PERGAMON

Phytochemistry 51 (1999) 1031–1037

PHYTOCHEMISTRY

Dammarane triterpenes and pregnane steroids from *Aglaia lawii* and *A. tomentosa*

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Received 25 November 1998; received in revised form 18 January 1999; accepted 20 January 1999

Abstract

Three known dammaranes, cabraleone, eichlerianic acid and shoreic acid, together with two new ones, aglinins A and B, were isolated from the bark of *Aglaia lawii*. *A. tomentosa* also contained dammarane triterpenes: the known, cabraleone, cabraleadiol 3-acetate, 3-epiocotillol, cabralealactone, cabralealactone 3-acetate and the new aglinins C and D. In addition, two new pregnane steroids, aglatomins A and B, were isolated from *A. tomentosa* along with the known cytotoxic cyclopentatetrahydrobenzofuran, rocaglaol. The structure of the new compounds was determined by spectral means, essentially 2D NMR experiments.

Keywords: *Aglaia lawii*; *Aglaia tomentosa*; Meliaceae; Dammarane triterpenoids; Pregnane steroids; Structural elucidation

1. Introduction

Our continuing researches on the *Aglaia* genus (Meliaceae) have led us to the present study of the constituents of the ethanol extracts of two species, *A. lawii* Sald. ex. Raman (leaves) and *A. tomentosa* Teijsm. and Binn. (bark), which were collected in Vietnam[1] and Malaysia[2], respectively. The extract of *A. tomentosa* showed cytotoxicity against KB cells (69% inhibition at 10 μg/ml), while the extract of *A. lawii* was inactive.

Two new 3,4-secodammarane triterpenes, aglinins A (**1a**) and B (**2a**), were isolated from *A. lawii*, together with the known compounds, spathulenol, 24*S*,25-epoxycycloartanol and the dammarane cabraleone (**3**), as well as the known 3,4-secodammaranes, eichlerianic acid (**4a**), shoreic acid (**4b**) and foveolin A (**5a**). *A. tomentosa* also contained cabraleone and related known triterpenes: cabraleadiol 3-acetate, 3-epiocotillol, cabralealactone and cabralealactone 3-acetate. In addition, two new dammaranes, aglinins C (**7**) and D (**8**), were isolated together with two pregnane steroids, aglatomins A (**9**) and B (**10**). Finally, the cyclopentatetrahydrobenzofuran, rocaglaol, a highly cytotoxic compound (IC_{50} againt KB 0.05 μg/ml), which also exists in other species of *Aglaia* (Ishibshi, Satasook, Isman, & Towers, 1993; Dumontet et al., 1996; Mulholland, & Nadoo, 1998), was found and is apparently the sole component responsible for the cytotoxicity of the crude extract.

2. Results and discussion

The 3,4 secodammaranes, aglinins A (**1a**) and B (**2a**), were isolated from the extract of *A. lawii* leaves

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[1] This work has been done in the framework of a collaborative program between CNRS (France) and the NCST (Hanoi, Vietnam).

[2] This work has been done in the framework of a collaborative program between CNRS France and the University of Malaya (Kuala Lumpur, Malaysia).

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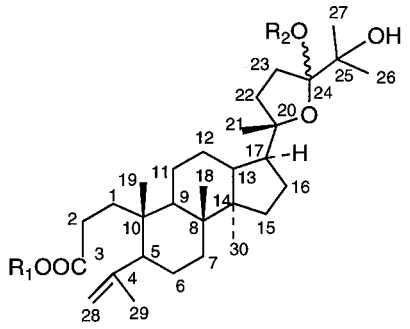
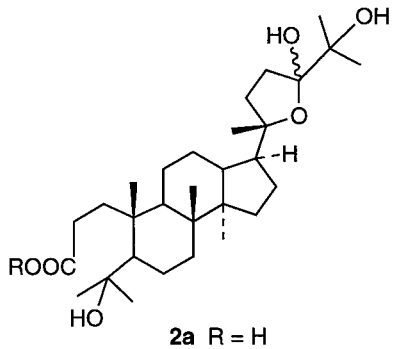
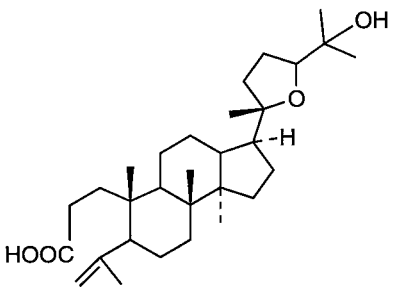
PII: S0031-9422(99)00053-9



