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JOANNESIALACTONE AND OTHER COMPOUNDS FROM *JOANNESIA PRINCEPS**

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Key Word Index—*Joannesia princeps*; Euphorbiaceae; root bark; joannesialactone; (−)-α-barbatenal; 4-hydroxy-10-epirotundone; new rhamnosides of dimeric proanthocyanidins; *E*- and *Z*-2-(4-hydroxyphenyl)ethenyl-α-L-rhamnoside; antibiotic principle cyperenal.

Abstract—The novel natural products joannesialactone, (−)-α-barbatenal, 4-hydroxy-10-epirotundone, and the *E*- and *Z*-isomers of 2-(4-hydroxyphenyl)ethenyl-α-L-rhamnopyranoside and the 3-*O*-rhamnosides of the dimeric proanthocyanidins afzelechin-(4α → 8)-epiafzelechin-3-*O*-vanillate, afzelechin-(4α → 8)-epicatechin-3-*O*-vanillate, afzelechin-(4α → 8)-epiafzelechin-3-*O*-syringate and afzelechin-(4α → 8)-epicatechin-3-*O*-syringate have been isolated from the root bark of *Joannesia princeps*, along with the antibiotic principle cyperenal, the colouring matter assufulvenal, curcusones C and D and 16 further known compounds. Structure determination was achieved mainly by spectroscopic studies and/or by comparison with authentic substances.

INTRODUCTION

Joannesia princeps (Euphorbiaceae) is native in Southern Brazil, where it grows as a tree up to 50 m high [2]. The Indians call it *Andá assú* [3]. Mainly because of the fatty oil content of its seeds [2, 4], the plant has been cultivated in tropical regions of Africa and Asia. Both the seed oil and the root bark are used as a laxative in folk medicine [5], and extracts of the seedlings exhibit strong anthelmintic activity [6]. Furthermore, the Brazilian Indians are reported to apply the stem bark and leaves to narcotize fish [5].

Previously reported phytochemical investigations described a group analysis of various plant parts [3] and resulted in the isolation of an 'alkaloidal compound' with significant anthelmintic activity from the seeds [6, 7]. A more recent publication reported the isolation of some flavonoid glycosides from the leaves [8].

In screening experiments, we observed strong antimicrobial and cytotoxic effects with extracts from the root bark and, subsequently, we isolated cyperenal (**1**) and cyperenol (**2**) as the active principles [9]. These results prompted us to investigate the constituents of *J. princeps* in more detail. This article reports the phytochemical investigation of extracts from the root bark, the stem bark and leaves of *J. princeps*.

RESULTS

The dried plant material was first extracted with petrol and then with methanol. Chromatographic separation of the petrol extract of the root bark gave cyperenal (**1**), cyperenol (**2**) and the further terpenes **3**–**10**, as well as lupeol, lupenone and seven known sitosterol- and stigmasterol-derived steroids (Table 1).

The dichloromethane soluble fraction of the methanol extract was shown by TLC to contain the same compounds as either the petrol extract or the ethyl acetate soluble fraction of the methanol extract. Therefore, only the petrol extract and the ethyl acetate soluble fraction were investigated further.

The chromatographic separation of the latter fraction yielded the compounds listed in Table 2. Whereas the glycosides **11**–**17**, pterolactam (**18**) and 3,4-dihydroxybenzaldehyde were found only in the extract of the root bark, rhamnose was detected in the extract of the stem bark also.

The structure determinations were based mainly on spectroscopic investigations and particularly on ^{1}H and ^{13}C NMR studies including HMBC (heteronuclear multiple bond correlation) and HMQC

*Dedicated to Prof. Dr W. Wiegrebe, Regensburg (Germany), on the occasion of his 65th birthday. This article is part 83 in the series 'Constituents of Tropical Medicinal Plants'. For part 82 see ref. [1].

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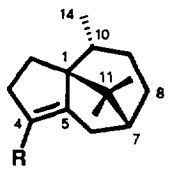
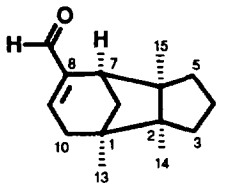


1: R=CHO
2: R=CH_2OH
4: R=CO_2H
5: R=CO_2Me



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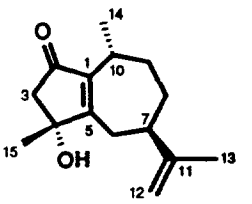
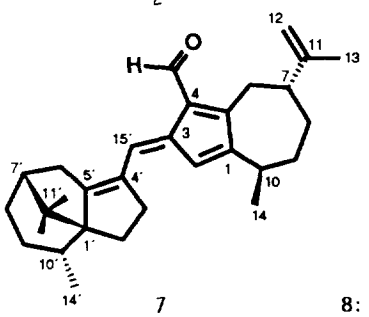


6 (rel. config.)



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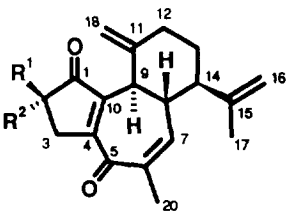
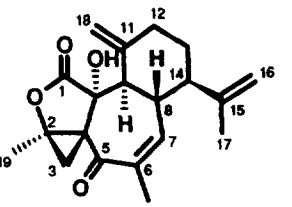
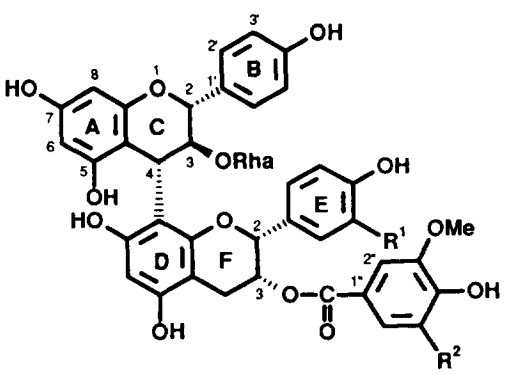


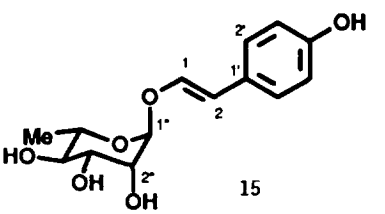
8: R^1=Me, R^2=OH (rel. config.)
9: R^1=OH, R^2=Me (rel. config.)



10 (rel. config.)



11: R^1=R^2=H
12: R^1=OH, R^2=H
13: R^1=H, R^2=OMe
14: R^1=OH, R^2=OMe
Rha=α-L-rhamnosyl



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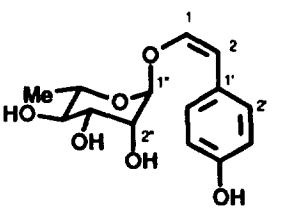

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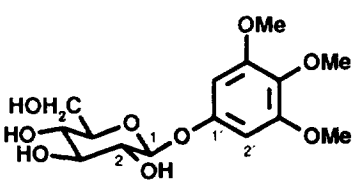

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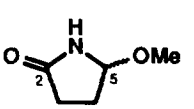

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(heteronuclear multiple quantum correlation) experiments. Known compounds were identified by comparison with their reported physico-chemical data and/or by proof of identity with authentic substances.

