ent-Kaurane and Beyerane Diterpenoids from *Excoecaria agallocha*[1]

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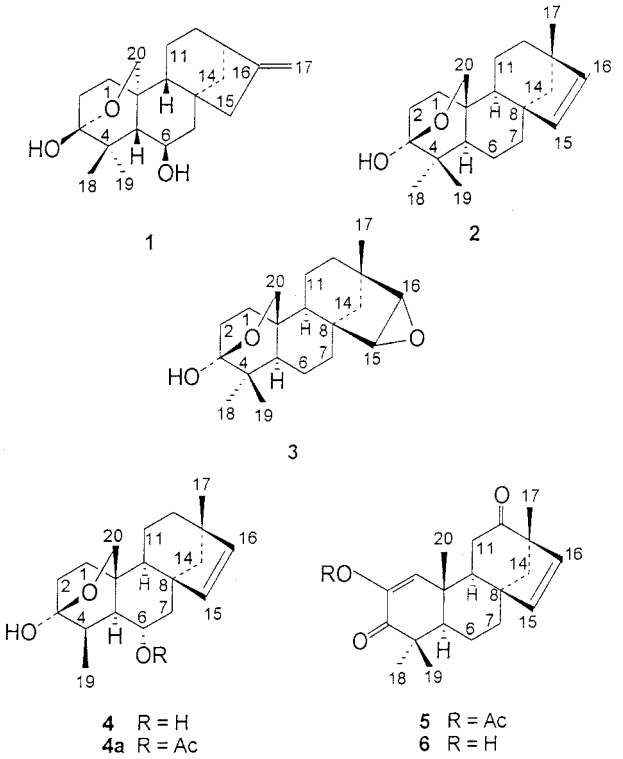
The roots of *Excoecaria agallocha* yielded four new diterpenoids, *ent*-3β,20-epoxy-3α,6α-dihydroxykaur-16-ene (agallochin F) (**1**), 3β,20-epoxy-3α-hydroxybeyer-15-ene (agallochin G) (**2**), 3β,20:15*R*,16*S*-diepoxy-3α-beyeranol (agallochin H) (**3**), and 3β,20-epoxy-3α,6α-dihydroxy-18-nor-beyer-15-ene (agallochin I) (**4**), along with three known derivatives, 2-acetoxy-1,15-beyeradiene-3,12-dione (**5**), 2-hydroxy-1,15-beyeradiene-3,12-dione (**6**), and *ent*-kauran-16β-ol-3-one. The structures of **1**−**4** were determined by spectroscopic (NMR and MS) data interpretation.

Agallochins A−E and six known diterpenoids[2] were recently reported from the hexane extract of the roots of the Indian mangrove plant *Excoecaria agallocha* L. (Euphorbiaceae). Further extraction of the roots with CH_3OH−CH_2Cl_2 has furnished four additional new diterpenoids, agallochins F−I (**1**−**4**), along with 2-acetoxy-1,15-beyeradiene-3,12-dione (**5**), 2-hydroxy-1,15-beyeradiene-3,12-dione (**6**), and *ent*-kauran-16β-ol-3-one. Compound **5** has now been reported for the first time from the nature, while it was reported earlier as a derivative of **6**. The details of the structure elucidation of **1**−**4** are presented here.



