Stevisalioside A, a Novel Bitter-Tasting ent-Atisene Glycoside from the Roots of Stevia salicifolia

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STEVISALIOSIDE A, A NOVEL BITTER-TASTING *ENT*-ATISENE GLYCOSIDE FROM THE ROOTS OF *STEVIA SALICIFOLIA*[1,2]

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ABSTRACT.—A new acetylated *ent*-atisene glycoside, stevisalioside A [**1**], has been isolated as a bitter-tasting principle from *Stevia salicifolia* roots. The structure was established by the interpretation of spectral data, with the nmr assignments of this compound being based on ^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, and selective INEPT experiments. A rearrangement product **4** of the aglycone moiety obtained by alkaline hydrolysis supported the structure of **1**. This is the first report of the occurrence of an atisane-type diterpene from the genus *Stevia*.

Stevia salicifolia Cav. (Asteraceae), indigenous to Mexico, is popularly known as "ronino" and "roninowa" among the Tarahumara Indians. Bitter-tasting infusions and decoctions of the roots are used respectively for alleviating gastrointestinal upsets and as a cathartic (2). The roots are also chewed for toothache in Mexico (3). In our previous work on *S. salicifolia*, a new dammarane triterpene was isolated from a hexane extract of the roots (4). Other phytochemical investigations on the aerial parts and roots of this species have afforded benzofurans (5), a chromene (5), flavonoids (7), monoterpenes (5), and sesquiterpenes (5,6), in addition to clerodane and labdane diterpenes (5,7).

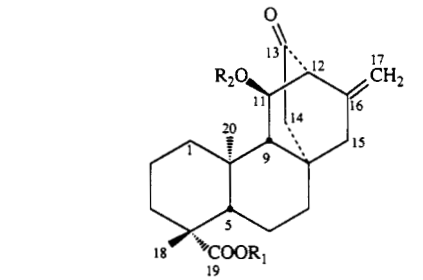
The genus *Stevia* is well-known as the source of the important sweet-tasting *ent*-kaurene glycosides, stevioside and rebaudioside A, which are extracted commercially from the South American plant, *Stevia rebaudiana* Bertoni (8). However, such sweet glycosides appear to have a very limited distribution in *Stevia*, since aside from *S. rebaudiana*, they were detected in only one other species (*Stevia phlebophylla* A. Gray) among 108 other *Stevia* species examined phytochemically, including *S. salicifolia* leaves (9). It has now been found that structural analogues exhibiting bitterness occur for all of the known naturally occurring diterpene sweeteners, embracing *ent*-kaurene glycosides from *S. rebaudiana* (10) and *Rubus suavissimus* S. Lee (Rosaceae) (11,12), and labdane glycosides from *Phlomis betonicoides* Diels (Labiatae) (13) and *Baccharis gaudichaudiana* DC. (Asteraceae) (14). Therefore, it was rationalized that the bitter taste of *S. salicifolia* roots might conceivably be due to either *ent*-kaurene or labdane glycosides. The present investigation, however, has revealed that the major bitter-tasting principle of *S. salicifolia* roots was an acetylated *ent*-atisene diterpene glycoside, stevisalioside A [**1**]. Reported herein are details of the isolation and structure elucidation of **1**, and of its enzymic and alkali hydrolysis products.

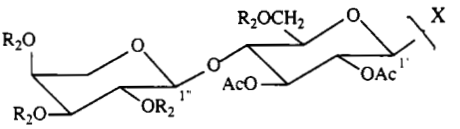
RESULTS AND DISCUSSION

The molecular formula of compound **1** was determined as $C_{35}H_{50}O_{15}$ (*m/z* 711.3228) in its high-resolution positive fabms spectrum. Its ir spectrum showed absorption maxima at 1740 cm^{-1} (carbonyl group) and at 1370 and 900 cm^{-1} (exo-

[1]Chemical Studies on Mexican Plants Used in Traditional Medicine, XXV. For the previous paper in this series, see R. Mata *et al.* (1).

