New Chemical Constituents from *Borreria verticillata* (Rubiaceae)

by **Vinicius F. Moreira**[a]), **Rodrigo R. Oliveira**[a]), **Leda Mathias**[a]), **Raimundo Braz-Filho**[b]), and **Ivo J. Curcino Vieira***[a])

[a]) Setor de Química de Produtos Naturais, Universidade Estadual do Norte Fluminense Darcy Ribeiro, 28013-602, Campos dos Goytacazes, Rio de Janeiro, Brazil (phone: +55-22-27397046; fax: +55-22-27397248; e-mail: curcino@uenf.br)

[b]) Pesquisador Visitante Emérito-FAPERJ/UENF/UFRRJ

A phytochemical study on *Borreria verticillata* has led to the isolation of two novel simple indole alkaloids, 6-methoxy-4-(3-methylbut-2-en-1-yl)-1*H*-indole, named verticillatine A (**1**), and 1-(1*H*-indol-6-yl)-3-methylbutan-1-one, named verticillatine B (**2**), one new iridoid, 6′-*O*-(2-glyceryl)scandoside methyl ester (**3**), with the glycerol unit linked to a glucose unit, and two known ones, asperuloside (**4**) and scandoside methyl ester (**5**). The structures of these compounds were elucidated on the basis of spectroscopic-data analyses, mainly ^{1}H- and ^{13}C-NMR, including 2D experiments (^{1}H,^{1}H-COSY, NOESY, HMBC, and HMQC), and HR-ESI-MS.

Introduction. – The Rubiaceae family has many pharmaceutically important plants. *Borreria verticillata* (L.) G. MEY., popularly known as 'Cordão-de-Frade' is a species which occurs over the entire Brazilian territory and is commonly used in traditional folk medicine as an antipyretic and analgesic [1–3]. Previous studies of *B. verticillata* by other research groups showed the presence of terpenoid indole alkaloids [4][5], and we have also reported the structure of a new iridoid named borreriagenin isolated from a MeOH extract of the flowers of *B. verticillata* [6]. In continuation of our phytochemical investigation of *B. verticillata*, we now report on the structural characterization of two new simple indole alkaloids, 6-methoxy-4-(3-methylbut-2-en-1-yl)-1*H*-indole, named verticillatine A[1]) (**1**), and 1-(1*H*-indol-6-yl)-3-methylbutan-1-one, named verticillatine B[1]) (**2**), and of a new iridoid, 6′-*O*-(2-glyceryl)scandoside methyl ester[1]) (**3**), from the MeOH extract of *B. verticillata* roots, isolated besides two known iridoids, asperuloside (**4**) and scandoside methyl ester (**5**), a mixture of aliphatic acids, a mixture of tri-*O*-acylglycerols, sucrose, and a mixture of glucose and sucrose identified after preparation of the corresponding acetyl derivatives. All structures were elucidated by spectroscopic methods, especially by 2D-NMR techniques and mass spectrometry.

Results and Discussion. – The phytochemical investigation of the MeOH extract from *B. verticillata* roots by classical chromatographic methods resulted in the isolation of the five compounds **1**–**5** (*Fig. 1*), together with a mixture of aliphatic acids, a mixture of tri-*O*-acylglycerols, sucrose, and a mixture of glucose and sucrose. The components of these three mixtures (aliphatic acids, tri-*O*-acylglycerols, and glucose +

