Abietane Diterpenes from *Illicium angustisepalum*

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Twelve novel (**1**, **2**, **4**, **5**, **7**−**14**) and two known (**3**, **6**) abietane diterpenes and have been isolated from the aerial parts of *Illicium angustisepalum*. These diterpenes are unusual in that they are oxygenated at the axial C-19 position of the *gem*-dimethyl group rather than the equatorial C-18 position.

Illicium angustisepalum A. C. Smith (Illiciaceae) is a medium-sized tree found in southern regions of the People's Republic of China.[1,2] In Hong Kong, its distribution is restricted to Lantau Island. It is used in traditional medicine for treating rheumatism and skin inflammation.[3] There have been no previous reports concerning the phytochemistry of *I. angustisepalum* or the biological activity of the extract.

Results and Discussion

Extraction of the aerial parts of *I. angustisepalum* with CH_2Cl_2 followed by column chromatography and HPLC has yielded 14 abietane-type diterpenes, of which 12 (**1**, **2**, **4**, **5**, **7**−**14**) are novel. Angustanoic acid A (**1**) was one of the most abundant constituents of the extract. HREIMS confirmed the molecular formula of **1** as $C_{20}H_{28}O_2$. Inspection of its 1D NMR spectra demonstrated the presence of a carboxylic acid group (δ_C 183.9) and three double bonds (δ_C 142.5 C, 140.2 C, 134.6 C, 126.0 C, 125.1 CH, and 111.0 CH_2), one of which was terminal [δ_H 5.07 (s), 4.93 (s)]. These structural features were incorporated into the abietane skeleton of **1** by means of correlations observed in HSQC (Tables 1 and 2), HMBC (Figure 1) and $^1H-^1H$ COSY (not shown) 2D NMR experiments. Rigorous NMR assignments for all other compounds reported in this paper were established in the same manner. Precise knowledge of ^1H NMR chemical shifts for each position in **1**, coupled with the expected comformational rigidity of the trans decalin system in **1**, allowed determination of relative stereochemistry at C-4, C-5, and C-10 by NOESY (Figure 2), which showed that the methyl group at C-4 was on the α-face of the molecule, that is, equatorial (C-18), and that the carboxylic acid was therefore axial (C-19). Although more than 20 abietanes incorporating a carboxylic acid substituent at the C-4 position[4] are known as natural products, only a handful contain an axial carboxylic acid[5−11] rather than the more common equatorial group.

Angustanal (**2**) is the C-19 aldehyde analogue of **1**, while compound **3** is the C-15,C-16 dihydro analogue of **1**. Both C-4 epimers of compound **3** are known from nature: in palustric acid[12] the carboxylic acid group is equatorial (C-18), while for epipalustric acid the carboxylic acid group is axial (C-19).[13] Although no NMR

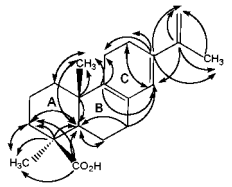

Figure 1. HMBC correlations used in establishing the abietane skeleton of **1** indicated by arrows from ^{13}C to ^1H.

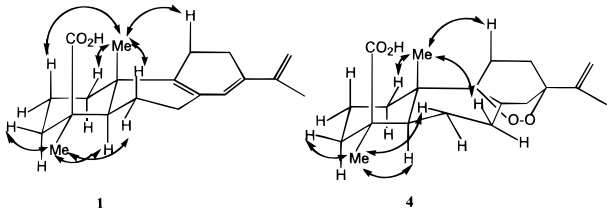

Figure 2. NOESY correlations used to establish the relative stereochemistry of **1** and **4** indicated by double headed arrows.

data are available for epipalustric acid in the literature to confirm the proposed stereochemistry at C-4 in compound **3**, close similarities in the NMR assignments for **1** and **3** established by 2D NMR (Tables 1 and 2) would seem to necessitate that **3** have the same relative stereochemistry as **1**.

