Three New *ent*-Labdane Diterpenoids from the Wood of *Excoecaria agallocha* LINN.

by **Ponnapalli Mangala Gowri***[a]), **Sri Vedavyasa Srirangaraja Radhakrishnan Bhattar**[a]), **Poreddy Guruva Reddy**[a]), **Yerraballi Rakesh**[a]), **Shaik Jeelani Basha**[b]), **AkellaVenkata Subrahmanya Sarma**[b]), and **Janaswamy Madhusudana Rao**[a])

[a]) Natural Products Laboratory, Indian Institute of Chemical Technology, 500007 Hyderabad, India (phone: +91-40-27191735; fax: +91-40-27160512; e-mail: mangala@iict.res.in)

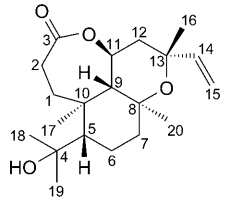
[b]) NMR Division, Indian Institute of Chemical Technology, 500007 Hyderabad, India

An extensive study of metabolites present in *Excoecaria agallocha* LINN. led to the isolation of three new *ent*-labdane-type diterpenoids, named agallochaexcoerins A–C (**1**–**3**), besides three known compounds. The skeleton present in compound **1** is rather unusual, containing of a seven-membered lactone. The structures were elucidated on the basis of spectroscopic studies and comparison with known related compounds. The isolated compounds **1**–**6** were not active against Raw 264.7 (macrophage-like), K 562 (leukemia), and COLO 205 (colon) human carcinoma cell lines.

Introduction. – The wide-spread genus *Excoecaria* of Euphorbiaceae comprises 40 species which are distributed on seashores, edge mangroves throughout tropical countries including Africa, Asia, Northwest Australia, and India [1]. It is well known that the milky latex exuded from the bark of this plant is poisonous and may cause temporary blindness and blistering of the skin [2]. In traditional Thai medicine, the bark and wood of the plant are used to combat flatulence. Several skin irritant daphnane and tigliane diterpene esters have been isolated from the latex of *E. agallocha* [3][4]. Recently, a new phorbol ester acting as an *anti*-HIV agent, was isolated from the stems and leaves of this species collected in Northwest Australia [5]. Furthermore, the *anti*-tumor activities of some of these diterpenes were investigated [6][7]. More recently, a series of diterpenoid derivatives with different kinds of carbon skeletons, such as labdane, beyerane, isopimarane, and kaurane types, were isolated from this plant [6][8–11]. We report herein the structure determination of three new diterpenoids, agallochaexcoerin A, a novel *seco*-labdanoid with a rare seven-membered lactone ring, and agallochaexcoerins B and C through spectral data and also by chemical correlation.

Results and Discussion. – The analysis of an acetone extract of the powdered wood of *E. agallocha* led to the isolation of three new *ent*-labdane diterpenoids **1**–**3**. Three known compounds were also identified by comparison of their spectral data with those reported in the literature as ribenone **4** [12], *ent*-8,13-epoxy-11α-hydroxy-3-oxo-13-*epi*-labd-14-ene **5** [12], and octacosyl (*E*)-ferulate **6** [13].

Compound **1** was obtained as colorless needles. The HR-ESI-MS of **1** exhibited the *pseudo*-molecular-ion peak at *m*/*z* 359.2183 ($[M+Na]^+$), which established the



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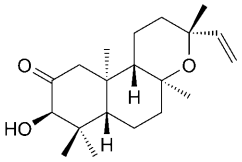

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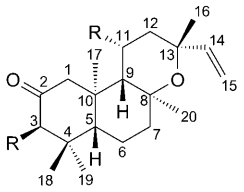

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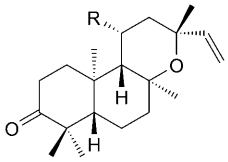
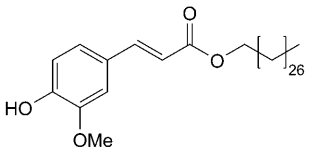
3a R = OAc



