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ALKALOIDS AND OTHER COMPOUNDS FROM *PSYCHOTRIA CORREAE**

HANS ACHENBACH,† MONIKA LOTTES, REINER WAIBEL, GEORGE A. KARIKAS,‡ MIREYA D. CORREA A.§ and MAHABIR P. GUPTA‡

Institute of Pharmacy and Food Chemistry, Department of Pharmaceutical Chemistry, University of Erlangen, 91052 Erlangen, Germany; ‡Research Center for the Study of Panamanian Flora (CIFLORPAN), College of Pharmacy, University of Panama, Estafeta Universitaria, Panama, Republic of Panama; §Herbarium of the University of Panama and Smithsonian Tropical Research Institute, Panama, Republic of Panama

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Key Word Index—*Psychotria correae* (= *Cephaelis correae*); Rubiaceae; isodolichantoside; correantoside; 10-hydroxycorreantoside; correantines A–C; 20-epi-correantine B; clethric acid; rotungenic acid; C_{13}-norisoprenoids; cerebrosides.

Abstract—From extracts of the leaves and/or the roots of *Psychotria correae*, isodolichantoside and the new alkaloids correantoside, 10-hydroxycorreantoside, correantines A to C, and 20-epi-correantine B were isolated, in addition to two cerebrosides and some isoprenoids. Structures were established by spectroscopic studies in combination with chemical interconversions and partial synthesis.

INTRODUCTION

The plant *Psychotria correae* (syn. *Cephaelis correae*) is only described from the Cordilleras de Guanacaste and Tilarán and from the Province of Coclé in Panama, where it grows as a small tree [2]. Various *Cephaelis* species are used in the traditional medicine of Middle America, e.g. against dizziness, hallucination, dementia and rubella [3]. In the European Pharmacopoea, preparations of *C. ipecacuanha* (= *Psychotria ipecacuanha*) are described as emetics and expectorants, and emetine, a major alkaloid from *Ipecacuanhae radix*, is used as an amoebicide [4].

In preliminary tests [5], a leaf extract of *P. correae* showed significant activity in the brine shrimp lethality test [6]. This observation led us to a study of the constituents of this species [7].

RESULTS AND DISCUSSION

Leaves were extracted with petrol and subsequently with methanol. The methanol extract, after addition of water and extraction with petrol to remove chlorophyll, was fractionated first with dichloromethane and then with ethyl acetate. In addition, the remaining aqueous layer was treated with Mayer's reagent [4].

The primary petrol extract contained a mixture of phytosterols, particularly β-sitosterol and stigmasterol. TLC analysis of the ethyl acetate fraction revealed only alkaloids, which were also contained in the dichloromethane fraction; therefore, it was not investigated further.

Repeated chromatography of the dichloromethane fraction yielded, as the major constituents, isodolichantoside (**1**) [8] and the new β-carboline-type alkaloid correantoside (**2**).** The further new alkaloids, correantines A (**3**) and B (**4**), 20-epi-correantine B (**5**) and correantine C (**6**) were isolated as minor compounds, besides the known terpenoids **8**, **9** and lutein. Furthermore, 10-hydroxycorreantoside (**7**) was precipitated with Mayer's reagent from the aqueous layer (Table 1).

The presented structures are the result of spectroscopic studies with the isolated compounds and suitable derivatives. The structure of the sugar moieties in **1** and **2** was recognized as glucose by NMR after acetylation [13]. Furthermore, the glucose units were confirmed to belong to the D-series by GC-analysis on a chiral column after enzymatic cleavage [14].

The determination of relative configurations is based mainly on the results of nuclear Overhauser experiments and on the observed $^1H/^1H$ coupling constants. Thus, the NMR and other spectroscopic data revealed structural elements of secologanin [15] in **1** and **2** besides a N_b-methyl-tetrahydro-β-carboline moiety, which was also present in **3**–**7**. Characteristic Cotton effects at 250–340 nm indicated the *R*-configuration at C-3 for all these compounds [8, 16, 17].

Structure **1** and, in addition, the absolute configuration of the substituted dihydropyrane ring system in **1**, were

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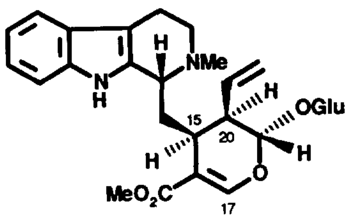
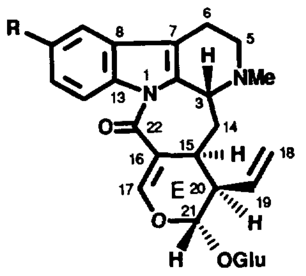
*Part 66 in the series 'Constituents of Tropical Medicinal Plants'. For Part 65 see ref. [1].

†Author to whom correspondence should be addressed.

**The structure of correantoside given in a poster presentation [7] has to be revised.



1



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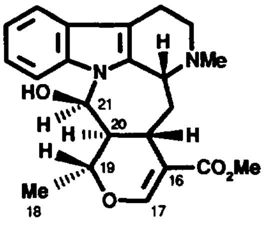
7: R = OH



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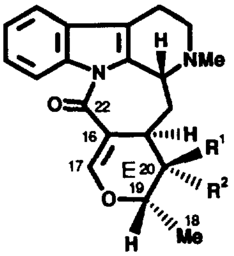
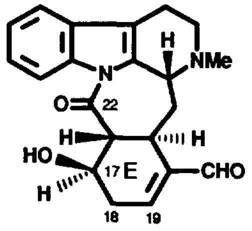


4: R^1 = H, R^2 = CHO
5: R^1 = CHO, R^2 = H



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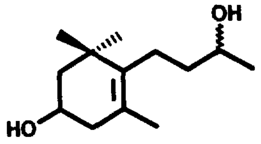

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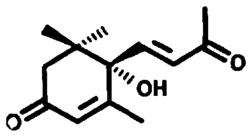

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Table 1. Compounds isolated from leaf extract of *Psychotria correae*

Classification	Compound	Content (%)*	Refs
Alkaloids	Isodolichantoside (**1**)	1.5	[8]
	Correantoside (**2**)	2.0	
	Correantine A (**3**)	0.01	
	Correantine B (**4**)	0.05	
	20-epi-Correantine B (**5**)	0.02	
	Correantine C (**6**)	0.006	
	10-Hydroxycorreantoside (**7**)	0.005	
C_{13}-Norisoprenoids	Megastigm-5-ene-3,9-diol (**8**)	0.007	[9]
	S(+)-Dehydrovomifoliol (**9**)	0.003	[10]
Carotenoids	Lutein	0.02	[11, 12]

*Dry weight of total leaf extract = 100%.

corroborated by the synthesis of tetraacetyl-**1** from N_b-methyltryptamine and (−)-(1*S*,2*R*,7*S*)-tetraacetylsecologanin; subsequent removal of the acetyl groups yielded **1** [18].

Owing to overlapping of the resonances of C-9 and C-18 in the NMR spectrum of **2** when measured in pyridine-d_5, as well as in methanol-d_4 solution, only 26 signals could be observed (Table 2). However, heteronuclear correlation measurements established the basic structure (Fig. 1).