Angustanoic acids B (**4**) and C (**5**) were determined to be diastereoisomers of the 9,13-epidioxy derivative of compound **1** from spectroscopic evidence. The relative stereochemistry at the epoxide for C-9 and C-13 in **4** was established as α,α by NOESY correlations (Figure 2); compound **5** was confirmed as the 9*β*,13*β* isomer by the same method. By analogy, compound **6** seems to be the 9,13-epidioxy derivative of epipalustric acid (**3**). Optical rotation and ^{13}C NMR data for **6** gave a good match with 4-*epi*-palustric acid-9α,13α-endoperoxide, previously isolated from *Juniperus sabina*[14] (erroneous literature assignments for C-6/C-11 and C-17/C-20 are corrected in Table 1). Full ^{13}C NMR data have also been reported for both the 9α,13α- and 9*β*,13*β*-endoperoxides of palustric acid.[15] As expected, the largest chemical shift differences reported between endoperoxides of palustric and epipalustric acid occurred in the vicinity of the C-4 position: ^{13}C NMR shifts for the C-4 methyl group were ca. 28 ppm when equatorial and ca. 17 ppm when axial, which is consistent with the equatorial (C-18)/axial (C-19) assignments of the methyl/carboxylic acid groups for all abietanes reported in this paper.

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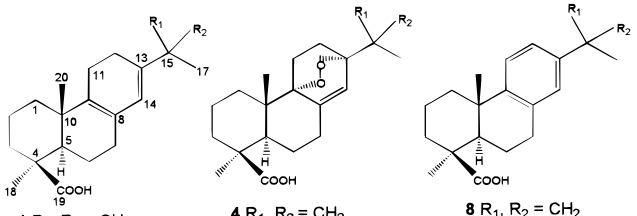
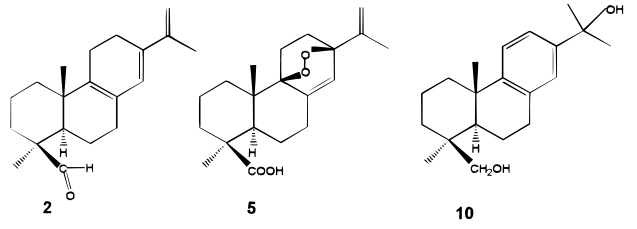
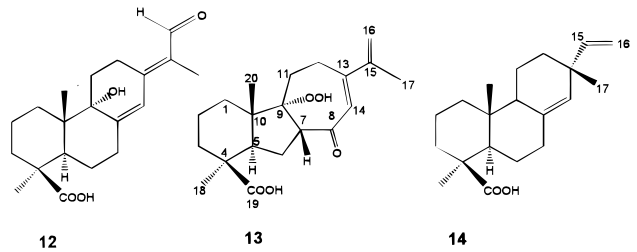
Table 1. ^{13}C NMR Assignments for Compounds **1**−**12** and **14**

