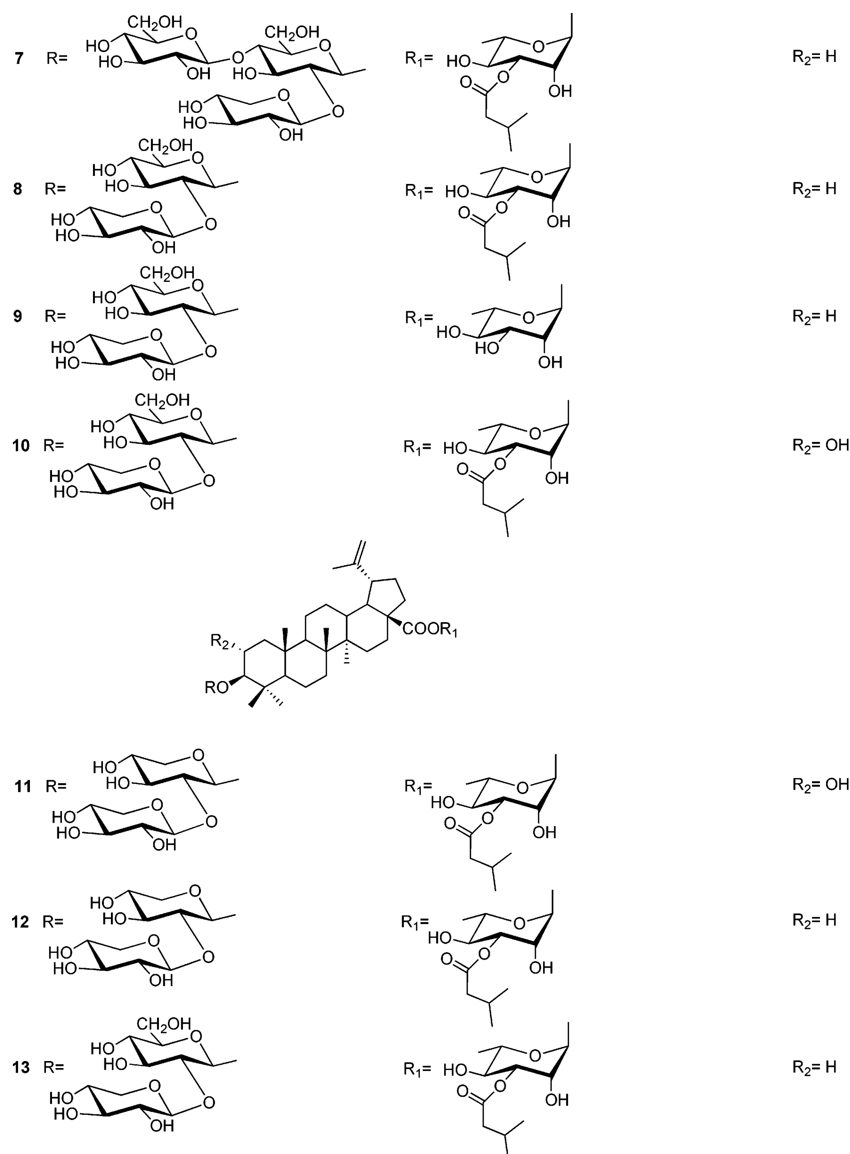


mental Section) showed 64 signals, of which 30 were assigned to a triterpenoid moiety and 34 to the saccharide portion. The following NMR data suggested the structural features of 2α,3β-dihydroxy-olean-12-en-28-oic acid (maslinic acid) for the aglycon of compound **3**: seven tertiary methyl group signals (δ 0.81, 0.92, 0.96, 1.00, 1.03, 1.13, 1.21), signals at δ 2.99 (d, J = 11.0 Hz) and 3.72 (ddd, J = 11.0, 9.0, 3.0 Hz), ascribable, respectively, to the 3α- and 2β-protons on carbons bearing a hydroxyl function, and a resonance for an olefinic hydrogen at δ 5.38 (t, J = 3.5 Hz).[8] In addition to the aglycon signals, the ^{13}C NMR spectrum exhibited 34 signals attributable to the sugar portion made up of three hexopyranosyl, two pentopyranosyl, and one deoxyhexopyranosyl unit. Analysis of the NMR data (Table 2) for the sugar portion of compound **3** and comparison with those of **1** revealed **3** to differ from **1** in the glycosidic chain at C-3. The proton-coupling network within each sugar residue was traced out, using a combination of 1D TOCSY, DQF-COSY, and HSQC experiments. Once again, direct evidence for the sugar sequence and the linkage sites was derived from the HSQC and HMBC data. These results established that the trisaccharide chain at C-3 of **3** contains a terminal β-glucopyranose, a terminal β-xylopyranose, and an inner β-xylopyranose disubstituted at C-2 and C-4. The configuration of the sugar units was determined as reported for compound **1**. On the basis of these data, the structure of **3** was established as 3β-*O*-{β-D-xylopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-xylopyranosyl}-2α-hydroxyolean-12-en-28-*O*-(β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl) ester.

The ESIMS of compound **4** (*m/z* 1043, corresponding to $C_{52}H_{84}O_{21}$ by elemental analysis) showed a $[M - H]^-$ at *m/z* 1043 and prominent fragments at *m/z* 897 $[M - H - 146]^-$ (cleavage of one deoxyhexose unit), 765 $[M - H - 146 - 132]^-$ (cleavage of one deoxyhexose and one pentose unit), and 603 $[M - H - 146 - 132 - 162]^-$ (cleavage of one deoxyhexose, one pentose, and one hexose unit). Analysis of NMR data of compound **4** and comparison with those of **3** showed **4** differs from **3** only in the absence of the two glucopyranosyl moieties linked at C-28 (Table 2). Therefore, the structure 3β-*O*-{β-D-xylopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-xylopyranosyl}-2α-hydroxyolean-12-en-28-*O*-α-L-rhamnopyranosyl ester was assigned to compound **4**.

