Secoatisane- and Isopimarane-Type Diterpenoids from the Chinese Mangrove *Excoecaria agallocha* L.

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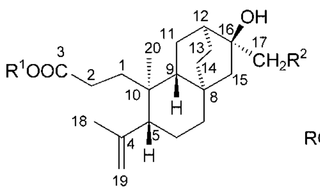
Phytochemical investigations of the stems and leaves of the Chinese mangrove *Excoecaria agallocha* L. yielded one new secoatisane-type diterpenoid, agallochaol C (**1**), three new isopimarane-type diterpenoids, agallochaols D–F (**2**–**4**), along with four known diterpenoids **5**–**8**. The structures of new compounds **1**–**4** were determined on the basis of spectroscopic-data interpretation and chemical evidence.

Introduction. – Agallochaols A and B are *ent*-isopimarane-type diterpenoids that have been isolated recently from the stems and leaves of the Chinese mangrove *Excoecaria agallocha* L. (Eupharbiaceae) [1]. Further chemical investigation of the AcOEt extract of the plant has now furnished four additional new diterpenoids, named agallochaols C–F (**1**–**4**)[1]), along with four known related diterpenoids (**5**–**8**). The details of structure elucidations of **1**–**4** are presented here.

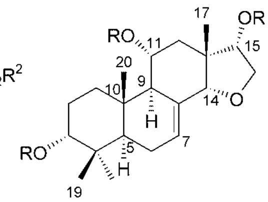
Results and Discussion. – The usual workup [1] of the AcOEt-soluble fraction of the MeOH extract of the stems and leaves of *E. agallocha* L. yielded the new compounds **1** and **2**, and the known compounds **5**–**8**, while new diterpenoids **3** and **4** were obtained as acetate derivatives **3a** and **4a**.

Agallochaol C (**1**) was isolated as a colorless oil, and its molecular formula was established as $C_{20}H_{32}O_4$ on the basis of HR-ESI-MS, which gave a quasi-molecular ion at *m/z* 359.2204 ($[M+Na]^+$). The IR spectrum of **1** showed absorption bands assignable to a OH group (3560 cm^{-1}), a C=O group (1715 cm^{-1}), and a 1,1-disubstituted alkene (1637, 760 cm^{-1}). The presence of carboxy and isopropenyl groups was also evident from the ^1H- and ^{13}C-NMR spectral data (*Tables 1* and *2*). The presence of a carboxylic acid group in **1** was further confirmed by treatment with CH_2N_2 to afford the expected methyl ester **1a**. The positions of the C(3)[1]) carboxy group and an isopropenyl group at C(5) were confirmed by HMBC correlations between the carbonyl C-atom at δ 179.0 and $C(2)H_2$ (δ 2.34, 2.26); between the C(4) methylene (δ 149.5) and the Me(18) group (δ 1.76), H–C(5), and $H_2C(19)$; and between C(5) (δ 52.6) and H–C(9), Me(20), and the isoprenyl Me(18). In addition, other correlations for the quaternary (C(8), C(10), and C(16)) and tertiary C-atoms (C(9), C(12)) were also observed in the HMBC spectrum. The above-mentioned

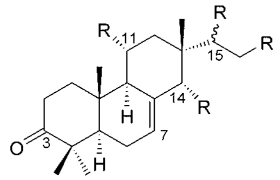
[1]) Trivial numbering.



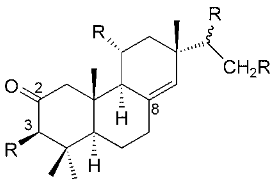
1 R^1 = H, R^2 = OH
1a R^1 = Me, R^2 = OH
5 R^1 = H, R^2 = H



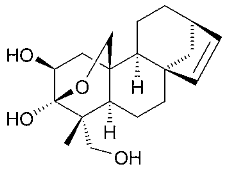
2 R = H
2a R = Ac



3 R = OH
3a R = OAc



4 R = OH
4a R = OAc



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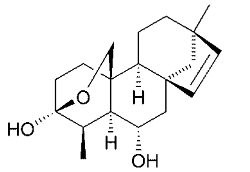

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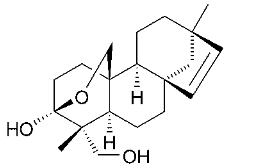

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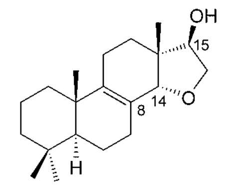

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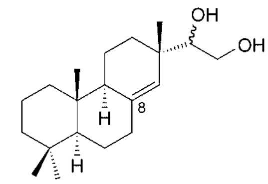