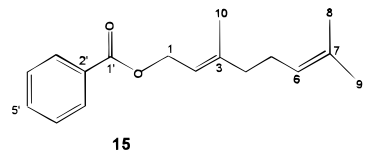
carbon	1	2	3	4	5	6	7	8	9	10	11	12	14
1	36.0	35.4	36.1	31.6	34.7	31.7	31.8	39.3	39.3	39.0	39.1	31.5	39.4
2	19.4	18.7	19.5	19.1	19.1	19.2	19.1	19.9	19.9	19.0	19.9	19.2	19.7
3	37.5	34.0	37.6	37.8	38.1	38.0	38.0	37.4	37.5	35.3	37.3	37.4	38.1
4	43.8	48.6	43.8	45.2	44.5	45.2	45.2	43.9	43.9	38.7	44.1	44.2	44.0
5	53.3	52.7	53.5	44.0	47.9	44.0	44.1	52.9	52.8	51.3	52.5	47.3	56.2
6	20.7	18.8	20.7	19.6	20.3	19.7	19.6	20.9	20.9	19.3	20.8	23.8	24.3
7	31.3	30.9	31.3	24.7	26.5	24.8	24.7	32.1	32.2	31.2	32.0	33.1	36.7
8	126.0	125.6	125.6	145.0	143.3	144.9	145.0	135.1	135.1	134.6	135.8	150.0	136.7
9	140.2	139.9	136.8	81.0	81.9	80.7	81.0	147.4	146.5	148.3	153.6	74.7	49.6
10	38.7	38.2	38.5	40.0	39.7	39.9	39.9	38.5	38.4	37.6	38.0	42.9	39.3
11	22.9	22.8	23.0	22.0	23.6	21.9	21.9	125.4	125.5	124.5	125.9	29.4	18.9
12	24.9	24.8	26.3	28.2	29.8	25.2	23.7	123.1	122.1	122.0	125.8	20.9	34.6
13	134.6	134.8	143.6	78.3	78.6	79.5	81.8	138.3	146.0	146.0	134.6	150.2	37.4
14	125.1	124.8	120.4	127.3	127.3	126.4	125.7	126.1	124.9	124.9	129.4	124.4	128.6
15	142.5	142.5	34.3	143.3	144.7	32.2	72.5	143.0	72.3	72.3	198.1	129.8	148.8
16	111.0	111.2	21.1[a]	112.9	113.2	17.4[a]	25.3[a]	111.7	31.64[a]	31.6		191.1	110.3
17	20.3	20.3	21.3[a]	19.3	19.4	17.2[a]	24.8[a]	21.7	31.62[a]	31.6	26.5	10.2	26.3
18	28.6	24.0	28.6	28.3	29.1	28.3	28.3	28.7	28.7	26.8	28.7	29.2	29.1
19	183.9	205.7	183.6	183.7	182.9	183.0	183.4	184.1	183.8	65.4	183.0	182.9	183.4
20	18.2	19.5	18.3	18.5	16.9	18.5	18.6	23.1	23.2	25.7	23.0	17.0	14.1

[a] Interchangeable within column.









Angustanoic acid D (**7**) is the 15-hydroxy analogue of compound **6**.

Angustanoic acid E (**8**) has undergone complete aromatization of the diene system present in compound **1**. A 1,2,4 substitution pattern for the aromatic C ring was easily recognized from inspection of the ^1H NMR spectrum of **8** (δ ^1H-12: 7.25, dd, J = 8.4, 1.7 Hz; δ ^1H-11: 7.20, d, J = 8.4 Hz; δ ^1H-14: 7.14, br d) and of all other C ring aromatized compounds (**9**−**11**). In angustanoic acid F (**9**), the terminal double bond in **8** has been replaced by a 15-hydroxyl group (as for compound **7**). The C-4 epimer of compound **9**, 15-hydroxy-dehydroabietane, has been reported previously as a natural product;[16−19] as discussed in the preceding paragraph, NMR data for this literature compound were in quite good agreement with our natural product for resonances in the C ring, but large differences (up to 10 ppm in the ^{13}C NMR spectrum) were noted in the vicinity of the C-4 position. Angustanol (**10**) is the C-19 alcohol analogue of **7**. The C-4 epimer of **10** (8,11,13-abietatriene-15,18-diol) has been reported from *Pinus* spp.[20] (as expected, the ^1H NMR chemical shifts for the axial C-4 methyl group of this literature compound were significantly different from those of **10**). Angustanoic acid G (**11**) is a norabietane, which may be derived by oxidative cleavage of the terminal bond in angustanoic acid E (**8**).

Angustanoic acid H (**12**) contains an extended enal functional group as demonstrated by resonances observed in its NMR spectrum [(δ_C 191.2 CH, 150.2 C, 150.0 C, 124.4 CH, 129.8 C; δ_H 10.19 (s), 6.42 (s)]. This functional group was located over the C ring and pendant C-15/C-17 substituent by means of 2D NMR spectroscopy. The stereochemistry about the C-13,C-15 double bond was established from a NOESY correlation between the aldehyde (C-16 position) and H-12β; NOESY experiments also confirmed that the C-9 hydroxy group was α, as expected if compound **12** were to be derived from one of the α-endoperoxides (**4**, **6**, **7**), which predominate in *I. angustisepalum*.

