New Cytotoxic Sterol Glycosides from the Octocoral *Carijoa* (*Telesto*) *riisei*

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Two new steroidal glycosides, 3*β*-*O*-(3′-*O*-acetyl-*β*-D-arabinopyranosyl)-25*ξ*-cholestane-3*β*,5α,6*β*,26-tetrol-26-acetate (riisein A, **2**) and 3*β*-*O*-(4′-*O*-acetyl-*β*-D-arabinopyranosyl)-25*ξ*-cholestane-3*β*,5α,6*β*,26-tetrol-26-acetate (riisein B, **3**), were isolated from extracts of the Brazilian telestacean octocoral *Carijoa* (*Telesto*) *riisei* collected near Rio de Janeiro. The new glycosides co-occur with the polyhydroxy sterol, 25*ξ*-cholestane-3*β*,5α,6*β*,26-tetrol-26-acetate (**1**), an inseparable diastereomeric mixture previously reported from *Telesto riisei* collected in Micronesia. The structures of the new glycosides were assigned by spectroscopic methods and by comparison with spectral data for sterol **1**. Riiseins A and B showed in vitro cytotoxicity toward HCT-116 human colon adenocarcinoma with IC_{50} values of 2.0 *μ*g/mL.

Octocorals or soft-corals (subclass Octocorallia) are common, soft-bodied invertebrates found throughout the world's oceans. This group of marine invertebrates is recognized to be an extremely rich source of bioactive secondary metabolites, and because these animals lack physical defenses, these compounds are generally hypothesized to function as chemical defenses.[1] Octocorals within the order Telestacea are rare, and chemical investigations have been reported from only two species, *Carijoa* (*Telesto) riisei*[2−5] and *Coelogorgia palmosa*.[6] Chemical investigations of geographically diverse collections of *C. riisei* revealed that this organism is capable of producing a diversity of secondary metabolites. While Hawaiian specimens yielded the unique prostanoids known as the punaglandins,[3,4] samples collected in the Marshall Islands and in Micronesia were reported to contain C_{21} pregnane derivatives[2] or phenylethylamides and polyhydroxylated steroids,[5] respectively.

The Brazilian coast is rich in soft-corals,[7] but studies of their natural products chemistry have been rare.[8−12] A previous investigation of *C. riisei*, collected in Brazil, generated three pregnane derivatives and several common C_{26}−C_{29} cholestanes.[12] In this paper, we describe another study of Brazilian *C. riisei* collected near Angra dos Reis, a region in proximity of Rio de Janeiro. From this collection, we isolated the previously described polyhydroxy sterol **1**[5] and two new sterol glycosides, riiseins A and B (**2** and **3**).

C. riisei was collected by surface-air-supply diving in July 1993. The animals were frozen and later freeze-dried prior to extraction with MeOH−CH_2Cl_2 (1:1). Si gel chromatography of the CH_2Cl_2 crude extract, eluting with mixtures of EtOAc in isooctane, led to a polar fraction (100% EtOAc), which was further purified by normal and reversed-phase HPLC to give sterol **1** (0,008% dry wt), riisein A (**2**, 0.003% dry wt), and riisein B (**3**, 0.005% dry wt).

Polyhydroxy sterol **1** (cholestane-3*β*,5α,6*β*,26-tetrol-26-acetate) was obtained as an amorphous white solid that showed mp 173−175 °C, $[\alpha]^{25}_D$ −4° (*c* 1.00, $CHCl_3$). The LRMS for **1** illustrated a molecular ion at *m*/*z* 478, which suggested the molecular formula $C_{29}H_{50}O_5$. This molecular formula was confirmed by HRFABMS mass measurement of the fragment ion at *m*/*z* 460.3549 (calcd for [$C_{29}H_{50}O_5$ − H_2O], 460.3553). NMR measurements revealed that **1** was cholestane-3*β*,5α,6*β*,26-tetrol-26-acetate, a sterol previously isolated by Lyanage and Schmitz from *Telesto riisei* collected in Micronesia.[5] This was confirmed by direct comparison of the NMR data from sterol **1** with that derived from an authentic sample provided by Professor Francis Schmitz. Although we conducted our NMR experiments in a different solvent, we observed the same diastereoisomeric mixture at C-25 as reported earlier.