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evidence suggests that **1** has a secoatisane-type structure with a 2-carboxyethyl group at C(10) and an isoproprenyl group at C(5). Comparison of the ^{1}H- and ^{13}C-NMR data revealed strong similarities between **1** and the co-occurring excoecarin V3 (**5**), isolated very recently from the same species of Japanese origin [2]. In fact, **1** differs from **5** only in substitution at C(16) (CH_2OH in **1**, Me in **5**). The CH_2OH group at C(16) was evidenced by the peaks at δ 70.1 in the ^{13}C-NMR spectrum and the typical *AB*-type CH_2 signals at δ 3.49 (*d*, $J = 11.4$) and 3.35 (*d*, $J = 11.4$) in the ^{1}H-NMR spectrum. The absolute configuration of **1** is tentatively assumed to be the same as that of **5** by comparison of optical rotations ($[\alpha]_D = -34$ for **1** and $[\alpha]_D = -53.7$) for **5**) [2]. Consequently, the structure of **1** is reported as (2*R*,3*R*,4a*R*,7*R*,8*R*,8a*R*)-octahydro-3-hydroxy-3-(hydroxymethyl)-8-methyl-7-(1-methylethenyl)-2*H*-2,4a-ethanonaphthalene-8-propanoic acid (= 3-[(1*R*,4*R*,5*R*,6*R*,8*R*,9*R*)-9-hydroxy-9-(hydroxymethyl)-5-methyl-4-(1-methylethenyl)tricyclo[6.2.2.0^{1,6}]dodec-5-yl]propanoic acid).

Agallochaol D (**2**) was isolated as a colorless oil. The positive-ion ESI-MS showed two pseudo-molecular-ion peaks at *m/z* 359 ($[M + Na]^+$), and 695 ($[2M + Na]^+$). The molecular formula $C_{20}H_{32}O_4$ of **2** was deduced from the HR-ESI-MS result of *m/z* 359.2201 ($[M + Na]^+$, calc. 359.2198), indicating five degrees of unsaturation. The structure and relative configuration of agallochaol D (**2**) were elucidated on the basis of

Table 1. *^{1}H-NMR Data of Compounds* **2**, **3a**, *and* **4a**. 400 MHz; δ in ppm. Assignments made by means of ^{1}H,^{1}H-COSY, HMQC, HMBC, and NOESY experiments.

Position[a])	**2**[b])	**3a**[c])	**4a**[c])
$H_α$–C(1)	2.03–2.05 (*m*)	1.67–1.69 (*m*)	2.62 (*d*, *J* = 12.2)
$H_β$–C(1)	1.63–1.66 (*m*)	2.13–2.16 (*m*)	2.16 (*d*, *J* = 12.2)
$H_α$–C(2)	1.50–1.53 (*m*)	2.20–2.22 (*m*)	–
$H_β$–C(2)	1.90–1.92 (*m*)	2.66–2.69 (*m*)	–
$H_α$–C(3)	–	–	4.96 (br. *s*)
$H_β$–C(3)	3.35 (br. *s*)	–	–
$H_α$–C(5)	1.55–1.58 (*m*)	1.52 (*dd*, *J* = 11.8, 4.3)	1.79 (*dd*, *J* = 11.9, 1.5)
$H_α$–C(6)	1.90–1.93 (*m*)	2.00–2.04 (*m*)	1.70–1.73 (*m*)
$H_β$–C(6)	1.90–1.93 (*m*)	2.07–2.09 (*m*)	1.44–1.47 (*m*)
$H_α$–C(7)	–	–	2.10–2.14 (*m*)
$H_β$–C(7)	–	–	2.38–2.42 (*m*)
H–C(7)	5.89 (br. *s*)	6.07 (*m*)	–
$H_α$–(9)	2.08–2.10 (*m*)	2.30–2.34 (*m*)	2.27 (*d*, *J* = 7.4)
$H_β$–C(11)	3.70 (*m*)	5.08 (*m*)	5.09 (*m*)
$H_α$–C(12)	1.66–1.69 (*m*)	1.78–1.81 (*m*)	1.32–1.36 (*m*)
$H_β$–C(12)	1.42–1.45 (*m*)	1.43–1.46 (*m*)	1.86–1.90 (*m*)
H–C(14)	3.62 (br. *s*)	5.05 (br. *s*)	5.36 (br. *s*)
H–C(15)	3.99 (*dd*, *J* = 6.6, 2.4)	5.13 (*dd*, *J* = 9.0, 2.4)	4.99 (*dd*, *J* = 9.0, 2.4)
H_a–C(16)	3.93 (*dd*, *J* = 9.2, 2.4)	4.37 (*dd*, *J* = 11.9, 2.4)	4.29 (*dd*, *J* = 12.1, 2.4)
H_b–C(16)	3.59 (*dd*, *J* = 9.2, 6.6)	3.91 (*dd*, *J* = 11.9, 9.0)	3.96 (*dd*, *J* = 12.1, 9.0)
Me(17)	0.98 (*s*)	0.99 (*s*)	1.04 (*s*)
Me(18)	0.91 (*s*)	1.11 (*s*)	0.83 (*s*)
Me(19)	0.91 (*s*)	1.06 (*s*)	1.11 (*s*)
Me(20)	0.91 (*s*)	1.10 (*s*)	0.83 (*s*)
3-AcO[d])	–	–	2.01 (*s*)
11-AcO[d])	–	1.99 (*s*)	2.01 (*s*)
14-AcO[d])	–	2.01 (*s*)	–
15-AcO[d])	–	2.03 (*s*)	2.09 (*s*)
16-AcO[d])	–	2.05 (*s*)	2.18 (*s*)