Compound **5** was assigned the molecular formula $C_{51}H_{82}O_{17}$, as shown by its ESIMS data (*m/z* 989 $[M + Na]^+$) in combination with the ^{13}C NMR spectrum and elemental analysis. The ^{13}C and ^{13}C DEPT spectra (Table 2 and Experimental Section) showed 51 signals, of which 30 were assigned to the aglycon, 16 to the sugar

Chart 2



portion, and five to an acyl group. It was apparent from the ^{1}H and ^{13}C NMR data of **5** that this compound is based on the same aglycon as **3**. Additionally for **5**, resonances of anomeric protons were observed in the ^{1}H NMR spectrum at δ 4.39 (d, $J = 7.5$ Hz), 4.63 (d, $J = 7.5$ Hz), and 5.96 (d, $J = 1.5$ Hz). 1D TOCSY, DQF-COSY, and HSQC NMR experiments showed the presence of two β-D-xylopyranosyl units (δ 4.39 and 4.63) and one α-L-rhamnopyranosyl unit (δ 5.96) (Table 2). The HSQC spectrum also showed glycosylation shifts for C-2 (δ 81.9) of one xylopyranosyl unit and acylation shifts for H-3 (δ 5.04) and C-3 (δ 74.3) of the rhamnopyranosyl unit. The acyl moiety was identified as an isovaleroyl group from the ^{1}H and ^{13}C NMR data.[9] An unambiguous determination of the sequence and linkage sites was obtained from HMBC correlations. The configurations of the sugar units were assigned after hydrolysis of **5** with 1 N HCl. The hydrolysate was trimethylsilylated, and GC retention times of each sugar were compared with those of authentic sugar samples prepared in the same manner. In this way, the sugar units of **5** were determined to be D-xylose and L-rhamnose in the ratio 2:1. On the basis of this evidence, **5** was established as the new compound 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-2α-hydroxyolean-12-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester.

Compound **6** ($C_{57}H_{82}O_{16}$) exhibited an ESIMS showing the $[M + Na]^+$ peak at *m/z* 973 and a fragmentation pattern similar to that of **5**. The NMR aglycon signals were identical to those of **1**, allowing the aglycon of **6** to be identified as oleanolic acid. Analysis of the sugar chain NMR data of compound **6** demonstrated that they were superimposable with those of **5**. Thus, the structure 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-olean-12-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester was assigned to compound **6**.

Compound **7** was assigned the molecular formula $C_{58}H_{94}O_{22}$, as determined by ^{13}C, ^{13}C DEPT, negative ion ESIMS, and elemental analysis. The ESIMS of **7** showed the $[M - H]^-$ ion at *m/z* 1141 and prominent fragments at *m/z* 1057 $[M - H - 84]^-$, 911 $[M - H - 84 - 146]^-$, 779 $[M - H - 84 - 146 - 132]^-$, 617 $[M - H - 84 - 146 - 132 - 162]^-$, and 455 $[M - H - 84 - 146 - 132 - 162 - 162]^-$. The ^{13}C NMR spectrum (Table 3 and Experimental Section) showed 58 signals, of which 30 were assigned to a triterpenoid moiety, 23 to the saccharide portion, and five to an isovaleroyl group. Analysis of the NMR data (Table 3) of compound **7** and comparison with those of **6** revealed **7** to differ from **6** only in the sugar chain at C-3. The structure of the oligosaccharide moiety at C-3 was then deduced using 1D TOCSY and DQF-COSY experiments, leading to the identification of two glucopyranosyl moieties (δ 4.47 and 4.44) and one xylopyranosyl moiety (δ 4.60). The absence of any glycosidation shift for one glucopyranosyl unit and one xylopyranosyl unit suggested that these

Table 1. ^{1}H and ^{13}C NMR Data for Sugar Moieties of Compounds **1** and **2** (CD_3OD, 600 MHz)[a]