Spectroscopic analyses of riiseins A and B (**2** and **3**) revealed that they had almost identical structures possessing the same molecular formulas and exhibiting similar NMR features. Riisein A analyzed for the molecular formula $C_{36}H_{60}O_{10}$ on the basis of HRFABMS and ^{13}C NMR data. The IR spectrum showed absorption bands due to hydroxyl (3436 cm^{-1}) and ester carbonyl groups (1734 cm^{-1}). Analysis of 2D NMR experiments (^1H−^1H COSY, HMQC, and HMBC) revealed that riisein A was a pentose glycoside derivative of **1**. This conclusion was supported by ^1H signals for the pentose pyranoside between *δ* 3.0 and 5.0 and by corresponding ^{13}C NMR bands between 60 and 73 ppm. NMR bands for the characteristic sugar anomeric carbon (97.8 ppm) and its corresponding proton (*δ* 5.0) were clearly observed (Table 2). ^1H NMR coupling-constant analysis of the pyranose ring indicated the presence of a pyranoarabinoside sugar linked to the steroidal polyol by a *β*-glycoside linkage (Table 2). The attachment of the sugar moiety at C-3 of the aglycon **1** in riisein A was based on ^2J and ^3J correlations observed in the HMBC spectrum. The sugar anomeric carbon C-1′ (97.8 ppm) and the aglycon carbon C-3 (74.6 ppm) showed correlations with the H-3 proton (*δ* 4.06) and H-1′ protons (*δ* 5.03), respectively. NMR data also indicated the presence of an additional acetate ester positioned at C-3′ (δ_H 5.07, dd, J = 3.0 and 9.8 Hz; and δ_C 73.1 ppm). Acetylation of riisein A yielded the triacetate **4**. This was an unexpected reaction that apparently occurred by acid-catalyzed hydrolysis of the arabinopyranoside ring and subsequent acetylation at C-3 and C-6. Triacetate **4**, produced by acetylation of riisein A, was

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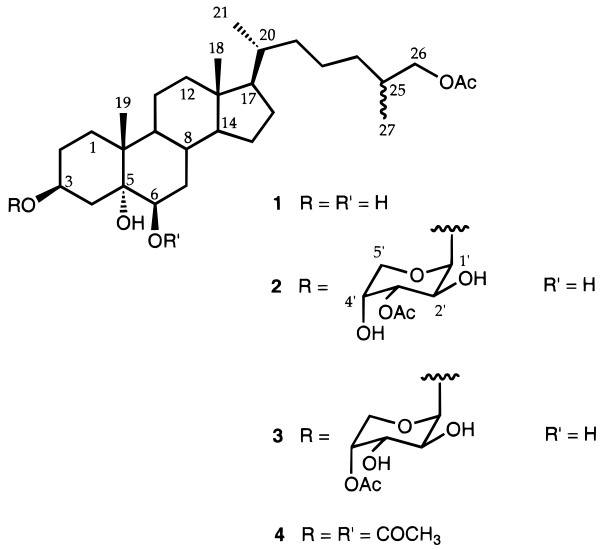
Table 1. NMR Data for the Sterol **1** and the Steroidal Aglycon Components of Riiseins A (**2**) and B (**3**) in $CDCl_3$

