190. A Novel Glyceryl Ester (Glyceryl Dendryphiellate A), a Trinor-eremophilane (Dendryphiellin A1), and Eremophilanes[1]) (Dendryphiellin E1 and E2) from the Marine Deuteromycete *Dendryphiella salina* (SUTHERLAND) PUGH *et* NICOT

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Continuing studies of the global extracts from cultures of the marine deuteromycete *Dendryphiella salina* have led to the isolation of novel compounds that add to the scarce list of marine fungal metabolites. Besides (22*E*)-ergosta-4,6,8(14),22-tetraen-3-one which, though known from basidiomycetes, was unknown in the sea, they are an unusual glyceryl ester, *i.e.* glycer-1-yl dendryphiellate A (= (+)-(2*R*)-2,3-dihydroxyprop-1-yl (6*S*,2*E*,4*E*)-6-methylocta-2,4-dienoate; (+)-**1**), a trinor-eremophilane, *i.e.* dendryphiellin A1 (= (+)-(3*R**,4*E*,6*E*)-7-{[(1*R**,2*S**,7*R**,8a*R**)-1,2,6,7,8,8a-hexahydro-7-hydroxy-1,8a-dimethyl-6-oxonaphthalen-2-yl]oxycarbonyl}-3-methylhepta-4,6-dienoic acid; (+)-**11**), and two eremophilanes, *i.e.* dendryphiellin E1 (= (+)-(1*R**,2*S**,7*S**,8a*R**)-1,2,6,7,8,8a-hexahydro-1,8a-dimethyl-7-(1-methylethenyl)-6-oxonaphthalen-2-yl (6*S*,2*E*,4*E*)-6-methylocta-2,4-dienoate; (+)-**13**) and dendryphiellin E2 (= (+)-(1*R**,2*S**,8a*R**)-1,2,6,7,8,8a-hexahydro-7-isopropylidene-1,8a-dimethyl-6-oxonaphthalen-2-yl (6*S*,2*E*,4*E*)-6-methylocta-2,4-dienoate; (+)-**14**). Absolute configurations have been established for (+)-**1** *via* total synthesis and for the acid portion of (+)-**13** and (+)-**14** *via* transesterification in NaOMe/MeOH which gave in both cases methyl dendryphiellate A ((+)-**16**) of known configuration and the free alcoholic moiety of (+)-**14**, *i.e.* (+)-**17**.

1. Introduction. – Although marine fungi have various habitats and often occur in association with other marine organisms [2], our knowledge of their natural-product chemistry is very limited. We have reviewed the secondary metabolism of marine fungi while reporting on novel trinor-eremophilanes [1] [3], eremophilanes [1], and branched C_9-carboxylic acids [1] isolated from global extracts of cultures of the marine deuteromycete *Dendryphiella salina*[2]).

Our continuing studies of extracts of *D. salina* have now led to the isolation of four novel significant metabolites: the glyceryl ester (+)-**1** of a C_9-carboxylic acid, two eremophilanes (+)-**13** and (+)-**14**, and a trinor-eremophilane (+)-**11**, besides the fluorescent steroid (22*E*)-ergosta-4,6,8(14),22-tetraen-3-one which was already isolated from basidiomycetes [7].

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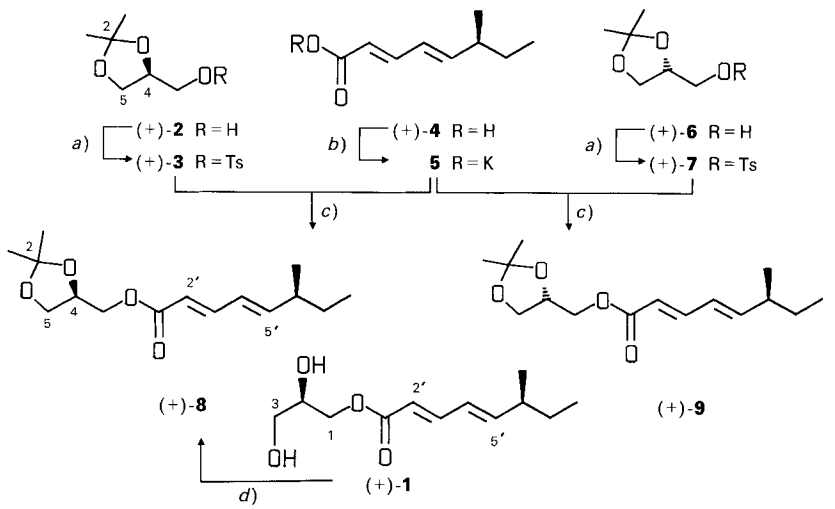
[1]) Eremophilane numbering [1] is used for data and discussion and IUPAC numbering for retrieval purposes.

