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ALKALOIDS AND OTHER COMPOUNDS FROM SEEDS OF *TABERNAEMONTANA CYMOSA**†

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Key Word Index—*Tabernaemontana cymosa* (= *T. psychotrifolia*); Apocynaceae; seeds; indole alkaloids; 9-(β-D-glucopyranosyloxy)tetrahydroalstonine; lignan glucosides; 5,5′-dimethoxy-9-*O*-(β-D-glucopyranosyl)lariciresinol; 2α-*O*-(β-D-glucopyranosyl)lyoniresinol; 3-*O*-(β-D-glucopyranosyl)-5-*O*-methylgallic acid.

Abstract—From the seeds of *Tabernaemontana cymosa* (= *T. psychotrifolia*) 17 indole alkaloids and six lignan glucosides were isolated, besides triacylglycerols, 9,12-octadecadienoic acid, lupeol, (+)-lyoniresinol, obtusifoliol, sweroside and a glucoside of 3-*O*-methylgallic acid. 9-(β-D-Glucopyranosyloxy)-tetrahydroalstonine, (+)-5,5′-dimethoxy-9-*O*-(β-D-glucopyranosyl)lariciresinol, (−)-2α-*O*-(β-D-glucopyranosyl)-lyoniresinol and 3-*O*-(β-D-glucopyranosyl)-5-*O*-methylgallic acid are described for the first time. Structural determination is based on spectroscopic studies and/or on comparison with authentic compounds. Some of the isolated substances exhibited significant antifungal and/or cytotoxic effects.

INTRODUCTION

The genus *Tabernaemontana* comprises *ca* 100 species distributed throughout the tropical regions of the world [3]. *Tabernaemontana cymosa* grows as a small tree in Colombia, Venezuela and Trinidad [4]. It is synonymous with *T. psychotrifolia* and *T. umbrosa* [4]. The plant is used in folk medicine against various diseases: the leaves and fruits are remedies against the sting of millepedes [4], the flowers are reported to have cardiotonic properties [3] and the latex is employed to remove warts [5]. The root and stem bark have occasionally been analyzed and various indole alkaloids have been isolated (from root: coronaridine, olivacine, voacamine and voacangine; from stem bark: affinine, 16-epivobasinic acid and taberpsychine) [6–8].

No previous phytochemical studies of the seeds of *T. cymosa* have been carried out. We report herein an investigation of this plant part, which was collected in Columbia.

RESULTS

Seeds were extracted with petrol and subsequently with methanol. The methanol extract, after addition of water, was fractionated first with petrol, then with dichloromethane and finally with ethyl acetate. Since TLC analysis of the petrol-soluble fraction of the methanol extract and the 'primary' petrol extract revealed identical compositions, it was not investigated further.

Chromatographic separation of the petrol extract, the dichloromethane and the ethyl acetate fractions yielded the individual constituents compiled in Tables 1–3 besides a mixture of triacylglycerols which was subjected to GC analysis.

The presented structures are the result of spectroscopic studies, especially of homo- and heteronuclear COSY measurements, done on the isolated compounds and appropriate derivatives thereof. Known substances were, as far as possible, identified by comparison with authentic compounds.

The glucose units of **18**, **19** and **21**–**27** have been confirmed to belong to the D-series by GC analysis on a chiral column after acidic cleavage, according to the method of König [43–45].

The known alkaloids **1**–**4**, **6**–**16** and **20** were identified from their physico-chemical data (UV, IR, mass spectra, ^{1}H, ^{13}C NMR, $[\alpha]_D$, mp and CD).

In the course of our spectroscopic studies for the

* Dedicated to Prof. Dr Gerhard Rücker, Bonn, on the occasion of his 65th birthday.

†Part 80 in the series 'Constituents of Tropical Medicinal Plants'. For part 79, see ref. [1]; for part 78 see ref. [2].

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Table 1. Compounds isolated from the petrol extract

Classification	Compound	Content (%)*	Refs
Alkaloids	Coronaridine (**1**)	1.5	[9, 10]
	7α-Hydroxyindolenine-voacangine (**2**)	0.3	[10, 11]
	Tabersonine (**3**)	3	[12–15]
	Voacangine (**4**)	6	[10]
Fatty acid	9,12-Octadecadienoic acid	2	
Triacylglycerols	Mixture (see Table 7)	*ca* 85	
Triterpenes	Lupeol	1.5	[16, 17]
	Obtusifoliol (**5**)	0.6	[18]

Compounds were also detected by TLC in the petrol-soluble fraction of the methanol extract.
* Roughly estimated concentrations as % of total petrol extract.

first time we publish the complete ^{13}C NMR data for stemmadenine (**12**), as well as for 3-oxotabersonine (**10**) (Table 4). For *N*-oxides **13** and **14**, respectively, neither ^{13}C nor ^{1}H NMR data had hitherto been published (for ^{13}C: Table 4; for ^{1}H NMR: Experimental).

Reduction ($Fe^{II}SO_4$) of the *N*-oxides **13** and **14** to stemmadenine (**12**) and tabersonine (**3**) corroborated the structures.

In spite of the consideration that the *N*-oxides might be genuine natural products [29, 46], it should be noted that model experiments performed with **3** and **12** showed that *N*-oxidation occurs easily in the presence of air. Similar studies revealed that **10** could have been derived from **3** during work-up of the plant extracts. Therefore, **10**, **13** and **14** cannot be excluded as artifacts.

For alkaloid **2**, the easy generation from **4** under mild oxidative conditions has been described [47].

The new heteroyohimbane-type alkaloid, 9-(β-D-glucopyranosyloxy)tetrahydroalstonine (**19**), was isolated from the ethyl acetate fraction. The characteristic ^{13}C NMR resonances revealed glucose as its sugar moiety [48]. The basic structure of the aglucone was determined by homo- and heteronuclear COSY studies (Figs 1 and 2). The determination of the relative configuration is mainly based on the results of nuclear Overhauser experiments and on the observed ^{1}H–^{1}H coupling constants (Table 5).

Comparison of the CD curves of **15** and **19**, and a positive Cotton effect measured at 292 nm for both compounds established the 3*S*-configuration [49, 50].

3-*O*-(β-D-Glucopyranosyl)-5-*O*-methylgallic acid (**27**) represents a major component of the ethyl acetate fraction; it was isolated as a natural product for the first time. Acetylation demonstrated the presence of the glucose unit, as well as one acetylable hydroxyl group in the aglucone. The IR ($\nu_{C=O}$ = 1690 cm^{-1}) in combination with a very broad ^{13}C resonance at δ 171.1 and the formation of a methyl ester on treatment with CH_2N_2 (which simultaneously methylated the

Table 2. Compounds isolated from dichloromethane-soluble fraction of the methanol extract

Classification	Compound	Content (%)*	Refs
Alkaloids	Condylocarpine (**6**)	0.1	[19, 20]
	Coronaridine (**1**)	2	[10]
	14,15-Dehydro-16-epi-vincamine (**7**)	0.007	[21–24]
	Heyneanine (**8**)	0.1	[10, 25]
	10-Hydroxycoronaridine (**9**)	0.07	[10, 26]
	3-Oxotabersonine (**10**)	0.03	[15]
	3-Oxovoacangine (**11**)	0.2	[27]
	Stemmadenine (**12**)	5	[19, 28]
	Stemmadenine-*N*-oxide (**13**)	0.5	[20, 29]
	Tabersonine (**3**)	0.2	[12–15]
	Tabersonine-*N*-oxide (**14**)	0.04	[15, 30]
	Tetrahydroalstonine (**15**)	0.13	[31–33]
	Voacangine (**4**)	24	[10]
	Voacristine (**16**)	0.9	[10]
Lignans and lignan glucosides	(+)-Lyoniresinol (**17**)	0.05	[34]
	(+)-5,5′-Dimethoxy-9-*O*-(β-D-glucopyranosyl)lariciresinol (**18**)	0.09	

*Roughly estimated concentrations as % of total dichloromethane extract.