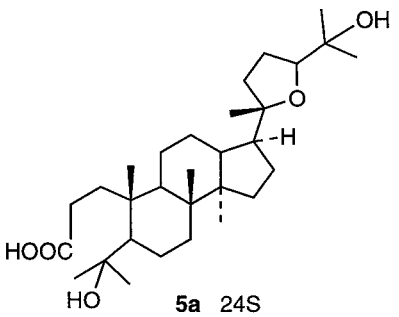
1a $R_1 = R_2 = H$,
1b $R_1 = Me$, $R_2 = H$
11 $R_1 = R_2 = Me$



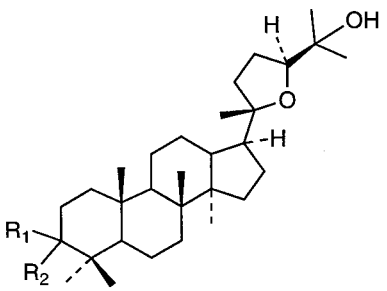
2a R = H
2b R = Me



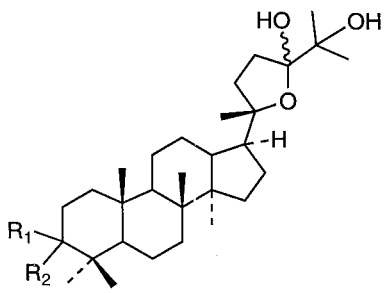
4a 24S
4b 24R



5a 24S
5b 24R



3 $R_1, R_2 = O$
6a $R_1, R_2 = H$, α-OH
6b $R_1, R_2 = H$, α-OAc



7 $R_1, R_2 = H$, α-OH
8 $R_1, R_2 = O$

by chromatography on silica gel, followed by HPLC on reverse phase and further purified in form of their methylesters **1b** and **2b**. The latter were obtained by esterification of the corresponding acids with diazomethane. All the other compounds were isolated either from the extracts of *A. lawii* or of *A. tomentosa* by repeated chromatography on silica gel.

Aglinin A methylester (**1b**), $[\alpha]_D$ +15°, showed an $[M+Na]^+$ peak in the HRFABMS at *m/z* 527.3722 corresponding to the molecular formula of $C_{31}H_{52}O_5$. The IR spectrum showed the absorption of a methyl ester at 1735 cm^{-1}. In the ^{13}C NMR spectrum (Table 1), the signal of the C-3 carbonyl appeared at δ 174.7, while the isopropenyl group attached to C-5 resonated at δ_C 113.5 (δ_H 4.82, 4.64, 2 brs, CH_2-28), δ 147.7 (C-4), δ 23.4 (δ_H 1.71, Me-29). These data as well as all the signals of the dammarane fused ring moiety were similar to the ones of the 3,4 secodammaranes eichleirianic and shoreic acid previously isolated from *A. foveolata* (Roux et al., 1998).