	1		**2**	
position	δ_H	δ_C	δ_H	δ_C
D-Glc I 1	4.47 d (7.6)	104.9	4.47 d (7.8)	104.9
2	3.53 dd (9.5, 7.6)	84.6	3.52 dd (9.5, 7.8)	84.9
3	3.64 t (9.5)	77.3	3.76 t (9.5)	76.7
4	3.67 t (9.5)	79.4	3.65 t (9.5)	79.6
5	3.42 m	75.6	3.46 m	75.0
6a	3.93 dd (12.0, 3.0)	62.4	3.91 dd (12.0, 3.0)	62.0
6b	3.71 dd (12.0, 5.0)		3.69 dd (12.0, 5.5)	
D-Glc II 1	4.62 d (8.0)	103.6	4.62 d (8.0)	103.6
2	3.48 dd (9.5, 8.0)	74.7	3.41 dd (9.5, 8.0)	75.6
3	3.47 t (9.5)	89.3	3.46 t (9.5)	89.4
4	3.37 t (9.5)	71.4	3.36 t (9.5)	71.6
5	3.41 m	78.4	3.40 m	78.2
6a	3.92 dd (12.0, 3.5)	62.5	3.90 dd (12.0, 3.5)	62.5
6b	3.70 dd (12.0, 5.0)		3.70 dd (12.0, 5.0)	
D-Glc III 1	4.64 d (8.0)	103.8	4.64 d (8.0)	103.6
2	3.59 dd (9.0, 8.0)	81.7	3.58 dd (9.5, 8.0)	81.7
3	3.78 t (9.0)	76.7	3.61 t (9.5)	77.1
4	3.40 t (9.0)	71.1	3.38 t (9.5)	71.0
5	3.42 m	77.4	3.34 m	77.7
6a	3.77 dd (12.0, 3.0)	62.1	3.77 dd (12.0, 2.5)	61.9
6b	3.69 dd (12.0, 5.0)		3.69 dd (12.0, 5.0)	
D-Xyl 1	4.81 d (7.5)	104.4	4.78 d (7.5)	105.0
2	3.28 dd (9.0, 7.5)	74.7	3.26 dd (9.5, 7.5)	74.7
3	3.42 t (9.0)	77.4	3.44 t (9.5)	77.7
4	3.58 m	69.0	3.58 m	69.6
5a	3.92 dd (11.0, 2.5)	66.5	3.91 dd (12.0, 2.5)	66.4
5b	3.21 dd (11.0, 5.0)		3.21 dd (12.0, 5.0)	
D-Glc IV 1	4.49 d (8.0)	104.2	4.45 d (7.8)	104.2
2	3.34 dd (9.5, 8.0)	75.0	3.30 dd (9.5, 7.8)	75.6
3	3.39 t (9.5)	77.4	3.35 t (9.5)	77.0
4	3.37 t (9.5)	71.4	3.34 t (9.5)	71.3
5	3.41 m	78.4	3.38 m	77.3
6a	3.93 dd (12.0, 2.5)	62.2	3.88 dd (12.0, 3.0)	61.7
6b	3.73 dd (12.0, 5.0)		3.69 dd (12.0, 5.0)	
L-Rha 1	6.37 d (1.5)	93.7	5.97 d (1.8)	94.7
2	3.84 dd (2.5, 1.5)	81.6	3.80 dd (2.5, 1.8)	71.0
3	3.81 dd (9.0, 2.5)	72.0	3.48 dd (9.0, 2.5)	73.2
4	3.47 t (9.0)	73.4	3.71 t (9.0)	72.2
5	3.85 m	69.7	3.72 m	72.0
6	1.25 d (6.0)	18.0	1.30 d (6.5)	18.3
D-Glc V 1	4.36 d (8.0)	104.6		
2	3.46 dd (9.5, 8.0)	74.7		
3	3.42 t (9.5)	77.4		
4	3.36 t (9.5)	71.0		
5	3.47 m	76.4		
6a	4.18 dd (12.0, 2.5)	69.0		
6b	3.83 dd (12.0, 5.5)			
D-Glc VI 1	4.33 d (8.0)	103.7		
2	3.42 dd (9.0, 8.0)	75.2		
3	3.38 t (9.0)	77.8		
4	3.37 t (9.0)	71.4		
5	3.47 m	78.0		
6a	3.90 dd (12.0, 3.0)	62.4		
6b	3.70 dd (12.0, 5.0)			

[a] *J* values are in parentheses and reported in Hz; chemical shifts are given in ppm; assignments were confirmed by DQF-COSY, 1D-TOCSY, HSQC, and HMBC experiments.

sugars were terminal units, while the glycosidation shift on C-2 and C-4 of the other glucopyranosyl unit indicated the presence of a glucopyranose residue glycosylated at C-2 and C-4. The position of each sugar unit was deduced from a 1D ROESY experiment that showed a cross-peak between the signal at δ 4.47 (H-1$_{glcI}$) and the signal at δ 3.19 (H-3) and other key correlation peaks between the signal at δ 4.44 (H-1$_{glcII}$) and the signal at δ 3.62 (H-4$_{glcI}$) and between the signal at δ 4.60 (H-1$_{xyl}$) and the signal at δ 3.54 (H-2$_{glcI}$). The ^{1}H and ^{13}C NMR data indicated the β configuration at the anomeric position for all these sugar units. Also in this case, the D configuration of the xylose and glucose units and the L configuration of the rhamnose units were determined by acid hydrolysis of **7** followed by GC analysis. Therefore, compound **7** was determined to be 3β-*O*-{β-D-xylopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-glucopyranosyl}-olean-12-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester.

The ESIMS of compound **8** ($C_{52}H_{84}O_{17}$) showed a $[M + Na]^+$ peak at *m/z* 1003 and fragment peaks at *m/z* 919 $[M + Na - 84]^+$, 773 $[M + Na - 84 - 146)]^+$, and 597 $[M + Na - 84 - 146 - 44 - 132]^+$. The analysis of NMR data (Table 3) of compound **8** and comparison with those of **7** showed **8** to differ from **7** only in the absence of the terminal glucopyranosyl unit linked at C-3. Therefore, the structure 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl]-olean-12-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester was assigned to **8**.

Compound **9** showed the molecular formula $C_{47}H_{76}O_{16}$, established unequivocally by the ESIMS (pseudomolecular ion peak at *m/z* 895 $[M - H]^-$), NMR data, and elemental analysis. The ^{1}H and ^{13}C NMR chemical shifts (Table 3) of compounds **9** and **8** were almost superimposable, with the absence of the isovaleroyl group linked at C-3 of the rhamnopyranosyl unit being the point of difference for compound **9** (H-3$_{rha}$ at δ 5.02 in **8** versus H-3$_{rha}$ δ 3.47 in **9**). Thus, the structure of compound **9** was established as 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl]-olean-12-en-28-*O*-α-L-rhamnopyranosyl ester.

Compound **10** showed a quasimolecular ion peak at *m/z* 1019 $[M + Na]^+$ in the positive ESIMS. In conjunction with the analysis of the ^{13}C NMR and HSQC spectrum, its molecular formula was deduced by elemental analysis to be $C_{52}H_{84}O_{18}$. The ^{1}H and ^{13}C NMR chemical shifts of the aglycon moiety of **10** were identical to those of **3**, while the ^{1}H and ^{13}C NMR signals of the sugar moieties were superimposable with those of **8**. Thus, compound **10** was identified as 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl]-2α-hydroxyolean-12-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester.