In the ^{1}H NMR spectrum of **2**, the signals of the geminal H-14 could be separated by running the spectrum in pyridine-d_5/D_2O solution and NOE studies then enabled not only the determination of the relative configuration of the secologanin part of the molecule, but also its sterical connection to the *R*-configurated H-3 (Fig. 2).

Similarly, the structures of the new alkaloids **3**–**7** were established.

Compound **1**, when treated with β-glucosidase, gave **3** and its 21-epimer in a 2:1 ratio (Scheme 1). This result

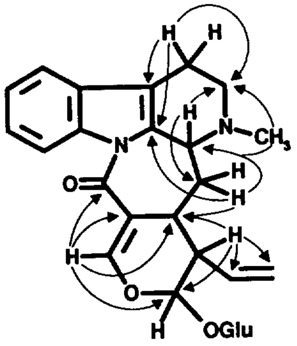


Fig. 1. Important couplings observed in the HMBC of compound **2** (in CD_3OD).

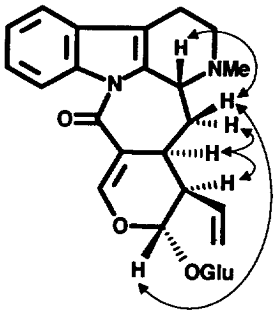


Fig. 2. Important NOEs observed for compound **2** (in pyridine-d_5/D_2O at 50°).

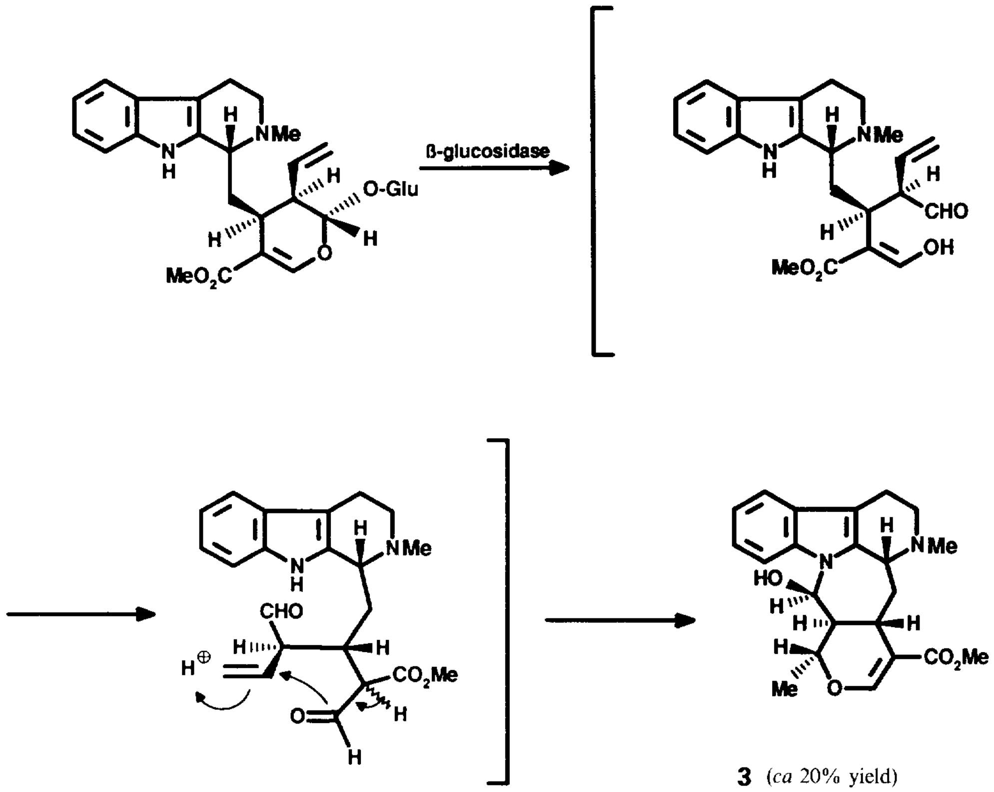
Table 2. ^{13}C NMR spectral data of compounds **1**–**7**

C	1*	2*	3†	4†	5†	6*	7*
2	134.0	134.3	136.2	132.9	133.0	134.6	133.8
3	58.8	57.8	61.4	56.4	56.7	58.5	58.2
5	47.9	46.4	52.0	45.5	45.5	48.0	46.7
6	17.9	18.8	20.9	17.6	17.7	19.6	18.8
7	106.5	115.7	108.0	114.8	114.8	117.4	115.3
8	128.1	130.4	126.8	129.1	129.1	130.6	131.3^a
9	118.7	119.2	118.5	118.1	118.0	117.8	104.4
10	119.9	124.2	119.8	123.2	123.2	119.0	155.1^b
11	122.3	125.5	121.5	124.6	124.6	125.0	114.2
12	111.8	116.0	109.2	115.4	115.2	126.0	116.8
13	137.8	137.3	137.1	136.0	136.0	137.7	131.4^a
14	34.5	34.4	36.7	39.1	35.3	35.9	34.1
15	30.5	35.7	30.8	29.7	29.2	34.5	35.6
16	112.0	112.2	111.2	108.6	109.6	52.0	112.0
17	154.0	155.7	155.2	158.0	156.4	67.5	155.5^b
18	119.8	119.2	18.6	18.3	19.3	33.8	119.3
19	135.8	135.1	74.8	70.2	69.4	149.7	135.0
20	45.5	45.4	52.0	51.8	53.9	144.2	45.4
21	97.8	97.4	75.5	199.5	199.2	194.3	97.3
22	169.8	168.2	167.5	166.2	166.2	174.8	167.8
1′	100.1	100.5	—	—	—	—	100.5
2′	74.7	74.7	—	—	—	—	74.7
3′	78.5	78.6	—	—	—	—	78.6
4′	71.6	71.6	—	—	—	—	71.7
5′	78.0	78.0	—	—	—	—	78.0
6′	62.8	62.9	—	—	—	—	62.9
$CO_2\underline{Me}$	51.9	—	51.1	—	—	—	—
NMe	40.6	41.4	43.0	41.5	41.5	41.9	41.2

*Measured in CD_3OD.

†Measured in $CDCl_3$.

^{a,b}Assignments may be interchanged.



Scheme 1. Correantine A (**3**) by enzymatic cleavage of isodolichantoside (**1**).

corroborated the absolute configuration of **3** in agreement with the CD-measurements.

The absolute configurations of **2**–**5** were all shown to agree with (−)-secologanin as far as ring E is concerned. This was achieved by studying the stereochemistry between the hydrogen at the *R*-configurated C-3 and H-14_A, as well as between H-14_B and H-15 using NOE studies and coupling constants.

However, this method did not work with **7**, since the geminal protons at C-14 were found to be magnetically equivalent in all solvents used. Owing to the fact that (i) the CD had established the *R*-configuration at C-3 and that (ii) all carbon atoms of the non-aromatic parts of **2** and **7** exhibited the same resonance values, formula **7** represents the absolute configuration.