Table 3. Compounds isolated from ethyl acetate-soluble fraction of methanol extract

Classification	Compound	Content [%]*	Refs
Alkaloids	Coronaridine (**1**)	0.6	[10]
	Voacangine (**4**)	0.2	[10]
	9-(β-D-Glucopyranosyloxy)-tetrahydroalstonine (**19**)	0.1	
	Isositsirikine (**20**)	0.04	[35–37]
	Stemmadenine (**12**)	5	[19, 28]
Lignan glucosides	(+)-3α-*O*-(β-D-Glucopyranosyl)-lyoniresinol (**21**)	3.5	[34, 38]
	(−)-3α-*O*-(β-D-Glucopyranosyl)-lyoniresinol (**22**)	2	[39]
	(−)-2α-*O*-(β-D-Glucopyranosyl)-lyoniresinol (**23**)	0.3	
	(−)-3α-*O*-(β-D-Glucopyranosyl)-5′-methoxyisolariciresinol (**24**)	0.4	[9, 39]
	(+)-8,8′-Dimethoxy-1-*O*-(β-D-glucopyranosyl)seco-isolariciresinol (**25**)	0.5	[40]
Others	Sweroside (**26**)	0.15	[41, 42]
	3-*O*-(β-D-Glucopyranosyl)-5-*O*-methylgallic acid (**27**)	2	

*Roughly estimated concentrations as % of total ethyl acetate extract.

phenolic hydroxyl group) gave evidence for a free carboxyl group. Eventually, heteronuclear COSY corroborated the structure (Fig. 3).

Among the isolated lignan and lignan glucosides, **18** and **23** represent new structures. Compound **25** has also to be regarded a new natural product, which hitherto had only been described from the methanolysis of hazaleanin A [40].

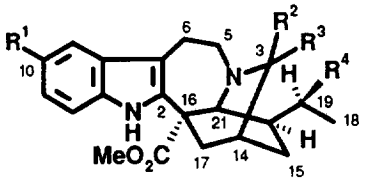
The ^{1}H NMR as well as the ^{13}C NMR resonances of **23** are very similar to those of the known com-

Table 4. ^{13}C NMR spectral data of compounds **10**, **12–14** and **28** (δ in CD_3OD)

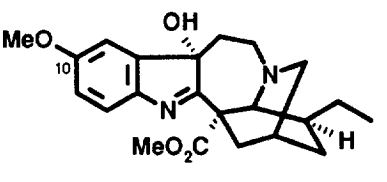
C	**10**	**12***	**13***	**14**	**28**
2	163.5[a]	133.8	134.8	164.3	135.6
3	166.5[a]	46.0	73.8[a]	69.5[a]	55.6
5	44.9[b]	56.4	64.4[a]	64.1[a]	65.4
6	44.4[b]	27.6	24.8	43.3	24.5
7	58.2	113.8	109.1	59.3	109.0
8	148.1[c]	128.3	127.8	137.3	128.0
9	122.6	118.4	118.2	122.3	118.8
10	122.3	119.3	120.4	119.1	120.9
11	129.8	122.0	123.0	129.8	123.5
12	111.2	111.5	112.1	110.3	112.7
13	144.7[c]	135.9	136.2	145.3	136.8
14	122.8	29.4	26.5	128.3	26.0
15	136.8[c]	38.0	34.6	132.8	34.5
16	90.6	61.5	60.9	89.7	61.4
17	27.2[d]	174.4	173.8	33.3[b]	174.0
18	7.6	14.4	14.5	8.0	14.6
19	27.9[d]	124.8	131.8	31.8[b]	135.2
20	41.7[b]	134.8	128.9	42.7	127.2
21	67.9	55.8	75.5	85.7	63.3
22	—	69.8	69.5	—	69.1
23	—	—	—	—	75.5
OMe	51.6	52.7	53.1	51.6	53.3
C=O	169.4			169.6	

* Measured in $CD_3OD/CDCl_3$ (1:1).

[a–d] Assignments interchangeable within a column.



1: $R^1 = R^2 = R^3 = R^4 = H$
4: $R^1 = OMe$; $R^2 = R^3 = R^4 = H$
8: $R^1 = R^2 = R^3 = H$; $R^4 = OH$
9: $R^1 = OH$; $R^2 = R^3 = R^4 = H$
11: $R^1 = OMe$; R^2, $R^3 = O$; $R^4 = H$
16: $R^1 = OMe$; $R^2 = R^3 = H$; $R^4 = OH$



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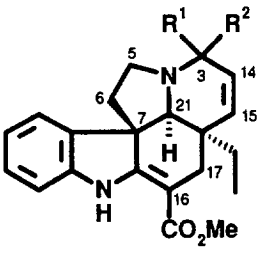
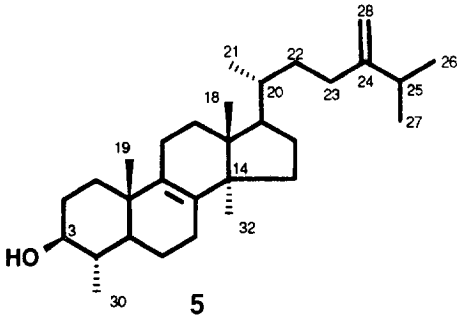


3: $R^1 = R^2 = H$
10: R^1, $R^2 = O$
14: 3-N_b-oxide



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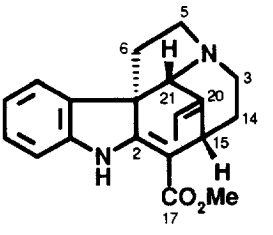

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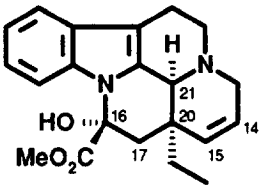

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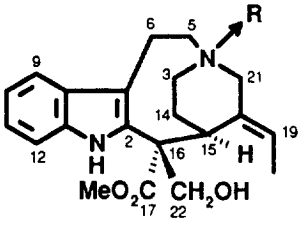
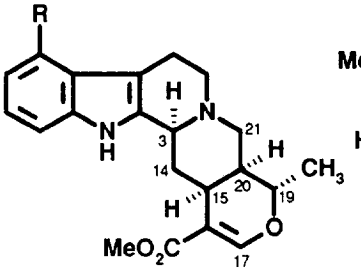
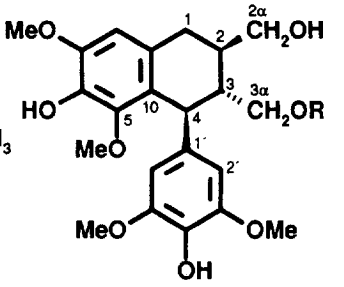


12: R = ·/·
13: R = O



15: R = H
19: R = O-ß-D-glucosyl



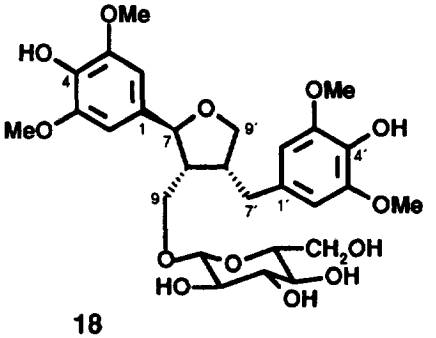
17: R = H
21: R = ß-D-glucosyl

pounds **21** or **22** and **24** [34, 38, 39]; only the ^{13}C signals for C-2, C-3, C-2α and C-3α exhibit significant differences (Table 6).