[a]) Trivial numbering. [b]) In $CD_3OD/CDCl_3$ 10 : 1; referenced to MeOH (δ(H) 3.30). [c]) In $CDCl_3$; referencing to $CHCl_3$ (δ(H) 7.26). [d]) Assignments may be interchanged.

extensive spectroscopic analyses and a comparison with the known compound (5*β*,14*α*,15*R*)-14,16-epoxypimar-8-en-15-ol (**9**) [3] as (3a*R*,5a*R*,7*R*,9a*S*,9b*S*,10*R*,11a*R*)-1,2,3a,5,5a,6,7,8,9,9a,9b,10,11,11a-tetradecahydro-6,6,9a,11a-tetramethylphenanthro[1,2-*b*]furan-1,7,10-triol (=(3*α*,11*α*,14*α*)-14,16-epoxypimar-7-ene-3,11,15-triol).

Analysis of the ^{13}C-NMR (*Table 2*) and DEPT spectra of **2** indicated that one degree of unsaturation is due to the trisubstituted C=C group with resonances at δ 133.4 (*d*) and 133.8 (*s*). Consequently, the remaining unsaturations are due to the presence of four rings. In addition, the ^{13}C-NMR spectrum showed signals of five O-atom-bearing C-atoms at δ 76.5 (*d*), 68.5 (*d*), 90.1 (*d*), 80.8 (*d*), and 71.6 (*t*). The remaining signals observed between δ 44.3 and 15.0 were attributed to 13 sp^3 C-atoms (4 Me, 4 CH_2, 2 CH, and 3 C). The ^{1}H-NMR spectrum (*Table 1*) shows six downfield signals at δ 5.89–3.35, assigned to olefinic and CH–O/CH_2–O protons, and four tertiary Me signals (δ 0.91, *s*, 3 Me; 0.98, *s*, Me). The *multiplet* integrating for ten protons at δ 2.10–1.45 is due to four CH_2 and two CH groups, as established by HMQC data. The proton signals at δ 3.99 (*dd*, *J* = 6.6, 2.4, 1 H), 3.93 (*dd*, *J* = 9.2, 2.4, 1 H), 3.59 (*dd*, *J* = 9.2, 6.6, 1 H), and 3.62 (*s*, 1 H) indicated the presence of a –OCH–CH_2–O–CH– moiety.

The spectral data of **2** resemble those of model compound **9**, implying an isopimarane-like skeleton [3]. ^{1}H,^{1}H-COSY Experiments allowed us to distinguish the separate spin systems of **2**, revealing connectivities

Table 2. *^{13}C-NMR Data of Compounds* **1**–**5**. 100 MHz; δ in ppm. Assignments made by means of ^{1}H,^{1}H-COSY, HMQC, HMBC, and NOESY experiments.