We regard all isolated alkaloids, except **5**, as genuine compounds and not artefacts (e.g. **4** an artefact derived from **3**), since they could be detected immediately after rapid extraction of the plant material with methanol at room temperature. Surprisingly, 21-epi-**3** could not be detected. However, **5** might be an artefact, since two-dimensional TLC and ^{1}H NMR experiments showed, that **4** undergoes easy epimerization at C-20 even at pH 7 forming a 3:1 equilibrium with **5**.

Correantoside (**2**) and its 10-hydroxy-analogue **7**, as well as correantines A (**3**), B (**4**), C (**6**) and 20-epi-correantine B (**5**) represent hitherto unknown alkaloids, whereas **1** has already previously been described from *Strychnos gossweileri* [8]. The occurrence of **6** with its alicyclic ring E, besides the other alkaloids with a 'corresponding' dihydropyrane ring system, is of interest from a biosynthetic point of view.

Megastigm-5-ene-3,9-diol (**8**) has been detected by GC-mass spectrometry in various aromatic fruits, like white-fleshed nectarines [19], apricots, peaches and yellow plums [20].

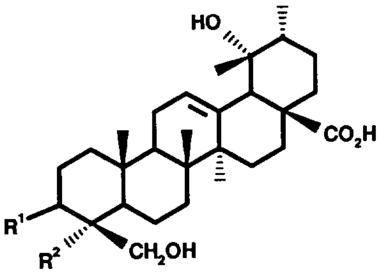
S-(+)-Dehydrovomifoliol (**9**) is structurally related to abscisic acid, a known plant growth regulator, and has been described in rice husks [10].

TLC comparison demonstrated a considerably larger number of alkaloidal constituents in the leaf extract than in the root extract. However, besides the alkaloids **1** and **2** from the equally prepared dichloromethane fraction of the roots, sitosterol glucoside, stigmasterol glucoside and **10**–**13** could be isolated (Table 3), which were not detectable (by TLC) in the leaf extracts.

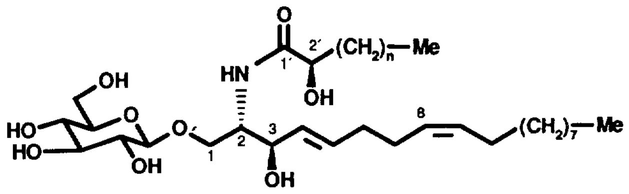
Compounds **12** and **13** are cerebrosides, a subgroup of neutral glycosphingolipids [27]. The length of the sphingadienine moieties in **12** and **13**, as well as of the *N*-acyl part, was determined from the characteristic fragment ions observed in the FAB-mass spectrum [28].

Compound **12** has been supposed to be the anti-ulcerogenic active principle of *Tetragonia tetragonoides* (Aizoaceae) [29].

Compound **13** has previously been isolated from wheat grain; it was tested for fruit-inducing activity on *Schizophyllum commune* [26].



10: R^1 = β-OH; R^2 = Me
11: R^1 = α-OH; R^2 = CH_2OH



12 (n = 13)
13 (n = 15)

Table 3. Compounds isolated from root extract of *Psychotria correae*

Classification	Compound	Content (%)*	Refs
Alkaloids	Isodolichantoside (**1**)	0.41	[8]
	Correantoside (**2**)	0.23	
Isoprenoids			
Triterpenes	Rotungenic acid (**10**)	0.07	[21]
	Clethric acid (**11**)	0.03	[22]
Sterols	Sitosterol glucoside	0.25	[23]
	Stigmasterol glucoside	0.38	[23]
Cerebrosides	Cerebroside B_{1b} (**12**)	0.17	[24, 25]
	Cerebroside (**13**)	0.05	[26]

*Dry weight of total leaf extract = 100%.

EXPERIMENTAL

General. Mps: uncorr. Analytical TLC was performed on precoated plates (HPTLC plates, silica gel 60 F_{254}, Merck) using the following systems: S-1 = CH_2Cl_2–MeOH (4:1), S-2 = CH_2Cl_2–MeOH (19:1), S-3 = CH_2Cl_2–Me_2CO (1:1), S-4 = CH_2Cl_2–MeOH (7:3), S-5 = CH_2Cl_2–MeOH (17:3), S-6 = CH_2Cl_2–MeOH (9:1), S-7 = cyclohexane–EtOAc (1:1); detection: UV, anisaldehyde reagent [30]. Unless otherwise stated, $[\alpha]_D$ in MeOH at 21°, CD and UV in MeOH, IR in $CHCl_3$. Unless otherwise stated, ^1H NMR were run at 360 MHz and ^{13}C NMR at 90 MHz in $CDCl_3$ with TMS as int. standard. EIMS were obtained at 70 eV; DCI-MS with NH_3 or isobutane, respectively; FAB-MS using a Xenon gun (8 kV). Unless key ions, only ions are given with rel. intensities > 15% and m/z > 100. CC and MPLC were carried out on silica gel 60 (Macherey–Nagel) and on LiChroprep® RP 18 (40–60 μm, Merck). For CC we also used Fractogel PVA 500 (Merck), Sephadex LH 20 (Pharmacia) and Fractogel TSK HW-40 (S) (Merck). HPLC was performed on LiChrosorb RP 18 (7 μm, Merck).

Plant material. Leaves and roots of *P. correae* (Dwyer & Hayden) C. M. Taylor (syn. *C. correae* Dwyer & Hayden) (Rubiaceae) were collected by Ms Carmen Galdames, Assistant botanist, CIFLORPAN, from El Valle de Anton, Panama, in May 1990 and 1991, respectively, and identified by M.D.C. A voucher specimen is held under No. FLORPAN 333 at the University of Panama.

Extraction and isolation. Dried, pulverized leaves (600 g) were extracted exhaustively at room temp., first with petrol (5 g extract) and then with MeOH (67 g extract). The MeOH extract was redissolved in 400 ml MeOH, 600 ml H_2O added and the obtained suspension was successively extracted with (i) petrol (10.2 g extract), (ii) CH_2Cl_2 (7.7 g extract) and (iii) EtOAc (4.9 g extract). After these extraction procedures, Mayer's reagent [4] was added to the aq. layer and the ppt. filtered off. Repeated CC on silica gel with CH_2Cl_2–MeOH–H_2O (24:16:1) and then on Sephadex LH 20 with MeOH yielded alkaloids **1**, **2** and **7**.

Roots (430 g) were extracted in the same way and yielded petrol (0.9 g), MeOH (13.5 g), CH_2Cl_2 (2.1 g) and EtOAc (0.6 g) extracts.

The CH_2Cl_2 extract (7.5 g) from leaves was sepd by MPLC on 550 g silica gel with CH_2Cl_2–MeOH mixts (5–50% MeOH) to give 5 frs, whose further sepn was achieved by repeated MPLC or CC using the following systems: (a) silica gel, CH_2Cl_2–EtOH (49:1), (b) LiChroprep RP 18, MeOH–H_2O (24:1, 3:1, 7:3, 3:2), (c) silica gel, cyclohexane–EtOAc (3:2), (d) Fractogel PVA 500, MeOH, (e) silica gel, CH_2Cl_2–MeOH (24:1, 9:1, 22:3, 3:2), (f) silica gel, CH_2Cl_2–Me_2CO (19:1), (g) Fractogel TSK HW-40 (S), MeOH. This yielded **1**–**6**, **8**, **9** and lutein.