[2]Taken in part from the M.S. thesis of V. Rodríguez.





1 R_1=X, R_2=H
2 R_1=X, R_2=Ac
3 R_1=R_2=H

methylene group). In addition, two tertiary methyl groups (δ 0.79 and 1.18), two acetyl groups (δ 2.16 and 2.22), an exo-methylene (δ 5.06 and 5.13), and two anomeric protons (δ 4.93 and 6.27) were observed in the ^{1}H-nmr spectrum. Thus, compound **1** was considered to be an acetylated diterpene glycoside.

^{13}C-nmr chemical shifts at δ 92.1 and 106.2, which correlated with two anomeric protons at δ 6.27 and 4.93, respectively, in a ^{1}H-^{13}C HETCOR nmr experiment, suggested that one of the sugar units was attached to a carboxylic acid in the aglycone, because anomeric chemical shifts of one sugar unit [δ 92.1 (^{13}C) and δ 6.27 (^{1}H)] were observed at resonances well removed from the other [δ 106.2 (^{13}C) and δ 4.93 (^{1}H)], owing to an esterification effect (15). Analysis of ^{1}H-^{1}H COSY nmr correlations and their coupling constants revealed that the spin systems corresponded to the presence of β-D-glucopyranosyl [δ 6.27 (H-1′), 5.63 (H-2′), 5.85 (H-3′), 4.59 (H-4′), 3.93 (H-5′), 4.20–4.27 (H-6′), 4.59 (H-4′)] and α-L-arabinopyranosyl [4.93 (H-1″), 4.35 (H-2″), 4.08 (H-3″), 4.20–4.27 (H-4″), 3.71 (H-5″), 4.20–4.27 (H-5″)] moieties, and that the esterified sugar unit was glucose. In addition, the identities of these sugars, when obtained by acid hydrolysis, were confirmed as D-glucose and L-arabinose by comparing with authentic sugar samples by tlc.

The presence of a disaccharide residue composed of one arabinose and one diacetylglucose (inner sugar) moiety was confirmed in the fabms spectra of **1**, which exhibited mass fragments at *m/z* 711 $[M+1]^+$, 579 $[M+1-\text{arabinose}]^+$, and 379 (disaccharide) in the positive mode, and at *m/z* 709 $[M-1]^-$, 667 $[M-1-\text{AcO}]^-$, and 331 (genin) in the negative mode. Information on the nature of the linkage between the sugars as well as on the position of the two acetyl groups in the inner sugar was determined by a selective INEPT experiment, an nmr technique which identifies vicinal ^{13}C-^{1}H coupling (16). Hence, irradiation ($^3J_{CH}$ = 6 Hz) of δ 5.63 (H-2′) and δ 5.85 (H-3′), which correlated in turn with δ 71.6 (C-2′) and 74.6 (C-3′) in the ^{1}H-^{13}C HETCOR nmr spectrum, resulted in selective enhancements of carbonyl carbons at δ 170.1 and 170.5, respectively. Furthermore, irradiation ($^3J_{CH}$ = 6 Hz) of δ 4.59 (H-4′), which also correlated with δ 76.8 (C-4′) in the ^{1}H-^{13}C HETCOR spectrum, selectively enhanced an anomeric carbon at δ 106.2 (C-1″). The anomeric carbon (δ 92.1) and carbons at C-2′, C-3′, and C-4′ of the glucosyl moiety were observed as resonances more upfield than those (δ 95.6–95.7) observed for other diterpene glucosyl esters (15),

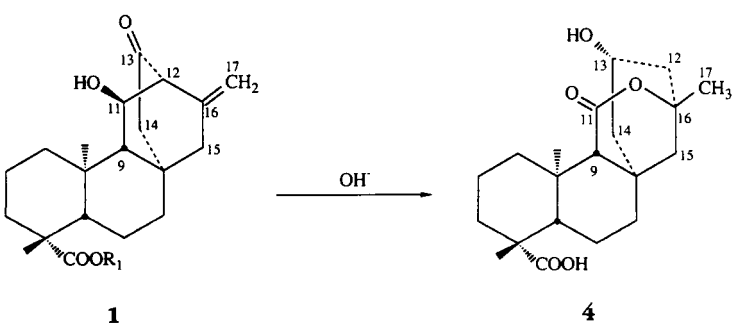
as may be explained by an acylation shift (17). Thus, the sugar unit of **1** was deduced as having α-L-arabinopyranosyl and 2,3-diacetyl-β-D-glucopyranosyl moieties that possessed a 1↦4 linkage.