Position[a])	**1**[b])	**2**[c])	**3**[d])	**4**[d])	**5**[d])
1	35.5 (*t*)	33.8 (*t*)	39.1 (*t*)	51.8 (*t*)	32.8 (*t*)
2	30.1 (*t*)	26.0 (*t*)	34.2 (*t*)	203.2 (*s*)	27.6 (*t*)
3	179.0 (*s*)	76.5 (*d*)	215.2 (*s*)	83.4 (*d*)	177.6 (*s*)
4	149.5 (*s*)	38.0 (*s*)	47.3 (*s*)	43.1 (*s*)	147.5 (*s*)
5	52.6 (*d*)	44.3 (*d*)	50.8 (*d*)	53.5 (*d*)	50.5 (*d*)
6	26.4 (*t*)	24.1 (*t*)	23.3 (*t*)	21.9 (*t*)	24.5 (*t*)
7	40.0 (*t*)	133.4 (*d*)	132.8 (*d*)	35.0 (*t*)	38.0 (*t*)
8	34.5 (*s*)	133.8 (*s*)	130.7 (*s*)	135.5 (*s*)	33.5 (*s*)
9	44.7 (*d*)	55.9 (*d*)	50.2 (*d*)	55.2 (*d*)	42.0 (*d*)
10	41.2 (*s*)	36.7 (*s*)	35.6 (*s*)	44.3 (*s*)	39.4 (*s*)
11	24.5 (*t*)	68.5 (*d*)	68.8 (*d*)	68.1 (*d*)	23.2 (*t*)
12	33.7 (*d*)	37.2 (*t*)	34.2 (*t*)	35.2 (*t*)	37.7 (*d*)
13	24.7 (*t*)	44.1 (*s*)	39.1 (*s*)	38.1 (*s*)	23.8 (*t*)
14	28.7 (*t*)	90.1 (*d*)	75.7 (*d*)	127.0 (*d*)	26.7 (*t*)
15	53.9 (*t*)	80.8 (*d*)	71.8 (*d*)	76.7 (*d*)	56.2 (*t*)
16	75.5 (*s*)	71.6 (*t*)	62.8 (*t*)	63.5 (*t*)	73.3 (*s*)
17	70.1 (*t*)	21.6 (*q*)	15.7 (*q*)	22.9 (*q*)	30.2 (*q*)
18	24.6 (*q*)	29.2 (*q*)	25.1 (*q*)	17.4 (*q*)	23.6 (*q*)
19	114.4 (*t*)	23.7 (*q*)	22.3 (*q*)	28.8 (*q*)	113.2 (*t*)
20	18.9 (*q*)	15.0 (*q*)	14.2 (*q*)	16.0 (*q*)	17.8 (*q*)
3-AcO[e])				21.6 (*q*)	
				170.9 (*s*)	
11-AcO[e])			21.1 (*q*)	20.9 (*q*)	
			170.1 (*s*)	170.6 (*s*)	
14-AcO[e])			20.6 (*q*)		
			169.8 (*s*)		
15-AcO[e])			20.4 (*q*)	20.6 (*q*)	
			169.6 (*s*)	170.2 (*s*)	
16-AcO[e])			21.4 (*q*)	20.8 (*q*)	
			170.5 (*s*)	170.5 (*s*)	

[a]) Trivial numbering. [b]) In CD_3OD; referenced to CD_3OD (δ(C) 49.0). [c]) In $CD_3OD/CDCl_3$ 10:1; referenced to CD_3OD (δ(C) 49.0). [d]) In $CDCl_3$; referenced to $CDCl_3$ (δ(C) 77.0). [e]) Me and C=O signals may be interchanged.

between H–C(3) and CH_2(2), between H–C(11) and CH_2(12), and among H–C(15), H_a–C(16), and H_b–C(16). An isopimarane-like skeleton similar to that of **9** was also suggested by the HMBC data showing the long-range correlations (*Figure*) between H–C(3) and C(1), C(4), and C(5); between Me_2C–(4) and C(3), C(4), and C(5); between H–C(11) and C(12) and C(13); between H–C(7) and C(6), C(9), and C(14); between H–C(14) and C(8), C(13), and C(16); between Me(17) and C(13) and C(16); and between H–C(15) and C(16) and C(17). The molecular framework of **2** was confirmed by NOE correlations (*Figure*). The presence of correlations between H–C(5) and H–C(9) and the absence of correlations between Me(20) and H–C(5) and H–C(9) indicated a *trans,trans* configuration at the C(5)/C(10) and C(9)/C(10) ring junctions. Further, the NOE correlations between H_β–C(3) and Me(19), between H_β–C(11) and Me–(20), between H_β–C(14) and Me–(17), and between H_β–C(15) and Me(17) indicated that all these H-atoms are β-oriented, implying the *trans*-relationship between Me(17) and H–C(9) corresponding to an isopimarane-like skeleton for the molecule.

The high polarity and structural similarity of new compounds **3** and **4**, both polyhydroxylated diterpenes, prevented us from separating them by means of the

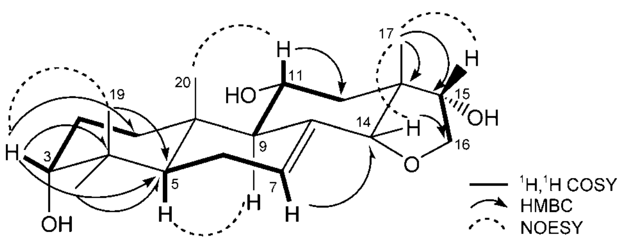

Figure. *Selected key ^{1}H,^{1}H-COSY, HMBC, and NOESY correlations for* **2**. Trivial numbering.

standard isolation procedure. Instead, the crude mixture of **3** and **4** was first acetylated, and the resulting product mixture was subjected to silica-gel column chromatography to afford the pure compounds **3a** and **4a** as the corresponding tetraacetate derivatives.