The side chain signals, however, differed from those of the latter. In the NMR spectra, the typical signals of the C-24 oxymethine were absent. Instead, a signal of a C–OH at low field (δ 108.6) was observed in the ^{13}C NMR suggesting that the tetrahydrofuran ring was replaced by a five membered hemiacetal ring. The 1D and 2D (COSY, HMQC, HMBC) NMR data were in agreement with the structure depicted in **1b**, especially the diagnostic HMBC correlations H-23/C-24, Me-21/C-17, C-20,C-22 and Me-26, Me-27/C-24. C-20 was assigned the *S* configuration similar to most of the

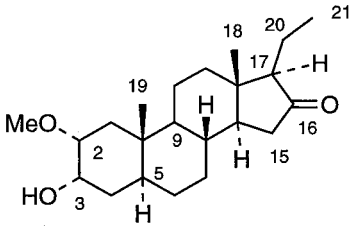
Table 1
^{13}C (75 MHz) and ^{1}H NMR (400 MHz) data for aglinin A methylester (**1b**)[a,b] and ^{13}C (75 MHz) data for aglinin B methylester and aglinins C and D (**2b**, **7** and **8**) ($CDCl_3$)[a].

Position	**1b**				**2b**	**7**	**8**
	δ C	δ H (*J* Hz)	HMBC	NOESY	δ C	δ C	δ C
1	34.7	1.58 m	2,5, 10, 19	2α	34.8	33.6	40.0
2	28.5	α 2.71 m	1,3	2β, 9	29.1	25.9	34.7
		β 2.31 m	1,3	5			
3	174.7			175.7	76.3	218.2	
4	147.7			76.0	37.2	47.5	
5	50.9	1.95 m		6α, 9, 28b	51.8	49.5 (49.3)	55.5
6	24.7	α 1.37 m		6β	22.7	18.2	19.8
		β 1.77 m		18, 19			
7	34.0	α 1.20 m		7β	34.8	34.5	34.2
		β 1.58 m		18, 19			
8	40.2				41.3	40.3	41.8
9	41.3	1.51 m		30	42.5 (42.3)	50.5	50.1
10	39.3				40.2	37.6	40.4
11	22.2 (22.0)	α 1.37 m		11β	21.4 (21.3)	21.3	22.1
		β 1.20 m		19, 18, 21			
12	27.4 (26.9)	α 1.20 m		12β	27.6 (27.1)	26.9 (26.3)	27.4
		β 1.74 m		21			
13	43.5 (43.0)	1.66 m		18, 21	43.5 (43.1)	43.2 (43.7)	43.5
14	50.9				50.5	50.3	50.5
15	31.7	α 1.45 m		15β, 16α	31.7	31.6	31.6
		β 1.07 m					
16	26.0	α 1.74 m		30	26.0	25.9 (25.4)	26.8
		β 1.38 m					
17	50.6 (49.5)	1.95 m		21, 22α,30	50.5 (50.0)	50.6 (50.4)	50.3
18	15.5	1.00 s	7, 8, 9, 14		15.5	15.5	15.3
19	20.3	0.82 s	1, 5, 9, 10	28b	20.7	16.0	16.2
20	88.8 (88.0)				88.8 (88.0)	88.8 (88.0)	88.8 (88.1)
21	24.4 (25.2)	1.09 (s)	17, 20, 22		24.3 (25.3)	24.2 (24.8)	24.4
22	34.7 (37.0)	α 2.06 m	23	22β	34.8 (37.0)	35.2 (36.8)	34.7 (37.0)
		β 1.66 m	23				
23	31.7.(31.2)	a 1.81 m	20, 24	23b	31.7 (32.8)	31.6	31.6 (31.1)
		b 2.06 m					
24	108.6				108.6	108.5	108.7
25	74.2 (74.8)				74.2 (74.9)	74.7 (74.0)	74.4 (74.2)
26	24.7 (25.0)	1.25 s	24, 25, 27		24.7 (25.0)	24.5	24.7
27	24.2	1.22 s	24, 25, 26	24.2	24.2	24.2	
28	113.5	a 4.82 brs	5, 29	29	34.3	28.3	26.0
		b 4.64 brs	5, 29				
29	23.4	1.71 s	4, 5, 28		27.6	22.1	21.1
30	16.5 (16.3)	0.86 s	8, 13, 14, 15		16.3 (16.2)	16.0	16.5 (16.2)
CO_2Me	51.7	3.64	3	29	52.0		

[a] Assignments based on 2D experiments (COSY, HMQC, HMBC, NOESY).
[b] ^{13}C values under brackets are for the minor C_{24}–OH epimer.

dammarane triterpenes particularly those isolated from the *Aglaia* genus. Compound **1b** was in fact a mixture of epimers at C-24 which were inseparable and probably interconvertible. This resulted in the doubling of the ^{13}C signals of the side chain except that of C-24. However, doubling of the C-24 acetal signal (δ 111.0 and 111.7) of the methoxylated derivatives **11** was observed. Attempts to separate these two isomers were unsuccessful.