Angustanoic acid I (**13**) is a tertiary hydroperoxide that is the first known example of a 9(8→7)-*abeo*-abietane. The novel skeleton of **13**, in which the B ring has been contracted to a five-membered system and the C ring has expanded to a seven-membered system, was determined by correlations observed in HMBC and ^1H−^1H COSY, as for all other compounds (Table 3), and the relative stereochemistry established by NOESY. As for compound **12**, the structure of **13** suggests it may be the rearrangement product of an α-endoperoxide.

Finally, compound **14** was shown to possess the closely related pimarane skeleton by 2D NMR, and its relative stereochemistry was established as being that

Table 2. ^{1}H NMR Assignments for Compounds **1**−**12** and **14**[a]

proton(s)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**14**
1α	1.08	1.11	1.09	1.48	1.57	1.46	1.48	1.38	1.39	1.43	1.41	1.45	1.08
1β	1.88	1.87	1.86	1.86	1.70	1.84	1.83	2.28	2.29	2.32	2.30	1.75	1.81
2α	1.53	1.55	1.51	1.52	1.58	1.52	1.53	1.62	1.62	1.68	1.65	1.57	1.49
2β	1.90	1.82	1.88	1.85	1.78	1.84	1.84	2.03	2.03	1.63	2.04	1.84	1.83
3α	1.06	1.04	1.03	1.09	1.08	1.09	1.09	1.09	1.08	1.02	1.11	1.10	1.06
3β	2.21	2.19	2.19	2.13	2.25	2.12	2.14	2.26	2.26	1.82	2.28	2.17	2.18
5	1.39	1.50	1.37	1.94	1.48	1.93	1.91	1.57	1.57	1.51	1.57	2.11	1.28
6α	2.04	2.07	2.01	1.94	1.80	1.91	1.92	2.19	2.19	1.99	2.23	1.98	1.89
6β	1.87	1.65	1.84	2.38	2.23	2.35	2.38	2.06	2.05	1.72	2.07	1.90	1.75
7α	2.05	2.19	2.08	2.47	2.29	2.40	2.50	2.80	2.81	2.83	2.83	2.56 (td, 13.9, 5.5)	1.98
7β	2.13	2.21	2.08	2.62	2.85	2.60	2.63	2.92 (dd, 16.3, 4.1)	2.91 (dd, 16, 5.6)	2.93 (dd, 16.2, 5.6)	2.99 (dd, 14.1, 7.0)	2.38	2.28
9													1.70
11α	2.02	2.12	1.99	2.18	2.37	1.96	2.17	7.20 (d, 8.4)	7.22 (s)	7.23 (s)	7.35 (d, 8.4)	1.78	1.54
11β	2.14	2.12	2.04	1.50	1.47	1.49	1.50					1.83	1.61
12α	2.19	2.20	2.01	2.15	2.22	2.13	2.17	7.25 (dd, 8.4, 1.7)	7.22 (s)	7.23 (s)	7.70 (dd, 8.4, 1.9)	2.38	1.37
12β	2.39	2.40	1.99	1.66	1.57	1.45	1.50					3.24 (dt, 14.8, 2.0)	1.44
14	5.81 (s)	5.80 (s)	5.43 (s)	6.18 (d, 2.3)	6.17 (s)	6.11 (d, 2.0)	6.32 (d, 2.2)	7.14 (br d)	7.16 (s)	7.15 (s)	7.65 (br d)	6.42 (s)	5.23 (s)
15			2.29 (sept, 6.8)			1.91							5.77 (dd, 17.4, 10.6)
16-a[c]	5.07 (s)	5.08 (s)	1.02 (3H, d, 6.8)	5.07 (s)	5.07 (s)	0.98 (3H, d, 6.9)	1.29[b] (3H, s)	5.32 (s)	1.56 (3H, s)	1.56 (3H, s)		10.19 (s)	4.90 (dd, 17.4, 1.6)
16-b[c]	4.93 (s)	4.94 (s)		5.00 (d, 1.4)	5.00 (s)			5.02 (t, 1.4)					4.88 (dd, 10.6, 1.6)
17	1.94 (3H, s)	1.94 (3H, s)	1.02 (3H, d, 6.8)	1.83 (3H, d, 0.9)	1.84 (3H, s)	0.98 (3H, d, 6.9)	1.30[b] (3H, s)	2.12 (3H, s)	1.56 (3H, s)	1.56 (3H, s)	2.57 (3H, s)	1.82 (3H, d, 1.3)	1.03 (3H, s)
18	1.28 (3H, s)	1.06 (3H, s)	1.27 (3H, s)	1.25 (3H, s)	1.29 (3H, s)	1.25 (3H, s)	1.26 (3H, s)	1.33 (3H, s)	1.33 (3H, s)	1.05 (3H, s)	1.35 (3H, s)	1.31 (3H, s)	1.25 (3H, s)
19										3.86 (d, 10.9) 3.56 (dd, 10.9, 0.8)			
20	0.97 (3H, s)	0.92 (3H, s)	0.94 (3H, s)	1.09 (3H, s)	1.07 (3H, s)	1.06 (3H, s)	1.08 (3H, s)	1.12 (3H, s)	1.11 (3H, s)	1.18 (3H, s)	1.14 (3H, s)	0.79 (3H, s)	0.72 (3H, s)