These data established structure **23**, which was finally corroborated by heteronuclear COSY measurements. The relative configuration followed from ^1H–^1H coupling constants. A positive Cotton effect at 285 nm determined the *R*-configuration at C-4 [51, 52].

NMR studies of peracetylated **18** revealed a glucose moiety and the lignan-type structure of the aglucone. The relative configuration of the tetrahydrofuran moiety came from comparison of its ^{13}C NMR resonances with the data for 5,5′-dimethoxylariciresinol [53]. Identical CD curves for **18** and 5,5′-dimethoxylariciresinol [53] proved the 7*S*,8*R*,8′*R*-configuration.

The ^1H NMR spectrum of the triacylglycerol mixture obtained by column chromatography from the petrol extract did not show any resonances indicating branched alkyls. Methanolysis converted the mixture of triacylglycerols to a mixture of the corresponding methyl esters, which was subjected to GC analysis (Table 7). Identification is based on co-injection with authentic methyl esters.



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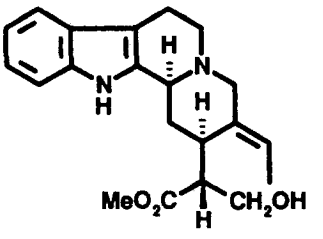

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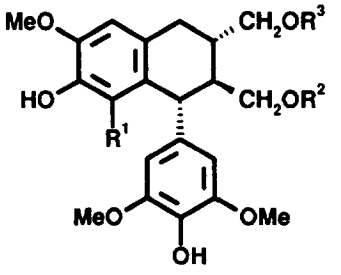
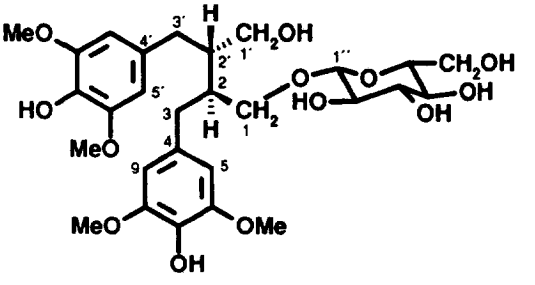


22: R^1 = OMe, R^2 = ß-D-glucosyl, R^3 = H
23: R^1 = OMe, R^2 = H, R^3 = ß-D-glucosyl
24: R^1 = H, R^2 = ß-D-glucosyl, R^3 = H



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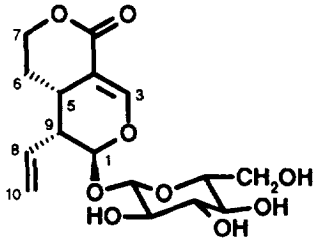

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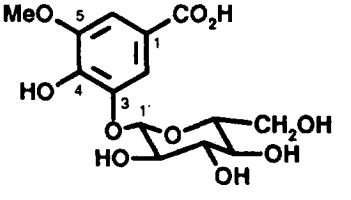

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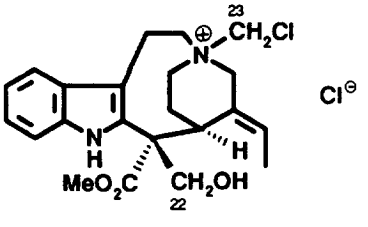

28

DISCUSSION

All structural types of the alkaloids isolated from the seeds of *T. cymosa* have been found earlier in other *Tabernaemontana* species and our results corroborate the botanical classification of the plant from a chemotaxonomical point of view [2]. Comparison of the results from the seeds of *T. cymosa* with those from former reports of the roots and the stem bark [6–8] revealed significant differences. Only two of the major alkaloids of the seeds—coronaridine (**1**) and voacangine (**4**)—had been isolated from the roots as well. All

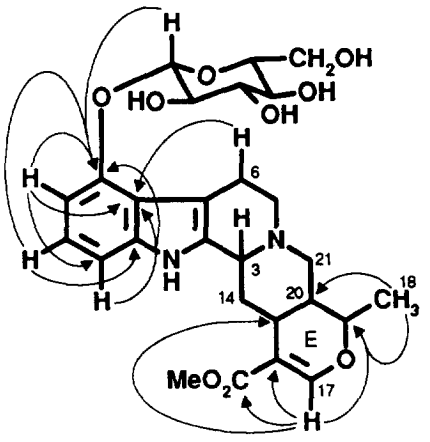

Fig. 1. Important couplings observed in the HMBC of compound **19** (in CD_3OD).

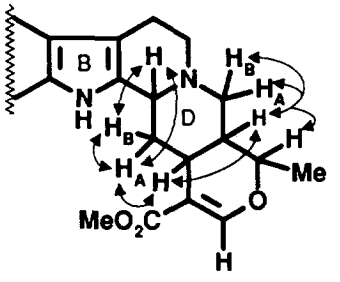

Fig. 2. Important couplings observed in the $^{2,3}J$ ^1H–^1H COSY of compound **19** (in CD_3OD).

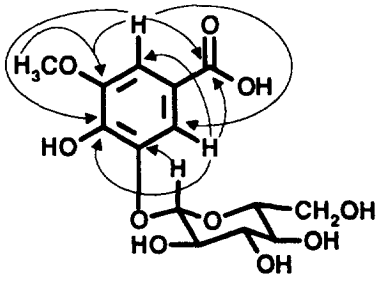

Fig. 3. Important couplings observed in the HMBC of compound **27** (in CD_3OD at 320 K to shift signal of H_2O).

other alkaloids isolated from the seeds had not been described in the other plant parts.

A further chlorine-containing compound isolated from the dichloromethane fraction was revealed as 4-*N*-chloromethylstemmadeninium chloride (**28**) by its FAB-mass spectrum and by NMR studies. Partial synthesis from **12** and CH_2BrCl according to ref. [54] corroborated the structure. Its obvious easy formation as an artifact by reaction of **12** with CH_2Cl_2 was supported by model experiments.

Biological tests with those constituents available in larger amounts revealed significant antifungal activity against *Rhizoctonia solani* for **1**, **2**, **3** and **11** in the plate diffusion test. Compounds **1** and **2** showed also significant antifungal activity against *Saprolegnia asterophora* but no antifungal effect was observed against *Botrytis cinerea*. In an antibacterial test against *Bacillus subtilis* only tabersonine (**3**) showed moderate activity. Furthermore, compounds **2**, **12** and **27** exhibited significant, and the alkaloids **1** and **4**, moderate toxicity in the brine shrimp bioassay [55].