The CH_2Cl_2 extract (2.1 g) from roots (430 g) was sepd by repeated CC using the following systems: (a) silica gel, CH_2Cl_2–MeOH (5–30% MeOH), (b) Sephadex LH 20, MeOH, (c) Fractogel PVA 500, MeOH, (d) silica gel, EtOAc. This yielded compounds **1**, **10**, **11** and mixts of **12** and **13**, and of the glucosides of sitosterol and stigmasterol, respectively, whose sepns were achieved by HPLC on silica gel RP 18 (LiChrosorb) using MeOH–H_2O (24:1) and MeOH–H_2O (97:3), respectively.

Isodolichantoside (**1**) (= [2S-[2α,3β,4β(S*)]]-3-*ethenyl*-2-(β-D-*glucopyranosyloxy*)-3,4-*dihydro*-4-[(2,3,4,9-*tetrahydro*-2-*methyl*-1H-*pyrido*[3,4-b]*indol*-1-*yl*)*methyl*]-2H-*pyran*-5-*carboxylic acid methyl ester*). Amorphous (20 mg). TLC: R_f 0.38 (S-1); anisaldehyde: blue. $[\alpha]_D$ − 113° (*c* 0.3). CD λ_{max} nm (Δε): 226 (− 3.8), 240 (+ 3.8), 270 (− 2.2), 280 (− 2.7), 290 (− 4.3). IR ν_{max} cm^{-1}: 3360 (OH), 1692 (C=O), 1630 (C=C). UV λ_{max} nm (log ε): 225 (4.50), 277 (3.85), 288 (3.79). ^{1}H NMR (CD_3OD): δ2.03 (1H, *ddd*, J_1 = 14, J_2 = J_3 = 7 Hz, H-14_A), 2.18 (1H, *ddd*, J_1 = 14, J_2 = J_3 = 7 Hz, H-14_B), 2.56 (3H, *s*, NMe), 2.66–2.76 (2H, *m*, H-6_A, H-20), 2.91 (1H, *ddd*, J_1 = 15, J_2 = 9, J_3 = 6 Hz, H-6_B), 3.05 (1H, *ddd*, J_1 = 13, J_2 = 6, J_3 = 3 Hz, H-5_A), 3.15–3.42 (6H, *m*, H-5_B, H-15, H-2′, H-3′, H-4′, H-5′), 3.66 (1H, *dd*, J_1 = 12, J_2 = 6 Hz, H-$6'_A$), 3.68 (3H, *s*, CO_2Me), 3.90 (1H, *dd*, J_1 = 12, J_2 = 2 Hz, H-$6'_B$), 4.00 (1H, *t*, *J* = 7 Hz, H-3), 4.71 (1H, *d*, *J* = 8 Hz, H-1′), 5.24 (2H, *m*, H-18_A, H-18_B), 5.62 (1H, *d*, *J* = 6.5 Hz, H-21), 5.82 (1H, *ddd*, J_1 = 17, J_2 = 10.5, J_3 = 8 Hz, H-19), 6.98 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-10), 7.06 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-11), 7.31 (1H, *br d*, *J* = 7.5 Hz, H-12), 7.41 (1H, *br d*, *J* = 7.5 Hz, H-9), 7.51 (1H, *s*, H-17). EIMS *m/z* (rel. int.): 544 $[M]^+$ (0.9), 185 (100), 184 (14), 165 (3), 58 (5). FAB-MS (neg. ion) *m/z* (rel. int.): 544 $[M]^-$ (19), 543 $[M - H]^-$ (43), 183 (100).

Correantoside (**2**) (= [11S-(11α,12β,12aα,13aβ)]-12-*ethenyl*-11-(β-D-*glucopyranosyloxy*)-1,2,3,11,12,12a,13,13a-*octahydro*-1-*methyl*-8H-10-*oxa*-1,7b-*diazabenzo*[5, 6]*cyclohepta*[1,2,3-jk]*fluoren*-8-*one*). Amorphous (46 mg). TLC: R_f 0.43 (S-1); anisaldehyde: red-violet. $[\alpha]_D$ − 83° (*c* 0.32). CD λ_{max} nm (Δε): 220 (+ 3.9), 250 (− 4.7), 267 (− 1.2), 275 (− 1.2), 315 (+ 5.7), 324 (+ 6.5). IR ν_{max} cm^{-1}: 3377 (OH), 1679 (C=O). UV λ_{max} nm (log ε): 262 (4.31), 308 (3.86). ^{1}H NMR (CD_3OD): δ1.96–2.12 (2H, *m*, H-14_A, H-14_B), 2.45 (3H, *s*, NMe), 2.51–2.67 (3H, *m*, H-6_A, H-15, H-20), 2.82–2.96 (2H, *m*, H-5_A, H-6_B), 3.13 (1H, *m*, H-5_B), 3.20–3.45 (4H, *m*, H-2′, H-3′, H-4′, H-5′), 3.69 (1H, *dd*, J_1 = 12, J_2 = 6 Hz, H-$6'_A$), 3.94 (1H, *dd*, J_1 = 12, J_2 = 2 Hz, H-$6'_B$), 3.90–3.97 (overlapped, H-3), 4.82 (1H, *d*, *J* = 8 Hz, H-1′), 5.16–5.25 (2H, *m*, H-18_A, H-18_B), 5.75 (1H, *d*, *J* = 9 Hz, H-21), 5.85 (1H, *ddd*, J_1 = 17.5, J_2 = 11, J_3 = 7.5 Hz, H-19), 7.22 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-10), 7.25 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-11), 7.46 (1H, *br dd*, J_1 = 7.5, J_2 = 1.5 Hz, H-9), 7.74 (1H, *s*, H-17), 8.14 (1H, *br dd*, J_1 = 7.5, J_2 = 1.5 Hz, H-12). ^{1}H NMR (pyridine-d_5–D_2O (*ca* 5 : 1)): δ2.08 (1H, *ddd*, J_1 = J_2 = 11.5, J_3 = 7.5 Hz, H-14_A), 2.29 (1H, *ddd*, J_1 = J_2 = 11.5, J_3 = 7.5 Hz, H-14_B), 2.40 (3H, *s*, NMe), 2.44–2.53 (2H, *m*, H-6_A, H-15), 2.65 (1H, *ddd*, J_1 = J_2 = 9, J_3 = 5 Hz, H-20), 2.74–2.90 (2H, *m*, H-5_A, H-6_B), 3.00 (1H, *m*, H-5_B), 3.93 (1H, *dd*, J_1 = 11, J_2 = 7.5 Hz, H-3), 4.01–4.15 (3H, *m*, H-2′, H-4′, H-5′), 4.25–4.34 (2H, *m*, H-3′, H-$6'_A$), 4.57 (1H, *dd*, J_1 = 12, J_2 = 2 Hz, H-$6'_B$), 5.16 (1H, *dd*, J_1 = 10.5, J_2 = 1.5 Hz, H-18_A), 5.27 (1H, *br d*, *J* = 17.5 Hz, H-18_B), 5.44 (1H, *d*, *J* = 8 Hz, H-1′), 6.07 (1H, *ddd*, J_1 = 17.5, J_2 = 10.5, J_3 = 8.5 Hz, H-19), 6.17 (1H, *d*, *J* = 9 Hz, H-21), 7.40 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-10), 7.44 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-11), 7.59 (1H, *br dd*, J_1 = 7.5, J_2 = 1.5 Hz, H-9), 7.98 (1H, *s*, H-17), 8.62 (1H, *br dd*, J_1 = 7.5, J_2 = 1.5 Hz, H-12). EIMS *m/z* (rel. int.): 512.2160 $[M]^+$ (3) (calcd for $C_{27}H_{32}N_2O_8$: 512.2159), 332 (23), 331 (16), 279 (15), 237 (15), 185 (56), 184 (100), 183 (72), 129 (18). FAB-MS (pos. ion) *m/z* (rel. int.): 513 $[M + H]^+$ (55), 308 (100).