Agallochin F (**1**) analyzed for $C_{20}H_{30}O_3$ by elemental analysis, consistent with the molecular ion at *m*/*z* 318 in its EIMS. Its IR spectrum indicated hydroxyl and exocyclic methylene groups. The ^{1}H NMR spectrum showed two tertiary methyls at δ 1.20 and 1.26, two exocyclic methylene protons at δ 4.81 and 4.76 (each, s), two hydroxymethylene protons at δ 3.82 and 4.25 (each, d, J = 8.7 Hz), and a hydroxymethine proton at δ 3.97 (td, J = 11, 4 Hz). The ^{13}C NMR spectrum showed 20 carbon signals, which were analyzed as two methyls, nine methylenes, four methines, and five quaternary carbons from its DEPT spectrum. The chemical shifts of the respective carbons were assigned on the basis of HMQC and ^{1}H−^{1}H COSY data and in comparison with values reported for the related compound *ent*-3α,7β,14α-trihydroxy-3β,20-epoxykaur-16-en-15-one.[3] The two signals at δ 104.0 and 153.8 and the two oxygenated carbons at δ 69.2 (C-20) and 98.7 (C-3) accounted for exocyclic methylene and hemiketal functionalities in the molecule. The third oxygenated carbon at δ 67.4 (d, C-6) accounted for the secondary hydroxyl at C-6, as in any other position the respective carbon would appear at a lower field,[4,5] whose configuration was fixed as equatorial from the coupling constants (J = 11, 4 Hz) of H-6.

The HMBC correlations (see Supporting Information) observed between C-3 (δ 98.7, s) and H_3-18, H_3-19, H_2-20, and H_2-2, C-20 (δ 69.2, t) and H-5, H_2-1, and H-9, C-6 (δ 67.4, d) and H-5 and H_2-7 and the NOESY correlations observed (cf. experimental) between H-9β and H-7β, and H-5β and H-7β, showing a *cis* relationship between H-5 and H-9 and between H_2-20 methylene protons and H-14 indicating their proximity in space are in support of the structure, 3,20-epoxy-3,6-dihydroxykaur-16-en (**1**), for agallochin F. The absolute configuration of agallochin F was taken as *ent*-kaurane in view of its levo specific rotation as noticed for several *ent*-kauranes[6] to establish its structure as *ent*-3β,20-epoxy-3α,6α-dihydroxykaur-16-ene (**1**).

Agallochin G (**2**), mp 152−154 °C, analyzed for $C_{20}H_{30}O_2$ by elemental analysis, consistent with the molecular ion at *m*/*z* 302 in its EIMS. Its IR spectrum indicated hydroxyl and symmetrically disubstituted alkene. Its ^{1}H NMR and ^{13}C NMR spectra are reminiscent of a beyerane diterpenoid,[7] showing the characteristic 15-H and 16-H at δ 5.46, 5.59 (each, d, J = 6 Hz) with the corresponding olefinic carbons at δ 133.1 (d, C-15) and 137.2 (d, C-16), respectively. The two oxygenated carbons at δ 98.2 (s) and 67.4 (t) accounted for the hemiketal carbons (C-3) and C-20, respectively, as in **1** to suggest the structure of agallochin G as **2**.

The HMBC correlations (see Supporting Information) observed between C-3 (δ 98.0) and H_2-2, H_2-1, H_3-18, H_3-19, and H_2-20, C-20 (δ 67.4) and H_2-1, H-5, and H-9, C-16 (δ 137.2) and H-15, H_2-14, H_2-12, and H_3-17, and C-15 (δ 133.1) and H_2-14, H-9, and H_2-7 and the NOESY correlations (cf. experimental) between H_3-18 and H-5, H-5 and

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H-9, and H-9 and H-1, showing their mutual *cis* relationship, and between H_2-20 and H-15 showing *cis* orientation of H_2-20 and ring D are consistent with structure **2**. The absolute configuration of agallochin G was taken as beyerane in view of its levo specific rotation, as noticed for all beyeranes, versus dextro rotation for *ent*-beyeranes[6] to derive its structure as 3β,20-epoxy-3α-hydroxybeyer-15-ene (**2**).