Compound **3** revealed the basic structure and the relative configuration (by nuclear Overhauser effect (NOE) measurements) of α-barbatenal [10].

To establish its absolute configuration, **3** was reduced with $LiAlH_4$ to give the corresponding alcohol barbatenol. Surprisingly, the circular dichroism (CD) curve of barbatenol exhibited a negative Cotton effect at 201 nm, whereas the literature data state for α-barbatene, the corresponding hydrocarbon with an 8-methyl group, a positive Cotton effect at that wavelength [10]. Therefore, we suggest for **3** the structure of (−)-α-barbatenal as shown in the formula.

Table 1. Compounds isolated from the petrol extract of the root bark of *J. princeps* or detected by TLC in stem bark (SB) and leaves (L), respectively

Compound class	Compound	Content in root bark* (%)	Also detected in	Refs
Sesquiterpenes	(−)-α-Barbatenal (**3**)	0.02	–	10
	Cyperenal (**1**)	0.5	–	11
	Cyperenol (**2**)	0.035	–	12, 13
	Cyperenoic acid (**4**)	0.35	–	13, 14
	Cyperenoic acid methyl ester (**5**)	0.07	–	14
	4-Hydroxy-10-epirotundone (**6**)	0.007	–	
bis-Sesquiterpene	Assufulvenal (**7**)	0.006		15, 16
Diterpenes	Curcusone C (**8**)	0.01	–	17
	Curcusone D (**9**)	0.02	–	17
	Joannesialactone (**10**)	0.004	–	
Triterpenes	Lupeol	0.45	SB, L	18, 19
	Lupenone	0.015	–	18, 20
Steroids	7α-Hydroxysitosterol	0.012	SB	21, 22
	7β-Hydroxysitosterol	0.01	SB	21, 22
	7α-Hydroxystigmasterol	0.01	SB	23
	7β-Hydroxystigmasterol	0.007	SB	24
	7-Oxositosterol	0.1	–	24, 25
	7-Oxostigmasterol	0.05	–	24
	5α-Stigmastane-3β,6α-diol	0.007	–	22, 26

*Estimated concentration in total extract (petrol + methanol).

Table 2. Compounds isolated from the ethyl acetate soluble fraction of the methanol extract from the root bark of *J. princeps*

Compound class	Compound	Content* (%)	Refs
Flavonoid rhamnosides	Proanthocyanidin I (**11**)	0.03	
	Proanthocyanidin II (**12**)	0.02	
	Proanthocyanidin III (**13**)	0.009	
	Proanthocyanidin IV (**14**)	0.01	
Other glycosides	(*E*)-2-(4-Hydroxyphenyl)ethenyl-α-L-rhamnopyranoside (**15**)	0.12	
	(*Z*)-2-(4-Hydroxyphenyl)ethenyl-α-L-rhamnopyranoside (**16**)	0.02	
	3,4,5-Trimethoxyphenyl-β-D-glucopyranoside (**17**)	0.01	27
Free sugar	L-Rhamnose	0.07	
Others	Pterolactam (**18**)	0.005	28, 29
	3,4-Dihydroxybenzaldehyde	0.009	30, 31

*Estimated concentration in total extract (petrol + methanol).

The spectra of compound **6** ($[M]^+$ *m/z* 234; $C_{15}H_{22}O_2$ by HRMS) required an enone chromophore, one exomethylene and three methyl groups. HMBC (Fig. 1) allowed the assignment of all ^{13}C resonances and established the basic structure with the relative configuration resulting from NOE measurements (Fig. 2).

The epimeric alcohols **8** and **9** have occasionally

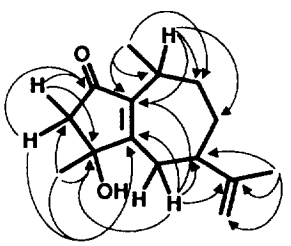

Fig. 1. Important couplings observed in the HMBC of compound **6**.

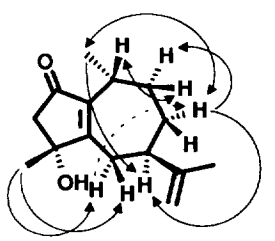

Fig. 2. Important nuclear Overhauser effects observed for compound **6**: (– – – –) in C_6D_6; (——) in $CDCl_3$.

Table 3. ^{13}C NMR resonances of curcusone C (**8**), curcusone D (**9**) and joannesialactone (**10**) (62.9 MHz, $CDCl_3$)

C	8	9	10*
1	212.2	209.1	174.1
2	74.5	72.9	71.4
3	43.3	42.9	28.6
4	145.3	145.8	41.3
5	198.2	197.3	199.1
6	141.1	140.7	140.7
7	136.8	137.4	140.9
8	43.6	43.6	44.0
9	45.3	45.5	58.3
10	158.0	158.2	78.5
11	148.5	148.1	146.1
12	36.6	36.2	38.5
13	34.5	34.1	33.9
14	51.9	51.4	52.4
15	146.6	146.8	146.4
16	113.4	113.3	113.4
17	18.7	18.7	18.8
18	108.2	109.0	110.5
19	26.1	23.9	14.7
20	19.4	19.5	18.2

*At 90 MHz.

been described as curcusone C and curcusone D, respectively [17]. We studied their NMR data and assigned the ^{13}C resonances (Table 3). This information was essential for the determination of the structure of compound **10**.

The ^1H NMR spectrum of **10** exhibited great similarity with those of **8** and **9**, and thereby we established the presence of the same annellated six- and seven-membered ring system. Homonuclear correlation spectroscopy (COSY) measurements corroborated these considerations. NMR studies also established the presence of a hydroxy group, a γ-lactone and an α,β-unsaturated carbonyl group, in agreement with the information from the IR spectrum. An observed $^1J(C,H)$ coupling constant of 165 Hz for CH_2-3 proved the presence of the cyclopropane moiety [32]. Heteronuclear COSY experiments taken in different solvents, to allow the observation of all signals, combined the partial structures and the 'remaining' proton signals to final structure **10** (Fig. 3).

NOE studies revealed the relative configuration of **10**, which represents a hitherto unknown diterpene, which we have named joannesialactone. Because of a lack of chiroptical data in the literature for compounds of related structure and confirmed absolute configuration, it was not possible to determine the absolute configuration for **10**.

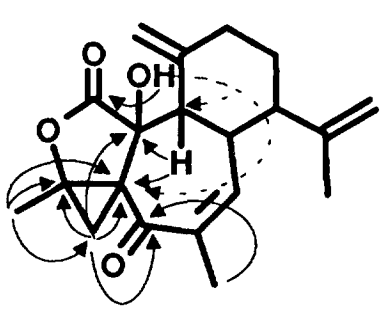

Fig. 3. Important couplings observed in the HMBC of compound **10**: (- - -) in Me_2CO-d_6; (——) in $CDCl_3$.