	1[a]		**2**		**3**	
position	δ ^{13}C (DEPT)[b]	δ ^{1}H (m, *J* in Hz)[b]	δ ^{13}C (DEPT)[b]	δ ^{1}H (m, *J* in Hz)[b]	δ ^{13}C (DEPT)[b]	δ ^{1}H (m, *J* in Hz)[b]
1a	32.3 (CH_2)	1.40 (m)	32.3 (CH_2)	1.42 (m)	31.7 (CH_2)	1.37 (m)
1b		1.52 (m)		1.55 (m)		1.57 (m)
2	30.7 (CH_2)	1.86 (m)	28.7 (CH_2)	1.86 (m)	28.2 (CH_2)	1.85 (m)
3	67.6 (CH)	4.08 (m)	74.6 (CH)	4.06 (m)	74.8 (CH)	4.01 (m)
4a	40.6 (CH_2)	1.63 (m)	37.3 (CH_2)	1.67 (m)	36.8 (CH_2)	1.64 (m)
4b		2.08 (m)		2.10 (m)		2.08 (m)
5	76.0 (C)		75.9 (C)		75.4 (C)	
6	75.8 (CH)	3.52 (br s)	76.1 (CH)	3.52 (br s)	75.1 (CH)	3.51 (br s)
7	34.3 (CH_2)	1.60 (m)	34.6 (CH_2)	1.60 (m)	33.7 (CH_2)	1.60 (m)
8	30.2 (CH)	1.72 (m)	30.3 (CH)	1.73 (m)	29.7 (CH)	1.71 (m)
9	45.7 (CH)	1.25	45.9 (CH)	1.24 (m)	45.3 (CH)	1.24 (m)
10	38.2 (C)		38.5 (C)		37.8 (C)	
11	21.1 (CH_2)	1.37 (m)	21.2 (CH_2)	1.34 (m)	20.5 (CH_2)	1.36 (m)
12a	39.9 (CH_2)	1.16 (m)	40.0 (CH_2)	1.15 (m)	39.4 (CH_2)	1.14 (m)
12b		1.98 (m)		1.98 (m)		1.98 (m)
13	42.7 (C)		42.7 (C)		42.2 (C)	
14	55.9 (CH)[c]	1.08 (m)	55.8 (CH)[c]	1.08 (m)	55.4 (CH)[c]	1.06 (m)
15a	24.1 (CH_2)	1.08 (m)	24.2 (CH_2)	1.06 (m)	24.2 (CH_2)	1.06 (m)
15b		1.56 (m)		1.57 (m)		1.57 (m)
16a	28.2 (CH_2)	1.22 (m)	28.3 (CH_2)	1.26 (m)	28.3 (CH_2)	1.25 (m)
16b		1.83 (m)		1.83 (m)		1.83 (m)
17	56.2 (CH)[c]	1.11 (m)	56.3 (CH)[c]	1.08 (m)	55.6 (CH)[c]	1.06 (m)
18	12.1 (CH_3)	0.67 (s)	12.2 (CH_3)	0.67 (s)	11.6 (CH_3)	0.66 (s)
19	17.0 (CH_3)	1.17 (s)	17.1 (CH_3)	1.18 (s)	16.2 (CH_3)[d]	1.18 (s)
20	36.0 (CH)	1.37 (m)	36.0 (CH)	1.37 (m)	35.5 (CH)[e]	1.36 (m)
21	18.6 (CH_3)	0.92 (d, $J = 7.0$)	18.7 (CH_3)	0.92 (d, $J = 6.5$)	18.1 (CH_3)	0.90 (d, $J = 6.0$)
22a	35.7 (CH_2)	1.00 (m)	35.8 (CH_2)	1.01 (m)	35.2 (CH_2)[e]	0.99 (m)
22b		1.37 (m)		1.37 (m)		1.36 (m)
23a	23.3 (CH_2)	1.37 (m)	23.4 (CH_2)	1.17 (m)	22.8 (CH_2)	1.36 (m)
23b				1.37 (m)		
24	33.7, 33.9 (CH_2)	1.72 (m)	33.8 (CH_2)	1.37 (m)	33.2, 33.3 (CH_2)	1.36 (m)
25	32.4, 32.5 (CH)	1.77 (m)	32.6, 32.6 (CH)	1.76 (m)	32.0 (CH)	1.75 (m)
26a	69.5, 69.6 (CH_2)	3.82, 3.84 (pair of dd, $J = 2.5, 10.5$)	69.5, 69.6 (CH_2)	3.82, 3.84 (pair of dd, $J = 2.5, 11.0$)	68.9, 69.0 (CH_2)	3.82, 3.84 (pair of dd, $J = 2.5, 11.0$)
26b		3.93, 3.95 (pair of dd, $J = 6.0, 10.5$)		3.93, 3.95 (m)		3.93, 3.95 (m)
27	16.8 (CH_3)	0.90, 0.91 (pair of d, $J = 6.0$)	16.9 (CH_3)	0.90, 0.91 (pair of d, $J = 6.5$)	16.5 (CH_3)[d]	0.91 (d, $J = 7.0$)
28	171.3 (C)		171.3 (C)		170.8 (C)	
29	21.0 (CH_3)	2.05 (s)	21.1 (CH_3)	2.05 (s)	20.5 (CH_3)	2.05 (s)