4 R = H
5 R = OH



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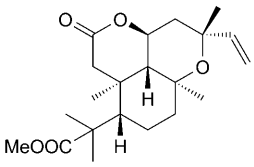

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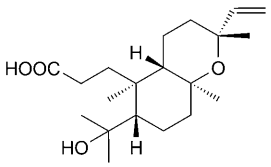

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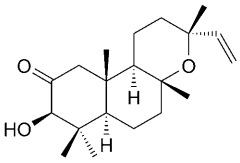

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molecular formula as $C_{20}H_{32}O_4$, indicating five degrees of unsaturation. The IR spectrum showed absorption bands ascribable to OH (3377 cm^{-1}), vinyl (1625, 949, 921 cm^{-1}), CO (1722, 1290 cm^{-1}), and ether (1136 cm^{-1}) functionalities. It was recognized as a new 13-*epi*-8,13-epoxy-*seco*-labdanoid by interpretation of the ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*). The presence of a vinyl group was evident from the spectra. The presence of five Me groups (*Tables 1* and *2*) of an intact labdane skeleton suggested that it might be a ring *A*-*seco*-derivative. The appearance of signals for geminal Me(18) and Me(19)[1]), deshielded at δ(H) 1.34 and 1.27, suggested the presence of tertiary OH group at C(4), *i.e.*, a 3,4-*seco*-labdanoid with the possibility of C(3) being part of an acid or a lactone. The location of the tertiary OH group at C(4) was also supported by the HMBC correlation between C(4) (δ(C) 75.8) and Me(18), Me(19), and H–C(5). The ^{13}C-NMR spectrum showed two O-bearing C-atoms with signals at δ(C) 72.9 (*s*) and at 72.1 (*s*) accounting for C(8) and C(13) of a 13-*epi*-manoyloxy partial structure [14], and two more O-bearing C-atoms with signals at δ(C) 70.9 (*d*) and at 75.8 (*s*). Compound **1** didn't react with diazomethane, suggesting the presence of a lactone, rather than of a carboxylic acid. The lactone could, therefore, be between C(3) and C(11), or C(3) and C(6). If the O-bearing CH group was at C(6), the ^{13}C-NMR signal for C(7) would be expected around δ(C) 50–53. However, if the O-bearing CH group was at C(11), the signal for C(12) would be around δ(C) 40–45. The