A quasi-molecular ion at *m/z* 843 in the FAB-MS fast atom bombardment MS together with extensive NMR studies and, particularly HMBC, revealed **11** as a proanthocyanidin dimer of the hitherto unknown afzelechin–epiafzelechin type. The glycosidically connected sugar moiety was recognized as rhamnose by the typical ^1H (Table 4) and ^{13}C NMR resonances; the coupling constant of the anomeric H-1‴ with H-2‴ indicated an α-rhamnoside. NOE studies and the $^1H,^1H$ coupling constants of the protons at the pyrane ring systems established the relative configurations within the two parts of the dimeric molecule.

An observed negative Cotton effect at 217 nm indicated the (4*S*) configuration for the 'upper' part of the molecule [33, 34]. For the 'lower' unit we presume the (2*R*) configuration, since according to our knowledge no proanthocyanidin dimers have been reported with the opposite absolute configuration at that position [e.g. 35, 36].

Structural elucidation of the dimers **12–14** was achieved by comparison of the spectroscopic data, especially ^1H NMR (Table 4), with those of the closely related dimer **11**, and by NOE studies.

Separation of the phenylethenyl rhamnosides **15** and **16** was achieved by HPLC. The ^1H NMR spectra again revealed the basic structures and the α-rhamnosidic linkages. The only significant difference between the ^1H NMR spectra of **15** and **16** was the coupling constant of the olefinic protons, which indicated *E*/*Z* isomers. ^{13}C NMR and electron impact (EI)-MS corroborated the structures of the *E* and *Z* configurated 2-(4-hydroxyphenyl)ethenyl-α-L-rhamnopyranosides.

HPLC using a polarimetric detector revealed the rhamnose isolated from *J. princeps* to belong to the L series. We therefore assume that the rhamnose moieties in the described rhamnosides also take the L configuration.

DISCUSSION

From a chemotaxonomic aspect, most of the isolated compounds have to be regarded as typical constituents of Euphorbiaceae plants; for example, up to now cyperenoic acid (**4**) has been found exclusively in this family [13, 14, 37]. Crotophorbolane-type diterpenes, like **8–10**, seem also to represent characteristic constituents of the Euphorbiaceae [17, 38]. For this reason, our results corroborate the botanical classification of *J. princeps* from a chemotaxonomical point of view.

Among the 29 isolated compounds, 4-hydroxy-10-epirotundone (**6**), assufulvenal (**7**), joannesialactone (**10**), the four proanthocyanidin rhamnosides **11–14** and the *E* and *Z* configurated 2-(4-hydroxyphenyl)

Table 4. ^{1}H NMR spectral data of the proanthocyanidin rhamnosides **11**–**14** (360 MHz, CD_3OD)

H	(Ring)	**11**		**12**		**13**		**14**	
2_{ax}	(C)	4.37 *d*	(9.5)	4.36 *d*	(9.5)	4.33 *d*	(9.5)	4.32 *d*	(9.5)
3_{ax}	(C)	4.60 *dd*	(9.5/7.5)	4.62 *dd*	(9.5/7.5)	4.59 *dd*	(9.5/7.5)	4.60 *dd*	(9.5/7.5)
4_{ax}	(C)	4.54 *d*	(7.5)	4.53 *d*	(7.5)	4.51 *d*	(7.5)	4.50 *d*	(7.5)
6	(A)	5.99 *s*		6.00[a] *d*	(2.0)	5.94[a] *d*	(2.5)	5.97[a] *d*	(2.5)
8	(A)	5.99 *s*		5.97[a] *d*	(2.0)	5.90[a] *d*	(2.5)	5.89[a] *d*	(2.5)
2′/6′	(B)	6.78 *m*	(AA′BB′)	6.80 *m*	(AA′BB′)	6.77 *m*	(AA′BB′)	6.78 *m*	(AA′BB′)
3′/5′	(B)	6.59 *m*	(AA′BB′)	6.61 *m*	(AA′BB′)	6.57 *m*	(AA′BB′)	6.60 *m*	(AA′BB′)
2_{ax}	(F)	5.12 *s*		5.02 *s*		5.17 *s*		5.08 *s*	
3_{eq}	(F)	5.40 *brd*	(4.0)	5.39 *brd*	(4.0)	5.42 *brd*	(4.0)	5.41 *brd*	(4.0)
4_{ax}	(F)	3.04 *dd*	(18.0/4.0)	3.03 *dd*	(18.0/4.0)	3.03–3.12 *m**		3.03–3.11 *m**	
4_{eq}	(F)	2.87 *brd*	(18.0)	2.85 *brd*	(18.0)	2.91 *brd*	(18.0)	2.90 *brd*	(18.0)
6	(D)	6.11 *s*		6.11 *s*		6.12 *s*		6.12 *s*	
2′	(E)	7.20 *m*	(AA′BB′)	6.84 *d*	(2.0)	7.25 *m*	(AA′BB′)	6.87 *d*	(2.0)
3′	(E)	6.74 *m*	(AA′BB′)			6.75 *m*	(AA′BB′)		
5′	(E)	6.74 *m*	(AA′BB′)	6.71 *d*	(8.0)	6.75 *m*	(AA′BB′)	6.73 *d*	(8.0)
6′	(E)	7.20 *m*	(AA′BB′)	6.77 *dd*	(8.0/2.0)	7.25 *m*	(AA′BB′)	6.81 *dd*	(8.0/2.0)
2″		7.26 *d*	(2.0)	7.28 *d*	(2.0)	7.02 *s*		7.04 *s*	
3″-OMe		3.80 *s*		3.80 *s*		3.78 *s*		3.79 *s*	
5″		6.86 *d*	(8.0)	6.85 *d*	(8.0)				
5″-OMe						3.78 *s*		3.79 *s*	
6″		7.16 *dd*	(8.0/2.0)	7.17 *dd*	(8.0/2.0)	7.02 *s*		7.04 *s*	
1‴		3.47 *d*	(1.5)	3.48 *d*	(1.5)	3.46 *d*	(1.5)	3.47 *d*	(1.5)
2‴		3.36 *dd*	(3.0/1.5)	3.36 *dd*	(3.0/1.5)	3.35 *dd*	(3.0/1.5)	3.35 *dd*	(3.0/1.5)
3‴		3.50 *dd*	(9.0/3.0)	3.50 *dd*	(9.0/3.0)	3.50 *dd*	(9.0/3.0)	3.50 *dd*	(9.0/3.0)
4‴		3.08 *dd*	(9.0/9.0)	3.09 *dd*	(9.0/9.0)	3.03–3.12 *m**		3.03–3.11 *m**	
5‴		3.13 *dq*	(9.0/6.0)	3.13 *dq*	(9.0/6.0)	3.03–3.12 *m**		3.03–3.11 *m**	
6‴		0.72 *d*	(6.0)	0.72 *d*	(6.0)	0.73 *d*	(6.0)	0.73 *d*	(6.0)

[a]Assignments interchangeable within a column.
*Signal overlapped.

ethenyl-α-L-rhamnopyranosides (**15**, **16**) represent hitherto unknown substances. (−)-α-Barbatenal (**3**) and cyperenoic acid methyl ester (**5**) are reported as natural products for the first time: to date, **3** and **5** have only been described as synthetic products [10, 14] and, in addition, compound **3** represents the (−) enantiomer of the published structure.