[a] Data included as a reference for NMR data of compounds **2** and **3** in $CDCl_3$. [b] ^{1}H and ^{13}C assignments ($CDCl_3$, 500 and 50 MHz, respectively) made on the basis of HMQC, HMBC, and ^{1}H−^{1}H COSY experiments (see experimental section). [c−e] Superscripts indicate that values in the same column may be interchanged.

found to be identical to triacetate **4** produced by acetylation of **1**.



Riisein B (**3**) was also analyzed for the molecular formula $C_{36}H_{60}O_{10}$ by HRFABMS and combined NMR data. Comprehensive NMR analyses, and comparison of overall spectral data to sterol **1** and riisein A (**2**), showed that **3** contained the same aglycon and β-pyranoarabinoside sugar as **2**. Like riisein A (**2**), riisein B was shown to be glycosylated at C-3 by interpretation of ^{2}J and ^{3}J correlations observed in the HMBC spectra. The anomeric carbon at C-1′ (97.6 ppm) and C-3 (74.8 ppm) showed correlations with the hydrogens H-3 (δ 4.01) and H-1′ (δ 5.01), respectively. Unlike **2**, however, riisein B was confirmed by HMBC NMR data (long-range coupling of the H-4′ proton to the ester carbonyl carbon) to possess an acetate ester positioned at 4′ on the pyranoarabinoside ring.

The arabinose sugar in riisein A was found to belong to the D series by chiral GC analysis of the corresponding trimethylsilylated (−)-2-butyl glycoside derivative.[13] Because riiseins A and B showed similar optical rotations, it is suggested that both have the same absolute configurations.

Riiseins A and B were examined for their in vitro cytotoxic properties toward HCT-116 human colon tumor cells. Both compounds showed significant cytotoxicity, with ED_{50} values of 2.0 μg/mL.

The generic nomenclature *Carijoa* and *Telesto* are synonymous in the literature. The variability of chemical components found from geographically diverse collections of

Table 2. NMR Data for the 3′- and 4′-*O*-Acetyl-Arabinopyranoside Components in Riiseins A (**2**) and B (**3**) in $CDCl_3$

	Riisein A (**2**)					Riisein B (**3**)				
	δ ^{13}C		^{1}H−^{1}H	HMBC (H$^{\#}$)[b]		δ ^{13}C		^{1}H−^{1}H	HMBC (H$^{\#}$)[b]	
position	(DEPT)[a]	δ ^{1}H (m, J in Hz)[a]	COSY	^2J	^3J	(DEPT)[a]	δ ^{1}H (m, J in Hz)[a]	COSY (H#)	^2J	^3J
1′	97.8 (CH)	5.04 (d, J = 4.5)	2′		3, 5ab′	97.6 (CH)	5.01 (d, J = 3.5)	2′		3, 5ab′
2′	67.3 (CH)	3.94 (m)	1′, 3′	3′	4′	68.8 (CH)	3.80 (dd, J = 3.5, 10.5)	1′, 3′	3′	4′
3′	73.1 (CH)	5.07 (dd, J = 3.0, 9.8)	2′, 4′		5ab′	67.8 (CH)	3.94 (m)	2′, 4′		1′, 5ab′
4′	68.3 (CH)	4.03 (br s)	3′, 5ab′	5ab′		71.1 (CH)	5.15 (br s)	3′, 5ab′	5ab′	5ab′
5a′	62.6 (CH_2)	3.66 (dd, J = 2.0, 12.5)	4′, 5b′		1′	60.5 (CH_2)	3.68 (br d, J = 11.0)	4′, 5b′		1′
5b′		3.94 (m)	4′, 5a′				3.93 (m)	4′, 5a′		
6′	170.9 (C)			7′	3′	170.9 (C)			7′	4′
7′	21.2 (CH_3)	2.17 (s)				21.2 (CH_3)	2.17 (s)			