Compound **11** was assigned the molecular formula $C_{51}H_{82}O_{17}$. The ESIMS showed the $[M + Na]^+$ ion at *m/z* 1003 and fragments at *m/z* 773 $[M + Na - 84 - 146]^+$ and 641 $[M + Na - 84 - 146 - 132]^+$, due to subsequent losses of an isovaleroyl group, a deoxyhexose, and a pentose unit. Analysis of the NMR data of compound **11** (Experimental Section) and comparison with those of **5** showed that they possess the same saccharide chains at C-3 and C-28, while the aglycon is the point of difference. The ^{1}H NMR spectrum for the triterpene skeleton of **11** showed, in addition to five methyl singlets assignable to tertiary methyls (δ 0.91, 0.95, 0.96, 1.06, 1.12), signals for an isopropylene function (δ 4.66 and 4.80, 1H each, br s, and 1.74 3H, s). Both OH-2α and OH-3β substitution was evident from the chemical shifts and *J* values of the C-2 proton at δ 3.61 (1H, ddd, $J = 11.5, 9.2, 3.0$ Hz) and the C-3 proton at δ 2.97 (1H, d, $J = 11.5$ Hz). Thus, the genin structure was assigned as 2α,3β-dihydroxylup-20(29)-en-28-oic acid (alphitolic acid) on the basis of the 1D and 2D NMR data.[10] On the basis of the above results, the structure of **11** was deduced to be 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-2α-hydroxylup-20-(29)-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester.

Compound **12** ($C_{51}H_{82}O_{16}$) was identified as a further triterpene derivative possessing two saccharide chains at C-3 and C-28. Comparison of the NMR spectroscopic data of compound **12** (Experimental Section) with those of **11** showed these to be identical in the sugar portion but different in the aglycon. In particular, the spectoscopic data for the aglycon moiety of **12** were identical to those of 3β-hydroxylup-20(29)-en-28-oic acid (betulinic acid).[11,12] Thus, compound **12** was determined to be 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-lup-20(29)-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester.

Compound **13** ($C_{52}H_{84}O_{17}$) exhibited a quasimolecular ion at *m/z* 1003 in its positive ESIMS spectrum, as well as fragments at *m/z* 773 $[M + Na - 84 - 146]^+$ and 641 $[M + Na - 84 - 146 - 132]^+$, corresponding to the sequential losses of an isovaleroyl group, a deoxyhexose, and a pentose unit. Comparison of the NMR

Table 2. ^{1}H and ^{13}C NMR Data for Sugar Moieties of Compounds **3**−**5** (CD_3OD, 600 MHz)[a]

	3		**4**		**5**	
position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
D-Xyl I 1	4.42 d (7.5)	104.6	4.42 d (7.5)	105.0	4.39 d (7.5)	105.2
2	3.62 dd (9.0, 7.5)	81.2	3.64 dd (9.5, 7.5)	81.1	3.56 dd (9.0, 7.5)	81.9
3	3.74 t (9.0)	76.6	3.75 t (9.5)	76.5	3.57 t (9.0)	78.1
4	3.87 m	77.7	3.80 m	77.7	3.60 m	70.4
5a	4.13 dd (10.5, 2.5)	64.3	4.11 dd (11.0, 3.0)	64.3	3.92 dd (11.0, 2.5)	66.0
5b	3.41 dd (10.5, 5.0)		3.40 dd (11.0, 5.0)		3.30 dd (11.0, 5.0)	
D-Xyl II 1	4.67 d (7.5)	105.8	4.68 d (7.5)	105.6	4.63 d (7.5)	105.8
2	3.24 dd (9.5, 7.5)	75.8	3.26 dd (9.0, 7.5)	75.8	3.25 dd (9.0, 7.5)	75.7
3	3.40 t (9.5)	77.7	3.38 t (9.0)	77.7	3.34 t (9.0)	77.6
4	3.47 m	71.1	3.48 m	70.8	3.48 m	70.8
5a	3.86 dd (11.0, 3.0)	66.7	3.84 dd (11.0, 2.5)	66.7	3.83 dd (10.5, 2.5)	67.6
5b	3.17 dd (11.0, 5.0)		3.17 dd (11.0, 5.0)		3.18 dd (10.5, 5.0)	
D-Glc I 1	4.44 d (7.8)	105.2	4.40 d (8.0)	103.1		
2	3.24 dd (9.0, 7.8)	74.9	3.23 dd (9.0, 8.0)	74.3		
3	3.34 t (9.0)	77.7	3.34 t (9.0)	77.7		
4	3.35 t (9.0)	71.4	3.32 t (9.0)	71.2		
5	3.40 m	77.6	3.36 m	77.7		
6a	3.93 dd (12.0, 3.5)	62.5	3.91 dd (12.0, 3.0)	62.4		
6b	3.72 dd (12.0, 5.0)		3.68 dd (12.0, 5.0)			
L-Rha 1	6.39 d (1.8)	93.9	5.96 d (1.8)	94.6	5.96 d (1.5)	94.3
2	3.83 dd (3.0, 1.8)	81.4	3.80 dd (3.0, 1.8)	71.0	3.94 dd (3.0, 1.5)	69.0
3	3.81 dd (9.0, 3.0)	72.0	3.48 dd (9.5, 3.0)	73.0	5.04 dd (9.0, 3.0)	74.3
4	3.47 t (9.0)	73.5	3.71 t (9.5)	72.2	3.70 t (9.0)	70.5
5	3.84 m	69.7	3.71 m	72.3	3.83 m	72.6
6	1.24 d (6.5)	18.0	1.27 d (6.0)	18.0	1.30 d (6.0)	18.0
Isoval 1′						174.0
2′					2.30 m	25.0
3′					2.35 m	44.0
4′/5′					1.03 d (6.5)	24.2
D-Glc II 1	4.46 d (7.8)	105.2				
2	3.35 dd (9.0, 7.8)	75.0				
3	3.40 t (9.0)	77.6				
4	3.47 t (9.0)	71.1				
5	3.45 m	76.6				
6a	4.17 dd (12.0, 3.0)	69.5				
6b	3.79 dd (12.0, 5.0)					
D-Glc III 1	4.39 d (7.8)	103.2				
2	3.24 dd (9.5, 7.8)	74.3				
3	3.34 t (9.5)	77.7				
4	3.35 t (9.5)	71.4				
5	3.40 m	77.6				
6a	3.88 dd (12.0, 3.5)	62.5				
6b	3.68 dd (12.0, 5.5)					

[a] *J* values are in parentheses and reported in Hz; chemical shifts are given in ppm; assignments were confirmed by DQF-COSY, 1D-TOCSY, HSQC, and HMBC experiments.

spectral data of **13** with those of **12** indicated that they have the same aglycon moiety, while the sugar portion of **13** was superimposable on those of compound **8**. Therefore, the structure 3β-*O*-[β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl]-lup-20(29)-en-28-*O*-(3-*O*-isovaleroyl)-α-L-rhamnopyranosyl ester was assigned to **13**.