[a] Multiplicity and coupling constant(s) in Hz for resonances clearly resolved in the ^{1}H NMR spectrum indicated in parentheses. [b] Interchangeable within column. [c] **16-a** *trans* to **17**-Me; **16-b** *cis* to 17-Me.

Table 3. NMR Data Used in Determining the Novel 9(8→7)-*abeo*-Abietane Skeleton of Compound **13**

position	δ_C [b]	δ_H [a]	HMBC correlation from ^{13}C to ^1H	COSY correlation from ^1H to ^1H	NOESY correlation from ^1H to ^1H
1	29.6 (CH_2)	1.30 (α)	0.86	1.84, 1.61, 1.53	1.53
		1.53 (*β*)		1.84, 1.61, 1.30	1.30
2	19.8 (CH_2)	1.61 (α)		2.14, 1.84, 1.53, 1.30, 1.08	1.84
		1.84 (*β*)		2.14, 1.61, 1.53, 1.30, 1.08	1.61, 0.86
3	37.2 (CH_2)	1.08 (α)	1.30	2.14, 1.84, 1.61	2.14
		2.14 (*β*)		1.84, 1.61, 1.08	1.08
4	43.8 (C)		1.30		
5	51.4 (CH)	2.08	0.86, 1.30	2.64, 2.35	2.64, 1.30
6	21.36 (CH_2)	2.64 (α)	3.32	3.32, 2.35, 2.08	3.32, 2.35, 2.08
		2.35 (*β*)		3.32, 2.64, 2.08	3.32, 2.64, 0.86
7	57.5 (CH)	3.32 (dd, 11.0, 4.9)	6.26, 1.65	2.64, 2.35	2.64, 2.35, 0.86
8	200.6 (C)		3.32		
9	83.7 (C)		0.86		
10	49.8 (C)		0.86		
11	33.3 (CH_2)	2.34 (α)		2.83, 2.58, 1.65	
		1.65 (*β*)		2.83, 2.58, 2.34	
12	27.9 (CH_2)	2.58 (α)	6.26	2.83, 2.34, 1.65	2.83
		2.83 (*β*)		2.58, 2.34, 1.65	5.36, 2.58
13	154.5 (C)		6.26, 5.36, 5.20, 1.97, 1.65		
14	129.6 (CH)	6.26 (s)	2.83		1.97
15	145.3 (C)		6.26, 5.36, 1.97		
16-a[c]	117.0 (CH_2)	5.36 (s)	1.97	5.20, 1.97	5.20, 2.83
16-b[c]		5.20 (s)		5.36, 1.97	5.36, 1.97
17	21.39 (CH_3)	1.97 (3H s)	5.36, 5.20		6.26, 5.20
18	28.4 (CH_3)	1.30 (3H s)			2.08
19	182.9 (C)		2.08, 1.30		
20	15.5 (CH_3)	0.86 (3H s)			3.32, 2.35, 1.84