[1]) Arbitrary numbering. For systematic names, see *Exper. Part.*

Table 1. *^{1}H-NMR Data of* **1**, **2**, **3**, *and* **3a**

	1[1])[a])	**2**[a])	**3**[b])	**3a**[b])
1α	1.52–1.62 (*m*)	2.10 (*d*, *J* = 12.2)	2.40 (*d*, *J* = 12.9)	2.48 (*d*, *J* = 13.9)
1β	3.04 (*dd*, *J* = 8.0, 13.2)	2.47 (*d*, *J* = 12.2)	3.23 (*d*, *J* = 12.9)	–
2α	2.47 (*dd*, *J* = 7.3, 13.2)	–	–	–
2β	2.76 (*t*, *J* = 13.2)	–	–	–
3		3.88 (br. *d*, *J* = 1.0)	3.91 (*d*, *J* = 3.6)	4.93 (br. *s*)
5	1.38–1.43 (*m*)	1.62[e])	1.68 (*dd*, *J* = 2.6, 13.3)	–
6α	1.65–1.72 (*m*)	1.81[d])	1.81 (*qd*, *J* = 3.4, 13.3)	–
6β	1.43–1.49 (*m*)	1.40–1.44 (*m*)	1.42 (*dq*, *J* = 3.0, 13.3)	–
7α	1.43–1.49 (*m*)	1.56[e])	1.54 (*dt*, *J* = 3.4, 13.3)	–
7β	1.81 (*dd*, *J* = 3.6, 9.5)	1.92 (*td*, *J* = 3.4, 12.5)	1.86 (*td*, *J* = 3.4, 13.3)	–
9	1.96 (*d*, *J* = 8.0)	1.64[c])	1.60 (*d*, *J* = 9.4)	–
11α	4.76 (*dd*, *J* = 7.3)	1.45–1.51 (*m*)	–	–
11β	–	1.56[e])	4.16 (*td*, *J* = 4.6, 9.4)	5.18–5.22 (*m*)
12α	2.05 (*d*, *J* = 15.4)	1.67 (*dd*, *J* = 6.4, 8.5)	–	–
12β	2.39 (*dd*, *J* = 6.6, 15.4)	1.81[d])	2.46 (*dd*, *J* = 4.6, 13.5)	2.40 (*d*, *J* = 13.9)
14	5.88 (*dd*, *J* = 10.7, 17.3)	5.87 (*dd*, *J* = 10.7, 17.3)	5.97 (*dd*, *J* = 12.9, 10.9)	5.90 (*dd*, *J* = 10.8, 17.5)
15a	5.18 (*dd*, *J* = 1.3, 17.3)	4.94 (*dd*, *J* = 1.5, 10.7)	4.96 (*d*, *J* = 11.1)	4.98 (*d*, *J* = 11.2)
15b	4.97 (*dd*, *J* = 1.3, 10.7)	5.16 (*dd*, *J* = 1.5, 17.3)	5.07 (*d*, *J* = 17.7)	5.23 (*d*, *J* = 17.9)
16	1.42 (*s*)	1.30 (*s*)	1.25 (*s*)	1.27 (*s*)
17	1.19 (*s*)	0.77 (br. *s*)	0.88 (*s*)	0.86 (*s*)
18	1.34 (*s*)	1.18 (*s*)	1.19 (*s*)	1.11 (*s*)
19	1.27 (*s*)	0.69 (*s*)	0.68 (*s*)	0.82 (*s*)
20	1.24 (*s*)	1.30 (*s*)	1.23 (*s*)	1.25 (*s*)
OH	–	3.43 (br. *s*)	3.48 (*d*, *J* = 4.9)	–

[a]) Measured at 500 MHz. [b]) Measured at 600 MHz. [c]), [d]), [e]) Overlapping signals.

C-atoms C(7) and C(12) appeared at δ(C) 42.9 (*t*) and 37.6 (*t*), respectively, to support a lactone bridge between C(3) and C(11). The CO group at δ(C) 175.9 (*s*) showed HMBC correlations with H–C(11), H–C(1), and H–C(2), supporting the presence of a seven-membered lactone ring between C(3) and C(11). The lactone was found to be a secondary lactone with the O-bearing CH group resonating at δ(C) 70.9 (*d*) and the corresponding CH group at δ(H) 4.76 (*dd*, *J* = 7.3) (coupling with H–C(9) and one of the vicinal H-atoms at C(12); the other H-atom at C(12) did presumably not show a coupling due to a dihedral angle of *ca.* 90°, with ring *C* in a *quasi*-chair form). A literature survey revealed that the first member of a 2,3-*seco*-labdanoid with δ-lactone between C(2) and C(11), agallochin N (**7**), has recently been reported from the same species of Indian origin [9]. The axial disposition of the O-bearing CH group at C(11) was comparable to agallochin N with an ^{1}H-NMR signal for the a 11β-oxymethine group at δ(H) 4.63 (*td*, *J* = 12.0, 4.0), while the corresponding signals for 13-*epi*-manoyloxide derivatives containing an 11α-OH group were noticed at 4.18 [14], 4.13 [15], and 4.17 ppm [12]. This is in accordance with the fact that an equatorial H-atom in a tetrahydropyran ring is more deshielded than its axial counterpart, as described in [16].

Agallochaexcoerin A thus appears to be the first example of a *seco*-tricyclic labdanoid containing a rare seven-membered lactone group between C(3) and C(11)[1]).