Compound **3a** was isolated as a colorless oil. The IR spectrum showed absorption bands attributable to ester carbonyl (1735 cm^{-1}), ketone (1700 cm^{-1}), and olefinic (1145, 1009 cm^{-1}) groups. The molecular formula $C_{28}H_{40}O_9$ was determined by HR-ESI-MS on the basis of the quasi-molecular ion peak observed at *m/z* 543 ($[M+Na]^+$) indicating nine degrees of unsaturation. The structure of **3a**, as for **2**, was elucidated on the basis of detailed analysis of 2D-NMR spectra and comparison to those of model compound (5*S*,6*R*,13*S*,14*S*)-9,19-didehydro-5,6,7,8,9,10,11,12,13,14-decahydro-14-hydroxy-5,10 : 13,19-dicycloretinol (**10**) [3]. The ^{1}H-NMR spectrum of **3a** (*Table 1*) showed a signal for an olefinic H-atom (δ 6.07, *m*, 1 H), signals for two oxymethines at δ 5.08 (*m*, 1 H) and δ 5.05 (br. *s*, 1 H), the signals of a $AcOCH_2$ substituent forming an *ABX* system at δ 5.13 (*dd*, $J = 9.0, 2.4$, 1 H), 4.37 (*dd*, $J = 11.9, 2.4$, 1 H) and 3.91 (*dd*, $J = 11.9, 9.0$, 1 H), and four tertiary Me signals (δ 0.99, 1.06, 1.10, 1.11), as well as signals for four Ac groups at δ 1.99, 2.01, 2.03, and 2.05. The ^{13}C-NMR spectrum of **3a** (*Table 2*) shows the presence of 28 C-atoms including four Ac and four ester C=O C-atoms. All of the above data suggests that **3a** is a polyoxygenated isopiramane-type diterpene. The ^{13}C-NMR chemical shift of the C=O C-atom at δ 215.2 (C(3))[1]) and the oxygenated C-atoms at δ 68.8 (C(11)), 75.7 (C(14)), 71.8 (C(15)), 62.8 (C(16)) as well as other C-atoms and ^{1}H-NMR data (*Table 1*) were found to be consistent with the structure **3a** proposed for the molecule. The ^{13}C-NMR assignments were made by comparison of HMQC and ^{1}H,^{1}H-COSY data with those of the co-occurring compound **2**, the triacetate derivative of **2** (**2a**), and the model compound **10** [4]. The proposed locations of the functional groups are supported by the HMBC data. For example, C(3) shows correlation with CH_2(2), Me(18), and Me(19), H–C(7) shows correlations with C(5), C(6), C(9) and C(14), H–C(11) shows correlations with C(9), C(12) and C(13), and H–C(14) shows correlations with C(8), C(13), C(15), and C(17).

Finally, the relative configuration of **3a**, deduced to be the same as that of **2** by means of a NOESY experiment, indicates that **2** could possibly be the biogenetic precursor of **3**. Thus, compound **3a** was identified as (4a*S*,4b*S*,5*R*,7*S*,8*R*,10a*S*)-5,8-bis(acetyloxy)-7-[(1*S*)-1,2-bis(acetyloxy)ethyl]-3,4,4a,4b,5,6,7,8,10,10a-decahydro-1,1,4a,7-tetramethylphenanthren-2(1*H*)-one (=(5*S*,6*S*,10*S*,11*R*,13*S*,14*S*,19*R*)-*O*^{15}-acetyl-11,14,19-tris(acetyloxy)-2-oxo-5,6,7,10,11,12,13,14-octahydro-5,10 : 13,19-dicycloretinol).