The presence of triterpenoid saponins from a plant belonging to the family Caesalpiniaceae is an unusual finding, since anthraquinones and flavonoids are the typical secondary metabolites biosynthesized by the genera of this family.[13] Moreover the saponins **1**−**13** have an unusual esterified side chain of the aglycon, made up of a rhamnopyranosyl unit linked at C-28.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 241 polarimeter equipped with a sodium lamp (589 nm) and a 1 dm microcell. NMR experiments were performed on a Bruker DRX-600 spectrometer at 300 K. All the 2D NMR spectra were acquired in CD_3OD in the phase-sensitive mode with the transmitter set at the solvent resonance and TPPI (time proportional phase increment) used to achieve frequency discrimination in the ω_1 dimension. The standard pulse sequence and phase cycling were used for DQF-COSY, TOCSY, HSQC, HMBC, and ROESY experiments. The NMR data were processed on a Silicon Graphic Indigo2 workstation using UXNMR software. ESIMS (positive and negative mode) were obtained from a LCQ Advantage ThermoFinnigan spectrometer, equipped with Xcalibur software. Elemental analysis was obtained from a Carlo Erba 1106 elemental analyzer. Column chromatography was performed over Sephadex LH-20. HPCPC (high-performance centrifugal partition chromatography) was performed on an EverSeiko CPC240 chromatograph. HPLC separations were conducted on a Shimadzu LC-8A series pumping system equipped with a Waters R401 refractive index detector and Shimadzu injector. GC analyses were performed using a Dani GC 1000 instrument on a 1-Chirasil-Val column (0.32 mm × 25 m).

Plant Material. The aerial parts of *C. guayanensis* were collected in August 2001 near Rio Cuao, Municipio Autana, in the Amazonian region of Venezuela, and were identified by Prof. Anibal Castillo, Universidad Central de Venezuela, Caracas, Venezuela. A voucher specimen (No. VEN 299.338) was deposited at Herbario Nacional de Venezuela, Caracas, Venezuela.

Extraction and Isolation. The dried, powdered aerial parts of *C. guayanensis* (560 g) were defatted with *n*-hexane and successively extracted for 48 h with $CHCl_3$, $CHCl_3$−MeOH (9:1), and MeOH, by exhaustive maceration (3 × 2 L), to give 2.9, 14.0, and 35.0 g of the respective residues. The methanol extract was partitioned between *n*-BuOH and H_2O, to afford a *n*-BuOH-soluble portion (12.0 g). The *n*-BuOH residue was submitted to a Sephadex LH-20 column (5 × 60 cm, 350 g) using MeOH as eluent to obtain eight major fractions (1−8) by TLC on silica 60 F_{254} gel-coated glass sheets with *n*-BuOH−

Table 3. ^{1}H and ^{13}C NMR Data for Sugar Moieties of Compounds **7**−**9** (CD_3OD, 600 MHz)[a]

	7		**8**		**9**	
position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
D-Glc I 1	4.47 d (8.0)	105.1	4.44 d (8.0)	105.1	4.44 d (8.0)	105.2
2	3.54 dd (9.5, 8.0)	83.0	3.45 dd (9.0, 8.0)	83.1	3.45 dd (9.0, 8.0)	83.0
3	3.75 t (9.5)	76.6	3.56 t (9.0)	78.0	3.56 t (9.0)	78.2
4	3.62 t (9.5)	80.4	3.34 t (9.0)	71.2	3.36 t (9.0)	71.3
5	3.41 m	75.9	3.25 m	77.0	3.26 m	77.4
6a	3.90 dd (12.0, 3.0)	62.3	3.87 dd (12.0, 2.5)	62.7	3.86 dd (11.0, 3.5)	62.6
6b	3.68 dd (12.0, 5.0)		3.69 dd (12.0, 5.5)		3.66 dd (11.0, 5.0)	
D-Xyl I 1	4.60 d (7.5)	105.9	4.54 d (7.5)	106.2	4.54 d (7.5)	106.1
2	3.24 dd (9.0, 7.5)	76.3	3.22 dd (9.0, 7.5)	76.5	3.25 dd (9.0, 7.5)	76.2
3	3.36 t (9.0)	77.8	3.34 t (9.0)	77.7	3.34 t (9.0)	77.8
4	3.45 m	71.1	3.47 m	71.1	3.48 m	71.1
5a	3.84 dd (11.0, 3.5)	67.0	3.83 dd (11.0, 2.5)	67.0	3.83 dd (10.5, 2.5)	67.0
5b	3.16 dd (11.0, 5.0)		3.18 dd (11.0, 5.0)		3.16 dd (10.5, 5.0)	
D-Glc II 1	4.44 d (8.0)	104.5				
2	3.24 dd (9.5, 8.0)	74.8				
3	3.36 t (9.5)	77.8				
4	3.33 t (9.5)	71.3				
5	3.38 m	78.0				
6a	3.87 dd (12.0, 2.5)	61.6				
6b	3.68 dd (12.0, 5.5)					
L-Rha 1	5.95 d (1.5)	94.7	5.98 d (1.5)	94.7	5.96 d (1.8)	94.7
2	3.90 dd (3.0, 1.5)	69.0	3.92 dd (3.0, 1.5)	69.0	3.80 dd (3.0, 1.8)	71.2
3	5.06 dd (9.0, 3.0)	74.9	5.02 dd (9.0, 3.0)	74.9	3.47 dd (9.0, 3.0)	73.2
4	3.69 t (9.0)	70.3	3.69 t (9.0)	70.3	3.77 t (9.0)	72.2
5	3.84 m	72.7	3.81 m	72.7	3.77 m	72.3
6	1.30 d (6.0)	18.0	1.28 d (6.0)	18.0	1.27 d (6.5)	18.3
Isoval 1′		174.0		173.0		
2′	2.30 m	24.5	2.33 m	24.4		
3′	2.35 m	44.0	2.37 m	44.0		
4′/5′	1.02 d (6.5)	23.0	1.01 d (6.5)	23.9		

[a] *J* values are in parentheses and reported in Hz; chemical shifts are given in ppm; assignments were confirmed by DQF-COSY, 1D-TOCSY, HSQC, and HMBC experiments.