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 = cyclohexane–EtOAc (9:1), S-2 = cyclohexane–EtOAc (4:1), S-3 = $CHCl_3$–MeOH (9:1), S-4 = CH_2Cl_2–MeOH (17:3), S-5 = $CHCl_3$–MeOH (17:3), S-6 = $CHCl_3$–MeOH (19:1), S-7 = cyclohexane–EtOAc (7:3), S-8 = cyclohexane–EtOAc (1:4), S-9 = cyclohexane–EtOAc (3:2), S-10 = CH_2Cl_2–MeOH (4:1), S-11 = CH_2Cl_2–MeOH (9:1), S-12 = $CHCl_3$–MeOH (4:1), S-13 = CH_2Cl_2–MeOH–H_2O (60:40:2.5), S-14 = cyclohexane–EtOAc (19:1); detection: UV, anisaldehyde reagent [56], Ce(IV) reagent [56]. Unless otherwise stated, $[\alpha]_D$ in $CHCl_3$ at 21°, CD and UV in MeOH, IR in $CHCl_3$. Unless otherwise stated, ^1H NMR at 360 MHz and ^{13}C NMR at 90 MHz in $CDCl_3$ with TMS as int. standard. EIMS at 70 eV; DCIMS with NH_3 or isobutane, respectively; FAB-MS using a xenon gun (8 kV). Unless key ions, only ions are given with rel. intensities $\geqslant 15\%$ and $m/z \geqslant 100$. CC and MPLC were carried out on silica gel 60 (Macherey-Nagel) or on LiChroprep® RP 18 (40–60 μm, Merck). For CC, in addition, we used Fractogel® PVA 500 (Merck), Sephadex® LH-20 (Pharmacia), Fractogel® TSK HW-40 (S) (Merck) or alumina B (activity grade III, ICN). HPLC was performed on LiChrosorb® RP 18 (7 μm, Merck). GC analysis of the fatty acid Me esters were performed on a column packed with polyethylene glycol succinate (EGS) on Chromosorb W (60–80 mesh), length: 2 m, He gas (33 ml/min^{-1}), temp. prog: 80° to 200° at 4° min^{-1}.

Plant material. Seeds of *T. cymosa* Jacquin were

Table 5. Important NOEs and coupling constants of compound **19**

Irradiation	M*	J [Hz] (Coupling partner)	Enhancement
H-14$_A$	*ddd*	12 (H-14$_B$), 12 (H-15), 12 (H-3)	H-14$_B$, H-19
H-15	*dd*	12 (H-14$_B$), 3.5 (H-20)	H-20, H-21$_A$
H-19	*dq*	11.5 (H-20), 6 (CH_3-18)	H-14$_A$

*M = multiplicity without irradiation.

Table 6. ^{13}C NMR data of compounds **21–24** (at 63 MHz, δ in CD_3OD)

C	21	22	23	24
1	33.8	33.8	34.1	33.6
2	40.6	41.2	38.2[a]	41.1
2α	66.2	66.2	74.9	65.5
3	46.7	46.5	*[a]	45.3
3α	71.4	71.5	63.3	70.8
4	42.8	43.2	42.7	*
5	148.6	148.7	147.7	117.3
6	138.9	138.9	138.9	145.3
7	147.6	147.5	148.6	147.4
8	107.8	107.7	107.7	112.4
9	130.2	130.2	130.1	129.2
10	126.4	126.2	126.5	133.5
1′	139.3	139.4	139.6	137.9
2′	106.9	107.1	107.0	108.0
3′	149.0	149.0	149.0	149.3
4′	134.5	134.6	134.6	135.1
5′	149.0	149.0	149.0	149.3
6′	106.9	107.1	107.0	108.0
1″	104.8	104.2	104.6	103.9
2″	75.1	75.0	75.2	75.0
3″	77.9	78.0	78.0	78.0
4″	71.6	71.5	71.7	71.5
5″	78.2	78.2	78.1	78.2
6″	62.8	62.7	62.8	62.5
OMe-5	60.1	60.1	60.0	—
OMe-7	56.6	56.6	56.6	56.4
OMe-3′	56.8	56.9[a]	56.8	56.9
OMe-5′	56.8	56.8[a]	56.8	56.9

[a] Assignments interchangeable within a column.
* Overlapped with solvent signal.

Table 7. Qualitative and quantitative composition of the mixture of fatty acid methyl esters obtained by methanolysis of triacylglycerols from the petrol extract

Methyl ester of:	Content (%)
9-Octadecenoic acid	53
9,12-Octadecadienoic acid	23
Hexadecanoic acid	15
Octadecanoic acid	6
9,12,15-Octadecatrienoic acid	2

collected in October 1992 at Campeche, Colombia, and identified by Mr R. Jaramillo (Herbario Nacional de Colombia). A voucher specimen is kept at the Herbario Nacional de Colombia under No. COL 12709.

Extraction and isolation. Dried, pulverized seeds (1 kg) were extracted exhaustively at room temp., first with petrol (203 g petrol extract) and then with MeOH (155 g MeOH extract). The MeOH extract was suspended in 800 ml MeOH–H_2O (1:1) and successively extracted with (i) petrol (20 g petrol fr.), (ii) CH_2Cl_2 (42 g CH_2Cl_2 fr.) and (iii) EtOAc (16 g EtOAc fr.). These extracts/frs were subjected to MPLC on silica gel, using cyclohexane–EtOAc or CH_2Cl_2–MeOH mixts. The crude frs were further separated by repeated CC, MPLC or HPLC using one of the following systems: (a) silica gel with cyclohexane–EtOAc or CH_2Cl_2–MeOH or $CHCl_3$–MeOH or CH_2Cl_2–MeOH–H_2O; (b) LiChroprep RP 18 with MeOH–H_2O or MeOH; (c) Fractogel PVA 500 with MeOH; (d) Fractogel TSK HW-40 (S) with MeOH; (e) Sephadex LH-20 with MeOH; (f) alumina B with cyclohexane–EtOAc.

These procedures yielded the pure compounds described below and a mixt. of triacylglycerols, which was converted to the corresponding fatty acid Me esters by methanolysis for GC analysis.

Isolated from petrol extract

Coronaridine (**1**). Amorphous (32 mg). TLC: R_f 0.44 (S-2); anisaldehyde: red–violet, Ce(IV) reagent: blue. $[\alpha]_D$ −34° (*c* 1.5) (ref. [9] $[\alpha]_D$ −41° (*c* 0.63)). IR, UV, ^1H NMR, ^{13}C NMR and MS identical with authentic sample.

7α-Hydroxyindoleninevoacangine (**2**). Oil (20 mg). TLC: R_f 0.24 (S-9); anisaldehyde: yellow, Ce(IV) reagent: yellow. $[\alpha]_D$ −43° (*c* 1.7) (ref. [11] $[\alpha]_D$ −18° (*c* 0.1)). CD, IR, UV, ^1H NMR and MS in agreement with published data [9–11].

Tabersonine (**3**). Oil (67 mg). TLC: R_f 0.37 (S-2); anisaldehyde: dark yellow. $[\alpha]_D$ −317° (*c* 1.0) (ref. [15] $[\alpha]_D$ −333° (MeOH; *c* 2.5)). IR, UV, ^1H NMR and MS in agreement with published data [9, 12–14].

Voacangine (**4**). Amorphous (49 mg). TLC: R_f 0.32 (S-2); anisaldehyde: red-violet, Ce(IV) reagent: green-brown. $[\alpha]_D$ −37° (*c* 1.6) (ref. [10] $[\alpha]_D$ −43° (for *c*: no data)). IR, UV, ^1H NMR, ^{13}C NMR and MS identical with authentic sample.