[2]) To be added to our previous list of fungal metabolites [1] [3] are gliovictin, helicascolide A and B, and ochracin. Gliovictin is a benzyl diketopiperazine isolated from both the marine deuteromycete *Asteromyces cruciatus* [4] and the terrestrial deuteromycete *Helminthosporium victoriae* [5]. Helicascolide A and B and ochracin are δ-lactones isolated from the ascomycete *Helicascus kanaloanus* which lives among Hawaiian mangroves [6]; ochracin is also produced by the terrestrial fungus *Aspergillus ochraceus* [6].

2. Results and Discussion. – 2.1. *Glyceryl Ester (+)-***1**. The NMR spectra of ester (+)-**1** (*Table* and *Exper. Part*) show up as the sum of the NMR spectra of a dendryphiellate A [1] and the glyceryl portion of a C(1) monoglyceride. In accordance, (+)-**1** has the UV absorption spectrum of dendryphiellic acid A [1]. The proposed structure (+)-**1** was confirmed by synthesis which also established its (2*R*,6′*S*)-configuration (see *Scheme 1*). Thus, the potassium salt **5** of dendryphiellic acid A (+)-**4** [1] reacted with either 4-toluenesulfonate (+)-**3** (obtained from commercial (+)-**2** of known (*S*)-configuration) or its enantiomer (+)-**7** (obtained from (+)-**6**) to give dioxolane (+)-**8** or (+)-**9**, respectively. Protection of (+)-**1** with acetone afforded (+)-**8**, as indicated by its [α] values and NMR data[3]).

Scheme 1



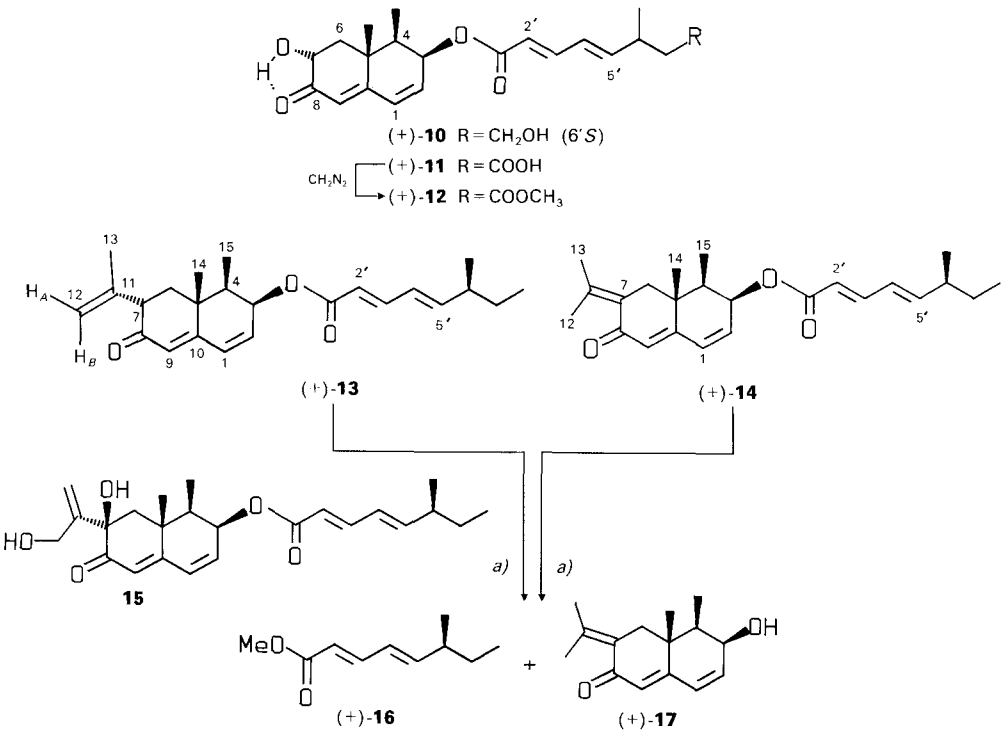
a) TsCl, pyridine, 0°. *b*) KOH. *c*) [18]Crown-6 and **5** in MeCN, then (+)-**3** (or (+)-**7**). *d*) Dry $CuSO_4$, Me_2CO.

Metabolite (+)-**1** is an unusual glyceryl ester owing to the peculiar structure of the component carboxylic acid which may be viewed either as a degraded monoterpene or a branched C_8-acetogenin [1] [3].