Table 2. *^{13}C-NMR Spectral Data of* **1**, **2**, **3**, *and* **3a**

	1[1])[a])	**2**[a])	**3**[b])	**3a**[b])
CH_2(1)	39.1	52.1	54.6	54.5
CH_2(2)	29.7	210.9	211.8	203.7
C(3)	175.9	82.9	82.3	83.7
C(4)	75.8	45.2	44.8	42.7
H–C(5)	58.3	54.4	54.4	55.2
CH_2(6)	23.6	19.6	19.3	19.3
CH_2(7)	42.9	42.6	42.7	42.9
C(8)	72.9	74.6	76.5	75.7
H–C(9)	56.7	55.3	62.2	59.1
C(10)	41.5	43.1	43.8	39.7
H–C(11) or CH_2(11)	70.9	15.6	64.9	67.7
CH_2(12)	37.6	35.5	44.9	39.4
C(13)	72.1	73.5	74.1	73.6
H–C(14)	146.8	147.5	147.2	146.4
CH_2(15)	110.9	110.6	110.2	111.1
Me(16)	29.5	28.3	31.9	31.9
Me(17)	16.7	16.3	16.2	17.1
Me(18)	34.9	29.3	29.4	28.9
Me(19)	27.8	16.2	17.3	17.2
Me(20)	25.8	24.9	25.1	25.6
MeO–*C*O–C(3)				170.5
*Me*O–CO–C(3)				20.6
MeO–*C*O–C(11)				170.1
*Me*O–CO–C(11)				21.7

[a]) Measured at 100 MHz. [b]) Measured at 150 MHz.

The ^{13}C-NMR spectral data of agallochaexcoerin A can be compared with a 3,4-*seco*-labdanoid (**8**), which was isolated from the same species, as well as synthesized from ribenone with *m*-CPBA in 7.6% yield along with (*R*)- and (*S*)-epoxides (20 and 25%, resp.) [17]. Unlike in **1**, compound **8** doesn't possess a OH group at C(11), and therefore no lactone between C(3) and C(11).

Agallochin N [9], agallochin E (8,13-epoxy-3-nor-2,3-*seco*-13-*epi*-labden-2,4-olide) [8], 2-oxo-3-oxamanoyl oxide [18], excoecarin H [7], *ent*-13-*epi*-8,13-epoxy-2-oxa-3-oxolabd-14-ene-(1*R*)-carboxylic acid [10], and excoecarin M [19] with each containing a δ-lactone moiety, were reported from the same species. The NOESY correlations of H–C(5) and H–C(9), Me(17) and Me(20), H–C(14) and Me(20), and H–C(11) and Me(20) established the relative configuration. Agallochaexcoerin A was considered as an *ent*-derivative in view of its laevo specific rotation [10][20] to derive its structure as *ent*-8,13-epoxy-4-hydroxy-3,4-*seco*-13-*epi*-labd-14-en-3,11-olide.

Compound **2** was isolated as colorless needles from aqueous EtOH. ESI-MS of **2** exhibited a *pseudo*-molecular-ion peak at *m*/*z* 355 ($[M+Cl]^+$), ascribable to a molecular formula $C_{20}H_{32}O_3$. The presence of OH (3440 cm^{-1}), CO (1714 cm^{-1}), mono-substituted C=C bond (1660, 1451, 1014, 918 cm^{-1}), and ether (1160 cm^{-1}) functionalities were noticed in the IR spectrum. A preliminary analysis of the ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*) suggested it to be a new 8,13-epoxy-13-*epi*-