Aglinin B methylester (**2b**), $[\alpha]_D$ +28°, exhibited an $[M+Na]^+$ peak in the HRFABMS at *m*/*z* 545.3811, which matched the molecular formula $C_{31}H_{54}O_6$. The IR showed the absorption of a methyl ester at 1735 cm^{-1} and the corresponding signal of the C=O group appears at δ 175.7 in the ^{13}C NMR spectrum. All ^{13}C NMR signals of the fused rings and the side chain were similar those of **1b** with the exception of those of the terminal isopropenyl group. The latter was replaced by a $C(OH)Me_2$ group as indicated by the presence of a C–OH signal at δ 76.0, the mass spectral data and the presence of an additional tertiary methyl in the molecule. Such a group was also present in foveolins A (**5a**) and B (**5b**) which have been isolated from *A. foveolata* (Roux et al., 1998).



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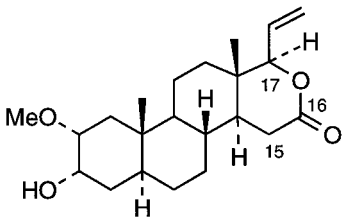

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Aglinin B methylester was a mixture of epimers at C-24 as shown by the doubling of a part of the ^{13}C NMR signals and was assigned structure **2b**.

Aglinin C (**7**), $[\alpha]_D$ +17°, showed an $[M+Na]^+$ peak in the HRFABMS at *m/z* 499.3704 corresponding to the molecular formula of $C_{30}H_{52}O_4$. The ^1H NMR showed an oxymethine proton at δ 3.40 (brs). The ^{13}C NMR signals of the fused rings were similar to the ones previously described for the dammarane cabraleadiol **6a** (Hisham, Ajitha Bai, Fujimoto, Hara, & Shimada, 1996), which possessed a 3α-OH group, while those of the side chain indicated a mixture of hemiacetals similar to those of aglinins A and B. Thus aglinin C was assigned structure **7**.

Aglinin D (**8**), $[\alpha]_D$ +14°, revealed an $[M+Na]^+$ peak in the HRFABMS at *m/z* 497.3606, which matched the molecular formula $C_{30}H_{50}O_4$. The IR spectrum exhibited a band at 1702 cm^{-1} assignable to a keto group, which gave an NMR signal at δ_C 218.2. Comparison of the ^{13}C NMR data Table 1 with those of aglinin C and known dammaranes with a 3-keto group as cabraleone (3) (Waterman, & Ampopo, 1985; Tori, Matsuda, Sono, & Asakawa, 1988), led to the assignment of structure **8** to aglinin D.