9,12-Octadecadienoic acid. Oil (41 mg). TLC: R_f 0.31 (S-2); anisaldehyde: blue. Methylation in MeOH soln with CH_2N_2 in Et_2O (room temp., 15 min) yielded the Me ester. Identification by GC (coinjection with authentic compound).

Mixture of triacylglycerols. Oil (*ca* 1.5 g). TLC: R_f 0.33 (S-14); anisaldehyde: green-blue. Methanolysis with methanolic HCl yielded a mixt. of fatty acid Me esters. Analysis by GC and identification by coinjection with authentic substances (see Table 7).

Lupeol. Crystals (13 mg), mp 214° (from MeOH) (ref. [16] mp 184–187°). TLC: R_f 0.19 (S-1); anisaldehyde: violet. $[\alpha]_D$ +28° (*c* 1.02) (ref. [16] $[\alpha]_D$ +28.5° (*c* 0.03)). IR, ^1H NMR, ^{13}C NMR and MS in agreement with published data [16, 17].

Obtusifoliol (**5**). Crystals (8 mg), mp 145° (from $CHCl_3$–MeOH) (ref. [18] mp 145–146°). TLC: R_f 0.24 (S-2); anisaldehyde: violet. $[\alpha]_D$ +69° (*c* 0.43) (ref. [18] $[\alpha]_D$ +72° (*c* 1.0)). IR, ^1H NMR, ^{13}C NMR and MS in agreement with published data [18].

Isolated from CH_2Cl_2-soluble fraction

Condylocarpine (**6**). Crystals (9 mg), mp 159° (from $CHCl_3$–MeOH) (ref. [34] mp 159–162°). TLC: R_f 0.35

(S-11); anisaldehyde: light pink, changes to light yellow. $[\alpha]_D$ +501° (*c* 0.7) (ref. [19] $[\alpha]_D$ +870° (EtOH; for *c*: no data)). IR, UV, ^{1}H NMR and MS in agreement with published data [19, 20].

14,15-*Dehydro*-16-*epi*-*vincamine* (**7**). Amorphous (1 mg). TLC: R_f 0.51 (S-11); anisaldehyde: violet. $[\alpha]_D$ +20° (*c* 0.08) (ref. [21] $[\alpha]_D$ +30° (*c* 1.2)). IR, UV, ^{1}H NMR, ^{13}C NMR and MS in agreement with published data [21–24].

Heyneanine (**8**). Crystals (7 mg), mp 158–160° (from MeOH) (ref. [10] mp 159–160°). TLC: R_f 0.32 (S-8); anisaldehyde: red. $[\alpha]_D$ −32° (*c* 0.62) (ref. [10] $[\alpha]_D$ −28° (for *c*: no data)). IR, UV, ^{1}H NMR and MS in agreement with published data [10, 25].

10-*Hydroxycoronaridine* (**9**). Oil (11 mg). TLC: R_f 0.29 (S-7); anisaldehyde: red violet. $[\alpha]_D$ −34° (*c* 0.87) (ref. [26] $[\alpha]_D$ −33° (*c* 0.5)). IR, UV, ^{1}H NMR and MS in agreement with published data [26].

3-*Oxotabersonine* (**10**). Oil (4 mg). TLC: R_f 0.20 (S-8); anisaldehyde: yellow. $[\alpha]_D$ −86° (*c* 0.35) (ref. [15] $[\alpha]_D$ −77° (for *c*: no data)). ^{13}C NMR: Table 4. IR, UV, ^{1}H NMR and MS in agreement with published data [15].

3-*Oxovoacangine* (**11**). Amorphous (16 mg). TLC: R_f 0.22 (S-8); anisaldehyde: red violet. $[\alpha]_D$ −52° (*c* 1.3) (ref. [27] $[\alpha]_D$ −56° (*c* 0.093)). IR, UV, ^{1}H NMR and MS in agreement with published data [27].

Stemmadenine (**12**). Crystals (875 mg). Mp 189–191° (from MeOH) (ref. [19] mp 189–191°). TLC: R_f 0.25 (S-10); anisaldehyde: red-violet. $[\alpha]_D$ +328° (pyridine; *c* 0.60) (ref. [19] $[\alpha]_D$ +329° (pyridine; for *c*: no data)). ^{13}C NMR: Table 4. IR, UV, ^{1}H NMR and MS in agreement with published data [19, 28].

Stemmadenine-N-oxide (**13**). Amorphous (72 mg). TLC: R_f 0.16 (S-12); anisaldehyde: grey–blue. $[\alpha]_D$ +98° (MeOH; *c* 0.63). IR ν_{max}^{KBr} cm^{-1}: 1728 (C=O). UV λ_{max} nm: 221 (log ε 4.41), 283 (log ε 3.70), 291 (log ε 3.66). ^{1}H NMR (250 MHz, $CDCl_3$–CD_3OD (1:1)): δ 1.80 (3H, *dd*, J_1 = 7, J_2 = 2 Hz, Me-18), 2.36 (1H, *ddd*, J_1 = 16, J_2 = 13, J_3 = 7 Hz, H-14$_A$), 2.65 (1H, *dddd*, J_1 = 16, J_2 = 13, J_3 = 7, J_4 = 4 Hz, H-14$_B$), 3.25–3.42 (2H, *m*, H-3$_A$ or H-5$_A$, H-6$_A$), 3.50–3.80 (6H, *m*, H-3$_A$ or H-5$_A$, H-3$_B$, H-5$_B$, H-6$_B$, H-15, H-21$_A$), 3.79 (3H, *s*, OMe), 3.93 (1H, *br d*, *J* = 15 Hz, H-21$_B$), 4.29 (1H, *d*, *J* = 11 Hz, H-22$_A$), 4.37 (1H, *d*, *J* = 11 Hz, H-22$_B$), 5.63 (1H, *q*, *J* = 7 Hz, H-19), 7.14 (2H, *m*, H-10, H-11), 7.39 (1H, *dm*, *J* = 8 Hz, H-12), 7.51 (1H, *dm*, *J* = 8 Hz, H-9). ^{13}C NMR: Table 4. EIMS *m/z* (rel. int. %): 324 (23), 123 (100), 122 (30), 121 (26), 108 (24), 42 (30).

Reduction of **13** *with* $FeSO_4$. **13** (4.4 mg) was heated under reflux in 1 ml of 10% aq. $FeSO_4$ soln for 15 min. After evapn, the residue was suspended in $CHCl_3$–MeOH (9:1) and passed over silica gel to yield 1.5 mg stemmadenine (**12**). Identification by TLC, $[\alpha]_D$; ^{1}H NMR and EIMS.