We regard all of the isolated compounds to be genuine natural products, since they can be detected by TLC immediately after rapid extraction of plant material at room temperature using inert solvents.

As reported recently [9], cyperenal (**1**) exhibits strong antibacterial and antifungal activity in several bioassays. Cyperenol (**2**) also has significant antifungal activity against various fungi, but does not show antibacterial effect against *Bacillus subtilis*. Cyperenoic acid (**4**) as well as its methyl ester (**5**) possess only moderate antifungal and no antibacterial activity.

The curcusones **8** and **9** both affected the test organisms (*Botrytis cinerea*, *Rhizoctonia solani* and *B. subtilis*) even in low doses (50 μg). 3,4-Dihydroxybenzaldehyde is reported to be a fungistatic agent [30].

The brine shrimp bioassay [39] revealed cyperenol (**2**), as well as curcusone C (**8**) and curcusone D (**9**), to be strongly effective compounds exceeding the activity of the standard podophyllotoxin considerably. The two latter compounds are already known for their cytotoxicity [40]. Also effective, but less so, in this test were cyperenal (**1**), cyperenoic acid (**4**) and its methyl ester (**5**).

EXPERIMENTAL

General. Mps: uncorr. Analytical TLC: precoated plates (HPTLC plates, silica gel 60 F_{254}, Merck) using the following systems: S-1, cyclohexane–EtOAc (19 : 1); S-2, cyclohexane–EtOAc (9 : 1); S-3, cyclohexane–EtOAc (4 : 1); S-4, cyclohexane–EtOAc (7 : 3); S-5, cyclohexane–EtOAc (3 : 2); S-6, cyclohexane–EtOAc (1 : 1); S-7, cyclohexane–EtOAc (3 : 7); S-8, cyclohexane–Me_2CO (9 : 1); S-9, $CHCl_3$–MeOH (19 : 1); S-10, $CHCl_3$–MeOH (4 : 1); S-11, $CHCl_3$–MeOH (3 : 2). Detection: UV, anisaldehyde reagent [41]. Unless otherwise stated, $[\alpha]_D$ in $CHCl_3$ at 21°; CD and UV VIS in MeOH; IR in $CHCl_3$; ^{1}H NMR at 360 MHz and ^{13}C NMR at 90 MHz in $CDCl_3$ with TMS as int. standard; inverse heteronuclear correlations were done with the sequences given in [42] for HMBC and in [43] for HMQC; NOEs were recorded by the difference technique. EI-MS: 70 eV; DCI-MS with isobutane; FAB-MS in glycerol using a xenon gun (8 kV). Unless key ions, only ions with rel. int. > 15% and m/z > 100 are given. CC and MPLC: silica gel 60 (Macherey-Nagel) and LiChroprep RP 18 (40–60

μm, Merck). CC: Fractogel PVA 500 (Merck) and Fractogel TSK HW-40 (S) (Merck). HPLC: LiChrosorb RP 18 (7 μm, Merck) and Eurospher 100-7 C18 (7 μm, Knauer).

Plant material. Root bark of *J. princeps* Vellozo was collected from Mazeras Botanical Gardens (near Mombasa, Kenya) in May 1995 and identified by Mr L. B. Mwasumbi, Curator of the herbarium at the University of Dar es Salaam, Tanzania. A voucher specimen is held at the Institute of Pharmacy and Food Chemistry, University of Erlangen under Code No. 95/03.

Extraction and isolation. Dried, pulverized root bark (1.95 kg) was extracted exhaustively at room temp. with petrol (5.6 g extract) and then with MeOH (63 g extract). The MeOH extract was redissolved in 200 ml MeOH, 500 ml H_2O added, and this suspension successively extracted with (i) CH_2Cl_2 (11.4 g CH_2Cl_2 fraction) and (ii) EtOAc (1.5 g EtOAc fraction).

The petrol extract and the EtOAc fraction were sepd by repeated CC or MPLC using the following systems: (a) silica gel, cyclohexane–Me_2CO; (b) silica gel, cyclohexane–EtOAc; (c) silica gel, CH_2Cl_2–MeOH; (d) silica gel, $CHCl_3$–MeOH; (e) silica gel RP-18 (LiChroprep), MeOH or MeOH–H_2O; (f) Fractogel PVA 500, MeOH; (g) Fractogel TSK HW-40 (S), MeOH. These procedures mostly yielded pure compounds. However, the phytosterols and the glycosides, apart from 5α-stigmastane-3β,6α-diol and 3,4,5-trimethoxyphenyl-β-D-glucopyranoside, needed final separation/purification by HPLC on LiChrosorb or Eurospher using MeOH–H_2O or MeCN–H_2O mixts.

Compounds from the petrol extract

Cyperenal (**1**). Oil (204 mg). TLC: R_f 0.43 (S-2); anisaldehyde: blue-violet. $[\alpha]_D$ +8 (*c* 0.3) (lit. [11] $[\alpha]_D$ +9.6 (*c* 0.4)). IR ν_{max} cm^{-1}: 1658 (C=O). UV λ_{max} nm (log ε): 262 (4.06). ^{1}H NMR, ^{13}C NMR, MS in agreement with published data [11].

Cyperenol (**2**). Crystals (15 mg). Mp 92–93 (lit. [12] 94). TLC: R_f 0.30 (S-3); anisaldehyde: red. $[\alpha]_D$ −12 (*c* 0.7) (lit. [12] $[\alpha]_D$ −12 (*c* 4.3)). IR, UV, ^{1}H NMR, ^{13}C NMR in agreement with published data [11, 13, 14].

(−)-α-*Barbatenal* (**3**). Oil (3 mg). TLC: R_f 0.28 (S-1); anisaldehyde: blue. $[\alpha]_D$ −103 (*c* 0.1). IR ν_{max} cm^{-1}: 1676 (C=O). UV λ_{max} nm (log ε): 242 (4.11). CD λ_{max} nm (Δε): 245 (−6.76). ^{1}H NMR: δ 0.89 (3H, *s*, Me-14), 0.98 (3H, *s*, Me-13), 1.07 (3H, *s*, Me-15), 1.00–1.55 (6H), 1.66 (1H, *br ddd*, J_1 = 12.5, J_2 = 6, J_3 = 4 Hz, H-3β), 1.97 (1H, *br dd*, J_1 = 11.5, J_2 = 4.5 Hz, H-11$_A$), 2.19 (1H, *dd*, J_1 = 21, J_2 = 3.5 Hz, H-10α), 2.55 (1H, *dd*, J_1 = 21, J_2 = 3.5 Hz, H-10β), 2.60 (1H, *d*, *J* = 4.5 Hz, H-7), 6.66 (1H, *t*, *J* = 3.5 Hz, H-9), 9.43 (1H, *s*, H-12). ^{13}C NMR: 23.9 (C-14), 24.3 (C-13), 26.8 (C-4), 27.0 (C-15), 37.0 (C-3), 38.7 (C-5), 41.6 (C-11), 41.7 (C-10), 42.6 (C-7), 44.7 (C-1), 55.7 (C-2), 58.0 (C-6), 147.2 (C-8), 151.2 (C-9), 192.7 (C-12). EI-MS *m/z* (rel. int.): 218 [M]$^+$ (13), 147 (17), 133 (17), 124 (45), 123 (26), 122 (38), 121 (31), 119 (20), 107 (42), 105 (19).