Aglatomin A (**9**), $[\alpha]_D$ −32°, showed an $[MH]^+$ peak at *m/z* 349.2738 in the HRCIMS corresponding to the molecular formula $C_{22}H_{36}O_3$. The IR spectrum showed the absorption of a five membered ring ketone at 1729 cm^{-1}. In the ^{13}C NMR spectrum, the signal of the carbonyl appeared at δ 220.0. The ^1H NMR spectra exhibited the singlets of two upfield tertiary methyls at δ_H 0.68 and δ_H 0.82 (δ_C 13.6 and δ_C 12.7), a triplet of a third methyl adjacent to a CH_2 group at δ_H 1.02 (J=7 Hz) and the singlet of an OMe group resonating at δ_H 3.38. These data together with the molecular formula suggested a pregnane type compound. In addition, in the ^1H NMR, two oxymethines protons resonated at δ 3.28 (ddd, J=11,3,3 Hz) and δ 4.13 (brs), respectively. The COSY spectrum aided by the HMQC experiment showed that the two oxymethine groups were adjacent, and that each was further coupled with a methylene group. These results suggested that the oxymethines were located at position 2 and 3 of the pregnane skeleton. A similar substitution pattern was found recently in a pregnane derivative isolated from *Aglaia grandis* (Inada, Murat, Yuka, Nakanishi, & Darnedi, 1997). Finally, careful analysis of the 2D NMR (COSY, HMBC, HMQC and NOESY) allowed the complete assignments of the carbons and protons of aglatomin A (**9**) (Table 2). The OMe group was located at position 2 owing to the observation of the spin system C_1–C_2–C_3–C_4–C_5 and the HMBC cross peak OMe/C-2, while the COSY spectrum and the HMBC correlations H-15/C-8, C-13 and H-15/C-16 indicated a C-16 ketone.

The 5α configuration was proved by the upfield shift of Me-19 (Hung et al., 1995) and the NOESY correlation H-5α/H-1α. The NOESY experiment further confirmed the usual H-14α and H-17α stereochemistry of pregnane derivatives, since the correlations H-15β/Me-18, H-15α/H-14α, H-15α/H-17 were observed. Finally the H-2β and H-3β configurations were deduced from the coupling pattern of both protons, as well as from the NOESY cross peaks H-2/H-19 and H-2/H-3.

Aglatomin B (**10**), $[\alpha]_D$ −6°, showed an $[MH]^+$ peak at *m/z* 363.2547 in the HRCIMS indicating a molecular formula of $C_{22}H_{34}O_4$. The IR spectrum showed a carbonyl band at 1731 cm^{-1} which corresponded to a lactone. In the ^{13}C NMR spectrum Table 2 the CO resonated at δ 173.0. Only two tertiary methyls were present, which were assigned to Me-18 and Me-19 (δ_H 0.83 and 0.77, δ_C 11.6 and 12.6) of a pregnane derivative. Aglatomin B further showed a similar substitution pattern of ring A with a 5α configuration as in aglatomin A. Analysis of the 2D spectra confirmed the pregnane skeleton with ring D being a six membered lactone. The oxymethine group (δ_H 4.32 and δ_C 90.6) was located at C-17 owing to the HMBC correlations H-17/C13, C14, C15 and the C=O at C-16 as in compound **9**. The $C_{20,21}$ pregnane chain was unsaturated, showing a Δ^{20} olefin with the typical coupling pattern of a vinyl group linked to a CH group Table 2. The COSY spectrum and the HMBC cross peak H-17/C-20 confirmed the attachment of the chain at C-17.

Tetracyclic triterpenes of the dammaranes or the tirucallane or cycloartane series are found in all *Aglaia* species, that have been studied until present. The cytotoxic cyclopentatetrahydrobenzofurans of the rocaglaol

Table 2
^{13}C (75 MHz) and ^{1}H NMR (400 MHz) data for aglatomin A (**9**) and B (**10**) ($CDCl_3$)[a]