[a] Multiplicity and coupling constants in Hz indicated in parentheses when resolved in 1D NMR. [b] Multiplicity determined from DEPT. [c] **16-a** *trans* to 17-Me; **16-b** *cis* to 17-Me.

of the C-4 epimer of sandaracopimaric acid. NMR data has been published for all three other diastereoisomers at the C-4 and C-13 positions, namely, pimaric acid (4*β*-methyl; 13*β*-vinyl),[21] sandaracopimaric acid (4*β*-methyl; 13α-vinyl),[21,22] and 4-*epi*-pimaric acid (4α-methyl; 13*β*-vinyl).[23] In addition to the above-mentioned diterpenes, *I. angustisepalum* also yielded the benzoyl ester of the linear sesquiterpene geraniol (**15**), which has not been reported previously as a natural product, as well as caryophyllene oxide, *β*-sitosterol, and methoxy eugenol.

The CH_2Cl_2 extract of *I. angustisepalum* consists predominantly of C-19 carboxy abietane diterpenes incorporating either a diene (**1**−**3**), an unsaturated endoperoxide (**4**−**7**), or a fully aromatized system (**8**−**11**) in the C ring. We speculate that the first group may be converted into the latter two groups as a result of autoxidation by molecular oxygen. Thus, direct Diels−Alder-type addition of singlet oxygen to the C ring diene simply accounts for the formation of the 9,13-endoperoxide system, while ene-type reaction with one of the C ring double bonds would generate a doubly allylic hydroperoxide that may then undergo elimination of hydrogen peroxide to generate the aromatic series of compounds (Figure 3).

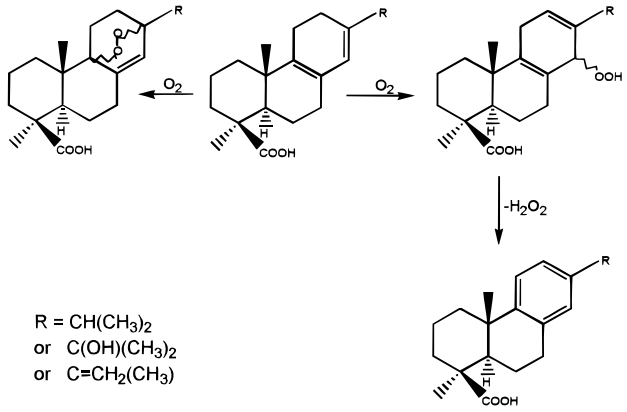


Figure 3. Possible biogenetic relationships among compounds **1**−**11**.

Experimental Section

General Experimental Procedures. Chemical shifts are expressed in parts per million (*δ*) relative to TMS as internal standard. All NMR experiments were run on a Bruker DRX 500 instrument. HSQC, HMBC, and $^1H-^1H$ COSY spectra were recorded with 1024 data points in F_2 and 256 data points in F_1. HRMS were recorded in EI mode at 70 eV on a Finnigan-MAT 95 MS spectrometer. IR spectra were recorded in $CHCl_3$ on a Bio-Rad FT S-7 IR spectrometer. Optical rotations were measured by a Perkin−Elmer 343 polarimeter with polarized light Na 589 nm, and $CHCl_3$ was used as the solvent. Column chromatography was performed using Si gel 60−200 μm (Merck). HPLC separations were performed using a Varaian chromatograph equipped with RI star 9040 and UV 9050 detectors and an Intersil PREP−SIL 20-mm × 25-cm column with a flow rate of 8 mL/min.

Plant Material. *Illicium angustisepalum* was collected from North Lantau Country Park in Hong Kong while in flower in February 1997. A voucher specimen (GDB 97/4) is held at the University of Hong Kong herbarium.