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

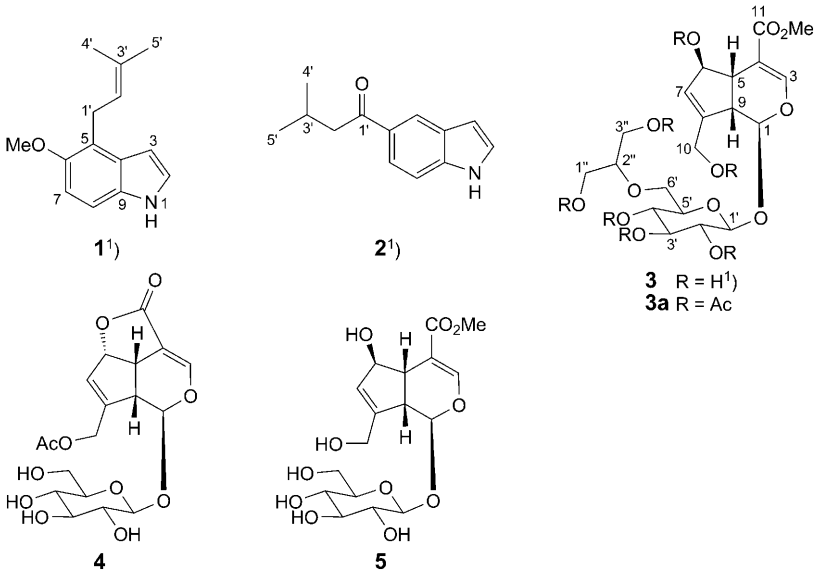


Fig. 1. *Compounds isolated from* Borreria verticillata

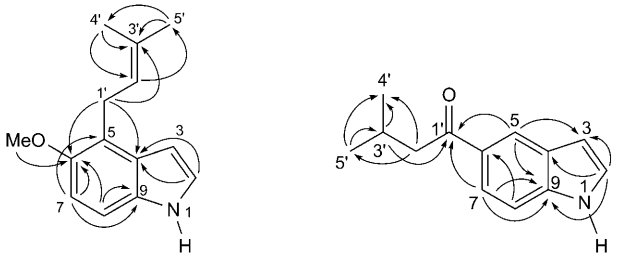
sucrose), sucrose [7], the known iridoids asperuloside (**4**) [8], and scandoside methyl ester (=(6β)-6-hydroxygeniposide; **5**) [9] were identified on the basis of 1D and 2D ^{1}H- and ^{13}C-NMR and MS data and comparison with the corresponding literature data. The 1D- and 2D-NMR (^{1}H and ^{13}C) and MS data of **1**–**3** allowed to characterize the two new simple indole alkaloids verticillatine A (**1**) and verticillatine B (**2**), and the new iridoid derivative of scandoside methyl ester, 6′-*O*-(2-glyceryl)scandoside methyl ester (**3**).

Verticillatine A (**1**) was obtained as an amorphous powder. Its IR spectrum exhibited a broad band at 3409 cm^{-1} typical for an N–H amine group and bands at 1272 and 1238 cm^{-1} for a C–O–C (MeO) group, at 2927 and 725 cm^{-1} for =CH, and at 1488 cm^{-1} typical for C=C of a benzene ring [10][11]. The UV spectrum showed an absorption band at 242 nm (log ε 1.86). The molecular formula of $C_{14}H_{17}NO$ was established by the EI-MS ($M^{+\cdot}$ at *m*/*z* 215) and was supported by NMR data. Comparative analysis of {^{1}H}- and DEPT(135°)-^{13}C-NMR spectra of **1** (*Table 1*) allowed to identify resonances for 14 C-atoms, including three Me groups (one linked to the O-atom at δ(C) 58.14 (MeO) and two linked to a sp^2 C-atom at δ(C) 25.76 (Me) and 17.92 (Me)), one CH_2 group at δ(C) 26.07, five sp^3 CH groups, and five quaternary sp^2 C-atoms, including an O-bearing one. The presence of a MeO group linked to C(6) was confirmed by a cross-peak correlation (^3J(H→C)) in the HMBC spectrum (*Fig. 2*), *i.e.*, δ(C) 151.00 (C(6))/δ(H) 3.85 (*s*, MeO). The fragment ions at *m*/*z* 200 ([*M* – Me]$^+$) and 184 ([*M* – MeO]$^+$) in the EI-MS were also used to confirm the presence of the MeO group. The prenyl (= 3-methylbut-2-en-1-yl) unit linked to C(5) was deduced by ^{1}H-NMR (1D and 2D ^{1}H,^{1}H-COSY) data, *i.e.*, by a *d* at δ(H) 3.85 (*J* = 7.0 Hz) of the CH_2(1′) group coupled to the olefinic H–C(2′) at δ(H) 5.24 (br. *t*, *J* = 7.0 Hz). Localization of the prenyl unit at C(5) (δ(C) 121.40) was confirmed by a

Table 1. *^{13}C- and ^{1}H-NMR* ($CDCl_3$) *Data of Verticillatine A* (**1**) *and Verticillatine B* (**2**)[a]). δ in ppm, J in Hz.