The ^{13}C resonances of the aglycone portion were consistent with those of an *ent*-atisene skeleton possessing a keto (δ 210.5), a secondary hydroxyl (δ 68.5), and a carboxyl (δ 175.9) group (18). The presence of the hydroxyl and the keto groups in rings C and D was deduced from the COSY (correlations between H-11 and H-12 and between H-15 and H-17) and the NOESY (correlations between H-11 and H-12 and between H-12 and H-17) nmr spectra. The position of the hydroxyl group was proved as being at C-11 by a selective INEPT nmr experiment, in which irradiation ($^3J_{CH} = 6$ Hz) of a multiplet at δ 4.20–4.27 gave clear enhancements of C-10 and C-16. The relative stereochemistry of the hydroxy group at C-11 was confirmed as β-hydroxy from the observed coupling constants of H-9 ($J = 1.5$ Hz) to H-11 and of H-12 ($J = 3.0$ Hz) to H-11. The coupling constant of H-11, which was overlapped with other protons in **1**, was clearly observed as a triplet at δ 5.26 ($J = 2.0$ Hz) in the ^{1}H-nmr spectrum of the heptaacetyl derivative **2**.

The positon of the keto group was also determined as being affixed to C-13, because of the enhancement of the resonances corresponding to C-9, C-11, and C-13 upon irradiation ($^3J_{CH} = 6$ Hz) of H-12 (δ 3.53) in a selective INEPT nmr experiment, as well as the downfield shifts of C-14 (δ 44.9) and H-14 (δ 1.91 and 2.77), which were comparable with analogous chemical shifts of other atisenes (18,19). The resonances of both C-4 (δ 44.2) and C-18 (δ 28.4) were consistent with the presence of a carboxyl group at C-19 (18), and since irradiation ($^3J_{CH} = 6$ Hz) of the glucosyl anomeric proton (δ 6.27) produced a strong enhancement of the carboxyl group at δ 175.9 in a further selective INEPT nmr experiment, it was concluded that the disaccharide portion of **1** was attached to the aglycone at C-19 through an ester linkage.

The absolute stereochemistry of the aglycone moiety in compound **1** was determined as an *ent*-atisane type, because its genin **3** obtained from enzyme hydrolysis (crude hesperidinase) demonstrated intense levo-rotations at 589 to 365 nm, a pattern consistent with other *ent*-atis-16-en-19-oic acid derivatives (20–23). Therefore, this new bitter-tasting *ent*-atisene glycoside, to which we have accorded the trivial name stevisalioside A [**1**], was elucidated as *ent*-11β-hydroxy-13-oxo-atis-16-en-19-oic acid α-L-arabinopyranosyl-(1↦4)-2′,3′-diacetyl-β-D-glucopyranosyl ester.

In initial attempts to acquire the genin compound **3**, acid and alkaline hydrolyses of **1** were carried out prior to enzymic hydrolysis. While acidic hydrolysis led to a complex mixture of decomposition products, alkaline treatment with KOH afforded a major compound **4** (yield 66%) (Figure 1). Compound **4** exhibited three singlet methyls (δ 1.13, 1.24, and 1.37) in the ^{1}H-nmr spectrum, suggesting that the aglycone moiety of



1 **4**

FIGURE 1. Conversion of **1** to **4** by alkaline hydrolysis (for R_1, see structures **1–3**).