Agallochin H (**3**), mp 164−66 °C, analyzed for $C_{20}H_{30}O_3$ by elemental analysis consistent with the molecular ion at *m*/*z* 318 in its EIMS. The ^{1}H NMR and ^{13}C NMR spectra of **3** were found to be very similar to those of **2** except for the replacement of two olefinic protons H-15 and H-16 by two epoxy protons, each as a doublet (J = 4.0 Hz) at δ 3.00 and 3.15, and the olefinic carbons C-15 and C-16 by epoxy carbons at δ 55.2 (d) and 59.6 (d), respectively, as documented for the related compounds[7,8] to suggest its structure as **3**. The location of the functional groups in agallochin H could be supported from the HMBC correlations (see Supporting Information) observed between C-3 (δ 98.2) and H_2-2, H_2-1, H_3-18, H_3-19, H_2-20, and H-5, C-20 (δ 67.8) and H_2-1, H-5, and H-9, C-15 (δ 55.2) and H_2-7, H_2-14, H-16, and H-9, and C-16 (δ 59.6) and H-15, H_2-14, H_3-17, and H_2-12. The relative and absolute configuration of agallochin H was taken as that of beyerane in view of its levo specific rotation[6] to establish its structure as 3β,20:15*R*,16*S*-diepoxy-3α-beyeranol (**3**).

Agallochin I (**4**), colorless oil, analyzed for $C_{19}H_{28}O_3$ by elemental analysis, consistent with the molecular ion at *m*/*z* 305 $[M^+ + H]^+$ in its positive FABMS. Its IR spectrum showed chelated hydroxyl and *cis* olefin groups. A preliminary examination of its ^{1}H and ^{13}C NMR spectral data revealed that it might be a new nor-beyerene diterpenoid. The appearance of only one tertiary methyl at δ 1.00 (3H) instead of four of a beyerane and the presence of a secondary methyl at δ 1.10 (3H, d, J = 6.3 Hz) indicated that it might be a 18-nor- or 19-nor-beyerene diterpenoid. The signal at δ 3.80 (m) accounted for three protons, which might include two of an oxymethylene and one of a hydroxymethine. Agallochin I on acetylation gave a monoaceate, $C_{21}H_{30}O_4$, (+) ve FABMS *m*/*z* 347 $[M^+ + H]^+$, where the hydroxymethine proton in **4** separated from the oxymethylene protons and appeared at δ 5.10 (1H, td, J = 11.5, 5.0 Hz) in support of the presence of a secondary hydroxyl. The coupling constants of the acetoxy methine proton and by inference that of the hydroxymethine proton suggested its axial orientation, with the acetate or hydroxyl being equatorial.

The ^{13}C NMR spectrum showed 19 carbons, which were analyzed as two methyls, seven methylenes, six methines, and four quaternary carbons. The oxygenated carbons at δ 68.5 (t, C-20) and 98.3 (s, C-3) confirmed the hemiketal linkage. The C-18 and C-19 carbons appear at ≅ δ 28.0 and 18.0, respectively, in agallochins F−H (**1**−**3**). But in agallochin I the secondary methyl carbon came at δ 19.3, suggesting that it is 18-nor-diterpenoid. The third oxygenated carbon appeared at δ 69.5 (d), a value close to the C-6 or C-11 carbons with a hydroxyl.[4,5] The hydroxyl was located at C-6 from the HMBC correlations (see Supporting Information) observed between C-6 (δ 69.5) and H-4, H-5, and H_2-7. The other HMBC correlations in support of the structure are those between C-3 (98.3) and H_2-2, H_2-1, H_3-19, and H-4 and C-20 (δ 68.5) and H-5 and H-9. The NOESY correlations (cf. Experimental Section) observed between H-5 and H-9, H-1 and H-9, and H_2-20 and H-15 established the relative stereochemistry of the beyerene diterpeniod skeleton. The absolute configuration of agallochin I was taken as for beyerane in view of its levo specific rotation as noticed for all beyeranes[6] to derive its structure as 3β,20-epoxy-3α,6α-dihydroxy-18-nor-beyer-15-ene (**4**).