2.2. *Trinor-eremophilane (+)-***11**. The NMR spectra of (+)-**11** (*Table* and *Exper. Part*) resemble much those of dendryphiellin A ((+)-**10**), a trinor-eremophilane previously isolated from *D. salina* [3] (see *Scheme 2*). The only differences lie in the signals for the side-chain terminus which arise from a CH_2COOH group in the case of (+)-**11** and from a CH_2CH_2OH group for (+)-**10**. Therefore, compound (+)-**11** is named dendryphiellin A1. Surprisingly, (+)-**11** showed broad ^{13}C-NMR signals for C(6′) and C(7′), and the signal for C(8′) could not be observed at all. Thus, (+)-**11** was esterified with diazomethane to give (+)-**12** for which no NMR ambiguities were observed and whose ^1H-NMR spectrum in $CDCl_3$ allowed the assignment of all protons (*Exper. Part*).

[3]) Not only (+)-**9** shows lower [α] values than (+)-**8**, but, more conclusively, 1H of CH_2–C(4) resonates at lower field in (+)-**9** than in (+)-**8**.

Scheme 2



a) 0.5M NaOMe, MeOH, 0°, 4 h, > 95%.

2.3. *Eremophilanes (+)-***13** *and (+)-***14**. The ^{13}C-NMR spectra of (+)-**13** and (+)-**14** (*Scheme 2*) are similar to those of (+)-**11**, though three more C-atoms are detected (*Table*). This suggests an intact eremophilane skeleton. The closest structural analog is the open form of dendryphiellin E (**15**), an eremophilane previously isolated from *D. salina* [1]. Therefore, (+)-**13** and (+)-**14** are named dendryphiellin E1 and E2, respectively. The proposed structures were corroborated by spectral data.

In the case of (+)-**13**, the 3 additional C-atoms constitute a 1-methylethenyl system (δ(H) = 1.74, 5.00, and 4.89 ppm; δ(C) = 19.80 (*q*), 143.63 (*s*), and 114.82 ppm (*t*)). The low-field resonance of H–C(7) (3.27 ppm) which, together with 2 H–C(6), is part of an *ABX* system, allows the assignment of the position of the 1-methylethenyl group, and the 7α-configuration of the latter is suggested by a 22% NOE on H–C(7)[4]) on irradiation at Me–C(5). NOE experiments (*Exper. Part*) also allow to assign the protons at C(12).

In the case of (+)-**14**, the 3 additional C-atoms constitute an isopropylidene system δ(H) = 1.90 (br. *s*) and 2.19 ppm (br. *s*); δ(C) = 22.89 (*q*), 23.14 (*q*), and 145.96 ppm (*s*). In accordance, C(7) shows up as a *s* at 127.97 ppm, whereas the 2 *H*–C(6) don't show ^3J couplings.

2.4. *Transesterification of the Eremophilanes*. On treatment of either (+)-**13** or (+)-**14** in 0.5M NaOMe in MeOH, the known methyl dendryphiellate A ((+)-**16**) [1] and the free alcohol (+)-**17** were obtained in high yield (*Scheme 2*), thus establishing the (6'*S*)-config-

[4]) According to *J* values obtained from ^{1}H experiments, H–C(7) is assigned to the axial position.

Table. *^{13}C-NMR Data for Glycer-1-yl Dendryphiellate A* ((+)-**1**) *and Dendryphiellins A1* ((+)-**11**), *E1* ((+)-**13**), *and E2* ((+)-**14**)

	(+)-**1**[a])	(+)-**11**[a])	(+)-**13**[b])	(+)-**14**[b])
C(1)	66.52 (*t*)	131.55 (*d*)	130.94 (*d*)	130.90 (*d*)
C(2)	71.22 (*d*)	134.10 (*d*)	132.72 (*d*)	131.98 (*d*)
C(3)	64.06 (*t*)	69.98 (*d*)	68.90 (*d*)	69.34 (*d*)
C(4)		42.46 (*d*)	40.99 (*d*)	40.31 (*d*)
C(5)		38.85 (*s*)	36.14 (*s*)	37.84 (*s*)
C(6)		44.56 (*t*)	40.29 (*t*)	40.18 (*t*)
C(7)		70.97 (*d*)	51.56 (*d*)	127.97 (*s*)
C(8)		201.36 (*s*)	198.88 (*s*)	191.41 (*s*)
C(9)		120.31 (*d*)	125.88 (*d*)	128.22 (*d*)
C(10)		163.92 (*d*)	160.87 (*s*)	158.72 (*s*)
C(11)			143.63 (*s*)	145.96 (*s*)
C(12)			114.82 (*t*)	22.89 (*q*)
C(13)			19.80 (*q*)	23.14 (*q*)
Me–C(4)		10.41 (*q*)	10.19 (*q*)	10.35 (*q*)
Me–C(5)		19.47 (*q*)	18.52 (*q*)	18.52 (*q*)
C(1′)	168.89 (*s*)	168.10 (*s*)	166.78 (*s*)	166.84 (*s*)
C(2′)	119.82 (*d*)	124.70 (*d*)	118.79 (*d*)	118.94 (*d*)
C(3′)	147.24 (*d*)	147.19 (*d*)	145.95 (*d*)	145.78 (*d*)
C(4′)	128.18 (*d*)	128.09 (*d*)	126.66 (*d*)	126.69 (*d*)
C(5′)	151.77 (*d*)	150.27 (*d*)	150.89 (*d*)	150.73 (*d*)
C(6′)	40.19 (*d*)	30.8 (br. *d*)	38.88 (*d*)	38.87 (*d*)
Me–C(6′)	19.96 (*q*)	19.96 (*q*)	19.52 (*q*)	19.54 (*q*)
C(7′)	30.40 (*t*)	35.5 (br. *t*)	29.29 (*t*)	29.29 (*t*)
C(8′)	12.08 (*q*)	not detected	11.71 (*q*)	11.71 (*q*)