1 was rearranged and the exo-methylene unit at C-17 had been converted into a methyl group. Furthermore, evidence for the disappearance of the keto group (δ 210.5) at C-13 and the presence of a lactone (δ 172.0) and a secondary hydroxyl group (δ 64.2) was noticed from the ^{13}C-nmr and eims (*m/z* 350) spectra. The linkage of the lactone was placed between C-11 and C-16, because a proton at δ 1.83 (H-9) was observed as a sharp singlet in the ^{1}H-nmr spectrum and an enhancement of the resonance corresponding to C-16 (δ 82.2, s) was observed upon irradiation ($^{3}J_{CH}$ = 4 Hz) of H-17 (δ 1.37) in a selective INEPT nmr experiment. It was also supported by the ^{1}H-nmr chemical shifts of H_{eq}-1 (δ 2.95, J = 13 Hz), H_{eq}-12 (δ 2.30, J = 13, 4 Hz) and H_{eq}-14 (δ 2.67, J = 12 Hz), which were shifted downfield by the influence of the carboxyl group at C-11. The position of a secondary hydroxyl group was also determined as at C-13 by a selective INEPT experiment. Thus, irradiation ($^{3}J_{CH}$ = 6 Hz) of H-14 (δ 2.67) led to enhancements of δ 37.5 (C-8), 46.7 (C-12), 49.0 (C-15), and 64.2 (C-13), and of δ 28.1 (C-17), 42.6 (C-14), 49.0 (C-15), 64.2 (C-13), and 82.2 (C-16) when H-12 (δ 2.30) was irradiated in a similar manner. The orientation of the secondary hydroxyl group at C-13 was established as equatorial by the observed diaxial coupling constants of H_{ax}-12 (J = 12 Hz) and H_{ax}-14 (J = 12 Hz) to H_{ax}-13. A representation of the preferred conformation of hydrolysis product **4** is shown in Figure 2. Interestingly, this type of rearrangement by alkali has already been observed in the alkaloid 11-acetyl-2,13-didehydrohetisine, which was first converted into a 11β-hydroxy-13-oxo-type derivative like compound **3** and then rearranged to a lactone compound, in a similar manner to compound **4** (24).

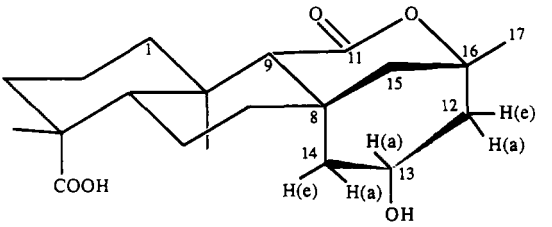


FIGURE 2. Preferred conformation of hydrolysis product **4**.

It is known that *Stevia* species produce a variety of diterpene compounds, whose basic structures are *ent*-kauranes, normal-labdanes, *ent*-labdanes, *ent*-clerodanes, *ent*-beyeranes, and a stevisalane (9, 10, 25–27). In spite of extensive phytochemical studies on *Stevia* species, no atisane derivative has yet been reported from this genus. Furthermore, only two atisane glycosides, from *Pteris purpureorachis* (Pteridaceae), have so far been reported previously in nature (28). Therefore, we believe that the discovery of stevisalioside A [**1**], a highly bitter *ent*-atisene glycoside from *S. salicifolia* roots, is significant both chemotaxonomically and in gaining a better understanding of the structural relationship between sweet and bitter diterpene glycosides.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points (uncorrected) were determined on a Fisher-Johns apparatus. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter. Ir spectra were obtained with a Midac Collegian FT-IR spectrophotometer. ^{1}H-nmr and ^{13}C-nmr spectra were measured with TMS as internal standard, employing a Varian XL-300 instrument operating at 300 MHz and 75.6 MHz, respectively. ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR nmr experiments were also performed on a Varian XL-300, using standard Varian pulse sequences. Selective INEPT nmr experiments were conducted on a Nicolet NT-360 spectrometer performing at 90.8 MHz. Eims and fabms spectra were obtained using a Finnegan MAT 90 instrument.