labdane diterpenoid. The presence of a vinyl and a keto group were evident from the spectra. The ^{13}C-NMR spectrum showed an O-bearing C-atom at δ(C) 82.9 (*d*), the CO group at δ(C) 210.9 accounted for the 2-keto group in addition to two O-bearing C-atoms at 74.6 (*s*), 73.5 (*s*), accounting for the 8,13-epoxymanoyloxy structure [8]. The presence of an isolated CH_2 group in α-position to a keto group was indicated by an *AB* system at δ(H) 2.10 and 2.47. The Me(18) and Me(19) attached to C(4) with resonances at δ(H) 1.18 and 0.69, respectively, indicated the presence of an α-ketol system when compared to the signals of those of 2-oxomanoyl oxide (δ(H) 0.87 and 1.08) [21]. The location of the keto CO group at C(2) was also supported by HMBC (*Table 3* and *Fig. 1*) data, where the C(2) showed correlation with H_{ax}–C(1), H_{eq}–C(1), H_{ax}–C(3), Me(18), and Me(19). The NOESY correlations between H–C(5) and H–C(9), Me(17) and Me(20), H–C(14) and Me(20), and H–C(6) and Me(20) established the relative configuration of **2**, as shown in *Fig. 2*. It was related to the *epi*-manoyl oxide skeleton by the correlations found in the ^{1}H,^{1}H-NOESY data (*Table 3* and *Fig. 2*). A search in the literature revealed that the isomeric manoyl oxide **9** has been isolated before from the plant *Lagarostrobos colensoi* (*Dacrydium colensoi*) [21] and *Euphorbia segetalis* [22]. A comparative study of **2** and **9** revealed that they have identical ^{1}H- and ^{13}C-NMR spectra, just like manoyl oxide and 13-*epi*-manoyl oxide, but that they differ in their physical properties, such as m.p. and CD. The circular dichroism (CD) spectrum of **2** showed a negative *Cotton* effect at 299 nm, analogous to that of **4**. The absolute configuration of **2** was assumed to be that of an *ent*-derivative in the light of its laevo specific rotation. An inspection of the vast literature [23] revealed

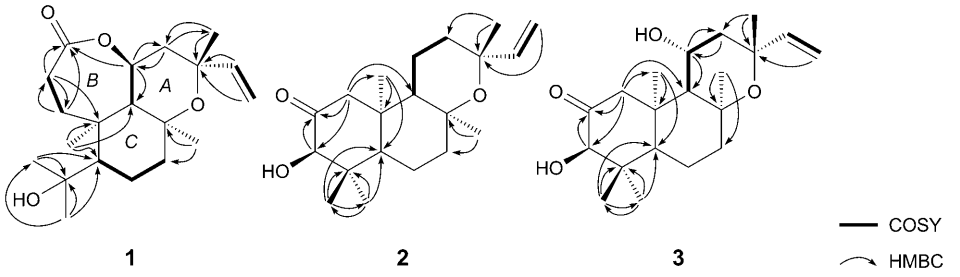

Fig. 1. *Key HMBC and COSY correlations of agallochaexcoecarins A, B, and C* (**1**–**3**)

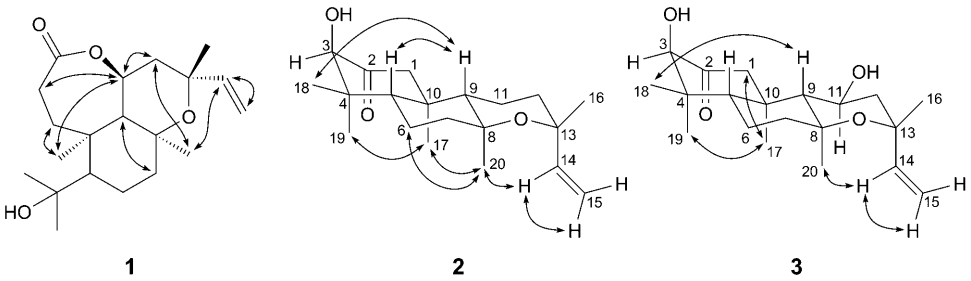

Fig. 2. *NOESY Correlations of agallochaexcoecarins A, B, and C* (**1**–**3**)

Table 3. *HMBC, COSY, and NOESY Correlations of Compounds* **1**, **2**, *and* **3**