Compound **5**, mp 136−138 °C, analyzed for $C_{22}H_{28}O_4$ by elemental analysis and the molecular ion at *m*/*z* 356 in its EIMS. A comparison of its physical and spectral characteristics (mp, IR, UV, $[\alpha]^{25}_D$, and ^{1}H NMR) with those of 2-acetoxy-1,15-beyeradiene-3,12-dione (**5**) proved their identity. This is the first report of its natural occurrence, although it was reported earlier as a derivative of the enol, 2-hydroxy-1,15-beyeradiene-3,12-dione (**6**), isolated from the plant *Androstachys johnsonii* Prain.[9] However, its ^{13}C NMR as well as 2-D NMR data were not reported earlier and hence are presented here (see Experimental Section). It is of interest to note that the chemical shift values of the olefinic carbons C-15 (138.8) and C-16 (137.4) are as in the related compounds[10] and those of C-1 and C-2 in **5** (δ 140.6, 143.2) are in agreement with the corresponding values in orthosiphol D[11] with an acetoxyl at C-2 and not with the values in 1-en-3-one derivatives (δ 150, 120)[12,13] and 1-en-2-hydroxy-3-one derivatives (δ 126 and ≅ 143 ppm) as in orthosiphol E.[11]

Compound **6** analyzed for $C_{20}H_{26}O_3$ by elemental analysis and the molecular ion at *m*/*z* 314 in its EIMS. Its physical characteristics (mp, $[\alpha]^{25}_D$) and spectral (IR, UV, ^{1}H NMR) data were identical with those reported for 2-hydroxy-1,-15-beyeradiene-3,12-dione (**6**) isolated from *A. johonsonii*.[9] Its ^{13}C NMR data were not, however, reported, and the same are presented in the Experimental Section.

Experimental Section

General Experimental Procedures. Melting points were determined on a VEB-Analytic Dreader HMK hot plate and are uncorrected. Optical rotations were determined on a Roudalph Autopol-III polarimeter. IR spectra were recorded on a Perkin-Elmer-841 IR spectrometer in $CHCl_3$ solution. UV spectra were recorded on a Milton Roy Spectronic 1201 spectrometer in $CHCl_3$. ^{1}H NMR spectra were measured on Bruker Advance DRX 300 and JEOL JNM EX-90 spectrometers. ^{13}C NMR spectra were measured on a Bruker Advance DRX 300 spectrometer at 75 MHz and JEOL JNM EX-90 spectrometer at 22.5 MHz using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. Mass spectra were obtained on a JEOL JMS-300 spectrometer. Elemental analyses were determined on a Carlo Erba 1108 instrument.

Plant Material. The roots of *Excoecaria agallocha* L. were collected from Corangi Mangrove forest near Bhiravapalem in the Godavari Estuary (16° 58′ N latitude and 82° 15′ E longitude) in March 1998 and were identified by Prof. B. Kondala Rao, Department of Marine Living Sources, Andhra University, Visakhapatnam. A voucher specimen (code: AU1/160) was deposited at the Marine Museum of the School of Chemistry, Andhra University, and the National Institute of Oceanography, Goa.

Extraction and Isolation. The air-dried and powdered plant material (4 kg) was extracted exhaustively with *n*-hexane. Removal of the solvent from the combined *n*-hexane extracts under reduced pressure gave a residue (35 g). The plant material was next extracted repeatedly with CH_2Cl_2−MeOH (1:1). Removal of solvent from the combined CH_2Cl_2−MeOH extracts gave a residue (60 g), which was extracted with EtOAc (500 mL × 3). Removal of solvent from the EtOAc extract under reduced pressure gave a residue (40 g). This residue was subjected to column chromatography over silica gel (Acme brand, 100−200 mesh, 350 g) using solvents of increasing polarity from *n*-hexane through EtOAc.

The residue from the respective column fractions on further purification by passage over silica gel or silver nitrate (20%) impregnated silica gel columns furnished compound F (**1**), 30 mg (fractions 46−65, *n*-hexanes−EtOAc, 4:1); compound G (**2**),

35 mg (fractions 66−71, *n*-hexanes−EtOAc, 4:1); compound H (**3**), 25 mg (fractions 80−92, *n*-hexanes−EtOAc, 3:2); compound I (**4**), 40 mg (fractions 138−147, *n*-hexanes−EtOAc, 2.5:2.5); compound **5**, 60 mg (fractions 80−92, *n*-hexanes−EtOAc, 7:3); compound **6**, 70 mg (fractions 100−128, *n*-hexanes−EtOAc, 3:2), and *ent*-kauran-16*β*-ol-3-one, 25 mg (fractions 73−77, *n*-hexanes−EtOAc, 3.5:1.5).