Extraction and Isolation. The sample (1.44 kg) was extracted with CH_2Cl_2 over several days. The organic extract was then dried and evaporated under reduced pressure to yield a pale yellow gum (40.8 g; 2.83% w/w). Compounds **1**−**15** were isolated by column chromatography using hexane and EtOAc (TLC plates used to monitor the column were visualized using *p*-anisaldehyde). In most cases, further purification was

required by HPLC, using EtOAc−hexane. Compound **1** (267.3 mg) (t_R 29.7 min in 1% EtOAc−hexane); **2** (45.7 mg) (t_R 14.5 min in 3% EtOAc−hexane); **3** (16.1 mg) (t_R 15.1 min in 11% EtOAc−hexane); **4** (745.7 mg) (t_R 21.7 min in 15% EtOAc−hexane); **5** (34.7 mg) (t_R 12.6 min in 26% EtOAc−hexane); **6** (66.3 mg) (t_R 14.1 min in 20% EtOAc−hexane); **7** (184.2 mg) (t_R 47.6 min in 20% EtOAc−hexane); **8** (373.5 mg) (t_R 13.6 min in 18% EtOAc−hexane); **9** (71.3 mg) (t_R 40.0 min in 20% EtOAc−hexane); **10** (9.6 mg) (t_R 28.6 min in 35% EtOAc−hexane); **11** (28.3 mg) (t_R 20.3 min in 25% EtOAc−hexane); **12** (69.4 mg) (t_R 19.9 min in 43% EtOAc−hexane); **13** (27.5 mg) (t_R 12.9 min in 43% EtOAc−hexane); **14** (125.1 mg) (t_R 14.3 min in 11% EtOAc−hexane); **15** (110.5 mg, t_R 16.5 min in 1% EtOAc−hexane).

Angustanoic acid A (1): oil; $[\alpha]_D$ +31.1° (*c* 0.56, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 2951, 2930, 2841, 1695, 1603, 1464, 1211 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 300.2076 [M^+, calcd for $C_{20}H_{28}O_2$, 300.2089] (58), 285 (100), 237 (85), 197 (40), 157 (35), 149 (50), 121 (62), 91 (60).

Angustanal (2): oil; $[\alpha]_D$ +6.3° (*c* 0.51, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 2998, 2937, 2872, 1713, 1678, 1231 cm^{-1}.

Epipalustric acid (3): oil; $[\alpha]_D$ +72.2° (*c* 0.69, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 2962, 2936, 2854, 1695, 1458, 1263 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 302.2253 [M^+, calcd for $C_{20}H_{30}O_2$, 302.2246] (50), 287 (100), 241 (20), 185 (15), 149 (10), 121 (10).

Angustanoic acid B (4): oil; $[\alpha]_D$ −44.5° (*c* 2.32, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 3028, 2932, 2856, 1693, 1460, 1232 cm^{-1};^1H and ^{13}C NMR data, see Table 1; HREIMS *m/z* 332.1989 [M^+, calcd for $C_{20}H_{28}O_4$, 332.1988] (2), 300 (100), 285 (72), 239 (15), 148 (18), 99 (33).

Angustanoic acid C (5): oil; $[\alpha]_D$ +20.3° (*c* 1.58, $CHCl_3$); ^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 332.1996 [M^+, calcd for $C_{20}H_{28}O_4$, 332.1988] (5), 316 (10), 315 (30), 300 (100), 285 (80), 248 (40), 147 (45), 131 (45), 109 (50), 105 (60).

4-*epi*-Palustric acid-9α,13α-endoperoxide (6): oil; $[\alpha]_D$ −23.2° (*c* 0.91, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3600−2400 (br), 3028, 2934, 2858, 1697 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 334.2142 [M^+, calcd for $C_{20}H_{30}O_4$, 334.2144] (1), 316 (10), 302 (70), 287 (20), 272 (20), 245 (30), 239 (55), 197 (30), 185 (25), 159 (35), 109 (70), 91 (75).

Angustanoic acid D (7): oil; $[\alpha]_D$ −42.3° (*c* 0.95, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 3576, 3026, 2984, 2943, 2876, 1695, 1464, 1231 cm^{-1};^1H NMR and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 350.2086 [M^+, calcd for $C_{20}H_{30}O_5$, 350.2093] (2), 332 (20), 314 (30), 292 (20), 274 (25), 246 (80), 213 (25), 123 (100).