Correantine A (**3**) (= [8R-(8α,8aβ,9β,12aα,13aα)]-1,2,3,8a,9,12a,13,13a-*octahydro*-8-*hydroxy*-1,9-*dimethyl*-8H-10-*oxa*-1,7b-*diazabenzo*[5, 6]*cyclohepta*[1,2,3-jk] *fluorene*-12-*carboxylic acid methyl ester*). Amorphous (7 mg). TLC: R_f 0.34 (S-2); anisaldehyde: blue. $[\alpha]_D$ + 211° (*c* 0.31). CD λ_{max} nm (Δε): 242 (+ 8.6), 268 (− 1.8), 287 (− 0.5), 295 (− 0.4), 335 (+ 0.3), 340 (+ 0.3). IR ν_{max} cm^{-1}: 3594 (OH), 1698 (C=O). UV λ_{max} nm (log ε): 226 (4.53), 273 (3.91), 290 (3.80). ^{1}H NMR (250 MHz): δ1.08 (1H, *ddd*, J_1 = 14, J_2 = J_3 = 11 Hz, H-14_A), 1.60 (3H, *d*, *J* = 6.5 Hz, Me-18), 1.66 (1H, *ddd*, J_1 = J_2 = 10, J_3 = 1.5 Hz, H-20), 2.54 (3H, *s*, NMe), 2.59–2.87 (3H, *m*, H-5_A, H-6_A, H-6_B), 2.92–3.04 (2H, *m*, H-5_B, H-14_B), 3.35 (1H, *br ddd*, J_1 = J_2 = 11, J_3 = 2 Hz, H-15), 3.46 (1H, *s*, OH), 3.69 (1H, *m*, H-3), 3.73 (3H, *s*, OMe), 3.98 (1H, *dq*, J_1 = 10, J_2 = 6.5 Hz, H-19), 6.28 (1H, *s*, H-21), 7.10 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-10), 7.18 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-11), 7.27 (1H, *br d*, *J* = 7.5 Hz, H-12), 7.43 (1H, *dd*, J_1 = 7.5, J_2 = 1.5 Hz, H-9), 7.53 (1H, *s*, H-17). Results of NOE measurements: Table 4. EIMS *m/z* (rel. int.): 382.1902 $[M]^+$ (30) (calcd for $C_{22}H_{26}N_2O_4$: 382.1892), 186 (15), 185 (100), 184 (33), 183 (20).

Correantine B (**4**) (= [11S-(11α,12α,12aα,13aβ)]-1,2,3,11,12,12a,13,13a-*octahydro*-1,11-*dimethyl*-8-*oxo*-8H-10-*oxa*-1,7b-*diazabenzo*[5, 6]*cyclohepta*[1,2,3-jk]*fluorene*-12-*carboxaldehyde*). Amorphous (4 mg). TLC: R_f 0.14 (S-3); anisaldehyde: red-violet. $[\alpha]_D$ − 81° (*c* 0.18). CD λ_{max} nm (Δε): 223 (+ 1.5), 250 (− 5.5), 276 (− 1.0), 311 (+ 4.6), 326 (+ 4.3). IR ν_{max} cm^{-1}: 1726 (C=O), 1676 (CO-N). UV λ_{max} nm (log ε): 264 (4.24), 308 (3.89). ^{1}H NMR: δ1.63 (3H, *d*, *J* = 6.5 Hz, Me-18), 1.92 (1H, *ddd*, J_1 = J_2 = 12, J_3 = 8 Hz, H-14_A), 2.19 (1H, *ddd*, J_1 = J_2 = 12, J_3 = 8 Hz, H-14_B), 2.32 (1H, *br s*, H-20), 2.47 (3H, *s*, NMe), 2.57 (1H, *m*, H-6_A), 2.80–3.01 (3H, *m*, H-5_A, H-6_B, H-15), 3.18 (1H, *m*, H-5_B), 3.88 (1H, *dd*, J_1 = 11, J_2 = 7 Hz, H-3), 4.42 (1H, *dq*, J_1 = 13.5, J_2 = 2.5 Hz, H-19), 7.26 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-10), 7.32 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-11), 7.46 (1H, *br d*, *J* = 8 Hz, H-9), 7.96 (1H, *s*, H-17), 8.25 (1H, *dd*, J_1 = 8, J_2

Table 4. Important NOEs of compound **3**

Irradiation	Enhancement
H-3	H-14_B, H-15
H-14_A	H-20
H-14_B	H-3, H-15
H-15	H-3, H-14_B, H-19
H-19	H-15
H-20	H-21
H-21	Me-18, H-20

= 1.5 Hz, H-12), 9.58 (1H, *d*, J = 3 Hz, H-21). EIMS *m/z* (rel. int.): 350.1644 $[M]^+$ (50) (calcd for $C_{21}H_{22}N_2O_3$: 350.1630), 349 (27), 322 (18), 321.1605 (23) (calcd for $C_{20}H_{21}N_2O_2$: 321.1603), 293 (15), 279 (26), 251 (25), 185 (37), 184 (100), 183 (66).