Position	**9**				**10**			
	δ C	δ H (*J* Hz)	HMBC	NOESY	δ C	δ H (*J* Hz)	HMBC	NOESY
1	37.6	α 1.25 m	2, 3, 5, 9, 10, 19	1β, 5, 9	37.5	α 1.75 m	2, 3, 5, 9, 10, 19	1β
		β 1.75 m	2, 3, 5, 9, 10, 19	2, 19, OMe		β 1.20 m	2, 3, 5, 9, 10	2, 19
2	78.3	3.28 ddd (11, 3, 3)	3, OMe	1β, 3, 19	78.2	3.28 ddd (11, 3, 3)	3, OMe	3, 4β, 19
3	65.7	4.13 brs		4α,β	65.5	4.11 brs	1	4α,β
4	33.5	α 1.65 m	2, 5		33.3	α 1.63 m		5
		β 1.40 m	5			β 1.40 m		19
5	54.4	0.97 m	19	6α, 9	53.0	0.86 m	19	
6	27.6	α 1.91 m	5		27.3	α 1.67 m		
		β 1.32 m	5			β 1.40 m		
7	32.2	α 1.57 m			30.0	α 1.07 m		15α
		β 1.65 m		15α		β 1.58 m		15α,β
8	34.1	1.45 m		19	35.5	1.25 m		15β, 19
9	38.3	1.60 m	11, 19		37.7	1.58 m		
10	37.0				37.5			
11	20.6	α 1.65 m			19.4	α 1.67 m		
		β 1.35 m		18, 19		β 1.20 m		
12	38.3	α 1.15 m		17	35.1	α 1.08 m		17
		β 1.35 m		18		β 1.37 m		
13	42.2				46.0			
14	50.6	1.42 m	8, 9, 15, 18	15α	45.9	1.40 m	8, 9, 15, 18	15α
15	38.6	α 2.20 dd (7, 18)	13, 14, 16	15β, 17	32.1	α 2.75 dd (6, 10)	8, 13, 14, 16	15β
		β 1.70 m	8, 13, 14, 16, 18	18		β 2.08 dd (11, 18)	8, 13, 14, 16	18
16	220.0				173.0			
17	65.7	1.65 m	8, 13, 15, 16, 18, 21		90.6	4.32 d (6)	12, 13, 14, 18, 20, 21	20, 21a
18	13.6	0.68 s	12, 13, 14, 17	20b	11.6	0.83 s	12, 13, 14, 17	20
19	12.7	0.82 s	1, 5, 9, 10		12.6	0.77 s	1, 5, 9, 10	
20	17.8	a 1.25 m	16, 17, 21	21	131.7	5.78 ddd (6, 10, 16)	17	21a,b
		b 1.60 m	16, 17, 21					
21	13.6	1.02 t (7)	17, 20		119.4	a 5.30 d (10)		
						b 5.37 d (16)		
OMe	56.1	3.38 s	2	56.1	3.37 s	2		

[a] Assignments based on 2D experiments (COSY, HMQC, HMBC, NOESY).

type are also frequently encountered. Pregnane steroids, which are relatively rare in the plant kingdom, have been isolated previously only from *A. grandis*.

3. Experimental

3.1. General

IR: $CHCl_3$; ^{1}H NMR: 400 MHz; ^{13}C NMR: 75 MHz; 2D experiments: 400 MHz; CC: Merck Silica gel 60 230–400 mesh. Semi-preparative HPLC: column Ultrasphere C-18 (10 × 250 mm), MeCN/H_2O/AcOH (65:35:0.5), flow rate 4 ml/min, RI detection.

3.2. Plant material

Leaves of *Aglaia lawii* (Wight) Sald. ex Raman (Meliaceae) were collected in Cho Don, Vietnam in December 1995, by one of us (VD) and identified. A voucher specimen (VN 051) was deposited at the Herbarium of the Institute of Ecology, NCST, Hanoi, Vietnam.

Bark material of *Aglaia tomentosa* Teijsm. and Binn. was collected in Kedah, Malaysia, in April 1995 by C. Wiart (Institut de Chimie des Substances Naturelles, Gif-sur-Yvette) and identified. Voucher specimens (KL 4493) are deposited at the Laboratoire de Phanérogamie, Muséum National d'Histoire Naturelle in Paris, at the Herbarium of Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia and at the Herbarium of the Forest Research Institute, Kepong, Malaysia.