PLANT MATERIAL.—The roots of *S. salicifolia* were collected in Municipio de Guachochic, Cusarare, Chihuahua, Mexico, in November 1988. The identity of the plant was confirmed by Dr. Robert Bye. Herbarium samples have been deposited at the ethnobotanical collection of the National Herbarium, Instituto de Biologia, Mexico City, Mexico (Voucher: Bye 16657).

EXTRACTION AND ISOLATION.—The dried and pulverized roots of *S. salicifolia* (3 kg) were exhaustively extracted with hexane at room temperature. The dried marc was repeatedly extracted with Me_2CO at room temperature to afford 76 g of a residue on removal of solvent under vacuum. This extract was column chromatographed over Si gel (760 g) using as eluents hexane with increasing amounts of $CHCl_3$ and then $CHCl_3$ gradually enriched with Me_2CO. Altogether, 379 fractions were collected, each of 500 ml. Fractions 87–94 were subjected to further chromatographic separation over a Si gel column by eluting with hexane-$CHCl_3$ (1:1) to give 52 mg of stigmasterol. Fractions 251–293, purified by elution with $CHCl_3$-Me_2CO (3:1), afforded 23 mg of daucosterol (β-D-glucositosterol). Fractions 294–340, which were chromatographed over Si gel with $CHCl_3$-Me_2CO (1:1), yielded 3.2 g (0.107% w/w) of compound **1**. Compound **1** was finally purified by crystallization from MeOH.

Stevisalioside A [**1**].—Mp 164–166° (colorless needles, MeOH); $[\alpha]^{25}D$ −42° (*c* = 0.24, MeOH); ir ν max (KBr) 3420, 2930, 1740, 1370, 1320, 1250, 1160, 1060, 900 cm^{-1}; ^1H nmr (C_5D_5N) δ 0.79 (3H, s, H-20), 1.18 (3H, s, H-18), 1.45 (1H, d, *J* = 1 Hz, H-9), 1.65 (1H, br d, *J* = 14 Hz, H_{eq}-6 or H_{eq}-7), 1.91 (1H, d, *J* = 20 Hz, H_{ax}-14), 2.16 (3H, s, OAc), 2.22 (3H, s, OAc), 2.27 (1H, d, *J* = 16 Hz, H_{eq}-15), 2.37 (1H, dd, *J* = 15, 2 Hz, H_{ax}-15), 2.77 (1H, dd, *J* = 19, 3 Hz, H_{eq}-14), 3.53 (1H, d, *J* = 3 Hz, H-12), 3.71 (1H, dd, *J* = 12, 1 Hz, H-5″), 3.93 (1H, dt, *J* = 9, 3 Hz, H-5′), 4.08 (1H, dd, *J* = 9, 3 Hz, H-3″), 4.20–4.27 (4H, m, H-11, H-6′, H-4″, H-5″), 4.35 (1H, dd, *J* = 8, 8 Hz, H-2″), 4.55 (1H, dd, *J* = 12, 2 Hz, H-6′), 4.59 (1H, dd, *J* = 10, 9 Hz, H-4′), 4.93 (1H, d, *J* = 7 Hz, H-1″), 5.06 (1H, br s, H-17), 5.13 (1H, br s, H-17), 5.63 (1H, dd, *J* = 9, 9 Hz, H-2′), 5.85 (1H, dd, *J* = 10, 9 Hz, H-3′), 6.27 (1H, d, *J* = 8 Hz, H-1′); ^{13}C nmr see Table 1; positive fabms *m/z* (rel. int.) $[M+1]^+$ 711 (8), $[M+1-arabinose]^+$ 579 (4), 379 (sugar) (100); negative fabms *m/z* (rel. int.) $[M-1]^-$ 709 (31), 667 $[M-1-AcO]^-$ (11), 331 (genin) (100); high-resolution positive fabms *m/z* $[M+1]^+$ 711.3228 (calcd for $C_{35}H_{51}O_{15}$, 711.3228).