The molecular formula, $C_{28}H_{40}O_9$, of compound **4a**, also obtained as a colorless oil, was identical to that of **3a**, as deduced by ESI-MS (*m/z* 543, ($[M+Na]^+$)). The ^{1}H- and ^{13}C-NMR spectra of **4a** were very similar to those of **3a** (*Tables 1* and *2*). The presence of a C=O group, a 1,2-diacetoxyethyl sidechain, two secondary AcO groups and a trisubstituted C=C group on the tricyclic isopimarane-like skeleton were obvious. Nevertheless, the spectroscopic properties of **4a** were somewhat different from those of **3a**. Detailed analysis of ^{1}H,^{1}H-COSY, HMQC, HMBC, and NOESY spectra allowed us to place the keto group at C(2)[1]), a β-AcO group at C(3), and C=C at C−8(14), whereas the remainder of the molecule is the same as **3a**. Thus, the structure of agallochaol F acetate (**4a**) is reported as (2*R*,4a*S*,4b*R*,5*S*,7*S*,10a*S*)-2,5-bis(acetyloxy)-7-[(1*S*)-1,2-bis(acetyloxy)ethyl]-1,4,4a,4b,5,6,7,9,10,10a-decahydro-1,1,4a,7-tetramethylphenanthren-3(2*H*)-one (=(2*R*,5*S*,6*S*,10*R*,11*S*,13*S*,14*S*)-*O*[15]-acetyl-2,11,14-tris(acetyloxy)-3-oxo-9,19-didehydro-5,6,7,8,9,10,11,12,13,14-decahydro-5,10:13,19-dicycloretinol).

Compounds **5**–**8** were characterized as excoecarin V3 (=3-[(1*S*,4*R*,5*S*,6*S*,8*R*,9*R*,10*S*)-9-hydroxy-5,10-dimethyl-4-(1-methylethenyl)tricyclo[6.2.2.0^{1,6}]dodec-5-yl]-propanoic acid; **5**) [2], excoecarin V1 (=(1*S*,2*R*,5*R*,8*S*,11*S*,12*S*,13*R*,17*S*)-12-(hydroxymethyl)-12-methyl-14-oxapentacyclo[11.2.2.1^{5,8}.0^{1,11}.0^{2,8}]octadec-6-ene-13,17-diol; **6**) [2], (3β,20-epoxy-3α,6α-dihydroxy-18-norbeyer-15-ene (=(1*S*,2*R*,5*R*,8*R*,10*R*,11*R*,12*R*,13*S*)-5,12-dimethyl-14-oxapentacyclo[11.2.2.1^{5,8}.0^{1,11}.0^{2,8}]octadec-6-ene-10,13-diol; **7**) [5], and excoecarin D (=(1*R*,2*R*,8*S*,11*R*,12*S*,13*S*)-12-(hydroxymethyl)-14-oxapentacyclo[11.2.2.1^{5,8}.0^{1,11}.0^{2,8}]octadec-6-en-13-ol; **8**) [6], by comparing their spectroscopic data with those reported in the literature.

Experimental Part

General. Column chromatography (CC): silica gel (*Qing Dao Hai Yang Chemical Group Co.*; 100–200 and 200–300 mesh); TLC: precoated silica-gel plates (*Yan Tai Zi Fu Chemical Group Co.*; *G60 F-254*). Optical rotation: *Perkin-Elmer 341* polarimeter. IR Spectra: *Nicolet Magna FT-IR 750* spectrometer; KBr pellets; ν_{max} in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker DRX-400* (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer; chemical shifts δ in ppm, with the residual $CHCl_3$ (δ(H) 7.26, δ(C) 77.0) or CD_3OD (δ(H) 3.30, δ(C) 49.0) as internal standards; coupling constants *J* in Hz; assignments supported by ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments. ESI-MS and HR-ESI-MS: *Q-TOF Micro LC-MS-MS* spectrometer in *m/z*.

Plant Material. Specimens were collected in Guangxi Province, China, in 1999, and identified as *E. agallocha* L. by Prof. *Jin-Gui Shen* of the Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences. A voucher specimen (No. 99PL-05) is available for inspection at the Institute of Materia Medica, SIBS-CAS.

Extraction and Isolation. Dried ground stems and leaves (4.0 kg) of *E. agallocha* L. were extracted with MeOH (3 × 5 l). The MeOH extract was concentrated *in vacuo* to give a residue (410 g), which was dissolved in H_2O (1000 ml), and the soln. was partitioned consecutively between H_2O and petroleum ether, H_2O and AcOEt, H_2O and BuOH. The AcOEt extract was evaporated *in vacuo* to give a residue (100 g), which was separated by CC (100–200 mesh, 1.5 kg; petroleum ether/AcOEt 90:10, 80:20, 70:30, 60:40, and 50:50, followed by Me_2CO). The eluted material was combined to yield 16 fractions on the basis of TLC evidence. *Fractions 10* and *13* were further purified by CC on silica gel ($CHCl_3$,MeOH), then on *Sephadex LH-20* (100% MeOH), yielding, in order of polarity, pure **2** (15 mg), **1** (12 mg), **5** (14 mg), **6** (12 mg), **7** (25 mg), **8** (28 mg), and a mixture of **3** and **4** (40 mg). This mixture was treated with Ac_2O/pyridine, then the reaction products were separated by CC (petroleum ether/AcOEt) to yield pure **3a** (7.2 mg) and **4a** (20 mg).