Tabersonine-N-oxide (**14**). Amorphous (4 mg). TLC: R_f 0.22 (S-3); anisaldehyde: blue, after 2 min heating yellow. $[\alpha]_D$ −59° (MeOH; *c* 0.33). ^{1}H NMR (CD_3OD): δ 0.77 (3H, *dd*, J_1 = J_2 = 7.5 Hz, Me-18), 1.14–1.34 (2H, *m*, H-19$_A$, H-19$_B$), 2.26 (1H, *d*, *J* = 16 Hz, H-17$_A$), 2.35 (1H, *ddd*, J_1 = 13, J_2 = 9, J_3 = 2 Hz, H-5$_A$ or H-6$_A$), 2.70–2.82 (1H, *m*, H-5$_A$ or H-6$_A$), 2.76 (overlapped 1H, *br d*, *J* = 16 Hz, H-17$_B$), 3.56 (1H, *m*, H-5$_B$ or H-6$_B$), 3.70 (1H, *br s*, H-21), 3.78 (3H, *s*, OMe), 3.81 (1H, *ddd*, J_1 = J_2 = 11, J_3 = 9 Hz, H-5$_B$ or H-6$_B$), 4.18 (1H, *ddd*, J_1 = 17, J_2 = J_3 = 1.5 Hz, H-3$_A$), 4.28 (1H, *dd*, J_1 = 17, J_2 = 4 Hz, H-3$_B$), 5.80–5.89 (2H, *m*, H-14, H-15), 6.92 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-10), 6.97 (1H, *br d*, *J* = 7.5 Hz, H-12), 7.19 (1H, *ddd*, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, H-11), 8.42 (1H, *br d*, *J* = 7.5 Hz, H-9). ^{13}C NMR: Table 4. EIMS *m/z* (rel. int. >25%): 353 $[M+H]^+$ (21), 352 $[M]^+$ (91), 336 (40), 335 (53), 303 (37), 233 (27), 232 (27), 229 (43), 228 (81), 227 (42), 218 (31), 214 (53), 206 (33), 205 (36), 204 (61), 196 (35), 195 (47), 194 (35), 168 (100), 167 (85), 166 (31), 154 (54), 138 (66), 135 (67), 125 (39), 124 (34), 122 (28), 121 (27), 108 (35), 107 (30). IR and UV in agreement with published data [15].

Reduction of **14** *with* $FeSO_4$. **14** (0.8 mg) was reduced with $FeSO_4$ as described for **13**. The aq. reaction mixt. on extraction with $CHCl_3$ yielded 0.3 mg tabersonine (**3**). Identification by TLC, $[\alpha]_D$ and EIMS.

Tetrahydroalstonine (**15**). Crystals (5 mg), mp 198–199° (from EtOH) (ref. [32] mp 199.5–200.5°). TLC: R_f 0.38 (S-7); anisaldehyde: red violet. $[\alpha]_D$ −89° (*c* 0.42) (ref. [33] $[\alpha]_D$ −108° (*c* 0.52)). CD λ_{max} nm: 230 ($\Delta\varepsilon$ +6.16), 243 ($\Delta\varepsilon$ −11.44), 287 ($\Delta\varepsilon$ +0.44), 295 ($\Delta\varepsilon$ +0.47). UV λ_{max} nm: 225 (log ε 4.58), 281 (3.88), 290 (3.81). IR, ^{1}H NMR, ^{13}C NMR and MS in agreement with published data [31, 32].

Voacristine (**16**). Oil (115 mg). TLC: R_f 0.31 (S-8); anisaldehyde: red violet. $[\alpha]_D$ −21° (*c* 1.66) (ref. [10] $[\alpha]_D$ −29° (for *c*: no data)). IR, UV, ^{1}H NMR and MS in agreement with published data [10].

(+)-*Lyoniresinol* (**17**). Oil (5 mg). TLC: R_f 0.24 (S-3); anisaldehyde: blue. $[\alpha]_D$ +52° (MeOH; *c* 0.37) (ref. [9] $[\alpha]_D$ +58° (MeOH, *c* 0.5)). CD, UV, ^{1}H NMR and MS in agreement with published data [34].

(+)-5,5′-*Dimethoxy*-9-O-(*β*-D-*glucopyranosyl*)-*laricitesinol* (**18**). Oil (6 mg). TLC: R_f 0.10 (S-5); anisaldehyde: blue. $[\alpha]_D$ +18° (MeOH; *c* 0.4). CD λ_{max} nm: 245 ($\Delta\varepsilon$ −0.28), 278 ($\Delta\varepsilon$ +0.12). UV λ_{max} nm: 208 (log ε 4.95), 237 (4.24), 271 (3.52). ^{1}H NMR (CD_3OD): δ 2.47–2.57 (2H, *m*, H-8, H-7$_A$), 2.77 (1H, *m*, H-8′), 2.96 (1H, *dd*, J_1 = 13.5, J_2 = 5 Hz, H-7$_B$), 3.19–3.40 (4H, *m*, H-2″, H-3″, H-4″, H-5″), 3.67 (1H, *dd*, J_1 = 12, J_2 = 6 Hz, H-6$_A$), 3.82 (6H, *s*, 2×OMe), 3.84 (6H, *s*, 2×OMe), 3.87 (1H, *dd*, J_1 = 12, J_2 = 2.5 Hz, H-6$_B$), 3.73–3.87 (2H, *m*, H-9$_A$, H-9′$_A$), 4.01 (1H, *m*, H-9$_B$), 4.08 (1H, *dd*, J_1 = 10, J_2 = 6.5 Hz, H-9′$_B$), 4.30 (1H, *d*, *J* = 8 Hz, H-1″), 4.86 (1H, *d*, *J* = 6.5 Hz, H-7), 6.51 (2H, *s*, H-2′, H-6′), 6.65 (2H, *s*, H-2, H-6). ^{13}C NMR (62.9 MHz, CD_3OD): δ 34.4 (C-7′), 43.9 (C-8′), 51.8 (C-8), 56.8 (4×OMe), 62.8 (C-6″), 68.6 (C-9), 71.7 (C-4″), 73.6 (C-9′), 75.2 (C-2″), 78.0, 78.2 (C-3″, C-5″), 84.4 (C-7), 104.4 (C-2, C-6), 104.8 (C-1″), 107.1 (C-2′, C-6′), 132.9 (C-1′), 134.9 (C-1, C-4′), 135.9 (C-4), 149.2, 149.3 (C-3, C-5, C-3′, C-5′).

DCIMS *m/z* (rel. int. %): 582 $[M]^+$ (12), 404 (32), 403 (100), 402 (45), 385 (16), 267 (66), 249 (67), 235 (51), 167 (77), 163 (79), 155 (15), 145 (23).

5,5′-*Dimethoxy*-9-O-(*β*-D-*glucopyranosyl*)*lariciresinolhexaacetate*. Oil (1 mg). TLC: R_f 0.79 (S-6); anisaldehyde: brown. $[\alpha]_D$ −20° (*c* 0.06). IR ν_{max} cm^{-1}: 1758 (C=O), 1605 (C=C). UV λ_{max} nm: 224 (log ε 4.61), 269 (3.69). ^1H NMR: δ 1.97 (3H, *s*, CO-Me), 2.01 (3H, *s*, CO-Me), 2.03 (3H, *s*, CO-Me), 2.06 (3H, *s*, CO-Me), 2.33 (6H, *s*, 2 × CO-Me), 2.50 (1H, *m*, H-8), 2.52 (1H, *dd*, J_1 = 13, J_2 = 11.5 Hz, H-$7_{A'}$), 2.67 (1H, *m*, H-8′), 2.88 (1H, *dd*, J_1 = 13, J_2 = 4 Hz, H-$7_{B'}$), 3.67–3.80 (3H, *m*, H-9_A, H-$9_{A'}$, H-5″), 3.81 (6H, *s*, 2 × OMe), 3.83 (6H, *s*, 2 × OMe), 4.00–4.14 (2H, *m*, H-9_B, H-$9_{B'}$), 4.15 (1H, *dd*, J_1 = 12.5, J_2 = 2.5 Hz, H-$6_{A'}$), 4.30 (1H, *dd*, J_1 = 12.5, J_2 = 4.5 Hz, H-$6_{B'}$), 4.59 (1H, *d*, *J* = 8 Hz, H-1″), 4.84 (1H, *d*, *J* = 6 Hz, H-7), 5.10 (1H, *dd*, J_1 = 10, J_2 = 8 Hz, H-2″), 5.13 (1H, *dd*, J_1 = J_2 = 10 Hz, H-4″), 5.24 (1H, *dd*, J_1 = J_2 = 10 Hz, H-3″), 6.41 (2H, *s*, H-2′, H-6′), 6.55 (2H, *s*, H-2, H-6).