20-*epi-Correantine B* (**5**) (= [11S-(11α,12β,12aα, 13aβ)]-1,2,3,11,12,12a,13,13a-*octahydro*-1,11-*dimethyl*-8-*oxo*-8H-10-*oxa*-1,7*b*-*diazabenzo*[5, 6]*cyclohepta*[1,2,3-jk] *fluorene*-12-*carboxaldehyde*). Amorphous (2 mg). TLC: R_f 0.30 (S-3); anisaldehyde: red-violet. $[\alpha]_D - 102°$ (*c* 0.10). CD λ_{max} nm ($\Delta\varepsilon$): 247 (− 7.5), 290 (+ 2.1), 312 (+ 7.7), 320 (+ 8.7). IR ν_{max} cm^{-1}: 1726 (C=O), 1676 (CO-N). UV λ_{max} nm (log ε): 265 (3.60), 308 (3.24). ^{1}H NMR: δ1.51 (3H, *d*, J = 6.5 Hz, Me-18), 1.94 (2H, *dd*, $J_1 = J_2$ = 9 Hz, H-14_A, H-14_B), 2.45 (3H, *s*, NMe), 2.55 (1H, *m*, H-6_A), 2.67 (1H, *ddd*, J_1 = 11, J_2 = 5, J_3 = 2 Hz, H-20), 2.82–3.02 (3H, *m*, H-5_A, H-6_B, H-15), 3.12 (1H, *m*, H-5_B), 3.83 (1H, *t*, J = 9 Hz, H-3), 4.54 (1H, *dq*, J_1 = 12, J_2 = 6.5 Hz, H-19), 7.26 (1H, *ddd*, $J_1 = J_2$ = 8, J_3 = 1.5 Hz, H-10), 7.32 (1H, *ddd*, $J_1 = J_2$ = 8, J_3 = 1.5 Hz, H-11), 7.45 (1H, *br d*, J = 8 Hz, H-9), 7.82 (1H, *s*, H-17), 8.24 (1H, *dd*, J_1 = 8, J_2 = 1.5 Hz, H-12), 9.74 (1H, *d*, J = 2 Hz, H-21). EIMS *m/z* (rel. int.): 350.1633 $[M]^+$ (56) (calcd for $C_{21}H_{22}N_2O_3$: 350.1630), 349 (26), 322 (22), 321.1608 (29) (calcd for $C_{20}H_{21}N_2O_2$: 321.1603), 293 (17), 279 (30), 267 (15), 252 (15), 251 (31), 209 (17), 185 (37), 184 (100), 183 (68).

Correantine C (**6**) (= [8aR-(8aα,9α,12aβ,13aα)]-1,2,3,8,8a,9,10,12a,13,13a-*decahydro*-9-*hydroxy*-1-*methyl*-8-*oxo*-1,7b-*diazabenzo*[5, 6]*cyclohepta*[1,2,3-jk] *fluorene*-12-*carboxyaldehyde*). Amorphous (3 mg). TLC: R_f 0.35 (S-6); anisaldehyde: yellow. $[\alpha]_D - 177°$ (*c* 0.2). CD λ_{max} nm ($\Delta\varepsilon$): 235 (− 5.60), 272 (− 2.03), 305 (+ 4.06), 312 (+ 2.73). IR ν_{max} cm^{-1}: 3546 (OH), 1685 (C=O). UV λ_{max} nm (log ε): 232 (4.18), 261 (sh, 3.98), 294 (3.64), 300 (sh, 3.62). ^{1}H NMR (CD_3OD): δ2.00 (1H, *ddd*, J_1 = 13, J_2 = 10.5, J_3 = 6.5 Hz, H-14_A), 2.37 (1H, *ddd*, J_1 = 13, J_2 = 10.5, J_3 = 7.5 Hz, H-14_B), 2.49 (1H, *m*, H-18_A), 2.49 (3H, *s*, NMe), 2.65–2.94 (5H, *m*, H-5_A, H-6_A, H-6_B, H-15, H-18_B), 3.13 (1H, *m*, H-5_B), 3.20 (1H, *t*, J = 9.5 Hz, H-16), 4.11–4.24 (2H, *m*, H-3, H-17), 6.95 (1H, *dd*, J_1 = 7.5, J_2 = 2.5 Hz, H-19), 7.25–7.35 (2H, *m*, H-11, H-12), 7.50 (1H, *dd*, J_1 = 8, J_2 = 1.5 Hz, H-10), 8.47 (1H, *dd*, J_1 = 8, J_2 = 2 Hz, H-9), 9.37 (1H, *s*, H-21). EIMS *m/z* (rel. int.): 350.1629 $[M]^+$ (25) (calcd for $C_{21}H_{22}N_2O_3$: 350.1630), 186 (16), 185 (100), 184 (45), 183 (62), 156 (30), 154 (24), 144 (22), 142 (17), 129 (17), 128 (16), 115 (15).

10-*Hydroxycorreantoside* (7) (= [11S-(11α,12β,12aα, 13aβ)]-12-*ethenyl*-11-(β-D-*glucopyranosyloxy*)-1,2,3,11, 12,12a,13,13a-*octahydro*-5-*hydroxy*-1-*methyl*-8H-10-*oxa*-1,7b-*diazabenzo*[5, 6] *cyclohepta*[1,2,3-jk]-*fluoren*-8-*one*). Amorphous (2.1 mg). TLC: R_f 0.28 (S-4); anisaldehyde: violet. $[\alpha]_D$ − 43° (*c* 0.11). CD λ_{max} nm ($\Delta\varepsilon$): 220 (+ 1.90), 250 (− 4.28), 285 (+ 1.58), 315 (+ 3.40), 327 (+ 3.83). IR ν_{max}^{KBr} cm^{-1}: 3354 (OH), 1667 (CO-N). UV λ_{max} nm (log ε): 272 (3.98), 320 (3.66). ^{1}H NMR (CD_3OD): δ2.02–2.16 (2H, *m*, H-14_A, H-14_B), 2.58 (3H, *s*, NMe), 2.55–2.69 (3H, *m*, H-6_A, H-15, H-20), 2.88 (1H, *ddd*, J_1 = 17, J_2 = 10, J_3 = 5 Hz, H-6_B), 3.05 (1H, *m*, H-5_A), 3.20–3.44 (5H, *m*, H-5_B, H-2′, H-3′, H-4′, H-5′), 3.68 (1H, *dd*, J_1 = 12, J_2 = 6.5 Hz, H-$6'_A$), 3.94 (1H, *dd*, J_1 = 12, J_2 = 2.5 Hz, H-$6'_B$), 4.10 (1H, *t*, J = 8.5 Hz, H-3), 4.81 (1H, *d*, J = 8 Hz, H-1′), 5.18–5.28 (2H, *m*, H-18_A, H-18_B), 5.75 (1H, *d*, J = 9 Hz, H-21), 5.85 (1H, *ddd*, J_1 = 17.5, J_2 = 11, J_3 = 7.5 Hz, H-19), 6.78 (1H, *dd*, J_1 = 9, J_2 = 2.5 Hz, H-11), 6.84 (1H, *d*, J = 2.5 Hz, H-9), 7.71 (1H, *s*, H-17), 7.97 (1H, *d*, J = 9 Hz, H-12). EIMS *m/z* (rel. int.): 528.2108 $[M]^+$ (8) (calcd for $C_{27}H_{32}N_2O_9$: 528.2108), 365 (23), 296 (15), 295 (28), 268 (16), 267 (32), 266 (19), 253 (34), 237 (20), 225 (15), 201 (59), 200 (100), 199 (78), 198 (17), 196 (21), 184 (18), 183 (18), 170 (15), 145 (19), 127 (19).