*Agallochaol C (=(2*R*,3*R*,4a*R*,7*R*,8*R*,8a*R*)-Octahydro-3-hydroxy-3-(hydroxymethyl)-8-methyl-7-(1-methylethenyl)-2*H*-2,4a-ethanonaphthalene-8-propanoic acid=3-[(1*R*,4*R*,5*R*,6*R*,8*R*,9*R*)-9-Hydroxy-9-(hydroxymethyl)-5-methyl-4-(1-methylethenyl)tricyclo[6.2.2.0^{1,6}]dodec-5-yl]propanoic Acid*; **1**). Colorless oil. $[\alpha]_D^{20}=-34.0$ ($c=0.50$, $CHCl_3$). IR: 3560, 3001, 1715, 1637, 1220, 760, 666. ^{1}H-NMR (CD_3OD)[1]): 0.82–0.85 (*m*, H_β–C(14)); 0.99 (*s*, Me(20)); 1.06 (*dd*, *J*=13.7, 2.7, H_a–C(15)); 1.16 (*d*, *J*=13.7, H_b–C(15)); 1.20–1.24 (*m*, H_β–C(7)); 1.20–1.24 (*m*, H_β–C(11)); 1.27–1.30 (*m*, H_β–C(6)); 1.27–1.30 (*m*, H_α–C(6)); 1.44–1.47 (*m*, H–C(9)); 1.44–1.47 (*m*, H_β–C(13)); 1.48–1.52 (*m*, H_a–C(1)); 1.63 (*m*, H_b–C(1)); 1.64–1.67 (*m*, H_α–C(13)); 1.76 (*s*, Me(18)); 1.80–1.83 (*m*, H_α–C(6)); 1.80–1.83 (*m*, H–C(12)); 1.92–1.96 (*m*, H_α–C(14)); 1.98–2.02 (*m*, H–C(5)); 1.98–2.02 (*m*, H_α–C(11)); 2.24–2.27 (*m*, H_a–C(2)); 2.34 (*m*, H_b–C(2)); 3.35 (*d*, *J*=11.4, H_a–C(17)); 3.49 (*d*, *J*=11.4, H_b–C(17)); 4.86 (br. *s*, H_a–C(19)); 4.92 (br. *s*, H_b–C(19)). ^{13}C-NMR (CD_3OD, 100 MHz): see Table 2. ESI-MS: 359 ([*M*+Na]$^+$), 695 ([2*M*+Na]$^+$), 335 ([*M*−H]$^+$), 671 ([2*M*−H]$^+$). HR-ESI-MS: 359.2204 ($C_{20}H_{32}O_4Na^+$; calc. 359.2207).

*Methyl (2*R*,3*R*,4a*R*,7*R*,8*R*,8a*R*)-Octahydro-3-hydroxy-3-(hydroxymethyl)-8-methyl-7-(1-methylethenyl)-2*H*-2,4a-ethanonaphthalene-8-propanoate (= Methyl 3-[(1*R*,4*R*,5*R*,6*R*,8*R*,9*R*)-9-Hydroxy-9-(hydroxymethyl)-5-methyl-4-(1-methylethenyl)tricyclo[6.2.2.0^{1,6}]dodec-5-yl]propanoate*; **1a**). Methylation of **1** (2.0 mg) by treatment with excess CH_2N_2 at r.t. yielded **1a** (1.8 mg). Colorless oil. ^{1}H-NMR ($CDCl_3$)[1]): 0.96 (*s*, Me(20)); 1.74 (br. *s*, Me(18)); 2.23 – 2.26 (*m*, H_a–C(2)); 2.35 – 2.38 (*m*, H_b–C(2)); 3.43 (*dd*, *J* = 11.0, 4.1, H_a–C(17)); 3.56 (*dd*, *J* = 11.0, 4.1, H_b–C(17)); 3.65 (br. *s*, MeO); 4.67 (br. *s*, H_a–C(19)); 4.86 (br. *s*, H_b–C(19)). ESI-MS: 373 ([*M* + Na]$^+$), 723 ([2*M* + Na]$^+$).