4-*Chloromethylstemmadeninium chloride* (**28**). Crystals (90 mg). Mp 159° (from MeOH). TLC: R_f 0.34 (tailing; S-10); anisaldehyde: orange. $[\alpha]_D$ +147° (MeOH; *c* 2.45). IR ν_{max}^{KBr} cm^{-1}: 1733 (C=O). UV λ_{max} nm: 222 (log ε 4.82), 275 (sh, 4.09), 282 (log ε 4.15), 290 (log ε 4.10). ^1H NMR (360 MHz, OD): δ 1.80 (3H, *dd*, J_1 = 7, J_2 = 2 Hz, Me-18), 2.51 (1H, *ddd*, J_1 = 17, J_2 = 13, J_3 = 7 Hz, H-14_A), 2.77 (1H, *dddd*, J_1 = 17, J_2 = 14, J_3 = 7, J_4 = 4 Hz, H-14_B), 3.33–3.86 (9H, *m*, H-3_A, H-3_B, H-5_A, H-5_B, H-6_A, H-6_B, H-15, H-21_A, H-21_B), 3.80 (3H, *s*, OMe). 4.32 (2H, *m*, H-22_A, H-22_B), 5.06 (2H, *m*, H-23_A, H-23_B), 5.71 (1H, *q*, *J* = 7 Hz, H-19), 7.11 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-10), 7.17 (1H, *ddd*, J_1 = J_2 = 8, J_3 = 1.5 Hz, H-11), 7.43 (1H, *dm*, *J* = 8 Hz, H-12), 7.52 (1H, *dm*, *J* = 8 Hz, H-9). ^{13}C NMR: Table 4: FAB-MS (pos. ions) *m/z* (rel. int. %): 405 $[M^1]^+$ (38), 403 $[M^2]^+$ (100), 367 $[M-HCl]^+$ (29).

Partial synthesis of **28**. Stemmadenine (**12**) (8 mg) was dissolved in 1 ml MeOH and 1 ml CH_2BrCl added. This mixt. was kept at 60° for 1 hr. Evapn *in vacuo* yielded 10 mg of **28**. Identification by TLC, FABMS, ^1H NMR and ^{13}C NMR.

Isolated from EtOAc-soluble fraction

9-(*β*-D-*Gluocopyranosyloxy*)*tetrahydroalstonine* (**19**). Amorphous (7 mg). TLC: R_f 0.63 (S-10); anisaldehyde: red–violet. $[\alpha]_D$ −16° (MeOH; *c* 0.20). CD λ_{max} nm: 230 (Δε +2.65), 242 (Δε −5.51), 292 (Δε +1.06). IR ν_{max}^{KBr} cm^{-1}: 3392 (OH), 1685 (C=O). UV λ_{max} nm: 226 (log ε 4.42), 266 (sh, 3.80), 291 (sh, 3.66). ^{1} NMR (CD_3OD): δ 1.39 (3H, *d*, *J* = 6 Hz, Me-18), 1.36–1.48 (overlapped 1H, *ddd*, J_1 = J_2 = J_3 = 12 Hz, H-14_A), 1.72 (1H, *m*, H-20), 2.51 (1H, *ddd*, J_1 = J_2 = 11.5, J_3 = 5 Hz, H-5_A), 2.60–2.80 (3H, *m*, H-14_B, H-15, H-21_A), 2.94–3.07 (2H, *m*, H-5_B, H-6_A), 3.16 (overlapped 1H, *br dd*, J_1 = 12.5, J_2 = 1.5 Hz, H-21_B), 3.13–3.25 (1H, *m*, H-6_B), 3.28–3.55 (5H, *m*, H-3, H-2′, H-3′, H-4′, H-5′), 3.70 (1H, *dd*, J_1 = 12, J_2 = 5 Hz, H-$6_{A'}$), 3.74 (3H, *s*, OMe), 3.88 (1H, *dd*, J_1 = 12, J_2 = 2 Hz, H-$6_{B'}$), 4.50 (1H, *dq*, J_1 = 11.5, J_2 = 6 Hz, H-19), 5.05 (1H, *d*, *J* = 7.5 Hz, H-1′), 6.68 (1H, *dd*, J_1 = 8, J_2 = 1.5 Hz, H-10), 6.91 (1H, *dd*, J_1 = J_2 = 8 Hz, H-11), 6.95 (1H, *dd*, J_1 = 8, J_2 = 1.5 Hz, H-12), 7.57 (1H, *s*, *H*-17). ^{13}C NMR (62.9 MHz, CD_3OD): δ 18.9 (C-18), 24.6 (C-6), 32.7 (C-15), 34.8 (C-14), 39.9 (C-20), 51.6 (OMe), 55.2 (C-5), 57.2 (C-21), 61.8 (C-3), 62.6 (C-6′), 71.5 (C-4′), 73.6 (C-19), 75.3 (C-2′), 78.1 (C-3′ or C-5′), 78.5 (C-3′ or C-5′), 102.4 (C-1′), 104.6 (C-10), 107.0 (C-12), 107.9 (C-7), 111.0 (C-16), 119.4 (C-8), 122.4 (C-11), 134.4 (C-2), 139.8 (C-13), 153.0 (C-9), 156.9 (C-17), 169.6 (C=O). FABMS (neg. ions) *m/z* (rel. int. %): 529 $[M-H]^-$ (20), 367 (100); FABMS (pos. ions) *m/z* (rel. int. ⩾ 20%): 531 $[M+H]^+$ (100), 528 (23), 371 (21), 370 (26), 369 (78), 368 (59), 367 (49), 365 (20), 353 (28).

Isositsirikine (**20**). Crystals (3 mg). Mp 105° (from $CHCl_3$–MeOH) (ref. [36] mp 105–107°). TLC: R_f 0.67 (S-4); anisaldehyde: red-violet. $[\alpha]_D$ −19° (MeOH; *c* 0.11) (ref. [36] $[\alpha]_D$ −23° (MeOH; *c* 0.107)). IR, UV, ^1H NMR and MS in agreement with published data [35–37].

(+)-3α-*O*-(*β*-D-*Glucopyranosyl*)*lyoniresinol* (**21**). Oil (45 mg). TLC: R_f 0.19 (S-4); anisaldehyde: black-blue. $[\alpha]_D$ +61° (MeOH; *c* 2.20) (ref. [38] $[\alpha]_D$ +22.4° (MeOH; *c* 1.01)). CD, IR, UV, ^1H NMR, ^{13}C NMR and MS in agreement with published data [34, 38].

(−)-3α-*O*-(*β*-D-*Glucopyranosyl*)*lyoniresinol* (**22**). Oil (16 mg). TLC: R_f 0.19 (S-4); anisaldehyde: black-blue. $[\alpha]_D$ −105° (MeOH; *c* 1.2) (ref. [39] $[\alpha]_D$ −110° (MeOH; *c* 0.7)). CD, UV, ^1H NMR and MS in agreement with published data [39].