AcOH−H_2O (60:15:25) and $CHCl_3$−MeOH−H_2O (40:9:1). Fraction 2 (400 mg) was purified by HPCPC with $CHCl_3$−MeOH−H_2O−*i*-PrOH (5:6:4:1) in which the stationary phase consisted of the upper phase (descending mode, flow rate 3 mL min^{-1}), with fractions of 3 mL collected. HPCPC fractions 150−200 (32 mg) were chromatographed by RP-HPLC on a C_{18} μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 mL min^{-1}) with MeOH−H_2O (7:3) to afford pure compound **2** (2.0 mg, t_R = 25 min). HPCPC fractions 201−300 (40 mg) and 301−320 (25 mg) were separately purified by RP-HPLC on a C_{18} μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 mL min^{-1}) with MeOH−H_2O (6.5:3.5) to yield pure compound **1** (2.5 mg, t_R = 22 min) from fractions 201−300 and compound **3** (2.0 mg, t_R = 29 min) from fractions 301−320. Part of the chloroform−methanol residue (10.0 g) was chromatographed on Sephadex LH-20 (5 × 60 cm, 350 g) using MeOH as eluent; fractions of 8 mL were collected and grouped into 10 major fractions (1−10), in the same way as the *n*-BuOH extract. Fraction 2 (800 mg) was purified by HPCPC with $CHCl_3$−MeOH−H_2O−*i*-PrOH (5:6:4:1) in which the stationary phase consisted of the upper phase (descending mode, flow rate 3 mL min^{-1}), again with fractions of 3 mL collected. HPCPC fractions 50−92 (45 mg) were subjected to RP-HPLC on a C_{18} μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 mL min^{-1}) with MeOH−H_2O (4:1) to yield pure compound **7** (2.2 mg, t_R = 31 min). HPCPC fractions 93−160 (103 mg), 161−210 (82 mg), 211−250 (30 mg), and 251−300 (50 mg) were further separated by RP-HPLC on a C_{18} μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 mL min^{-1}) with MeOH−H_2O (7.5:2.5) to give pure compounds **10** (2.4 mg, t_R = 30 min), **11** (3.1 mg, t_R = 33 min), **5** (7.8 mg, t_R = 39 min), **13** (1.8 mg, t_R = 44 min), and **8** (5.5 mg, t_R = 48 min) from fractions 93−160, compound **9** (2.3 mg, t_R = 25 min) from fractions 161−210, compounds **12** (1.3 mg, t_R = 15 min), **6** (1.2 mg, t_R = 24 min), and **5** (4.5 mg, t_R = 40 min) from fractions 211−250, and compound **4** (2.6 mg, t_R = 17 min) from fractions 251−300.

Compound 1: white solid; $[\alpha]_D^{25}$ −17 (*c* 0.1, MeOH); ^{1}H NMR data of the aglycon (CD_3OD, 600 MHz) δ 0.81 (3H, s, Me-26), 0.86 (3H, s, Me-24), 0.95 (3H, s, Me-29), 0.97 (3H, s, Me-25), 1.02 (3H, s, Me-30), 1.08 (3H, s, Me-23), 1.20 (3H, s, Me-27), 2.96 (1H, dd, *J* = 12.0, 5.0 Hz, H-18), 3.19 (1H, dd, *J* = 11.5, 4.0 Hz, H-3), 5.38 (1H, t, *J* = 3.5 Hz, H-12); ^{13}C NMR data of the aglycon (CD_3OD, 150 MHz) δ 16.0 (C-25), 16.5 (C-24), 18.0 (C-26), 19.5 (C-6), 23.5 (C-16), 23.8 (C-30), 24.6 (C-11), 26.2 (C-27), 26.6 (C-2), 28.0 (C-23), 28.2 (C-15), 30.8 (C-20), 33.4 (C-29), 33.7 (C-7), 34.0 (C-22), 34.5 (C-21), 37.7 (C-10), 39.0 (C-4), 39.9 (C-1), 40.3 (C-8), 42.3 (C-14), 42.8 (C-18), 46.7 (C-19), 47.0 (C-17), 48.8 (C-9), 57.0 (C-5), 90.8 (C-3), 124.3 (C-12), 144.2 (C-13), 177.8 (C-28); ^{1}H and ^{13}C NMR of the sugar moieties, see Table 1; ESIMS *m/z* 1707 [M + H]$^+$, 1545 [M + H − 162]$^+$, 1383 [M + H − 162 − 162]$^+$, 1251 [M + H − 162 − 162 − 132]$^+$, 1237 [M + H − 162 − 162 − 146]$^+$, 1089 [M + H − 162 − 162 − 132 − 162]$^+$, 927 [M + H − 162 − 162 − 132 − 162 − 162]$^+$, 765 [M + H − 162 − 162 − 132 − 162 − 162 − 162]$^+$, 619 [M + H − 162 − 162 − 132 − 162 − 162 − 162 − 146]$^+$, 457 [M+H-162−162−132−162−162−162−146−162]$^+$; *anal.* C 54.10%, H 7.46%, calcd for $C_{77}H_{126}O_{41}$, C 54.15%, H 7.44%.