	1[1])		**2**[1])	
	δ(C)	δ(H)	δ(C)	δ(H)
H–C(2)	124.77	7.18 (*d*, *J* = 2.9)	125.77	7.29 (br. *s*)
H–C(3)	101.20	6.51 (*d*, *J* = 2.9)	104.59	6.68 (br. *s*)
C(4)	128.32	–	138.58	–
C(5) or H–C(5)	121.40	–	122.94	8.33 (br. *s*)
C(6)	151.00	–	130.53	–
H–C(7)	110.14	6.92 (*d*, *J* = 8.7)	122.53	7.89 (*dd*, *J* = 8.6, 1.3)
H–C(8)	108.73	7.19 (*d*, *J* = 8.7)	111.16	7.43 (*d*, *J* = 8.6)
C(9)	131.57	–	138.58	–
CH_2(1′) or C(1′)	26.07	3.62 (*d*, *J* = 7.0)	200.68	–
H–C(2′) or CH_2(2′)	123.39	5.24 (*t*, *J* = 7.0)	47.73	2.92 (*d*, *J* = 6.9)
C(3′) or H–C(3′)	130.98	–	25.87	2.34–2.37 (*m*)
Me(4′)	17.92	1.84 (br. *s*)	23.10	1.02 (br. *s*)
Me(5′)	25.76	1.67 (br. *s*)	23.10	1.03 (br. *s*)
*Me*O–C(6)	58.14	3.85 (*s*)	–	–
NH	–	8.02 (br. *s*)	–	8.33 (br. *s*)

[a]) Number of H-atoms bound to C-atoms deduced by comparative analysis of {^{1}H}- and DEPT-^{13}C-NMR spectra; δ and J from 1D ^{1}H-NMR; assignments confirmed by 2D-NMR data (^{1}H,^{1}H-COSY, HMQC, and HMBC).



1[1]) **2**[1])

Fig. 2. *Selected HMBCs* (H → C) *for verticillatine A* (**1**) *and verticillatine B* (**2**)

cross-peak correlation (^{2}J(H → C)) in the HMBC spectrum (*Fig. 2*), *i.e.*, δ(C) 121.40 (C(5))/δ(H) 3.62 (J = 7.0 Hz, CH_2(1′)). The complete analysis of the HMBCs (*Fig. 2*) in combination with additional NMR data (*Table 1*) allowed to characterize verticillatine A as a simple indole alkaloid, 6-methoxy-4-(3-methylbut-2-en-1-yl)-1*H*-indole (**1**).

Verticillatine B (**2**) was obtained as an amorphous powder. Its IR spectrum exhibited a broad band at 3390 cm^{-1} typical for an N–H amine group, a band at 1730 cm^{-1} for a C=O group, and at 1500 cm^{-1} typical for C=C of a benzene ring [10][11]. The UV spectrum showed an absorption band at 242 nm (log ε 4.13). The molecular formula of $C_{13}H_{15}NO$ was established by EI-MS ($M^{+\cdot}$ at m/z 201) in combination with NMR data. The {^{1}H}^{13}C-NMR spectrum (*Table 1*) combined with DEPT experiments exhibited resonances for 13 C-atoms, including two Me groups at