Acetylation of **1**.—Compound **1** (100 mg) was acetylated with 2.5 ml of Ac_2O-C_5H_5N (3:2) for 24 h at room temperature to afford a heptaacetyl derivative **2** (83 mg): Mp 116–118° (colorless needles, MeOH); $[\alpha]^{25}D$ −33° (*c* = 0.72, $CHCl_3$); ir ν max (KBr) 3450, 2940, 1750, 1370, 1220, 1070 cm^{-1}; ^1H nmr (C_5D_5N) δ 0.78 (3H, s, H-20), 1.23 (3H, s, H-18), 1.40 (1H, d, *J* = 2 Hz, H-9), 1.92 (1H, d, *J* = 20 Hz, H_{ax}-14), 1.96–2.18 (21H, s, 7 × OAc), 2.74 (1H, dd, *J* = 20, 3 Hz, H_{eq}-14), 3.65 (1H, d, *J* = 3 Hz, H-12), 3.85 (1H, dd, *J* = 12, 1 Hz, H-5″), 4.10–4.25 (4H, m, H-4′, H-5′, H-3″, H-5″), 4.45 (1H, dd, *J* = 12, 3 Hz, H-6′), 4.60 (1H, dd, *J* = 12, 6 Hz, H-6′), 4.92 (1H, d, *J* = 7 Hz, H-1″), 4.98 (1H, br s, H-17), 5.01 (1H, br s, H-17), 5.26 (1H, t, *J* = 2 Hz, H-11), 5.48–5.65 (3H, m, H-2′, H-2″, H-4″), 5.82 (1H, dd, *J* = 10, 9 Hz, H-3′), 6.30 (1H, d, *J* = 8 Hz, H-1′); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) $[M-42]^+$ 878 (3), 646 (11), 547 (41), 487 (8), 317 (20), 269 (29), 259 (100), 227 (37), 169 (50), 157 (44), 139 (60). *Anal.* calcd for $C_{45}H_{60}O_{20}$, C 58.70%, H 6.52%; found C 58.64%, H 6.54%.

Enzyme hydrolysis of **1**.—A mixture of **1** (100 mg), crude hesperidinase (Tanabe Pharmaceutical Co., Lot. No. EzBK-N-30) (500 mg) and a few drops of toluene in 50 ml of phosphate buffer (0.2 M, pH 4.0) was incubated at 40° for 7 days followed by extraction with Et_2O. The extract was subjected to preparative Si gel tlc, by developing with $CHCl_3$-MeOH (20:1), to give a genin **3** (1 mg): colorless solid; ir ν max (KBr) 3430, 2920, 2850, 1720, 1470, 1180, 890 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.75 (3H, s, H-20), 1.27 (3H, s, H-18), 2.60 (1H, dd, *J* = 19, 3 Hz, H_{eq}-14), 3.12 (1H, d, *J* = 3 Hz, H-12), 3.95 (1H, t, *J* = 2 Hz, H-11), 5.07 (1H, s, H-17), 5.08 (1H, s, H-17); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) $[M]^+$ 332 (49), 304 (13), 257 (12), 166 (20), 151 (46), 135 (38), 12 (100);

$$[\alpha]\lambda^{25} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365 \text{ nm}}{-86° \quad -92° \quad -98° \quad -196° \quad -491°} \qquad (c = 0.06, CHCl_3).$$