3.3. Extraction and isolation

Dried ground leaves (500 g) of *A. lawii* were extracted exhaustively with EtOH at room temperature. The extract (48 g) was repeatedly chromatographed on silica gel yielding (+)-spathulenol (158 mg (1) CH_2Cl_2/MeOH, 99.5:0.5, (2) heptane/EtOAc, 95:5), cabraleone (**3**) (103 mg (1) CH_2Cl_2/MeOH,

99.5:0.5, (2) heptane/EtOAc, 90:10) and 24,25-epoxycycloartanol (33 mg (1) CH_2Cl_2/MeOH, 99.5:0.5, (2) heptane/EtOAc, 90:10, (3) CH_2Cl_2/MeOH, 99:1), a mixture of shoreic acid (**4a**) and eichlerianic acid (**4b**) (1.61 g CH_2Cl_2/MeOH 98-2, not further purified, see Dumontet et al. (1996) for the separation method), aglinin A (**1a**) (317 mg, crude, CH_2Cl_2/MeOH, 95:5) and a mixture (200 mg) containing foveolin A (**5a**) and aglinin B (**2a**) (CH_2Cl_2/MeOH/H_2O, 80:20:1). Semi-preparative HPLC of the crude aglinine A gave a purified fraction (44 mg), which was esterified with diazomethane and further purified by chromatography on silica gel yielding aglinin A methylester (**1b**) (14 mg (1) CH_2Cl_2/MeOH, 99:1, (2) heptane/EtOAc, 90:10). The mixture of crude foveolin A and aglinin B was submitted to semi-preparative HPLC yielding pure foveolin A (20 mg) and aglinin B (13 mg), which was esterified with diazomethane to give aglinin B methylester (**2b**).

Dried ground leaves (500 g) of *A. tomentosa* were extracted with EtOH at room temperature. VLC on silica gel of the crude extract (20.0 g) afforded a fraction (6.51 g, CH_2Cl_2) which was further submitted to repeated CC and PTLC on silica gel, yielding cabraleactone 3-acetate (17 mg) and aglatomin A (**9**) (12 mg) ((1) CH_2Cl_2/MeOH, 99:1, (2) heptane/AcOEt, 90:10, (3) PTLC heptane/AcOEt, 40:60); cabrealactone (41 mg (1) CH_2Cl_2/MeOH, 99:1, (2) heptane/AcOEt, 80:20, (3) PTLC heptane/AcOEt, 40:60); cabraleadiol 3-acetate (**6b**) (89 mg), cabraleone (**3**) (79 mg) and 3-epiocotillol (70 mg) ((1) CH_2Cl_2/MeOH, 98:2, (2) heptane/AcOEt, 90:10); aglinin D (**8**) (16 mg (1) CH_2Cl_2/MeOH, 98:2, (2) heptane/AcOEt, 80:20, (3) PTLC heptane/AcOEt, 40:60); aglinin C (**7**) (23 mg (1) CH_2Cl_2/MeOH, 98:2, (2) heptane/AcOEt, 60:40, (3) PTLC heptane/AcOEt, 40:60); rocaglaol (8 mg) and aglatomine B (**10**) (10 mg (1) CH_2Cl_2/MeOH, 98:2, (2) heptane/AcOEt, 40:60, (3) PTLC heptane/AcOEt, 60:40).

3.4. Aglinin A methylester (*1b*)

$[\alpha]_D$ +15° (*c* 1, $CHCl_3$); IR ν cm−1 3415, 1735; ^{1}H NMR and ^{13}C NMR see Table 1; HRFABMS *m/z* 527.3714 $[M+Na]^+$ ($C_{31}H_{52}O_5Na$, Δ 0.2 mmu).

3.5. Aglinin B methylester (*2b*)

$[\alpha]_D$ +28° (*c* 1, $CHCl_3$); IR ν cm−1 3415, 1735; ^{1}H NMR ($CDCl_3$): δ 2.50, 2.20 (2 × 1H, 2 × m, H-2), 1.02 (3H, s, Me-18), 1.02 (3H, s, Me-19), 1.12 (3H, s, Me-21),1.32 (3H, s, Me-26), 1.27 (9H, s, Me-27, Me-28, Me-27), 0.88 (3H, s, Me-30), 3.70 (3H, s, COOMe); ^{13}C NMR see Table 1; HRFABMS *m/z* 45.3811 $[M+Na]^+$ ($C_{31}H_{54}O_6Na$, Δ −0.7 mmu).