δ(C) 23.10, one CH_2 group at δ(C) 47.73 linked to a C=O group, five CH groups (4 arom. sp^2 and 1 sp^3), and four sp^2 quaternary C-atoms, including one C=O at δ(C) 200.68. The presence of the C=O group was inferred by the signal at δ(C) 200.68 in the ^{13}C-NMR spectrum (*Table 1*). The position of the C=O group within an isopentyl group linked to C(6) was confirmed by cross-peaks in the HMBC spectrum (*Fig. 2*), *i.e.*, δ(C) 200.68 (C(1′))/δ(H) 2.92 (*d*, $J = 6.9$ Hz, CH_2(2′)) and 2.34–2.37 (*m*, H–C(3′)). The presence of the isopentyl group was corroborrated by the HMBCs δ(C) 47.73 (C(2′))/δ(H) 1.03 and 1.02, (2*s*, Me(5′) and Me(4′), resp.). The substitution at the indole moiety was confirmed by the HMBCs δ(C) 138.58 (C(9))/δ(H) 8.33 (H–C(5)), 7.89 (*dd*, $J = 8.6$ and 1.3 Hz, H–C(7)), 2.29 (br. *s*, H–C(2)), and 6.68 (br. *s*, H–C(3)). The complete analysis of the HMBCs (*Fig. 2*) in combination with additional NMR data (*Table 1*) also allowed the identification of the features of the unprecedented skeleton of verticillatine B, *i.e.*, of the simple indole alkaloid 1-(1*H*-indol-6-yl)-3-methylbutan-1-one (**2**).

The iridoid 6′-*O*-(2-glyceryl)scandoside methyl ester (**3**) was obtained as an optically active amorphous powder. The IR spectrum showed bands at 3386 (O–H stretching), 2923 (C–H stretching), 1693 (ester C=O), and 1195–1157 and 1080 cm^{-1} (stretching C–O) [10][11]. Comparative analysis of the {^{1}H}- and DEPT(135°)-^{13}C-NMR spectra of **3** (*Table 2*) revealed signals corresponding to 20 C-atoms,

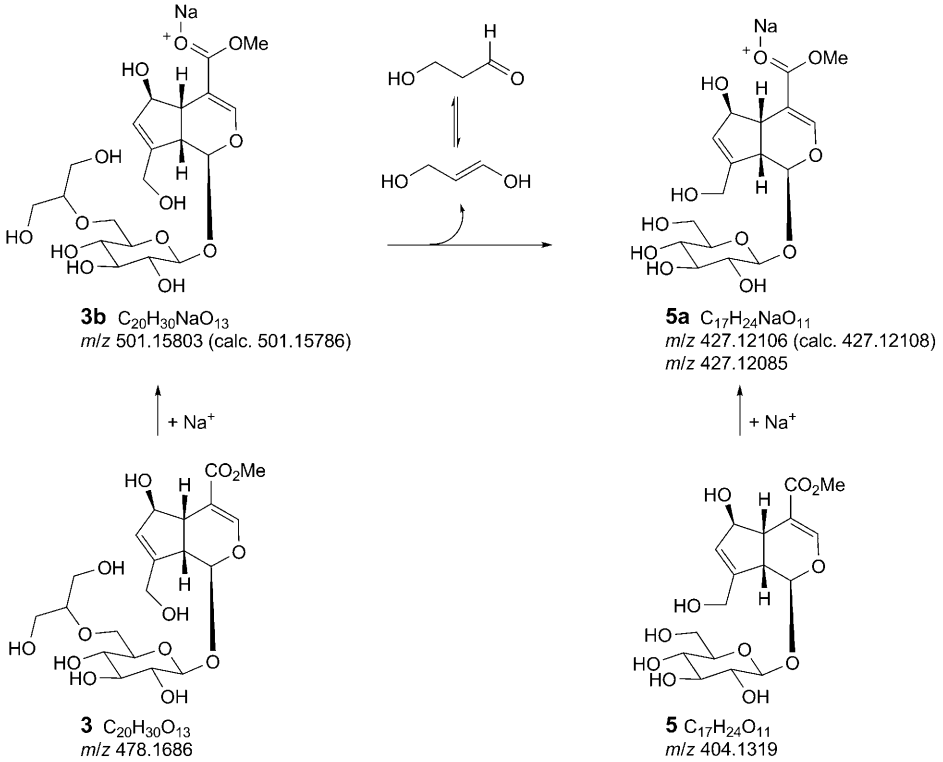
Table 2. *^{13}C- and ^{1}H-NMR* ((D$_5$)pyridine) *Data of Iridoids* **3** *and* **5**[a]). δ in ppm, J in Hz.