	1[1])				**2**				**3**		
	HMBC	COSY	NOESY		HMBC	COSY	NOESY		HMBC	COSY	NOESY
1α	3, 17	1β, 2β	17	1α	2, 9, 10, 17	1β	–	1α	2, 3, 10, 17	1β	17
1β	2, 3, 9, 10	1α, 2α	–	1β	2, 3, 5, 10, 17	1α	19	1β	2, 9, 10, 17	1α	–
2α	3, 10	1β, 2β	11α, 17	3α	2, 4, 18, 19	–	1α, 12α, 18	3α	2, 4, 18, 19	–	18
2β	1, 3, 10	1α, 2α	–	5β	–	–	–	5β	4, 17, 19	6β	–
5α	4	6	9α	6α	–	–	9α	6α	–	6β	–
6α	–	7	–	6β	–	–	–	6β	–	6α	–
6β	–	7	–	7α	–	7β	–	7α	–	7β	–
7α	–	6	9α	7β	–	7α	–	7β	–	7α	–
7β	–	–	–	9β	–	–	–	9β	8, 10, 11, 17, 20	–	–
9α	8, 10, 11, 17, 20	11α	5α, 7α	11α	–	–	5α	11β	–	12α	12α, 17, 20
11α	3, 10, 12, 13	12β, 9α	2β, 12β, 17, 20	11β	–	–	–	12α	9, 11, 13	11β, 12β	11β
12α	9, 11, 16	12β, 11α	–	12α	–	11α, 12β	–	12β	11, 13	12α	20
12β	13, 14, 16	12α	11α, 20	12β	–	12α	–	14	–	15a, 15b	15a, 20
14	13	15a, 15b	15a, 20	14	–	15a, 15b	15a, 20	15a	13, 14	14, 15b	14
15a	13, 14	14, 15b	–	15a	–	14, 15b	14	15b	13	14, 15a	–
15b	13	14, 15a	–	15b	–	14, 15a	–	16	12, 13	–	–
16	12, 13, 14	–	–	16	12, 13, 14	–	–	17	1, 5, 9, 10	–	1α, 11β
17	1, 5, 9, 10	–	1β, 2β, 11β, 20	17	1, 5, 9, 10	–	–	18	3, 4, 5, 19	–	3α
18	4, 5, 19	–	–	18	2, 3, 4, 5, 19	–	–	19	3, 4, 5, 18	–	–
19	4, 5, 18	–	–	19	2, 3, 4, 5, 18	–	–	20	7, 8, 9	–	11β, 12β
20	7, 8, 9	–	11, 12β, 14, 17	20	7, 8, 9	–	–				

that *ent*-labdanes are laevo-rotatory, while labdanes are dextro-rotatory [24]. Therefore, the absolute configuration of agallochaexcoerin B was tentatively fixed as *ent*-8,13-epoxy-3β-hydroxy-13-*epi*-labd-14-en-2-one.

Compound **3** was obtained as colorless needles. The ESI-MS of **3** displayed a *pseudo*-molecular-ion peak at *m*/*z* 359 ($[M+Na]^+$), corresponding to a molecular formula of $C_{20}H_{32}O_4$. The IR spectrum of **3** revealed the presence of OH (3443 cm^{-1}), CO (1716 cm^{-1}), olefinic (1661, 1453, 1114, 919 cm^{-1}), and ether (1160 cm^{-1}) groups. On acetylation with pyridine and acetic anhydride, **3** gave a diacetate **3a**. The molecular formula $C_{24}H_{36}O_6$ of **3a** was deduced from *quasi*-molecular-ion peak, at *m*/*z* 443.2407 ($[M+Na]^+$) in the HR-ESI-MS. The IR spectrum of **3a** showed acetate (1735, 1225 cm^{-1}) and ether (1125 cm^{-1}) moieties, but no OH absorption, suggesting that **3** has two acylable OH groups but no free tertiary OH group, which might be present as an ether.