*Agallochaol D (= 3a*R*,5a*R*,7*R*,9a*S*,9b*R*,10*R*,11a*R*)-1,2,3a,5,5a,6,7,8,9,9a,9b,10,11,11a-Tetradecahydro-6,6,9a,11a-tetramethylphenanthro[1,2-*b*]furan-1,7,10-triol = (3α,11α,14α)-14,16-Epoxypimar-7-ene-3,11,15-triol*; **2**). Colorless oil. $[\alpha]^{20}_D = +28.0$ (*c* = 0.79, MeOH/$CHCl_3$ 4 : 1). IR: 3408, 2927, 1630, 1460, 1385, 1066, 1020, 906, 827. ^{1}H-NMR: see *Table 1*. ^{13}C-NMR: see *Table 2*. ESI-MS: 359 ([*M* + Na]$^+$), 695 ([2*M* + Na]$^+$). HR-ESI-MS: 359.2201 ($C_{20}H_{32}O_4Na^+$; calc. 359.2198).

*(3a*R*,5a*R*,7*R*,9a*S*,9b*R*,10*R*,11a*S*)-1,2,3a,5,5a,6,7,8,9,9a,9b,10,11,11a-Tetradecahydro-6,6,9a,11a-tetramethylphenanthro[1,2-*b*]furan-1,7,10-triol Triacetate (= (3α,11α,14α)-14,16-Epoxypimar-7-ene-3,11,15-triyl triacetate*; **2a**). Acetylation of **2** (1.5 mg) by treatment with Ac_2O/pyridine 1 : 1 (3 ml) at r.t. for 48 h yielded **2a** (1.4 mg). White powder. ^{1}H-NMR ($CDCl_3$): 6.04 (*m*, H–C(7)); 4.96 (*m*, H_β–C(11)); 4.92 (*dd*, *J* = 8.2, 6.7, H_β–C(15)); 4.64 (br. *s*, H_β–C(3)); 4.21 (*dd*, *J* = 9.6, 8.2, H_α–C(16)); 3.71 (br. *s*, H_β–C(14)); 3.63 (*dd*, *J* = 9.6, 6.7, H_β–C(16)); 2.07, 2.06, 2.05 (3*s*, 3 Ac); 1.09, 0.99, 0.89, 0.86 (3*s*, 4 Me). ESI-MS: 485 ([*M* + Na]$^+$).

*Agallochaol E Tetraacetate (= (4a*S*,4b*S*,5*R*,7*S*,8*R*,10a*S*)-5,8-Bis(acetyloxy)-7-[(1*S*)-1,2-bis(acetyloxy)ethyl]-3,4,4a,4b,5,6,7,8,10,10a-decahydro-1,1,4a,7-tetramethylphenanthren-2(1*H*)-one = (5*S*,6*S*,10*S*,11*R*,13*S*,14*S*,19*R*)-O^{15}-Acetyl-11,14,19-tris(acetyloxy)-2-oxo-5,6,7,10,11,12,13,14-octahydro-5,10 : 13,19-dicycloretinol*; **3a**). Colorless oil. $[\alpha]^{20}_D = +54$ (*c* = 0.70, $CHCl_3$). IR: 2974, 1735, 1700, 1433, 1369, 1145, 1009, 980, 602. ^{1}H-NMR ($CDCl_3$): see *Table 1*. ^{13}C-NMR ($CDCl_3$): see *Table 2*. ESI-MS: 543 ([*M* + Na]$^+$). HR-ESI-MS: 543.2214 ($C_{20}H_{32}O_4Na^+$; calc. 543.2218).

*Agallochaol F Tetraacetate (= (2*R*,4a*S*,4b*R*,5*S*,7*S*,10a*S*)-2,5-Bis(acetyloxy)-7-[(1*S*)-1,2-bis(acetyloxy)ethyl]-1,4,4a,4b,5,6,7,9,10,10a-decahydro-1,1,4a,7-tetramethylphenanthren-3(2*H*)-one = (2*R*,5*S*,6*S*,10*R*,11*S*,13*S*,14*S*)-O^{15}-Acetyl-2,11,14-tris(acetyloxy)-3-oxo-9,19-didehydro-5,6,7,8,9,10,11,12,13,14-decahydro-5,10 : 13,19-dicycloretinol*; **4a**). Colorless oil. $[\alpha]^{20}_D = -21$ (*c* = 0.76, $CHCl_3$). IR: 2974, 1741, 1705, 1437, 1371, 1238, 1045, 960, 754. ^{1}H-NMR ($CDCl_3$): see *Table 1*. ^{13}C-NMR ($CDCl_3$): see *Table 2*. ESI-MS: 543 ([*M* + Na]$^+$).

This research is financially supported by the *National Science Foundation for Outstanding Chinese Youth* (No. 30125044), National 863 project (2003AA624030 and 2005AA624040).

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Received December 15, 2004