[a] ^{1}H and ^{13}C assignments made on the basis of HMQC and HMBC experiments ($CDCl_3$, 500 and 50 MHz, respectively). [b] HMBC J_{CH} = 8 Hz.

this animal is not fully understood. Certainly, different approaches in extraction and purification of natural products can lead to the isolation of different classes of natural products. The variability of secondary metabolites found in *C. riisei*, however, may indicate temporal or geographic variations in the production of such chemicals as a consequence of environmental conditions, phenotype differences, or other biotic factors. Typically, the systematics of octocorals represent difficulties not yet clarified by gene sequence-based systematics.

Although different classes of compounds have been isolated from Pacific specimens, the southwest Atlantic populations of this animal appear closely related to those populations studied from the southwest Pacific Ocean. The isolation of compounds **1**−**3**, as well as the previously described pregnanes from the Brazilian *Carijoa* (*Telesto*) *riisei*, indicates the similarity of the Brazilian, Enewetak, and Chuuk Atoll collections, all of which contain 18-acetoxypregna-1,4,20-trien-3-one[2] and 25ξ-cholestane-3β,5α,6β-26-tetrol-26-acetate (**1**).[5]

Experimental Section

General Experimental Procedures. Corrected melting points were observed on a Thomas-Hoover capillary apparatus. IR spectra (film, $CHCl_3$) were recorded on a Perkin-Elmer model 1600 FTIR spectrometer. Optical rotations were measured on a Perkin-Elmer 243B (D_{25} = 589 nm, *c* 1.0, $CHCl_3$ or MeOH). Mass measurements were obtained on a HP5989A spectrometer. NMR spectra were recorded on a Varian Unity-500 (^{1}H, ^{1}H−^{1}H COSY, HMQC, and HMBC experiments) and Brucker 200 [PND (proton noise decoupled) and DEPT ^{13}C experiments)] spectrometers (with $CDCl_3$ solutions using TMS as internal standard). GC analyses were performed on a Varian model 3400 equipped with DB-5 glass capillary column (30 m) using hydrogen as carrier gas and temperature programming from 120 to 240 °C at a rate of 2 °C/min. Normal (Si gel) and reversed-phase (C_{18}) HPLC separations were carried out using semipreparative columns (9.4 mm i.d.) using a Waters model M6000 pump and a model R401 refractive index detector.

Extraction and Isolation. Colonies of *Carijoa* (*Telesto*) *riisei* were collected by surface-air-supply diving, in July 1993, at Mangaratiba, Rio de Janeiro State, Brazil, at a depth of 6 m. After collection, the specimens were immediately frozen. The animals were freeze-dried (235 g) and subsequently extracted at room temperature 3 times with MeOH−CH_2Cl_2 (1:1). After removal of the solvents from the combined extracts under reduced pressure, 15.0 g of a brownish gum was obtained. The CH_2Cl_2-soluble portion of the crude extract (5.64 g) was fractionated by flash chromatography on Si gel (230−400 mesh, Merck) employing a gradient of 0−100% of EtOAc in isooctane and pure MeOH as eluents. The EtOAc-soluble compounds obtained from the MeOH fraction (983 g) were subjected to semipreparative normal-phase HPLC separation, with EtOAc as eluent, to yield **1**−**3** as impure compounds. Compounds **1**−**3** were further purified by reversed-phase (C_{18}) HPLC using MeOH−H_2O (94:6, flow rate of 2.5 mL/min) to furnish sterol **1** (19 mg, 0.008% dry wt), riisein A (**2**, 8 mg, 0.003% dry wt), and riisein B (**3**, 12 mg, 0.005% dry wt).