The ^{1}H-NMR spectrum of **3** was similar to that of **2**, except for the presence of an extra signal for an O-bearing CH group at δ(H) 4.16, and three Me *singlet*s at δ(H) 1.25, 1.23, and 0.88, which were shifted upfield by 0.05, 0.07, and downfield by 0.11 ppm, respectively, compared with the corresponding Me signals of **2**. Comparison of the ^{13}C-NMR spectra (*Table 2*) of **3** and **2** suggested that the OH group was located at the C(11), based on the substitution effects at the respective α and β positions. The configuration at C(11) in **3** was assigned from the ^{1}H,^{1}H coupling constant and ^{13}C chemical shifts. The signal of H–C(11) at δ(H) 4.16 (*dt*, $J = 4.6, 9.4$) was identical to the corresponding signal for *ent*-11α-hydroxy-3-oxo-13-*epi*-manoyl oxide [12]. Further, the corresponding signal in the diacetate at δ(H) 5.18–5.22 (*m*), was deshielded. A *trans*-diaxial relationship between the two H-atoms H–C(9) and H–C(11) was assumed, based on the coupling constant between these two H-atoms. Therefore, the orientation of the OH group at C(11) was presumed to be equatorial. The relative configuration was deduced by the NOESY spectrum (*Fig. 2*, *Table 3*). The absolute configuration of **3** was considered as an *ent*-derivative in view of its laevo-specific rotation to derive the structure as *ent*-3β,11α-dihydroxy-2-oxo-13-*epi*-manoyl oxide. The CD spectrum of **3** showed a negative *Cotton* effect at 288 nm analogous to that of **4**. Therefore, the absolute configuration of **3** was tentatively fixed as *ent*-8,13-epoxy-3β,11α-dihydroxy-13-*epi*-labd-14-en-2-one.

In cytotoxic studies, compounds **1**–**6** were tested against human carcinoma cell lines using the MTT (=(3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. However, none of the compounds showed statistically significant cytotoxicity ($IC_{50} > 50$ μg/ml) for the cell lines tested.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 100–200 or 230–400 mesh, *Acme*). Analytical TLC: Silica gel *60 F254* plates (0.25 mm, *Merck*). M.p.: *Fischer–John micro* melting point apparatus; uncorrected. Optical rotations: *Horiba DIP-370* digital polarimeter. CD Spectra: *Jasco J-810* spectrometer. IR Spectra: *Thermo Nicolet Nexus 670* spectrometer; with KBr pellets. ^{1}H-NMR (300, 500, and 600 MHz) and ^{13}C-NMR (75, 100, and 150 MHz) spectra: *Bruker Avance-300*, *Varian INOVA-400*, *Varian INOVA-500*, or *Bruker Avance-600* spectrometer in $CDCl_3$ with TMS as internal standard; coupling constants (*J*) in Hz. MS: *JEOL MS-BU 20* or a *JEOL LMS-SX-120A QQ* mass spectrometer.

Plant Material. The wood of *Excoecaria agallocha* (1.5 kg) was collected from Visakhapatnam coast (latitude 17° 42′ 0″ N, longitude 83° 18′ 0″ E), Andhra Pradesh, India in August 2007, and was identified by Assoc. Prof. Dr. *Venkiah*, Dept. of Botany, Andhra University, Visakhapatnam. A voucher specimen (IIC-101) has been deposited with the Herbarium of the Indian Institute of Chemical Technology.

Extraction and Isolation. The chopped resinous wood (1.2 kg) was exhaustively extracted three times with acetone in a *Soxhlet* apparatus (3 × 5 l). Removal of the solvent from the combined acetone extracts gave a brown syrup (25 g). A portion (22 g) of this brown syrup was subjected to CC over SiO_2 using solvent mixtures of increasing polarity from hexane through acetone to yield several fractions. *Fr. 5* (500 mg) was chromatographed on SiO_2 with 5% acetone to afford ribenone (**4**; 10 mg), 6% acetone to afford agallochaexcoerin C (**3**; 6 mg), and 7% acetone to afford octacosyl (*E*)-ferulate (**6**; 5 mg). *Fr. 10* (100 mg) was subjected to SiO_2 CC using 10% acetone to afford *ent*-11α-hydroxy-3-oxo-13-*epi*-manoyl oxide (**5**; 3 mg), 12% acetone to afford agallochaexcoerin B (**2**; 5 mg), and 14% acetone to afford agallochaexcoerin A (**1**; 10 mg).