(−)-α-*Barbatenol by reduction of* **3**. Compound **3** (2 mg) was stirred in dry Et_2O with $LiAlH_4$ (room temp., 30 min). After addition of H_2O and neutralization (1 M H_2SO_4), the product was extracted with Et_2O and purified by CC on silica gel. Oil (1.5 mg). TLC: R_f 0.38 (S-4); anisaldehyde: pink. $[\alpha]_D$ −87 (*c* 0.08). IR ν_{max} cm^{-1}: 3613 (OH). UV λ_{max} nm (log ε): 205 (3.57). CD λ_{max} nm (Δε) (pentane): 201 (−4.77), 228 (+0.02), 240 (−0.01), 301 (+0.05). ^{1}H NMR: δ 0.86 (3H, *s*, Me-14), 0.92 (3H, *s*, Me-13), 1.01 (3H, *s*, Me-15), 1.05 (1H, *m*, H-3α), 1.20 (1H, *ddd*, J_1 = 12.5, J_2 = J_3 = 6.5 Hz, H-5α), 1.44 (1H, *d*, *J* = 11 Hz, H-11$_A$), 1.50–1.72 (4H, *m*, H-3β, H-4α, H-4β, H-5β), 1.83 (1H, *d*, *J* = 4.5 Hz, H-7), 1.94 (1H, *ddd*, J_1 = 11, J_2 = 4.5, J_3 = 1 Hz, H-11$_B$), 1.95 (1H, *dddd*, J_1 = 19, J_2 = J_3 = J_4 = 2.5 Hz, H-10α), 2.23 (1H, *br d*, *J* = 19 Hz, H-10β), 3.92–4.04 (2H, *m*, H-12$_A$, H-12$_B$), 5.50 (1H, *m*, H-9). ^{13}C NMR (62.9 MHz): δ 23.6 (C-14), 24.7 (C-13), 27.2 (C-4), 27.5 (C-15), 37.2 (C-3), 38.4 (C-5), 40.3 (C-10), 42.8 (C-11), 43.9 (C-1), 47.1 (C-7), 55.5 (C-2), 58.5 (C-6), 67.3 (C-12), 121.3 (C-3), 143.5 (C-8). EI-MS *m/z* (rel. int.): 220 [M]$^+$ (24), 189 (16), 124 (67), 123 (27), 122 (16), 106 (26).

Cyperenoic acid (**4**). Crystals (31 mg). Mp 162–164° (lit. [13] mp 162–164°). TLC: R_f 0.23 (S-4); anisaldehyde: violet. $[\alpha]_D$ −10 (*c* 0.5) (lit. [14] $[\alpha]_D$ −8 (*c* 0.25)). CD λ_{max} nm (Δε): 232 (+4.77), 264 (−0.47). IR, UV, ^{1}H NMR, ^{13}C NMR in agreement with published data [14].

Cyperenoic acid methyl ester (**5**). Oil (37 mg). TLC: R_f 0.42 (S-1); anisaldehyde: violet. $[\alpha]_D$ −8 (*c* 1.1). IR ν_{max} cm^{-1}: 1697 (C=O). UV λ_{max} nm (log ε): 241 (3.96). CD λ_{max} nm (Δε): 232 (+4.66), 260 (−0.55). ^{1}H NMR (250 MHz): δ 0.81 (3H, *s*, Me-12), 0.85 (3H, *d*, *J* = 6.5 Hz, Me-14), 0.99 (3H, *s*, Me-13), 1.12 (1H, *m*, H-9α), 1.36 (1H, *m*, H-8α), 1.44–1.58 (2H, *m*, H-2α, H-9β), 1.74 (1H, *ddd*, J_1 = 13, J_2 = J_3 = 10 Hz, H-2β), 1.80–1.99 (2H, *m*, H-7, H-8β), 2.05 (1H, *ddq*, J_1 = 13, J_2 = J_3 = 6.5 Hz, H-10β), 2.21 (1H, *br d*, *J* = 19 Hz, H-6α), 2.61–2.90 (3H, *m*, H-3α, H-3β, H-6β), 3.72 (3H, *s*, COOMe). ^{13}C NMR (62.9 MHz): δ 17.9 (C-14), 19.3 (C-13), 25.7 (C-2), 26.2 (C-12), 27.0 (C-8), 27.9 (C-9), 31.1 (C-6), 35.9 (C-10), 36.7 (C-3), 41.6 (C-11), 48.2 (C-7), 50.9 (COOMe), 67.8 (C-1), 123.3 (C-4), 166.0 (C-15), 169.3 (C-5). EI-MS *m/z* (rel. int. >25%): 248 [M]$^+$ (98), 217 (32), 216 (100), 205 (56), 201 (39), 192 (56), 173 (26), 145 (44), 133 (42), 131 (36), 117 (46), 115 (30), 105 (35).

4-*Hydroxy*-10-*epirotundone* (**6**). Amorphous (3 mg). TLC: R_f 0.34 (S-6); anisaldehyde: brown. $[\alpha]_D$ −69° (*c* 0.2). IR ν_{max} cm^{-1}: 3600 (OH), 1698 (C=O), 1644. UV λ_{max} nm (log ε): 236 (4.15). CD λ_{max} nm (Δε): 240 (+3.51), 317 (−2.34). ^{1}H NMR: δ 1.16 (3H, *d*, *J* = 7 Hz, Me-14), 1.44 (3H, *s*, Me-15), 1.60–1.73 (2H, *m*, H-8β, H-9α), 1.76 (3H, *br s*, Me-13), 1.86 (1H, *m*, H-9β), 1.99 (1H, *m*, H-8α), 2.41–2.67 (5H, *m*, H-3α, H-3β, H-6α, H-6β, H-7), 2.79 (1H, *m*, H-10), 4.72 (1H,

m, H-12$_A$), 4.75 (1H, *m*, H-12$_B$). ^{13}C NMR (62.9 MHz): δ 17.7 (C-14), 20.1 (C-13), 26.5 (C-15), 28.3 (C-6, C-10), 28.9 (C-8, C-9), 44.5 (C-7), 51.4 (C-3), 75.8 (C-4), 109.6 (C-12), 145.5 (C-1), 149.6 (C-11), 174.4 (C-5), 204.4 (C-2). EI-MS *m/z* (rel. int.): 234.1619 $[M]^+$ (24) (calcd for $C_{15}H_{22}O_2$: 234.1620), 191 (48), 149 (21), 135 (17), 133 (34), 119 (17), 111 (18), 43 (100).