Megastigm-5-*ene*-3,9-*diol* (= 3-*hydroxy*-7,8-*dihydro*-β-*ionol*) (**8**). Oil (5 mg). TLC: R_f 0.33 (S-2); anisaldehyde: blue. $[\alpha]_D - 26°$ ($CHCl_3$; *c* 0.42). IR ν_{max} cm^{-1}: 3609, 3436, 3028, 3011, 2967, 2929, 2873, 1469, 1458, 1378. ^{1}H NMR: δ1.03 (3H, *s*, Me-11), 1.06 (3H, *s*, Me-12), 1.22 (3H, *d*, J = 6 Hz, Me-10), 1.43 (1H, *dd*, $J_1 = J_2$ = 12 Hz, H-2_{ax}), 1.45–1.56 (2H, *m*, H-8_A, H-8_B), 1.63 (3H, *br s*, Me-13), 1.71 (1H, *ddd*, J_1 = 12, J_2 = 3.5, J_3 = 2.5 Hz, H-2_{eq}), 1.90 (1H, *m*, H-7_A), 1.96 (1H, *dd*, J_1 = 16, J_2 = 10 Hz, H-4_{ax}), 2.10 (1H, *m*, H-7_B), 2.25 (1H, *ddd*, J_1 = 10, J_2 = 6, J_3 = 1.5 Hz, H-4_{eq}), 3.80 (1H, *m*, H-9), 3.94 (1H, *dddd*, J_1 = 12, J_2 = 10, J_3 = 6, J_4 = 3.5 Hz, H-3_{ax}). ^{13}C NMR (62.9 MHz): δ19.7 (C-13), 23.4 (C-10), 24.4 (C-7), 28.5 (C-11), 29.7 (C-12), 37.9 (C-1), 39.7 (C-8), 42.3 (C-4), 48.6 (C-2), 65.0 (C-3), 66.7 (C-9), 124.1 (C-5), 136.9 (C-6). EIMS in agreement with published data [9].

S(+)-*Dehydrovomifoliol* (**9**). Light yellow oil (2 mg). TLC: R_f 0.25 (S-7); anisaldehyde: red-brown. $[\alpha]_D$ + 149° (*c* 0.16) (ref. [10] $[\alpha]_D^{25}$ + 142.7° (MeOH; *c* 0.782)). ^{1}H, ^{13}C NMR, IR, UV, CD, MS in agreement with published data [10].

Lutein. Yellow crystals (6 mg). Mp 182° (from dioxane) (ref. [11], mp 183°). TLC: R_f 0.43 (S-2); anisaldehyde: blue. $[\alpha]_D$ + 62° ($CHCl_3$; *c* 0.04). IR ν_{max} cm^{-1}: 3674, 3608, 3034, 3011, 2964, 2926, 2858, 2361, 1723. UV, ^{1}H and ^{13}C NMR in agreement with published data [11, 12]. EIMS *m/z* (rel. int. > 25): 568 $[M]^+$ (23), 550 (40), 209 (27), 197 (27), 183 (27), 173 (38), 171 (38), 169 (31), 159 (46), 157 (56), 145 (79), 143 (52), 133 (53), 131 (45), 129 (27), 121 (52), 119 (100), 117 (26), 109 (28), 107 (53), 105 (90).

Rotungenic acid (**10**). Crystalline (8 mg). Mp 292° (from MeOH) (ref. [21] mp 295–298° (dec)). TLC: R_f 0.19 (S-2); anisaldehyde: blue. $[\alpha]_D$ + 38° (*c* 0.12) (ref. [21] $[\alpha]_D$ + 16° (MeOH)). IR, UV, ^{13}C NMR, MS in agreement with published data [21]. ^{1}H NMR correlates well with the data published for the Me ester [21].

Clethric acid (**11**). Crystalline (5 mg). Mp 280–283° (from $CHCl_3$–MeOH) (ref. [22], mp 284–287°). TLC: R_f 0.25 (S-6); anisaldehyde: blue. $[\alpha]_D$ + 21° (*c* 0.27) (ref. [22] $[\alpha]_D^{17}$ + 50° (MeOH; *c* 0.69)). IR, EIMS in agreement with published data [22]. ^{1}H and ^{13}C NMR correlate well with the data published for the Me ester [22].

Cerebroside B_{1b} (= (2S,3R,4E,8Z)-3-*hydroxy*-2-[(2R)-2-*hydroxyhexadecanoylamino*]-1-β-D-*glucopyranosyloxy*-4,8-*octadiene*) (**12**). Crystalline (18 mg). Mp 197–201° (from MeOH) (ref. [24] mp 192–194°, ref. [25] mp 183°). TLC: R_f 0.37 (S-5); anisaldehyde: blue. $[\alpha]_D$ + 6.6°

(*c* 0.68) (ref. [25] $[\alpha]_D + 4.6°$ ($CHCl_3$–MeOH (1:1); *c* 1.76)). IR, ^1H NMR (in pyridine-d_5), ^{13}C NMR (CD_3OD–$CDCl_3$ (9:11)), FAB-MS in agreement with published data [24, 25]. ^1H NMR (CD_3OD): δ 0.90 (6H, *t*, $J = 6.5$ Hz, Me-18, Me-16′), 1.20–1.77 (40H, *m*, CH_2), 2.0–2.17 (6H, *m*, H-6_A, H-6_B, H-7_A, H-7_B, H-10_A, H-10_B), 3.19 (1H, *dd*, $J_1 = 9$, $J_2 = 8$ Hz, H-2″), 3.25–3.39 (2H, *m*, H-4″, H-5″), 3.35 (1H, *dd*, $J_1 = J_2 = 9$ Hz, H-3″), 3.67 (1H, *m*, H-$6''_A$), 3.71 (1H, *dd*, $J_1 = 11$, $J_2 = 3.5$ Hz, H-1_A), 3.86 (1H, *dd*, $J_1 = 12$, $J_2 = 2$ Hz, H-$6''_B$), 3.96–4.02 (2H, *m*, H-2, H-2′), 4.11 (1H, *dd*, $J_1 = 11$, $J_2 = 5.5$ Hz, H-1_B), 4.14 (1H, *br t*, $J = 7$ Hz, H-3), 4.26 (1H, *d*, $J = 8$ Hz, H-1″), 5.35 (1H, *dd*, $J_1 = 10.5$, $J_2 = 6$ Hz, H-8 or H-9), 5.39 (1H, *dd*, $J_1 = 10.5$, $J_2 = 6$ Hz, H-9 or H-8), 5.49 (1H, *dd*, $J_1 = 15.5$, $J_2 = 7.5$ Hz, H-5), 5.74 (1H, *ddd*, $J_1 = 15.5$, $J_2 = J_3 = 6$ Hz, H-4). ^{13}C NMR (CD_3OD): δ 14.4 (C-16′), 14.4 (C-18), 23.7 (C-15′), 26.2 (C-4′), 27.9 (C-7), 28.3 (C-10), 30.4 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 30.8 (CH_2), 30.9 (CH_2), 33.1 (C-17), 33.7 (C-6), 35.9 (C-3′), 54.6 (C-2), 62.7 (C-6″), 69.7 (C-1), 71.6 (C-5″), 72.8 (C-3), 73.1 (C-2′), 75.0 (C-2″), 77.92 and 77.98 (C-3″, C-4″), 104.7 (C-1″), 129.9 (C-8 or C-9), 131.3 (C-9 or C-8), 131.4 (C-4), 134.3 (C-5), 177.2 (C-1′).