Angustanoic acid E (8): oil; $[\alpha]_D$ +104.3° (*c* 2.74, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 3033, 2934, 2874, 1697, 1418, 1456, 1267 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 298.1935 [M^+, calcd for $C_{20}H_{26}O_2$, 298.1933] (60), 283 (95), 237 (100), 181 (25).

Angustanoic acid F (9): oil; $[\alpha]_D$ +113.7° (*c* 0.02, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3412, 3400−2600 (br), 3030, 2966, 2936, 2874, 2854, 1697, 1468, 1217, 1148 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 316.2036 [M^+, calcd for $C_{20}H_{28}O_3$, 316.2038] (6), 301 (100), 298 (35), 283 (85), 255 (25), 237 (100), 197 (30), 181 (39), 141 (30).

Angustanol (10): oil; $[\alpha]_D$ +37.0° (*c* 0.73, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3427 (br), 2966, 2937, 2862, 1711, 1458, 1238, 1015 cm^{-1};^1H NMR and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 302.2245 [M^+, calcd for $C_{20}H_{30}O_2$, 302.2246] (18), 287 (100), 269 (50), 175 (18), 141 (15).

Angustanoic acid G (11): oil; $[\alpha]_D$ +44.2° (*c* 1.45, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600, 3028, 2937, 2855, 1695, 1605, 1468, 1273, 1213, 1042 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 300.1726 [M^+, calcd for $C_{19}H_{24}O_3$, 300.1725] (40), 285 (100), 239 (90).

Angustanoic acid H (12): oil; $[\alpha]_D$ +154.7° (*c* 0.81, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 3391 (br), 3026, 2937, 2870, 1695, 1651, 1618, 1460, 1375, 1238, 1167 cm^{-1};^1H and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 332.1986 [M^+, calcd for $C_{20}H_{28}O_4$, 332.1988] (13), 285 (50), 253 (15), 239 (20), 197 (10), 164 (100), 131 (30), 123 (59).

Angustanoic acid I (13): oil; $[\alpha]_D$ +22.1° (*c* 0.72, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 3026, 2930, 2862, 1699, 1643, 1458, 1230, 1213, 1174 cm^{-1};^1H NMR and ^{13}C NMR data, see Table 3; HREIMS *m/z* 348.1932 [M^+, calcd for $C_{20}H_{28}O_5$, 348.1937] (1), 330 (25), 316 (30), 315 (60), 301 (100), 283 (57), 269 (45), 237 (57), 213 (25), 181 (30), 167 (20), 123 (55), 91 (57).

4-*epi*-Sandaracopimaric acid (14): oil; $[\alpha]_D$ +1.9° (*c* 1.03, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400−2600 (br), 2931, 2874, 1693, 1467, 1211 cm^{-1};^1H NMR and ^{13}C NMR data, see Tables 1 and 2; HREIMS *m/z* 302.2250 [M^+, calcd for $C_{20}H_{30}O_2$, 302.2246] (50), 287 (35), 257 (20), 167 (35), 123 (35), 121 (100).

Geraniol Benzoyl Ester (15). ^{13}C NMR data δ ($CDCl_3$) 166.7 (C, C-1′), 142.0 (C, C-3), 132.8 (CH, C-5′), 132.0 (C, C-2′), 131.7 (C, C-7), 129.6 (CH, C3′/7′), 128.3 (CH, C-4′/6′), 123.8 (CH, C-6), 118.5 (CH, C-2), 61.9 (CH_2, C-1), 39.6 (CH_2, C-4), 26.4 (CH_2, C-5), 25.6 (CH_3, C-9), 17.7 (CH_3, C-8); ^1H NMR δ ($CDCl_3$) ppm 8.05 (2H, dd, J = 8.4, 1.1 Hz, H-3′/7′), 7.54 (1H, t, J = 7 Hz, H-5′), 7.43 (2H, dd, J = 8 Hz, H-4′/6′), 5.47 (1H, td, J = 7.0, 1.2 Hz, H-2), 5.09 (1H, m, H-6), 4.82 (2H, d, J = 7.0 Hz, H-1), 1.77 (3H, s, H-10), 1.67 (3H, d, J = 0.6 Hz, H-9), 1.61 (3H, s, H-8).

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