3.6. Aglinin C (*7*)

$[\alpha]_D$ +17° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.40 (1H, brs, H-3), 0.98 (3H, s, Me-18), 0.83 (3H, s, Me-19), 1.13 (3H, s, Me-21), 1.32 (3H, s, Me-26), 1.27 (3H, s, Me-27), 0.96 (3H, s, Me-28), 0.80 (3H, s, Me-29), 0.90 (3H, s, Me-30); ^{13}C NMR see Table 1; HRFABMS *m/z* 483 $[M+Na]^+$ ($C_{30}H_{52}O_4Na$, Δ 0.1 mmu).

3.7. Aglinin D (*8*)

$[\alpha]_D$ +14° (*c* 1, $CHCl_3$); IR ν cm−1 3415, 1702; ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, s, Me-18), 0.92 (3H, s, Me-19), 1.10 (3H, s, Me-21), 1.25 (3H, s, Me-26), 1.22 (3H, s, Me-27), 1.04, 1.08 (2 × 3H, 2 × s, Me-28, Me-29), 0.90 (3H, s, Me-30); ^{13}C NMR see Table 1; HRFABMS *m/z* 497.3606 $[M+Na]^+$ ($C_{30}H_{50}O_4Na$, Δ −0.1 mmu).

3.8. Aglatomin A (*9*)

$[\alpha]_D$ −32° (*c* 1, $CHCl_3$); IR ν cm−1 3395, 1729; ^{1}H NMR and ^{13}C NMR see Table 2; HRCIMS *m/z* 349.2738 $[MH]^+$ ($C_{22}H_{37}O_3$, Δ −0.4 mmu).

3.9. Aglatomin B (*9*)

$[\alpha]_D$ −6° (*c* 1, $CHCl_3$); IR ν cm−1 3395, 1731; ^{1}H NMR and ^{13}C NMR see Table 2; HRCIMS *m/z* 363.2547 $[MH]^+$ ($C_{22}H_{35}O_4$, Δ 1.2 mmu).

3.10. Methoxy derivatives *11*

A solution of **1b** (20 mg) in absolute methanol (2 ml) was kept at RT during one night and evaporated to dryness under reduced pressure, yielding **11** (20 mg), $[\alpha]_D$ +19° (*c* 1, MeOH); IR ν cm−1 3415, 1735; ^{1}H NMR (CD_3OD): δ 2.20, 2.40 (2 × 1H, 2 × m, H_2-2), 1.05 (3H, s, Me-18), 0.84 (3H, s, Me-19), 1.18 (3H, s, Me-21), 1.22 (3H, s, Me-26), 1.20 (3H, s, Me-27), 4.64, 4.82 (2 × H, 2 × brs, H_2-28): 1.75 (3H, s, Me-29), 0.92 (3H, s, Me-30), 3.62 (3H, s, COOMe), 3.48 (3H, s, OMe); ^{13}C (CD_3OD): δ 34.5 (C-1), 28.0 (C-2), 174.9 (C-3), 147.5 (C-4), 50.9 (C-5), 24.8 (C-6), 33.8 (C-7), 39.9 (C-9), 40.8 (C-9), 38.9 (C-10), 22.4 (C-11), 26.4 (C-12), 43.1 (C-13), 50.8 (C-14), 31.6 (C-15), 26.0 (C-16), 50. 6, 49.3 (C-17), 15.2 (C-18), 19.5 (C-19), 88.8, 88.2 (C-20), 21.7, 22.4 (C-21), 37.7, 37.0 (C-22), 31.70 (C-23), 111.0, 111.7 (C-24), 74.7, 74.8 (C-25), 24.8 (C-26), 24.1 (C-27), 112.7 (C-28), 23.9 (C-29), 14.6 (C-30), 51.6 (COOMe), 48.2 (OMe); FABMS *m/z* 541 $(M+Na)^+$.

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