***ent*-3*β*,20-Epoxy-3α,6α-dihydroxykaur-16-ene (agallochin F) (1):** colorless oil; $[\alpha]^{25}_D$ −21.6° (*c* 1.2, $CHCl_3$); IR (Nujol) ν_{max} 3450, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *δ* 2.20 (1H, m, H-1α), 1.20 (1H, m, H-1*β*), 2.18 (1H, m, H-2α), 1.72 (1H, m, H-2*β*), 1.20 (1H, m, H-5), 3.97 (1H, dt, *J* = 11.0, 4.0 Hz, H-6α), 1.68 (1H, m, H-7α), 1.48 (1H, m, H-7*β*), 1.19 (1H, m, H-9), 1.70 (1H, m, H-11α), 1.50 (1H, m, H-11*β*), 1.22 (1H, m, H-12α), 1.50 (1H, m, H-12*β*), 2.62 (1H, m, H-13), 1.23 (1H, m, H-14α), 1.45 (1H, m, H-14*β*), 1.50 (1H, m, H-15α), 2.10 (1H, m, H-15*β*), 4.81 (1H, s, H-17), 4.76 (1H, s, H-17), 1.20 (3H, s, H_3-18), 1.26 (3H, s, H_3-19), 3.82 (1H, d, *J* = 8.0, 7.0 Hz, H-20), 4.25 (1H, d, *J* = 8.0, 7.0 Hz, H-20); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 35.7 (t, C-1), 29.3 (t, C-2), 98.7 (s, C-3), 40.7 (s, C-4), 56.4 (d, C-5), 67.4 (d, C-6), 48.5 (t, C-7), 43.9 (s, C-8), 49.2 (d, C-9), 38.8 (s, C-10), 18.5 (t, C-11), 32.8 (t, C-12), 43.2 (d, C-13), 40.1 (t, C-14), 47.9 (t, C-15), 153.8 (s, C-16), 104.0 (t, C-17), 28.5 (q, C-18), 17.5 (q, C-19), 69.2 (t, C-20); partial correlations observed in the $^1H-^1H$ COSY spectrum, H-1α with H-1*β* and H-2α; H-2*β* with H-1α; H-6*β* with H-7α, H-7*β*, and H-5; H-13 with H-12α, H-12*β*, and H-14α; H-17 with H-13; H_3-20 with H-1α; partial correlations observed in the $^1H-^1H$ NOESY spectrum, H-9*β* with H-7*β*, H-5*β* with H-7*β*, H-5*β* with H-9*β*, H_2-20 with H-14, H-9*β*, and H-15*β*; EIMS *m*/*z* 318 $[M]^+$, 300, 243, 182, 132, 104, 85; *anal*. C 75.22%, H 9.23%, calcd for $C_{20}H_{30}O_3$, C 75.47%, H 9.43%.