Assufulvenal (**7**). Red crystals (4 mg). Mp 225–230 °. TLC: R_f 0.43 (S-1); anisaldehyde: red-brown. $[\alpha]_D$ −171 (*c* 0.2). Spectroscopic data as summarized in [15].

Curcusone C (**8**). Crystals (7 mg). Mp 203–205° (lit. [17] mp 204–205 °). TLC: R_f 0.36 (S-5); anisaldehyde: blue. $[\alpha]_D$ −235 (CH_2Cl_2; *c* 0.3) (lit. [17] $[\alpha]_D$ −432 (CH_2Cl_2)). CD λ_{max} nm ($\Delta\varepsilon$): 233 (+2.12), 257 (−11.23), 315 (−5.74), 395 (+1.62). ^{13}C NMR: Table 3. IR, UV, ^{1}H NMR, MS in agreement with published data [17].

Curcusone D (**9**). Crystals (9 mg). Mp 158–160 (lit. [17] mp 158–160 °). TLC: R_f 0.34 (S-4); anisaldehyde: blue. $[\alpha]_D$ −399 (CH_2Cl_2; *c* 0.4) (lit. [17] $[\alpha]_D$ −518 (CH_2Cl_2)). CD λ_{max} nm ($\Delta\varepsilon$): 225 (−4.24), 253 (−9.11), 313 (−5.87), 395 (+1.25). ^{13}C NMR: Table 3. IR, UV, ^{1}H NMR, MS in agreement with published data [17].

Joannesialactone (**10**). Amorphous (2 mg). TLC: R_f 0.39 (S-4); anisaldehyde: blue. $[\alpha]_D$ −37 (*c* 0.2). IR ν_{max} cm^{-1}: 3567 (OH), 1785 (γ-lactone), 1665 (C=O). UV λ_{max} nm (log ε): 255 (3.60). CD λ_{max} nm ($\Delta\varepsilon$): 253 (−3.35), 303 (+0.60), 337 (−0.20). ^{1}H NMR: δ 1.45 (1H, *dddd*, $J_1 = J_2 = J_3 = 13$, $J_4 = 4$ Hz, H-13β), 1.51 (1H, *d*, $J = 7$ Hz, H-3$_A$), 1.59 (3H, *br s*, Me-17), 1.86 (overlapped 1H, *m*, H-13α), 1.88 (3H, *t*, $J = 1.5$ Hz, Me-20), 1.98 (3H, *s*, Me-19), 2.16 (1H, *br ddd*, $J_1 = J_2 = 13$, $J_3 = 4$ Hz, H-12α), 2.23 (1H, *d*, $J = 7$ Hz, H-3$_B$), 2.35 (1H, *ddd*, $J_1 = J_2 = 11$, $J_3 = 4$ Hz, H-14), 2.36 (1H, *dt*, $J_1 = 13$, $J_2 = 3.5$ Hz, H-12β), 2.60 (1H, *dddq*, $J_1 = J_2 = 11$, $J_3 = 6$, $J_4 = 1.5$ Hz, H-8), 2.76 (1H, *br d*, $J = 11$ Hz, H-9), 2.83 (1H, *br s*, OH), 4.33 (1H, *s*, H-18$_A$), 4.81 (1H, *br s*, H-16$_A$), 4.85 (1H, *m*, H-16$_B$), 4.99 (1H, *s*, H-18$_B$), 6.19 (1H, *dq*, $J_1 = 6$, $J_2 = 1.5$ Hz, H-7). ^{13}C NMR: Table 3. EI-MS *m/z* (rel. int.): 328.1673 $[M]^+$ (1) (calcd for $C_{20}H_{24}O_4$: 328.1674), 257 (19), 173 (18), 159 (19), 145 (18), 124 (41), 121 (16), 119 (21), 107 (19), 105 (20), 43 (100).

Lupeol. Crystals (161 mg). Mp 214–215° (lit. [18] mp 215 °). TLC: R_f 0.32 (S-8); anisaldehyde: violet. $[\alpha]_D$ +24 (*c* 1.0) (lit. [18] $[\alpha]_D$ +27 °). IR, ^{1}H NMR, ^{13}C NMR, MS identical with an authentic sample.

Lupenone. Crystals (7 mg). Mp 164–167 (lit. [18] mp 171–172 °). TLC: R_f 0.27 (S-1); anisaldehyde: violet $[\alpha]_D$ +52 (*c* 0.2) (lit. [18] $[\alpha]_D$ +57 °). IR, ^{1}H NMR, MS identical with an authentic sample. ^{13}C NMR in agreement with published data [20].

7α-Hydroxysitosterol. Crystals (4 mg). Mp 205–208 (lit. [21] mp 207–210 °). TLC: R_f 0.19 (S-7); anisaldehyde: blue. $[\alpha]_D$ −61° (*c* 0.3) (lit. [21] $[\alpha]_D$ −63 (MeOH; *c* 0.1)). ^{1}H NMR, ^{13}C NMR, MS in agreement with published data [22].

7β-Hydroxysitosterol. Crystals (2 mg). Mp 151–154 (lit. [21] mp 155–158 °). TLC: R_f 0.26 (S-7); anisaldehyde: blue. $[\alpha]_D$ +12 (*c* 0.2) (lit. [21] $[\alpha]_D$ +25 (MeOH; *c* 0.02)). ^{1}H NMR, ^{13}C NMR, MS in agreement with published data [22].

7α-Hydroxystigmasterol. Crystals (2 mg). Mp 200–204 °. TLC: R_f 0.19 (S-7); anisaldehyde: blue. $[\alpha]_D$ −64 (*c* 0.2). IR ν_{max} cm^{-1}: 3605 (OH). ^{1}H NMR: δ 0.70–2.40 (43H) within 0.71 (3H, *s*, Me-18), 1.00 (3H, *s*, Me-19), 3.59 (1H, *m*, H-3), 3.85 (1H, *br s*, H-7), 5.03 (1H, *dd*, $J_1 = 15$, $J_2 = 8.5$ Hz, H-23), 5.17 (1H, *dd*, $J_1 = 15$, $J_2 = 8.5$ Hz, H-22), 5.61 (1H, *dd*, $J_1 = 5$, $J_2 = 1.8$ Hz, H-6). EI-MS *m/z* (rel. int.): 428 $[M]^+$ (10), 411 (31), 410 (100), 398 (32).

7β-Hydroxystigmasterol. Crystals (2 mg). Mp 154–157 (lit. [24] mp 154–157 °). TLC: R_f 0.26 (S-7); anisaldehyde: blue. $[\alpha]_D$ −15 (*c* 0.2) (lit. [24] $[\alpha]_D$ −28 (*c* 0.04)). IR ν_{max} cm^{-1}: 3606 (OH). ^{1}H NMR: δ 0.65–2.40 (43H) within 0.71 (3H, *s*, Me-18), 1.05 (3H, *s*, Me-19), 3.55 (1H, *m*, H-3), 3.85 (1H, *m*, H-7), 5.03 (1H, *dd*, $J_1 = 15$, $J_2 = 8.5$ Hz, H-23), 5.17 (1H, *dd*, $J_1 = 15$, $J_2 = 8.5$ Hz, H-22), 5.29 (1H, *t*, $J = 2$ Hz, H-6). EI-MS *m/z* (rel. int.): 428 $[M]^+$ (9), 411 (33), 410 (100), 398 (22).