25ξ-Cholestane-3β,5α,6β-26-tetrol-26-acetate (1): amorphous white powder; mp 173−175 °C; $[\alpha]^{25}_D$ −4° (*c* 0.1, $CHCl_3$); IR (film, $CHCl_3$) ν_{max} 3424, 1742 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 1; EIMS *m/z* (rel int) [M]$^+$ 478 (4), 460 (30), 442 (100) 424 (17), 383 (4), 320 (26); HREIMS (70 eV) [M − H_2O]$^+$ obsd 460.3549, calcd for $C_{29}H_{48}O_4$, 460.3553.

Riisein A (2), 3β-*O*-(3′-*O*-Acetyl-β-D-arabinopyranosyl)-25ξ-cholestane-3β,5α,6β,26-tetrol-26-acetate: white powder; mp 187−189 °C; $[\alpha]^{25}_D$ −61° (*c* 0.1, $CHCl_3$); IR (film, $CHCl_3$) ν_{max}: 3436, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz), see Tables 1 and 2; ^{1}H−^{1}H COSY ($CDCl_3$, 500 MHz) *H* no. cross-peaks *H-1a*: H-1b,2; *H-1b*: H-1a,2; *H-2*: H-1ab,3; *H-3*: H-2,-4ab; *H-4a*: H-3,-4b; *H-4b*: H-3,-4a; *H-6*: H-7; *H-7*: H-6,-8; *H-8*: H-7,-9,-14; *H-9*: H-8; *H-11*: H-12ab; *H-12a*: H-11,-12b; *H-12b*: H-11,-12a; *H-14*: H-8,-15ab; *H-15a*: H-14,-15b,-16ab; *H-15b*: H-14,-15a, -16ab; *H-16a*: H-15ab,-16b; *H-16b*: H-15ab,-16a,-17; *H-17*: H-16b,-20; *H-20*: H-17,-21; *H-21: H*-20; *H-22a*: H-22b; *H-22b*: H-22a; *H-25*: H-26ab,-27; *H-26a*: H-25,-26b; *H-26b*: H-25,-26a; *H-27*: H-25; for pyranoarabinosyl sugar data, see Table 2; HMBC ($CDCl_3$, 500 MHz, J_{CH} = 8 Hz) *C* no., ^2J and ^3J correlations *C-1*: H-19; *C-2*: H-4ab; *C-3*: H-1′,-4ab; *C-4*: H-6; *C-5*: H-4a,-6,-7,-19; *C-6*I H-4a,-7; *C-7*: H-8; *C-8*: H-6,-7,-14; *C-9*: H-7,12ab,-14,-19; *C-10*: H-4a,-6,-19; *C-11*: H-12b; *C-12*: H-14,-17,-18; *C-13*: H-14,-16,-18; *C-14*: H-12b,-17,-18; *C-15*: H-14,-17; *C-16*: H-14,-17; *C-17*: H-12a,-14,-21,-22; *C-18*: H-14,-17; *C-20*: H-21; *C-21*: H-17; *C-22*: H-21; *C-24*: H-25,-27; *C-25*: H-26ab,-27; *C-26*: H-27; *C-27*: H-24,-25,-26ab; *C-28*: H-26ab,-29; for arabinosyl moiety, see Table 2; FABMS *m/z* (rel int) [M + Na]$^+$ 675 (10), 443 (12), 425 (10), 383 (4), 154 (100); HRFABMS (70 eV) [M + Na]$^+$ obsd 675.4084, calcd for $C_{36}H_{60}O_{10}Na$, 675.4058.