Compound 2: white solid; $[\alpha]_D^{25}$ −20 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **1**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 1; ESIMS *m/z* 1383 [M + H]$^+$, 1221 [M + H − 162]$^+$, 1059 [M + H − 162 − 162]$^+$, 927 [M + H − 162 − 162 − 132]$^+$, 781 [M + H − 162 − 162 − 132 − 146]$^+$, 619 [M + H − 162 − 162 − 132 − 146 − 162]$^+$, 457 [M + H − 162 − 162 − 132 − 146 − 162 − 162]$^+$; *anal.* C 56.40%, H 7.73%, calcd for $C_{65}H_{106}O_{31}$, C 56.43%, H 7.72%.

Compound 3: white solid; $[\alpha]_D^{25}$ −12 (*c* 0.1, MeOH); ^{1}H NMR data of the aglycon (CD_3OD, 600 MHz) δ 0.81 (3H, s, Me-26), 0.92 (3H, s, Me-24), 0.96 (3H, s, Me-29), 1.00 (3H, s, Me-30), 1.03 (3H, s, Me-25), 1.13 (3H, s, Me-23), 1.21 (3H, s, Me-27), 2.96 (1H, dd, *J* = 10,5, 4.0 Hz, H-18), 2.99 (1H, d, *J* = 11.0 Hz, H-3), 3.72 (1H, ddd, *J* = 11.0, 9.0, 3.0 Hz, H-2), 5.38 (1H, t, *J* = 3.5 Hz, H-12); ^{13}C NMR data of the aglycon (CD_3OD, 150 MHz) δ 16.6 (C-25), 17.0 (C-24), 17.7 (C-26), 19.4 (C-6), 23.5 (C-16), 23.6 (C-30), 24.4 (C-11), 27.0 (C-27), 28.2 (C-23), 28.4 (C-15), 31.0 (C-20), 33.4 (C-29), 33.5 (C-7), 33.6 (C-22), 34.4 (C-21), 37.8 (C-10), 40.0 (C-4), 40.1 (C-8), 42.5 (C-14), 42.7 (C-18), 46.8 (C-19), 47.0 (C-17), 47.4 (C-1), 48.8 (C-9), 56.6 (C-5), 67.3 (C-2), 96.0 (C-3), 124.0 (C-12), 144.0 (C-13), 177.5 (C-28); ^{1}H and ^{13}C NMR of the sugar moieties, see Table 2; ESIMS *m/z* 1391 [M + Na]$^+$, 921 [M + Na − 162 − 162 − 146]$^+$, 877 [M

+ Na − 162 − 162 − 146 − 44]$^+$, 789 [M + Na − 162 − 162 − 146 − 132]$^+$; *anal*. C 56.16%, H 7.66%, calcd for $C_{64}H_{104}O_{31}$, C 56.13%, H 7.65%.

Compound 4: white solid; $[\alpha]_D^{25}$ +56 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **3**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 2; ESIMS: *m/z* 1043 [M − H]$^-$, 897 [M − H − 146]$^-$, 765 [M − H − 146 − 132]$^-$, 735 [M − H − 146 − 162]$^-$, 603 [M − H − 146 − 132 − 162]$^-$, 471 [M − H − 146 − 132 − 162 − 132]$^-$; *anal*. C 59.70%, H 8.13%, calcd for $C_{52}H_{84}O_{21}$, C 59.75%, H 8.10%.

Compound 5: white solid; $[\alpha]_D^{25}$ −17 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **3**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 2; ESIMS *m/z* 989 [M + Na]$^+$, 759 [M + Na − 84 − 146]$^+$, 715 [M + Na − 84 − 146 − 44]$^+$, 583 [M + Na − 84 − 146 − 44 − 132]$^+$; *anal*. C 63.30%, H 8.56%, calcd for $C_{51}H_{82}O_{17}$, C 63.33%, H 8.55%.

Compound 6: white solid; $[\alpha]_D^{25}$ −29 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **1**; ^{1}H and ^{13}C NMR of the sugar moieties were identical to those of compound **5**; ESIMS *m/z* 973 [M + Na]$^+$, 889 [M + Na − 84]$^+$, 743 [M + Na − 84 − 146]$^+$, 699 [M + Na − 84 − 146 − 44]$^+$; *anal*. C 64.43%, H 8.66%, calcd for $C_{51}H_{82}O_{16}$, C 64.40%, H 8.69%.

Compound 7: white solid; $[\alpha]_D^{25}$ +33 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **1**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 3; ESIMS *m/z* 1141 [M − H]$^-$, 1057 [M − H − 84]$^-$, 911 [M − H − 84 − 146]$^-$, 779 [M − H − 84 − 146 − 132]$^-$, 617 [M − H − 84 − 146 − 132 − 162]$^-$, 455 [M − H − 84 − 146 − 132 − 162 − 162]$^-$; *anal*. C 60.97%, H 8.31%, calcd for $C_{58}H_{94}O_{22}$, C 60.93%, H 8.29%.

Compound 8: white solid; $[\alpha]_D^{25}$ +52 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **1**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 3; ESIMS *m/z* 1003 [M + Na]$^+$, 919 [M + Na − 84]$^+$, 773 [M + Na − 84 − 146]$^+$, 729 [M + Na − 84 − 146 − 44]$^+$, 597 [M + Na − 84 − 146 − 44 − 132]$^+$; *anal*. C 63.62%, H 8.65%, calcd for $C_{52}H_{84}O_{17}$, C 63.65%, H 8.63%.

Compound 9: white solid; $[\alpha]_D^{25}$ −35 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **1**; ^{1}H and ^{13}C NMR of the sugar moieties, see Table 3; ESIMS *m/z* 895 [M − H]$^-$; *anal*. C 62.97%, H 8.50%, calcd for $C_{47}H_{76}O_{16}$, C 62.93%, H 8.54%.