	3[1])				**5**
	HMQC (H → C)		HMBC (H → C)		
	δ(C)	δ(H)	^2J	^3J	δ(C)
CH(1)	97.67	5.82 (*d*, $J = 5.6$)	C(9)	C(3), C(1′)	98.26
H–C(3)	152.96	7.70 (*s*)		C(1), C(5)	153.85
C(4)	110.31	–	C(3), C(5)		110.74
H–C(5)	44.99	3.46 (*dd*, $J = 6.7$, 3.0)	C(9)	C(1), C(7)	45.50
H–C(6)	81.21	4.94–4.95 (*m*)	C(5), C(7)		83.20
H–C(7)	130.21	6.33 (br. *s*)		C(9), C(10)	130.06
C(8)	147.21	–	C(7), C(9), C(10)		147.47
H–C(9)	47.00	3.51 (br. *t*, $J = 5.8$)	C(5)	C(7)	47.44
CH_2(10)	60.38	4.80 (br. *d*, $J = 15.2$), 4.51 (br. *d*, $J = 15.2$)		C(7)	60.93
C(11)	168.69	–		C(3), MeO	170.17
*Me*O–C(11)	51.26	3.59 (*s*)			52.07
H–C(1′)	101.01	5.38 (*d*, $J = 7.8$)	C(2′)	C(1)	100.24
H–C(2′)	74.78	4.04–4.08 (*m*)	C(3′)		74.71
H–C(3′)	78.39	4.26–4.28(*m*)	C(2′)		77.78
H–C(4′)	71.36	4.18–4.21 (*m*)	C(3′)		71.45
H–C(5′)	78.81	3.96–3.99 (*m*)		C(3′), C(4′)	78.32
CH_2(6′)	64.79	4.26–4.20 (*m*)		C(2″), C(4′)	62.61
CH_2(1″,3″)	62.46	4.47–4.49 (*m*), 4.26–4.29 (*m*)	C(2″)		–
H–C(2″)	74.04	4.41 (*quint.*, $J = 5.4$)	C(1″)/C(3″)	C(6′)	–

[a]) Number of H-atoms bound to C-atoms deduced by comparative analysis of {^{1}H}- and DEPT-^{13}C-NMR spectra; δ and J from 1D ^{1}H-NMR; assignments confirmed by 2D-NMR data (^{1}H,^{1}H-COSY, HMQC, and HMBC).

corresponding to three nonhydrogenated sp^2 C-atoms (including one COOMe at δ(C) 168.69), twelve CH groups (eight sp^3 C-atoms linked to an O-atom and two sp^2 C-atom at δ(C) 152.96 (C(3)) and 130.21 (C(7))), four sp^3 CH_2 groups linked to an O-atom, and one MeO at δ(C) 51.26/δ(H) 3.59, characteristic of a MeO group of an ester function. These data, together with the HR-ESI-MS (pos. mode) furnishing the quasi-molecular-ion peak at *m/z* 501.15803 ($[M+Na]^+$, **3b** in the *Scheme*) and indicating a molecular mass M_r of 478, were compatible with a molecular formula $C_{20}H_{30}O_{13}$. Another significant positive-ion peak was observed at *m/z* 427.12106 ($[M+Na-C_3H_6O_2]^+$, **5a** in the *Scheme*) corresponding to a fragmentation involving the glyceryl moiety and a H-atom rearrangement (*Scheme*). All these data suggested a close similarity of **3** with the known iridoid **5**, which was identified as part of the structure of **3**, after comparative analysis of the {^{1}H}- and DEPT-^{13}C-NMR data of **5** establishing the number of signals corresponding to quaternary C-atoms and CH, CH_2, and Me groups. Additional spectral data of **3**, mainly 1D- and 2D-NMR (*Table 2*), the HR-ESI-MS of **5** ($[M+Na]^+$ at *m/z* 427.12085, **5a** in the *Scheme*, indicating a molecular mass M_r of 404 compatible with a molecular formula $C_{17}H_{24}O_{11}$ for **5**), comparison with similar data described in [8], and the 1D- and 2D-NMR data of **5** were also used to identify the structure of **3**.