(2S,3R,4E,8Z)-3-*Hydroxy*-2-[(2R)-2-*hydroxyoctadecanoylamino*]-1-β-D-*glucopyranosyloxy*-4,8-*octadiene* (**13**). Crystalline (5 mg). Mp 194–197° (from MeOH). TLC: R_f 0.36 (S-5); anisaldehyde: blue. $[\alpha]_D + 4.8°$ (*c* 0.27). IR, ^1H, ^{13}C NMR in agreement with the corresponding data of **12**. FAB-MS (pos. ion) *m/z* (rel. int.): 725 (17), 724 $[M - H_2O]^+$ (57), 564 (28), 563 (54), 562 (23), 546 (15), 545 (23), 544 (40), 300 (15), 280 (41), 263 (84), 262 (100), 260 (18), 250 (21); FAB-MS (neg. ion) *m/z* (rel. int.): 742 $[M + H]^-$ (16), 741 $[M]^-$ (58), 740 $[M - H]^-$ (100), 739 (54), 579 (16), 578 (45), 577 (24), 560 (26), 341 (22), 340 (25), 325 (19), 324 (38), 323 (16), 322 (16), 300 (15), 299 (15), 298 (15), 293 (17), 291 (15), 281 (19), 265 (19), 255 (22), 253 (49), 227 (16).

Sitosterol glucoside. Crystalline (4 mg). Mp 160–164° (from $CHCl_3$–MeOH) (ref. [23] mp 164°). TLC: R_f 0.49 (S-1); anisaldehyde: violet. $[\alpha]_D - 32°$ ($CHCl_3$–MeOH, 1:1; *c* 0.25) (ref. [23] $[\alpha]_D - 35°$ ($CHCl_3$; *c* 0.1)). IR, ^1H NMR, DCI-MS in agreement with published data [23].

Stigmasterol glucoside. Crystalline (6 mg). Mp 299° (from MeOH) (ref. [23] mp 299°). TLC. R_f 0.49 (S-1); anisaldehyde: violet. $[\alpha]_D - 41°$ ($CHCl_3$–MeOH, 1:1; *c* 0.39 (ref. [23] $[\alpha]_D - 45°$ ($CHCl_3$–MeOH, 1:1; *c* 0.21)). IR, ^1H NMR, DCI-MS in agreement with published data [23].

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REFERENCES

1. Achenbach, H., Zwanzger, M., Domínguez, X. A., Espinosa B., G., Verde S. J., Sánchez, V. H. and Touché E. M. G. (1995) *H. Planta Med.* (in press).
2. Burger, W. and Taylor, C. M. (1993) *Fieldiana Botany, New Series No.* 33, Flora Costaricensis, Family No. 202 Rubiaceae, p. 244. Field Museum of Natural History, Chicago.
3. Joly, L. G., Guerra, S., Séptimo, R., Solis, P. N., Correa, M., Gupta, M., Levy, S. and Sandberg, F. (1987) *J. Ethnopharmacol.* **20**, 145.
4. Deutsches Arzneibuch, 10. Ausgabe (1991) mit 2. Nachtrag (1993). Deutscher Apotheker Verlag, Stuttgart, Govi, Frankfurt.
5. Gupta, M. P., Monge, A., Karikas, G. A., Lopez de Serrain, A., de Leon, E., Trujillo, M., Suarez, O., Wilson, F., Montenegro, G., Noriega, Y., Santana, A. and Correa, M. (1994) *Int. J. Pharmacogn.* (in press).
6. Meyer, B. N., Ferrigni, N. R., Putnam, J. E., Jacobsen, L. B., Nichols, D. E. and McLaughlin, J. L. (1982) *Planta Med.* **45**, 31.
7. Achenbach, H., Lottes, M., Waibel, R., Karikas, G. A. and Gupta, M. P. (1993) *Planta Med.* **59**, Suppl. Issue, A 619.
8. Coune, C. A. and Angenot, L. J. G. (1980) *Herba Hung.* **19**, 189.
9. Winterhalter, P. and Schreier, P. (1988) *J. Agric. Food Chem.* **36**, 1251.
10. Kato, T., Tsunakawa, M., Sasaki, N., Aizawa, H., Fujita, K., Kitahara, Y. and Takahashi, N. (1977) *Phytochemistry* **16**, 45.
11. Buchecker, R., Hamm, P. and Eugster, C. H. (1974) *Helv. Chim. Acta* **57**, 631.
12. Moss, G. P. (1976) *Pure Appl. Chem.* **47**, 97.
13. Achenbach, H., Waibel, R., Raffelsberger, B. and Addae-Mensah, I. (1981) *Phytochemistry* **20**, 1591.
14. König, W. A., Mischnik-Lübbecke, P., Brassat, B., Lutz, S. and Wenz, G. (1988) *Carbohydr. Res.* **183**, 11.
15. El-Naggar, L. J. and Beal, J. L. (1980) *J. Nat. Prod.* **43**, 649.
16. Legrand, M. and Rougier, M. J. (1977) in *Stereochemistry, Fundamentals and Methods*, Vol. 2, p. 33 (Kagan, H.-B., ed.). Georg Thieme, Stuttgart.
17. Brown, R. T., Chapple, C. L. and Lashford, A. G. (1975) *J. Chem. Soc. Chem. Commun.* **8**, 295.
18. Kocsis, Á., Patthy, A., Pál, Z., Szabó, L., Varga, J. and Téténvi, P. (1988) *Hung. Teljes* HU 46032A2.
19. Takeoka, G. R., Flath, R. A., Buttery, R. G., Winterhalter, P., Güntert, M., Ramming, D. W. and Teranishi, R. (1992) *ACS Symp. Ser.* **490**, 116.
20. Krammer, G., Winterhalter, P., Schwab, M. and Schreier, P. (1991) *J. Agric. Food Chem.* **39**, 778.
21. Nakatani, M., Miyazaki, Y., Iwashita, T., Naoki, H. and Hase, T. (1989) *Phytochemistry* **28**, 1479.
22. Takahashi, K. and Takani, M. (1978) *Chem. Pharm. Bull.* **26**, 2689.
23. Schwinn, A. (1993) Dissertation. Univ. Erlangen-Nürnberg.

24. Mori, K. and Kinsho, T. (1988) *Liebigs Ann. Chem.* 807.
25. Kodato, S., Nakagawa, M. and Hino, T. (1989) *Tetrahedron* **45**, 7263.
26. Kawai, G., Ohnishi, M., Fujino, Y. and Ikeda, Y. (1986) *J. Biol. Chem.* **261**, 779.
27. Tkaczuk, P. and Thornton, E. R. (1981) *J. Org. Chem.* **46**, 4393.
28. Ohashi, Y., Iwamori, M., Ogawa, T. and Nagai, Y. (1987) *Biochemistry* **26**, 3990.
29. Singh, N. P. and Schmidt, R. R. (1989) *J. Carbohydr. Chem.* **8**, 199.
30. Stahl, E. (1967) *Dünnschichtchromatographie*, 2. Aufl., p. 817. Springer, Berlin.