Compound 10: white solid; $[\alpha]_D^{25}$ −44 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **3**; ^{1}H and ^{13}C NMR of the sugar moieties were identical to those of compound **8**; ESIMS *m/z* 1019 [M + Na]$^+$, 935 [M + Na − 84]$^+$, 789 [M + Na − 84 − 146]$^+$, 745 [M + Na − 84 − 146 − 44]$^+$, 613 [M + Na − 84 − 146 − 44 − 132]$^+$; *anal*. C 62.60%, H 8.50%, calcd for $C_{52}H_{84}O_{18}$, C 62.63%, H 8.49%.

Compound 11: white solid; $[\alpha]_D^{25}$ −30 (*c* 0.1, MeOH); ^{1}H NMR data of the aglycon (CD_3OD, 600 MHz) δ 0.91 (3H, s, Me-24), 0.95 (3H, s, Me-25), 0.96 (3H, s, Me-26), 1.06 (3H, s, Me-27), 1.12 (3H, s, Me-23), 1.74 (3H, s, Me-30), 2.97 (1H, d, J = 11.5 Hz, H-3), 3.07 (1H, dd, J = 11.5, 8.0 Hz, H-18), 3.61 (1H, ddd, J = 11.5, 9.2, 3.0 Hz, H-2), 4.66 (1H, brs, H-29a), 4.80 (1H, br s, H-29b); ^{13}C NMR data of the aglycon (CD_3OD, 150 MHz) δ 14.9 (C-27), 16.5 (C-26), 16.9 (C-24), 17.6 (C-25), 19.2 (C-6), 19.4 (C-30), 22.0 (C-11), 26.6 (C-15), 28.0 (C-23), 30.7 (C-16), 31.6 (C-12), 33.0 (C-7), 35.0 (C-13), 37.6 (C-22), 38.8 (C-10), 39.8 (C-21), 40.1 (C-8), 40.4 (C-4), 43.0 (C-14), 47.6 (C-1), 48.7 (C-18), 50.4 (C-19), 51.1 (C-9), 56.3 (C-17), 56.7 (C-5), 67.0 (C-2), 96.1 (C-3), 110.4 (C-29), 151.0 (C-20), 177.5 (C-28); ^{1}H and ^{13}C NMR of the sugar moieties were superimposable on those of **5**; ESIMS *m/z* 1003 [M + Na]$^+$, 819 [M + Na − 84]$^+$, 773 [M + Na − 84 − 146]$^+$, 641 [M + Na − 84 − 146 − 132]$^+$; *anal*. C 63.35%, H 8.53%, calcd for $C_{51}H_{82}O_{17}$, C 63.33%, H 8.55%.

Compound 12: white solid; $[\alpha]_D^{25}$ −11 (*c* 0.1, MeOH); ^{1}H NMR data of the aglycon (CD_3OD, 600 MHz) δ 0.83 (3H, s, Me-24), 0.88 (3H, s, Me-25), 0.96 (3H, s, Me-26), 1.05 (3H, s, Me-27), 1.06 (3H, s, Me-23), 1.74 (3H, s, Me-30), 3.07 (1H, dd, J = 11.5, 8.0 Hz, H-18), 3.12 (1H, dd, J = 11.5, 4.0 Hz, H-3), 4.65 (1H, br s, H-29a), 4.80 (1H, br s, H-29b); ^{13}C NMR data of the aglycon (CD_3OD, 150 MHz) δ 15.0 (C-27), 16.4 (C-25), 16.5 (C-26), 16.8 (C-24), 19.3 (C-6), 19.6 (C-30), 22.0 (C-11), 26.7 (C-2), 27.0 (C-15), 28.1 (C-23), 30.7 (C-16), 31.5 (C-12), 33.0 (C-7), 35.2 (C-13), 37.8 (C-22), 38.3 (C-10), 38.6 (C-4), 39.8 (C-1), 39.9 (C-21), 40.5 (C-8), 42.1 (C-14), 47.0 (C-18), 50.5 (C-19), 51.0 (C-9), 56.3 (C-17), 57.1 (C-5), 90.7 (C-3), 110.4 (C-29), 151.0 (C-20), 177.5 (C-28); ^{1}H and ^{13}C NMR of the sugar moieties were identical to those of compound **5**; ESIMS *m/z* 973 [M + Na]$^+$, 743 [M + Na − 84 − 146]$^+$; *anal*. C 64.42%, H 8.65%, calcd for $C_{51}H_{82}O_{16}$, C 64.40%, H 8.69%.

Compound 13: white solid; $[\alpha]_D^{25}$ −23 (*c* 0.1, MeOH); ^{1}H and ^{13}C NMR data of the aglycon were superimposable on those reported for **12**; ^{1}H and ^{13}C NMR of the sugar moieties were identical to those of compound **8**; ESIMS *m/z* 1003 [M + Na]$^+$, 819 [M + Na − 84]$^+$, 773 [M + Na − 84 − 146]$^+$, 641 [M + Na − 84 − 146 − 132]$^+$; *anal*. C 63.63%, H 8.66%, calcd for $C_{52}H_{84}O_{17}$, C 63.65%, H 8.63%.

Acid Hydrolysis of Compounds 1−13. A solution of each compound **1**−**13** (2.0 mg) in 1 N HCl (1 mL) was stirred at 80 °C in a stoppered reaction vial for 4 h. After cooling, the solution was evaporated under a stream of N_2. Each residue was dissolved in 1-(trimethylsilyl)imidazole and pyridine (0.2 mL), and the solution was stirred at 60 °C for 5 min. After drying the solution, the residue was partitioned between water and $CHCl_3$. The $CHCl_3$ layer was analyzed by GC using a 1-Chirasil-Val column (0.32 mm × 25 m). Temperatures of both the injector and detector were 200 °C. A temperature gradient system was used for the oven, starting at 100 °C for 1 min and increasing up to 180 °C at a rate of 5 °C/min. Peaks of the hydrolysate were detected by comparison with retention times of authentic samples of D-glucose, D-xylose, and L-rhamnose (Sigma Aldrich) after treatment with 1-(trimethylsilyl)imidazole in pyridine.

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