3*β*,20-Epoxy-3α-hydroxybeyer-15-ene (agallochin G) (2): colorless needles (MeOH); mp 152−54 °C; $[\alpha]^{25}_D$ −59.2° (*c* 1.9, $CHCl_3$); IR (Nujol) ν_{max} 3450, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *δ* 1.18 (1H, m, H-1α), 2.12 (1H, m, H-1*β*), 1.72 (1H, m, H-2α), 2.12 (1H, m, H-2*β*), 1.24 (1H, d, *J* = 5.0 Hz, H-5), 1.64 (1H, m, H-6α), 1.08 (1H, m, H-6*β*), 1.28 (1H, m, H-7α), 1.62 (1H, m, H-7*β*), 1.08 (1H, m, H-9), 1.63 (1H, m, H-11α), 1.49 (1H, m, H-11*β*), 1.24 (1H, m, H-12α), 1.68 (1H, m, H-12*β*), 1.02 (1H, m, H-14α), 1.47 (1H, m, H-14*β*), 5.59 (1H, d, *J* = 6.0 Hz, H-15), 5.46 (1H, d, *J* = 6.0 Hz, H-16), 1.00 (3H, s, H_3-17), 1.02 (3H, s, H_3-18), 0.96 (3H, s, H_3-19), 3.82 (2H, ABq, *J* = 8.0, 7.0 Hz, H_2-20); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 32.5 (t, C-1), 29.4 (t, C-2), 98.2 (s, C-3), 40.2 (s, C-4), 51.4 (d, C-5), 21.0 (t, C-6), 35.7 (t, C-7), 48.5 (s, C-8), 45.8 (d, C-9), 35.3 (s, C-10), 21.7 (t, C-11), 32.5 (t, C-12), 43.8 (s, C-13), 60.2 (t, C-14), 133.1 (d, C-15), 137.2 (d, C-16), 24.6 (q, C-17), 27.9 (q, C-18), 18.0 (q, C-19), 67.4 (t, C-20); partial correlations observed in the $^1H-^1H$ COSY spectrum, H-1α with H-1*β* and H-2α; H-2*β* with H-1*β*; H-6*β* with H-7*β*; H-11*β* with H-12*β*; H-11α with H-9; H-15 with H-16 and H_2-20; partial correlations observed in the $^1H-^1H$ NOESY spectrum, H-$_3$-19 with H-5α, H-5α and H-9α, H-9α and H-1α, H_2-20 and H-15; EIMS *m*/*z* 302 $[M]^+$, 287, 259, 233, 173, 131, 105; *anal*. C 79.30%, H 9.71%, calcd for $C_{20}H_{30}O_2$, C 79.47%, H 9.93%.

3*β*,20:15*R*,16*S*-Diepoxy-3α-beyeranol (agallochin H) (3): colorless needles (*n*-hexanes−EtOAc); mp 164−166 °C; $[\alpha]^{25}_D$ −76.4° (*c* 0.7, $CHCl_3$); IR (Nujol) ν_{max} 3450, 1210,970 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *δ* 1.22 (1H, m, H-1α), 2.20 (1H, m, H-1*β*), 1.80 (1H, m, H-2α), 2.22 (1H, m, H-2*β*), 1.30 (1H, m, H-5), 1.60 (1H, m, H-6α), 1.32 (1H, m, H-6*β*), 1.38 (1H, m, H-7α), 1.68 (1H, m, H-7*β*), 1.28 (1H, m, H-9), 1.72 (1H, m, H_2-11), 1.20 (1H, m, H-12α), 1.90 (1H, m, H-12*β*), 0.53 (1H, m, H-14α), 1.24 (1H, m, H-14*β*), 3.15 (1H, d, *J* = 4.0 Hz, H-15), 3.00 (1H, d, *J* = 4.0 Hz, H-16), 1.02 (3H, s, H_3-17), 1.04 (3H, s, H_3-18), 1.00 (3H, s, H_3-19), 3.89 (1H, d, *J* = 8.0 Hz, H-20), 4.05 (1H, d, *J* = 8.0 Hz, H-20); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 33.7 (t, C-1), 29.4 (t, C-2), 98.2 (s, C-3), 40.4 (s, C-4), 51.1 (d, C-5), 20.1 (t, C-6), 35.6 (t, C-7), 43.6 (s, C-8), 49.5 (d, C-9), 35.5 (s, C-10), 21.2 (t, C-11), 31.7 (t, C-12), 39.0 (s, C-13), 46.0 (t, C-14), 55.2 (d, C-15), 59.6 (d, C-16), 21.3 (q, C-17), 27.6 (q, C-18), 18.1 (q, C-19), 67.8 (t, C-20); partial correlations observed in the $^1H-^1H$ COSY spectrum, H-1α with H-2*β*; H-2α with H-1*β*; H-6α with H-6*β*; H-7α with H-7*β*; H-12α with H-12*β* and H_2-11; H-14α with H-14*β*; H-15 with H-16; H-20 with H-9 and H-1*β*; EIMS *m*/*z* 318 $[M]^+$, 300, 285, 144; *anal*. C 75.35%, H 9.32%, cacld for $C_{20}H_{30}O_3$, C 75.47%, H 9.43%.