Scheme. *Proposed Fragmentation Mechanisms of* **3** *by MS/MS of Peak at* m/z *501.15803* ($[M+Na]^+$) *and Quasimolecular Ion of* **5** *at* m/z *427.12106* ($[M+Na]^+$). Values observed in the HR-ESI-MS of **3** and **5**.



Comparison of the ^{1}H- and ^{13}C-NMR data of iridoid **3** and **5** (*Table 2*) indicated that the CH_2(6′)OH group of **5** at δ(C) 62.61 (δ(H) 3.76 (br. *d*, $J = 11.7$ Hz) and 3.55 (superimposed with other signals)) was linked to glyceryl (=2-hydroxy-1-(hydroxymethyl)ethyl) in **3**, *i.e.*, CH_2(1″,3″) of **3** appeared at δ(C) 62.46 and δ(H) 4.47 – 4.49 and 4.26 – 4.29, CH(2″) at δ(C) 74.04 and δ(H) 4.41, and CH_2(6′) at δ(C) 64.79 and δ(H) 4.26 – 4.20. The presence of a glycerol unit linked to O−CH_2(6′) of **3** was confirmed by the presence of the HMQCs δ(H) 4.41 (*quint.*, $J = 5.4$ Hz, H−C(2″))/δ(C) 74.04 (C(2″)) and δ(H) 4.47 – 4.49 and 4.26 – 4.29 (CH_2(1″,3″))/δ(C) 62.46 (C(1″,3″)) and by the HMBC δ(C) 64.79 (C(6′))/δ(H) 4.41 (H−C(2″)) (*Table 2*). Other important HMBCs were δ(C) 62.46 (C(1″,3″))/δ(H) 4.41 (H−C(2″)) and δ(C) 74.04 (C(2″))/δ(H) 4.47 – 4.49 and 4.26 – 4.29 (CH_2(1″,3″)). Moreover, the ^{1}H,^{1}H-COSY plot of **3** was used to establish homonuclear H-atom interactions (geminal and vicinal). The complete analysis of the HMBC spectrum of **3** confirmed the presence of the basic skeleton of scandoside methyl ester (**5**) with a glycerol unit and allowed the complete ^{1}H- and ^{13}C-NMR chemical shift assignments (*Table 2*) of 6′-*O*-(2-glyceryl)scandoside methyl ester (**3**).

Acetylation of **3** with pyridine/Ac_2O 1:2 (*v*/*v*) overnight yielded acetyl derivative **3a** confirming the presence of the OH groups in **3**, among others by the $\Delta\delta$(C) of the C-atoms of the glucose unit showing the protection due to the γ-effect [7][10] (see *Exper. Part*).

The known iridoid **4** was identified as asperuloside on the basis of spectral data, mainly 1D- and 2D-NMR and ESI-MS, and comparison with values described in [6].

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Experimental Part

General. TLC: silica gel (SiO_2) *60* F_{254}. Column chromatography (CC): SiO_2 *60* (70 – 230 mesh). M.p.: *Microquímica MQRPF*; uncorrected. Optical rotation: *Perkin-Elmer-343* digital polarimeter. FT-IR Spectra: *FT-IR-8300-Shimadzu* spectrometer; KBr disk; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-DRX-500* spectrometer equipped with inverse probes and field gradient, at 500 (^{1}H) and 125 (^{13}C) MHz; in $CDCl_3$ or (D_5)pyridine soln.; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; 1D spectra were acquired under standard conditions by using a direct detection 5-mm ^{1}H/^{13}C dual probe; standard pulse sequences were used for 2D spectra by using a multinuclear inverse-detection 5-mm probe with field gradient. EI-MS: *Shimadzu-QP5050A* mass spectrometer; at 70 eV; in *m*/*z* (rel. %). HR-ESI-MS: *VG7070E-HF* mass spectrometer; in *m*/*z*.

Plant Material. The roots of *Borreria verticillata* (L.) G. MEY. were collected in November 2007 at Campos dos Goytacazes City, Rio de Janeiro State, Brazil, and identified by *I. J. C. V.*, Brazil. A voucher specimen was deposited with the Universidade Estadual do Norte Fluminense Darcy Ribeiro, Brazil.