Agallochaexcoerin A (=*(2*R,*3a*S,*7a*R,*8*S,*10a*S,*10b*R*)-2-Ethenyldecahydro-8-(2-hydroxypropan-2-yl)-2,7a,10a-trimethyloxepino[2,3,4-*de*]chromen-5(2*H*)-one*; **1**). Colorless needles. M.p. 106–108°. $[\alpha]_D^{27} = -32.0$ ($c = 1.0$, $CHCl_3$). UV (EtOH): 230 (4.03), 320 (4.05). IR (KBr): 3377, 1722, 1625, 1290, 1136, 949, 921. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 359.2183 ($[M+Na]^+$, $C_{20}H_{32}NaO_4^+$; calc. 359.2192).

Agallochaexcoerin B (=*(3*R,*4a*S,*6a*S,*8*R,*10a*R,*10b*S*)-3-Ethenyldodecahydro-8-hydroxy-3,4a,7,7,10a-pentamethyl-9*H*-benzo[*f*]chromen-9-one*; **2**). Colorless needles. M.p. 72–74°. $[\alpha]_D^{27} = -59.9$ ($c = 1.0$, $CHCl_3$). CD (2×10^{-4}, MeOH): 0 (325), -0.47×10^{-4} (299), 0 (243). IR (KBr): 3440, 1660, 1451, 1160, 1014, 918. ^{1}H- and ^{13}C-NMR spectra: *Tables 1* and *2*. ESI-MS: 355 ($[M+Cl]^+$).

Agallochaexcoerin C (=*(1*R,*3*R,*4a*S,*6a*S,*8*R,*10a*R,*10b*R*)-3-Ethenyldodecahydro-1,8-dihydroxy-3,4a,7,7,10a-pentamethyl-9*H*-benzo[*f*]chromen-9-one*; **3**). Colorless needles. M.p. 128–130°. $[\alpha]_D^{27} = -69.9$ ($c = 1.0$, $CHCl_3$). CD (2×10^{-4}, MeOH): 0 (329), -0.45×10^{-4} (288), 0 (239). IR (KBr): 3443, 1716, 1661, 1453, 1160, 1114, 919. ^{1}H- and ^{13}C-NMR spectra: *Tables 1* and *2*. ESI-MS: 359 ($[M+Na]^+$).

3β,11α-Diacetoxyagallochaexcoerin C (=*(1*R,*3*R,*4a*S,*6a*S,*8*R,*10a*R,*10b*R*)-3-Ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-9-oxo-1*H*-benzo[*f*]chromene-1,8-diyl Diacetate*; **3a**). Colorless needles. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 443.2407 ($[M+Na]^+$, $C_{24}H_{36}NaO_4^+$; calc. 443.2409).

Ribenone (=*(3*R,*4a*S,*6a*S,*10a*R,*10b*S*)-3-Ethenyldecahydro-3,4a,7,7,10a-pentamethyl-1*H*-benzo[*f*]-chromen-8(4a*H*)-one*; **4**). White needles. M.p. 109–110°. $[\alpha]_D^{27} = -53.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2941, 2858, 1705, 1458, 1383, 1082, 1007. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS: 327 ($[M+Na]^+$).

ent-*11α-Hydroxy-3-oxo-13*-epi-*manoyl Oxide* (=*(1*R,*3*R,*4a*S,*6a*S,*10a*R,*10b*R*)-3-Ethenyldecahydro-1-hydroxy-3,4a,7,7,10a-pentamethyl-1*H*-benzo[*f*]chromen-8(4a*H*)-one*; **5**). Colorless needles. M.p. 114–116°. $[\alpha]_D^{27} = -59.2$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3450, 1699, 1677, 1412, 1130, 960, 912. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS: 321 ($[M+Na]^+$).

*Octacosyl (*E*)-Ferulate* (=*Octacosyl (2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate*; **6**). White needles. M.p. 78–80°. IR (KBr): 3325, 2941, 2858, 1742, 1625, 1383, 1225, 1082, 1007. ESI-MS: 587 ($[M+H]^+$).

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