3*β*,20-Epoxy-3α,6α-dihydroxy-18-nor-beyer-15-ene (agallochin I) (4): colorless oil; $[\alpha]^{25}_D$ −52.2° (*c* 1.0, $CHCl_3$); IR (Nujol) ν_{max} 3340, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *δ* 2.00 (1H, m, H_2-1), 1.70 (1H, m, H-2α), 1.98 (1H, m, H-2*β*), 2.05 (1H, m, H-4), 0.98 (1H, m, H-5), 3.80 (1H, m, H-6*β*), 1.40 (1H, m, H-7α), 1.86 (1H, m, H-7*β*), 1.10 (1H, m, H-9), 1.70 (1H, m, H_2-11), 1.21 (1H, m, H_2-12), 1.05 (1H, m, H-14α), 1.52 (1H, m, H-14*β*), 5.49 (1H, d, *J* = 5.4 Hz, H-15), 5.57 (1H, d, *J* = 5.4 Hz, H-16), 1.00 (3H, s, H_3-17), 1.13 (3H, d, *J* = 6.3 Hz, H_3-19), 3.80 (2H, m, H_2-20); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 31.2 (t, C-1), 26.9 (t, C-2), 98.3 (s, C-3), 41.5 (d, C-4), 56.9 (d, C-5), 69.5 (d, C-6), 44.7 (t, C-7), 49.4 (s, C-8), 44.5 (d, C-9), 36.3 (s, C-10), 20.7 (t, C-11), 31.9 (t, C-12), 43.7 (s, C-13), 60.4 (t, C-14), 133.3 (d, C-15), 137.9 (d, C-16), 24.4 (q, C-17), 19.3 (q, C-19), 68.5 (t, C-20); partial correlations observed in the $^1H-^1H$ COSY spectrum, H_2-1 with H-2α; H-2α with H-2*β*; H-4 with H_3-19 and H-5; H-7α with H-7*β*; H_2-11 with H_2-12; H-14α with H-14*β*; H-6α with H_2-7 and H-5; H-16 with H-15; partial correlations observed in the $^1H-^1H$ NOESY; H-5α with H-9α, H-9α with H-1α, and H_2-20 with H-15; FABMS (+ve) *m*/*z* 305 $[M + H]^+$, 279, 257, 239, 213, 167, 149. *anal*. C 74.74%, H 8.95%, calcd for $C_{19}H_{28}O_3$, C 75.00%, H 9.21%.

Acetylation of Agallochin I. Formation of the Acetate (4a). Agallochin I (**4**) (25 mg) was acetylated with a mixture of acetic anhydride (1.5 mL) and pyridine (1.5 mL) at room temperature for 24 h. After usual workup, it yielded the monoacetyl derivative **4a** (20 mg): colorless oil, $[\alpha]^{25}_D$ −60.4° (*c* 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 90 MHz), 1.05 (3H, s, Me), 1.15 (3H, d, *J* = 6 Hz), 2.05 (3H, s, acetate methyl), 3.92 (2H, m, H_2-20), 5.08 (1H, dt, *J* = 11.5, 5.0 Hz, H-6), 5.52 (1H, d, *J* = 5.6 Hz, H-15), 5.72 (1H, d, *J* = 5.6 Hz, H-16); FABMS (+ve) *m*/*z* 347 $[M^+ + H]^+$, 287, 269, 239, 207, 178, 165, 154; *anal*. C 72.61%, H 8.48%, calcd for $C_{21}H_{30}O_4$, C 72.83%, H 8.67%.