Alkaline hydrolysis of **1**.—Compound **1** (80 mg) was refluxed for 1 h with 10 ml of 1 N KOH/H_2O. After cooling, the mixture was acidified with HOAc and extracted with Et_2O. The Et_2O extract was chromatographed over Si gel by elution with $CHCl_3$-MeOH (20:1) to afford a rearranged genin **4** (26 mg): colorless powder; $[\alpha]^{25}D$ −32° (*c* = 0.52, $CHCl_3$); ir ν max (KBr) 3420, 2930, 2850, 1710, 1460, 1140, 1050, 730 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.88 (1H, dt, *J* = 13, 3 Hz, H_{ax}-1), 1.03 (1H, dt, *J* = 14, 4 Hz, H-3), 1.10 (1H, dd, *J* = 12, 12 Hz, H_{ax}-14), 1.13 (3H, s, H-20), 1.24 (3H, s, H-18), 1.35 (1H, dd, *J* = 12, 12 Hz, H_{ax}-12), 1.37 (3H, s, H-17), 1.57 (1H, d, *J* = 14 Hz, H-15), 1.66 (1H, d, *J* = 13 Hz, H-15), 1.83 (1H, s, H-9), 2.14 (1H, br d, *J* = 13 Hz, H-3), 2.30 (1H, dd, *J* = 13, 4 Hz, H_{eq}-12), 2.67 (1H, br d, *J* = 12 Hz, H_{eq}-14), 2.95 (1H, br d, *J* = 13 Hz, H_{eq}-1), 3.95 (1H, m, H-13); ^{13}C nmr see Table 1; eims *m/z* (rel. int.) $[M]^+$ 350 (33), 332 (41), 295 (58), 277 (43), 151 (60), 137 (82), 119 (80), 105 (100).

TABLE 1. ^{13}C-nmr Spectra of Compounds **1–4**.[a]

Carbon	Compound			
	1[b]	**2**[b]	**3**[c]	**4**[c]
C-1	39.6 t	38.5 t	39.4 t	40.2 t
C-2	18.9 t	18.7 t	18.4 t	18.9 t
C-3	38.2 t	37.9 t	37.7 t	37.7 t
C-4	44.2 s	44.2 s	43.5 s	43.8 s
C-5	56.4 d	55.8 d	56.4 d	57.7 d
C-6	20.3 t	20.8 t	19.8 t	18.9 t
C-7	37.8 t	37.9 t	37.7 t	42.8 t
C-8	36.7 s	36.4 s	36.4 s	37.5 s
C-9	62.6 d	58.3 d	63.0 d	59.5 d
C-10	37.9 s	37.4 s	37.7 s	38.5 s
C-11	68.5 d	70.5[d] d	68.2 d	172.0 s
C-12	66.1 d	61.0 d	64.4 d	46.7 t
C-13	210.5 s	208.2 s	209.9 s	64.2 d
C-14	44.9 t	44.9 t	44.8 t	42.6 t
C-15	46.2 t	45.6 t	45.8 t	49.0 t
C-16	139.9 s	138.4 s	137.2 s	82.2 s
C-17	113.4 t	114.0 t	115.1 t	28.1 q
C-18	28.4 q	28.5 q	28.8 q	29.0 q
C-19	175.9 s	175.5 s	181.2 s	182.5 s
C-20	14.5 q	14.3 q	14.2 q	13.2 q
C-1′	92.1 d	91.6 d		
C-2′	71.6 d	71.0[d] d		
C-3′	74.6 d	73.9[d] d		
C-4′	76.8 d	77.5 d		
C-5′	77.6 d	73.8[d] d		
C-6′	60.4 t	62.5 t		
C-1″	106.2 d	102.0 d		
C-2″	72.7 d	71.1[d] d		
C-3″	74.6 d	70.1[d] d		
C-4″	69.5 d	68.3[d] d		
C-5″	67.6 t	63.9 t		
$CH_3C{=}O$	21.0 (q × 2)	20.5–21.0 (q × 7)		
$CH_3C{=}O$	170.1 s 170.5 s	169.8-170.4 (s × 7)		

[a]Measured at 75.6 MHz, δ TMS = 0.
[b]Obtained in pyridine-d_5.
[c]Obtained in $CDCl_3$.
[d]May be reversed with a close signal in the same column.

Acid hydrolysis of **1**.—A solution of **1** (200 mg) in 1 N HCl (20 ml) was refluxed for 3 h, the solvent was removed at 40° in vacuo, and the reaction mixture was partitioned between $CHCl_3$ and H_2O. The aqueous layer contained glucose and arabinose (tlc) and the organic phase a mixture of several compounds, indicating substantial decomposition of the aglycone portion.

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