(−)-2α-*O*-(*β*-D-*Glucopyranosyl*)*lyoniresinol* (**23**). Oil (4 mg). TLC: R_f 0.19 (S-4); anisaldehyde: blue. $[\alpha]_D$ −23° (MeOH; *c* 0.3). CD λ_{max} nm: 230 (Δε +0.58), 242 (Δε −5.06), 257 (Δε −0.70), 272 (Δε −1.63), 285 (Δε +0.52). UV λ_{max} nm: 208 (log ε 4.73), 238 (sh, 4.04), 281 (3.53). ^1H NMR (CD_3OD): δ 1.78–1.94 (2H, *m*, H-2, H-3), 2.57 (1H, *dd*, J_1 = 15.5, J_2 = 11 Hz, H-1_A), 2.79 (1H, *dd*, J_1 = 15.5, J_2 = 4.5 Hz, H-1_B), 3.17 (1H, *dd*, J_1 = 9, J_2 = 8 Hz, H-2″), 3.21–3.35 (3H, *m*, H-3″, H-4″, H-5″), 3.35 (3H, *s*, OMe-5), 3.49–3.65 (3H, *m*, H-$2\alpha_A$, H-$3\alpha_A$, H-$3\alpha_B$), 3.65 (1H, *dd*, J_1 = 12, J_2 = 5.5 Hz, H-6A″), 3.74 (6H, *s*, OMe-2′, OMe-6′), 3.81–3.89 (overlapped 1H, *m*, H-$6_{B'}$), 3.85 (3H, *s*, OMe-7), 3.93 (1H, *dd*, J_1 = 10, J_2 = 5.5 Hz, H-$2\alpha_B$), 4.25 (1H, *d*, *J* = 8 Hz, H-1″), 4.30 (1H, *d*, *J* = 6 Hz, H-4), 6.39 (2H, *s*, H-2′, H-6′), 6.57 (1H, *s*, H-8). ^{13}C NMR: Table 6. DCIMS *m/z* (rel. int. %): 582 $[M]^+$ (19), 285 (20), 267 (100), 257 (60), 249 (19), 237 (15), 167 (16), 163 (56), 155 (48), 145 (21).

(−)-3α-*O*-(*β*-D-*Glucopyranosyl*)-5′-*methoxyisolariciresinol* (**24**). Oil (6 mg). TLC: R_f 0.13 (S-4); anisaldehyde: black-blue. $[\alpha]_D$ −17° (MeOH; *c* 0.47) (ref. [39] $[\alpha]_D$ −4° (MeOH; *c* 0.16)). CD, UV, ^1H NMR ^{13}C NMR and MS in agreement with published data [39].

(+)-8,8′-*Dimethoxy*-1-*O*-(*β*-D-*glucopyranosyl*) *secoisolariciresinol* (**25**). Oil (7 mg). TLC: R_f 0.16 (S-

4); anisaldehyde: green-blue. $[\alpha]_D$ +30° (MeOH; *c* 0.13) (ref. [40] $[\alpha]_D$ +8.9° (MeOH; *c* 1.12)). CD λ_{max} nm: 235 ($\Delta\varepsilon$ +3.21), 248 ($\Delta\varepsilon$ −0.29), 260 ($\Delta\varepsilon$ −0.17), 282 ($\Delta\varepsilon$ +0.99), 310 ($\Delta\varepsilon$ +0.16). IR, UV, ^{1}H NMR and ^{13}C NMR in agreement with published data [40].

Sweroside (**26**). Oil (12 mg). TLC: R_f 0.16 (S-5); anisaldehyde: light brown. $[\alpha]_D$ −205° (MeOH; *c* 0.77) (ref. [42] $[\alpha]_D$ −236° (H_2O)). IR ν_{max} cm^{-1}: 3386 (OH), 1698 (C=O). UV, ^{1}H NMR, ^{13}C NMR and MS in agreement with published data [41, 42].

3-O-(β-D-Glucopyranosyl)-5-O-methylgallic acid (**27**). Amorphous (178 mg). TLC: R_f 0.58 (tailing) (S-13); anisaldehyde: brown-grey. $[\alpha]_D$ −56° (MeOH; *c* 0.88). IR ν_{max}^{KBr} cm^{-1}: 3392 (OH), 1690 (C=O). UV λ_{max} nm: 211 (log ε 4.41), 259 (log ε 3.91); +NaOH: 203 (log ε 4.62), 225 (sh, 4.04), 293 (4.08); +HCl: 216 (log ε 4.37), 266 (3.96). ^{1}H NMR (CD_3OD, 320K): δ 3.39–3.55 (4H, *m*, H-2′, H-3′, H-4′, H-5′), 3.76 (1H, *dd*, J_1 = 12, J_2 = 4.5 Hz, H-6$_{A'}$), 3.89 (1H, overlapped *dd*, J_1 = 12, J_2 = 2 Hz, H-6$_{B'}$), 3.89 (3H, *s*, OMe), 4.85 (1H, *d*, *J* = 7.5 Hz, H-1′), 7.40 (1H, *br s*, H-6), 7.56 (1H, *br s*, H-2). ^{13}C NMR (62.9 MHz, CD_3OD): δ 56.8 (OMe), 62.2 (C-6′), 71.1, 74.9, 77.6, 78.2 (C-2′, C-3′, C-4′, C-5′), 104.1 (C-1′), 109.6 (C-6), 113.6 (C-2), 124.0 (C-1), 142.1 (C-4), 146.3 (C-3), 149.2 (C-5), 171.1 (broad, C=O). FABMS (neg. ions) *m/z* (rel. int. %): 345 $[M-H]^-$ (100).

3-O-(β-D-Glucopyranosyl)-5-O-methylgallic acid pentaacetate. Amorphous (7.5 mg). TLC: R_f 0.47 (S-5); anisaldehyde: brown. $[\alpha]_D$ −24° (MeOH; *c* 0.52). IR ν_{max} cm^{-1}: 1758 (C=O). UV λ_{max} nm: 206 (log ε 4.86), 243 (4.17), 286 (log ε 3.65); +NaOH: 207 (log ε 5.09), 231 (sh, 4.06), 288 (3.65); +HCl: 208 (log ε 4.83), 248 (4.21), 290 (3.71). ^{1}H NMR (CD_3OD): δ 1.99 (3H, *s*, CO-Me), 2.03 (6H, *br s*, 2 × CO-Me), 2.07 (3H, *s*, CO-Me), 2.25 (3H, *s*, CO-Me), 3.85 (3H, *s*, OMe), 4.17 (1H, *m*, H-5′), 4.20 (1H, *dd*, J_1 = 12, J_2 = 2 Hz, H-6$_{A'}$), 4.28 (1H, *dd*, J_1 = 12, J_2 = 6 Hz, H-6$_{B'}$), 5.07 (1H, *dd*, $J_1 = J_2$ = 9 Hz, H-3′ or H-4′), 5.19 (1H, *dd*, J_1 = 9, J_2 = 8 Hz, H-2′), 5.33 (1H, *d*, *J* = 8 Hz, H-1′), 5.40 (1H, *dd*, $J_1 = J_2$ = 9 Hz, H-3′ or H-4′), 7.46 (2H, *s*, H-2, H-6). FABMS (neg. ions) *m/z* (rel. int. %): 556 $[M]^-$ (21), 555 $[M-H]^-$ (81), 513 (37), 471 (48), 437 (24), 429 (26), 411 (25), 309 (100).

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