2-Acetoxy-1,15-beyeradiene-3,12-dione (5): colorless needles (MeOH); mp 136−138 °C; $[\alpha]^{25}_D$ −294.2° (*c* 2.1, $CHCl_3$); IR (Nujol) ν_{max} 1750, 1210, 1670, 1685, 720, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *δ* 6.46 (1H, s, H-1), 1.85 (1H, dd, *J* = 11.0, 12.0 Hz, H-5), 1.70 (1H, m, H-6α), 1.62 (1H, m, H-6*β*), 1.56 (1H, m, H-7α), 2.00 (1H, m, H-7*β*), 1.99 (1H, dd, *J* = 11.0, 6.0 Hz, H-9), 2.60 (1H, dd, *J* = 16.0 11.0 Hz, H-11α), 2.45 (1H, dd, *J* = 16.0, 6.0 Hz, H-11*β*), 1.68 (1H, d, *J* = 11.0 Hz, H-14α), 1.96 (1H, d, *J* = 11.0 Hz, H-14*β*), 6.08 (1H, d, *J* = 5.5 Hz, H-15), 5.72 (1H, d, *J* = 5.5 Hz, H-16), 1.12 (3H, s, H_3-17), 1.22 (3H, s, H_3-18), 1.14 (3H, s, H_3-19), 1.11 (3H, s, H_3-20), 2.18 (3H, s, OCO*CH*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.6 (d, C-1), 143.2 (s, C-2), 196.8 (s, C-3), 45.4 (s, C-4), 52.3 (d, C-5), 20.3 (t, C-6), 35.7 (t, C-7), 49.6 (s, C-8), 49.5 (d, C-9), 39.5 (s, C-10), 35.8 (t, C-11), 209.9 (s, C-12), 58.1 (s, C-13), 57.5 (t, C-14), 133.8 (d, C-15), 137.4 (d, C-16), 17.3 (q, C-17), 27.3 (q, C-18), 21.6 (q, C-19), 16.9 (q, C-20), 168.7 (s, *OCO*CH$_3$), 20.2 (s, OCO*CH*$_3$); partial correlations observed in the $^1H-^1H$ COSY spectrum, H-7α with H-7*β* and H-6α; H-11α with H-11*β* and H-9; H-14α with H-14*β*; H-15 with H-16; EIMS *m*/*z* 356 $[M]^+$, 314, 298, 270, 215, 154, 119, 93; *anal*. C 73.90%, H 7.74%, calcd for $C_{22}H_{28}O_4$, C 74.15%, H 7.86%.

2-Hydroxy-1,15-beyeradiene-3,12-dione (6): colorless oil; $[\alpha]^{25}_D$ −22.4° (*c* 0.53, $CHCl_3$); IR (Nujol) ν_{max} 3450, 1670, 1690, 720, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz);[9] ^{13}C NMR ($CDCl_3$, 22.5 MHz) *δ* 124.4 (d, C-1), 144.0 (s, C-2), 200.2 (s, C-3), 43.7 (s, C-4), 52.9 (d, C-5), 19.8 (t, C-6), 35.7 (t, C-7), 50.4 (s, C-8), 49.3 (d, C-9), 39.3 (s, C-10), 35.8 (t, C-11), 210.3 (s, C-12), 57.2 (s, C-13), 58.0 (t, C-14), 138.9 (d, C-15), 136.9 (d, C-16), 17.4 (q, C-17), 26.6 (q, C-18), 21.7 (q, C-19), 16.7 (q, C-20); EIMS *m*/*z* 314 $[M]^+$, 271, 271, 201, 173, 135, 119, 105, 93; *anal*. C 76.18%, H 8.10%, calcd for $C_{20}H_{26}O_3$, C 76.43%, H 8.28%.

***ent*-Kauran-16*β*-ol-3-one:** colorless needles (MeOH); mp 155−160 °C; $[\alpha]^{25}_D$ −65.2° (*c* 0.32, $CHCl_3$); spectral data (IR, ^1H, and ^{13}C NMR) were identical with literature values.[14]

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Supporting Information Available: The HMBC data of compounds **1**−**5** are available free of charge via the Internet at http://pubs.acs.org.

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