7-Oxositosterol. Crystals (18 mg). Mp 152–154 (lit. [24] mp 152–154 °). TLC: R_f 0.20 (S-6); anisaldehyde: red-brown. $[\alpha]_D$ −81 (*c* 0.6) (lit. [24] $[\alpha]_D$ −83 (*c* 0.03)). IR, ^{1}H NMR, ^{13}C NMR, MS identical with an authentic sample.

7-Oxostigmasterol. Crystals (12 mg). Mp 160–161 (lit. [24] mp 158–161 °). TLC: R_f 0.19 (S-6); anisaldehyde: red-brown. $[\alpha]_D$ −81 (*c* 0.6) (lit. [24] $[\alpha]_D$ −76 (*c* 0.03)). IR, ^{1}H NMR, ^{13}C NMR, MS identical with an authentic sample.

5α-Stigmastane-3β,6α-diol. Crystals (2 mg). Mp 102–104 (lit. [22] mp 102–104 °). TLC: R_f 0.29 (S-9); anisaldehyde: blue-violet. $[\alpha]_D$ +42 (*c* 0.2) (lit. [26] $[\alpha]_D$ +42 (EtOH; *c* 0.7)). IR, ^{1}H NMR, ^{13}C NMR, MS in agreement with published data [22].

Compounds from the EtOAc-soluble fraction of the MeOH *extract*

Proanthocyanidin I (3-O-(α-L-*rhamnopyranosyl*)*afzelechin*-(4α → 8)-*epiafzelechin*-3-O-*vanillate*, **11**). Amorphous (6 mg). TLC: R_f 0.47 (S-11); anisaldehyde: red. $[\alpha]_D$ −284 (MeOH; *c* 0.5). UV λ_{max} nm (log ε): 205 (4.92), 266 (4.09), 281 (sh, 3.91), 295 (sh, 3.77); + NaOH: 212 (5.37), 236 (sh, 4.39), 291 (sh, 3.78), 313 (4.25). CD λ_{max} nm ($\Delta\varepsilon$): 217 (−45.47), 260 (−0.27), 297 (−0.72). ^{1}H NMR: Table 4. ^{13}C NMR (62.9 MHz, CD_3OD): δ 18.1 (C-6‴), 27.5 (C-4(F)), 37.2 (C-4(C)), 56.5 (OMe), 69.8 (C-5‴), 70.6 (C-3(F)), 71.8 (C-2″), 72.2 (C-3‴), 73.9 (C-4‴), 78.9 (C-2(F)), 79.9 (C-3(C)), 83.2 (C-2(C)), 96.5 (C-5(A) or C-7(A)), 97.0 (C-5(D)), 97.6 (C-7(A) or C-5(A)), 101.1 (C-8a(D) or C-1‴), 101.2 (C-1‴ or C-8a(D)), 107.2 (C-8a(A)), 108.7 (C-7(D)), 113.3 (C-2″), 115.6 (C-3′(E), C-5′(E)), 116.1 (C-3′(B), C-5′(B)), 116.3 (C-5″), 122.3 (C-1″), 125.6 (C-6″), 129.7 (C-2′(E), C-6′(E)), 129.9 (C-2′(B), C-6′(B)), 130.6 (C-1′(E)), 131.6 (C-1′(B)), 148.5

(C-3″), 152.7 (C-4″), 155.3 (C-6(D)), 155.7 (C-8(D)), 156.5 (C-4a(D)), 157.6, 157.7, 158.1 (C-4a(A), C-6(A), C-8(A)), 158.5 (C-4′(B) or C-4′(E)), 158.6 (C-4′(E) or C-4′(B)), 167.5 (C=O). FAB-MS *m/z* (rel. int.): 843 $[M + H]^+$ (8), 369 (100).

Proanthocyanidin II (3-O-(α-L-*rhamnopyranosyl*)*afzelechin*-(4α → 8)-*epicatechin*-3-O-*vanillate*, **12**). Amorphous (5 mg). TLC: R_f 0.39 (S-11); anisaldehyde: red. $[\alpha]_D$ −257 (MeOH; *c* 0.2). UV λ_{max} nm (log ε): 204 (4.97), 265 (4.12), 281 (sh, 4.03); +NaOH: 210 (5.34), 236 (sh, 4.60), 292 (sh, 4.21), 313 (4.23). CD λ_{max} nm (Δε): 217 (−41.18), 255 (−4.63), 292 (−4.03). ^{1}H NMR: Table 4. ^{13}C NMR (62.9 MHz, CD_3OD): δ 18.1 (C-6‴), 27.7 (C-4(F)), 37.2 (C-4(C)), 56.6 (OMe), 69.8 (C-5‴), 70.6 (C-3(F)), 71.8 (C-2‴), 72.2 (C-3‴), 73.9 (C-4‴), 79.1 (C-2(F)), 80.0 (C-3(C)), 83.2 (C-2(C)), 96.6 (C-5(A) or C-7(A)), 97.0 (C-5(D)), 97.6 (C-7(A) or C-5(A)), 101.2 (C-8a(D) or C-1‴), 101.4 (C-1‴ or C-8a(D)), 107.3 (C-8a(A)), 108.9 (C-7(D)), 113.3 (C-2″), 115.4 (C-2′(E)), 115.9 (C-5′(E)), 116.1 (C-3′(B), C-5′(B)), 116.2 (C-5″), 120.8 (C-6′(E)), 122.4 (C-1″), 125.6 (C-6′), 130.0 (C-2′(B), C-6′(B)), 131.2 (C-1′(E)), 131.6 (C-1′(B)), 145.8 (C-3′(E) or C-4′ (E)), 146.0 (C-4′ (E) or C-3′ (E)), 148.5 (C-3″), 152.7 (C-4″), 155.2 (C-6(D)), 155.8 (C-8(D)), 156.4 (C-4a(D)), 157.4, 157.5, 158.5 (C-4a(A), C-6(A), C-8(A)), 158.6 (C-4′ (E)), 167.6 (C=O). FAB-MS *m/z* (rel. int.): 859 $[M + H]^+$ (7), 369 (100).

Proanthocyanidin III (3-O-(α-L-*rhamnopyranosyl*) *afzelechin*-(4α → 8)-*epiafzelechin*-3-O-*syringate*, **13**). Amorphous (2 mg). TLC: R_f 0.47 (S-11); anisaldehyde: red. $[\alpha]_D$ −218 (MeOH; *c* 0.07). UV λ_{max} nm (log ε): 205 (4.95), 275 (4.17); +NaOH: 210 (5.36), 236 (sh, 4.63), 293 (sh, 4.10), 322 (4.21). CD λ_{max} nm (Δε): 217 (−40.10), 265 (−2.88), 285 (−2.62). ^{1}H NMR: Table 4. FAB-MS *m/z* (rel. int.): 873 $[M + H]^+$ (6), 369 (100).