Riisein B (3), 3β-*O*-(4′-*O*-acetyl-β-D-arabinopyranosyl)-25ξ−cholestane-3β,5α,6β,26-tetrol-26-acetate: white powder, mp 188−191 °C; $[\alpha]^{25}_D$ −85° (*c* 0.1, $CHCl_3$); IR (film, $CHCl_3$) ν_{max} 3436, 1731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz), see Tables 1 and 2; ^{1}H−^{1}H COSY ($CDCl_3$, 500 MHz) *H* no. cross-peaks *H-1a*: H-1b,-2; *H-1b*: H-1a,-2; *H-2*: H-1ab,-3; *H-3*: H-2,-4ab; *H-4a*: H-3,-4b: *H-4b*: H-3,-4a; *H-6*: H-7; *H-7*: H-6,-8; *H-8*: H-7,-9,-14; *H-9*: H-8; *H-11*: H-12ab; *H-12a*: H-11,-12b; *H-12b*: H-11,-12a; *H-14*: H-8,-15ab; *H-15a*: H-14,-15b; *H-15b*: H-14,-15a; *H-16a*: H-16b,-17; *H-16b*: H-16a; *H-17*: H-16a,-20; *H-20*: H-17,-21; *H-21*: H-20; *H-22a*: H-22b; *H-22b*: H-22a; *H-24*: H-25; *H-25*: H-24,-26ab,-27; *H-26a*: H-25,-26b; *H-26b*: H-25,-26a; *H-27*: H-25; for arabinosyl moiety, see Table 2; HMBC ($CDCl_3$, 500 MHz, J_{CH} = 8 Hz) *C* no. ^2J and ^3J correlations *C-1*: H-19; *C-2*: H-1b,-4a; *C-3*: H-1′,-4b; *C-4*: H-6; *C-5*: H-4a,-6,-7,-19; *C-6*: H-4a,-7; *C-8*: H-6,-9; *C-9*: H-7,-12ab,-14,-19; *C-10*: H-6,-19; *C-11*: H-12b; *C-12*: H-14,-17; *C-13*: H-12b,-14,- 16b,-18,-20; *C-14*: H-12b,-17,-18; *C-15*: H-14,-17; *C-16*: H-14,-17; *C-17*: H-18,-20,-21; *C-18*: H-14,-17; *C-19*: H-1ab; *C-20*: H-17,-21,-22a; *C-21*: H-17; *C-22*: H-17,-21; *C-23*: H-25; *C-24*: H-25,-27; *C-25*:

H-26ab,-27; *C-26*: H-25,-27; *C-27*: H-24,-25,-26ab; *C-28*: H-29,-26ab; for arabinosyl moiety see Table 2; FABMS *m/z* (rel int) $[M + Na]^+$ 675 (5), 460 (12), 443 (22), 425 (25), 383 (15), 154 (100).

Acetylation of Compounds 1, 2, and 3. In separate experiments, a solution of 2 mg of compounds **1**, **2**, or **3** were combined with Ac_2O−pyridine (0.5 mL each) and allowed to stand at room temperature for 24 h. The solvents were removed under reduced pressure, and the reaction products were chromatographed by Si gel HPLC, eluting with EtOAc, to give the triacetate **4**. Compound **4**, which was also prepared by Lyanage and Schmitz as part of their structure analysis of sterol **1**,[5] provided the following NMR data (in $CDCl_3$): ^1H NMR (500 MHz) δ 0.67 (3H, s), 0.90 (3H, d, $J = 6.5$ Hz,), 0.91 (3H, d, $J = 6.5$ Hz), 0.92 (3H, d, $J = 7.0$ Hz), 1.18 (3H, s), 2.01 (3H, s), 2.05 (3H, s), 3.84 (1H, m), 3.95 (1H, m), 4.68 (1H, br s), 5.14 (1H, m).

Absolute Configuration of Arabinose. Riisein B (**2**, 1 mg) was treated with (−)-2-butanol (0.5 mL) in 0.5 M HCl at 80 °C for 18 h. The solution was washed with heptane (3 × 2 mL) and evaporated to dryness under N_2. Bistrimethylsilyltrifluoroacetamide (25 μL) in dry pyridine (25 μL) was added to the resulting residue. After 1 h at room temperature, the solution was analyzed by GC. The same procedure was used to prepare the authentic trimethylsylilated (±)-2-butyl glycosides of D-(−)-arabinose. The chromatograms obtained were compared with literature data, which indicated the preparation of the corresponding D-arabinose derivatives.[13]

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