Extraction and Isolation. Dried and powdered root (505 g) from *B. verticillata* was extracted with MeOH at r.t., furnishing, after solvent evaporation, 29 g of crude MeOH extract. MeOH Extract was subjected to CC (SiO_2, gradient MeOH/CH_2Cl_2): *Fractions 1 – 10*. *Fr. 2* (99 mg) was submitted to prep. TLC (hexane/AcOEt 9:1): verticillatine A (**1**; 13.8 mg). *Fr. 5* (628.7 mg) was subjected to CC (SiO_2, gradient AcOEt/hexane): verticillatine B (**2**; 9.0 mg). *Fr. 9* (410.9 mg) was subjected to CC (*RP-18*, gradient H_2O/MeOH): iridoids **3** (70.0 mg), **4** (20.0 mg), and **5** (34.0 mg).

Verticillatine A (=*6-Methoxy-4-(3-methylbut-2-en-1-yl)-1*H-*indole*; **1**): Amorphous powder. IR: 3409 (N–H), 1272 and 1238 (C–O–C, MeO), 2927 and 725 (=CH), 1488 (C=C, benzene). ^{1}H- and ^{13}C-NMR (500 and 125 MHz, resp., $CDCl_3$): *Table 1*. EI-MS: 215 (100, $M^{+\bullet}$), 200 (25), 184 (22), 169 (20).

Verticillatine B (=*1-(1*H-*Indol-6-yl)-3-methylbutan-1-one*; **2**): Amorphous powder. IR (KBr disk): 3390 (N–H), 1730 (C=O), 1500 (C=C, benzene). ^{1}H- and ^{13}C-NMR (500 and 125 MHz, resp., $CDCl_3$): *Table 1*. EI-MS: 201 (20, $M^{+\bullet}$), 159 (15), 144 (100), 116 (25).

6′-O-*(2-Glyceryl)scandoside Methyl Ester* (=*(1*S,*4a*S,*5*R,*7a*S*)-1,4a,5,7a-Tetrahydro-5-hydroxy-1-{{6-*O*-*[2-hydroxy-1-(hydroxymethyl)ethyl]-β*-D-*glucoyranosyl}oxy}-7-(hydroxymethyl)cyclopenta[*c*]pyran-4-carboxylic Acid Methyl Ester*; **3**): Amorphous powder. $[\alpha]_D^{20} = -25.5$ ($c = 0.009$, MeOH). IR (KBr): 3386 (O–H), 2923 (C–H), 1693 (ester C=O), 1195–1157 and 1080 (C–O). ^{1}H- and ^{13}C-NMR (500 and 125 MHz, resp., (D_5)pyridine): *Table 2*. HR-ESI-MS (pos. mode): 501.15803 ($[M+Na]^+$, see *Scheme*; calc. 501.15841).

6′-O-*(2-Glyceryl)scandoside Methyl Ester Heptaacetate* (=*(1*S,*4a*S,*5*R,*7a*S*)-5-(Acetyloxy)-1-{{2,3,4-tri*-O-*acetyl-6*-O-*{2-(acetyloxy)-1-[(acetyloxy)methyl]ethyl}-β*-D-*glucopyranosyl}oxy}-7-[(acetyloxy)-methyl]-1,4a,5,7a-tetrahydrocyclopenta[*c*]pyran-4-carboxylic Acid Methyl Ester*; **3a**): ^{13}C-NMR (100 MHz, $CDCl_3$): 94.74 (C(1)); 151.73 (C(3)); 109.16 (C(4)); 39.13 (C(5)); 81.36 (C(6)); 128.73 (C(7)); 142.81 (C(8)); 46.34 (C(9)); 61.14 (C(10)); 166.83 (C(11)); 51.51 (*Me*O–C(11)); 96.46 (C(1′)); 70.71 (C(2′)); 72.40 (C(3′)); 70.71 (C(4′)); 72.43 (C(5′)); 61.51 (C(6′)); 62.47 (C(1″,3″)); 68.11 (C(2″)); 21.18–22.55 (7 *Me*C=O)); 170.26 (7 Me*C*=O).

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