Proanthocyanidin IV (3-O-(α-L-*rhamnopyranosyl*) *afzelechin*-(4α → 8)-*epicatechin*-3-O-*syringate*, **14**). Amorphous (2 mg). TLC: R_f 0.39 (S-11); anisaldehyde: red. $[\alpha]_D$ −247 (MeOH; *c* 0.1). UV λ_{max} nm (log ε): 204 (5.01), 277 (4.20); +NaOH: 210 (5.37), 237 (sh, 4.64), 294 (sh, 4.16), 323 (4.25). CD λ_{max} nm (Δε): 217 (−51.50), 260 (−2.40), 288 (−5.33). ^{1}H NMR: Table 4. FAB-MS *m/z* (rel. int.): 889 $[M + H]^+$ (9), 369 (100).

(*E*)-2-(4-*Hydroxyphenyl*)*ethenyl*-α-L-*rhamnopyranoside* (**15**). Amorphous (22 mg). TLC: R_f 0.38 (S-10); anisaldehyde: green. $[\alpha]_D$ −106 (MeOH; *c* 0.8). UV λ_{max} nm (log ε): 206 (4.41), 263 (4.38), 295 (sh, 3.53); +NaOH: 209 (4.85), 281 (4.39), 314 (sh, 3.22). ^{1}H NMR (CD_3OD): δ 1.27 (3H, *d*, J = 6 Hz, Me-6″), 3.41 (1H, *dd*, $J_1 = J_2$ = 9.5 Hz, H-4″), 3.62 (1H, *dq*, J_1 = 9.5, J_2 = 6 Hz, H-5″), 3.71 (1H, *dd*, J_1 = 9.5, J_2 = 3.5 Hz, H-3″), 3.90 (1H, *dd*, J_1 = 3.5, J_2 = 1.5 Hz, H-2″), 5.05 (1H, *d*, J = 1.5 Hz, H-1″), 6.02 (1H, *d*, J = 13 Hz, H-2), 6.69 (2H, *m*, AA′BB′, H-3′, H-5′), 6.89 (1H, *d*, J = 13 Hz, H-1), 7.08 (2H, *m*, AA′BB′, H-2′, H-6′). ^{13}C NMR (62.9 MHz, CD_3OD): δ 18.0 (C-6″), 70.5 (C-5″), 71.6 (C-2″), 72.2 (C-3″), 73.7 (C-4″), 101.5 (C-1″), 111.7 (C-2), 116.4 (C-3′, C-5′), 127.5 (C-2′, C-6′), 128.5 (C-1′), 143.2 (C-1), 157.0 (C-4′). EI-MS *m/z* (rel. int.): 282 $[M]^+$ (4), 136 (100), 107 (28).

(*Z*)-2-(4-*Hydroxyphenyl*)*ethenyl*-α-L-*rhamnopyranoside* (**16**). Amorphous (4 mg). TLC: R_f 0.36 (S-10); anisaldehyde: green. $[\alpha]_D$ +108 (MeOH; *c* 0.3). UV λ_{max} nm (log ε): 204 (4.34), 261 (4.32), 270 (sh, 4.22); +NaOH: 208 (4.82), 280 (4.33). ^{1}H NMR (CD_3OD): δ 1.25 (3H, *d*, J = 6 Hz, Me-6″), 3.43 (1H, *dd*, $J_1 = J_2$ = 9.5 Hz, H-4″), 3.58 (1H, *dq*, J_1 = 9.5, J_2 = 6 Hz, H-5″), 3.82 (1H, *dd*, J_1 = 9.5, J_2 = 3.5 Hz, H-3″), 4.00 (1H, *dd*, J_1 = 3.5, J_2 = 1.5 Hz, H-2″), 5.04 (1H, *d*, J = 1.5 Hz, H-1″), 5.30 (1H, *d*, J = 7 Hz, H-2), 6.28 (1H, *d*, J = 7 Hz, H-1), 6.70 (2H, *m*, AA′BB′, H-3′, H-5′), 7.38 (2H, *m*, AA′BB′, H-2′, H-6′). ^{13}C NMR (62.9 MHz, CD_3OD): δ 18.0 (C-6″), 70.9 (C-5″), 71.6 (C-2″), 72.5 (C-3″), 73.6 (C-4″), 102.7 (C-1″), 108.6 (C-2), 116.0 (C-3′, C-5′), 128.6 (C-1′), 130.7 (C-2′, C-6′), 141.3 (C-1), 156.8 (C-4′). EI-MS *m/z* (rel. int.): 282 $[M]^+$ (6), 136 (100), 107 (33).

3,4,5-*Trimethoxyphenyl*-β-D-*glucopyranoside* (**17**). Crystals (4 mg). Mp 199–202° (lit. [27] mp 201–203°). TLC: R_f 0.33 (S-10); anisaldehyde: red. $[\alpha]_D$ −53° (MeOH; *c* 0.3) (lit. [27] $[\alpha]_D$ −22.3° (MeOH; *c* 0.38)). UV λ_{max} nm (log ε): 205 (4.58), 223 (sh, 3.91), 271 (2.99). ^{13}C NMR (62.9 MHz, CD_3OD): δ 56.6 (OMe-3′, OMe-5′), 61.2 (OMe-4′), 62.8 (C-6), 71.7 (C-4), 75.0 (C-2), 78.1 (C-3 or C-5), 78.4 (C-5 or C-3), 96.2 (C-2′, C-6′), 103.2 (C-1), 134.5 (C-4′), 154.8 (C-3′, C-5′), 156.1 (C-1′). IR, ^{1}H NMR, MS in agreement with published data [27]. There is no explanation for the discrepancy between the resonance signal observed for C-4′ and the value reported in [27].

Pterolactam (**18**). Solid (1 mg). Mp 54–56° (lit. [28] mp 56–57°). TLC: R_f 0.58 (S-10); anisaldehyde: yellow. $[\alpha]_D$ +10 (*c* 0.1) (lit. [28] $[\alpha]_D$ +2° (for *c*: no data)). EI-MS *m/z* (rel. int.): 115 $[M]^+$ (24), 84 (100), 71 (17), 60 (26), 56 (19). IR, ^{1}H NMR in agreement with published data [28, 29].

3,4-*Dihydroxybenzaldehyde*. Crystals (5 mg). Mp 153–154° (lit. [30] mp 153–154°). TLC: R_f 0.62 (S-10); anisaldehyde: colourless. UV λ_{max} nm (log ε): 206 (4.21), 231 (4.14), 278 (4.01), 312 (3.95); +NaOH: 210 (4.57), 250 (3.97), 297 (sh, 3.87), 347 (4.35). IR, ^{1}H NMR, MS in agreement with published data [30, 31].

L-(+)-*Rhamnose*. Crystals (17 mg). Identified by HPLC analysis on APS Hypersil (5 μm, Bischoff) using MeCN–H_2O (4 : 1) with a chiralyser (IBZ) and by comparison with an authentic sample.

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