[a]) In CD_3OD. [b]) In $CDCl_3$.

uration for both (+)-**13** and (+)-**14** and revealing a double-bond shift in the alcohol moiety of (+)-**13** to the more stable position.

2.5. *Isolation of Steroids.* Chromatographic fractions of lower polarity than those containing the sesquiterpenes afforded the fluorescent sterone (22*E*)-ergosta-4,6,8(14),22-tetraen-3-one. Although this sterone has widespread occurrence in terrestrial basidiomycetes, *e.g. Astraeus hygrometricus* [7a], *Ganoderma australe* [7b], and *Scleroderma polyrhizum* [7c], it was never found in deuteromycetes nor, in general, in marine fungi.

Experimental Part

1. *General.* See [1] [3]. NMR: 'small' means $J < 0.5$; ^{13}C multiplicities from DEPT [8], assignments of *CH* from ^{13}C,^{1}H-COSY [9]; 90/45 ^{1}H,^{1}H-COSY [10a] (and delayed ^{1}H,^{1}H-COSY [10b] for small couplings) for (+)-**13** and (+)-**14** and ^{1}H,^{1}H-COSY-RCT (relayed coherence transfer) [10c] for (+)-**14**. Differential NOE [11]: only for negative NOE, the algebraic sign is indicated. MS: see [12].

2. *Isolation.* Fraction 8 of the previous flash chromatography (FC) [3] was evaporated (< 40°) and the residue subjected to CN HPLC (hexane/EtOH/AcOH 92:8:1): (+)-**1** (2.2 mg) at t_R = 5 min and (+)-**11** (9.0 mg) at t_R = 11 min. The combined hexane and AcOEt extracts (10.6 g) [3] were subjected to gradient FC (hexane→AcOEt); fraction 8 (collected at hexane/AcOEt 7:3) was evaporated and the residue subjected to gradient, reversed-phase FC (EtOH/H_2O 7:3→EtOH). The fraction eluted at EtOH/H_2O 4:1 was evaporated: 37 mg of (+)-**13**/(+)-**14**. Further purification by HPLC with hexane/AcOEt 9:1 gave pure (+)-**13** (t_R = 12.9 min; 1.4 mg) and (+)-**14** (t_R = 15.4 min; 2.3 mg). From slightly more polar fractions, 2.5 mg of (22*E*)-ergosta-4,6,8(14),22-tetraen-3-one were isolated.

3. *Glycer-1-yl Dendryphiellate A* (= *(+)-(2*R*)-2,3-Dihydroxyprop-1-yl (6*S*,2*E*,4*E*)-6-Methylocta-2,4-dienoate;* (+)-**1**). Colorless oil. $[\alpha]_{20}$ = +23.6 (589), +30.0 (577), +36.4 (546), +70.9 (435; *c* = 0.22, EtOH). UV (EtOH): 260 (16800). ^{1}H-NMR (CD_3OD): 4.13, 4.21 (*AB* of *ABX*, *J*(*AB*) = 11.5, *J*(*AX*) = 4.3, *J*(*BX*) = 6.1, 2 H–C(1)); 3.85 (*m*, H–C(2)); 3.58 (*m*, 2 H–C(3)); 5.88 (br. *d*, *J*(2′,3′) = 15.3, *J*(2′,4′) small, H–C(2′)); 7.32 (*dd*, *J*(3′,2′) = 15.3, *J*(3′,4′) = 10.8, H–C(3′)); 6.24 (br. *dd*, *J*(4′,5′) = 15.3, *J*(4′,3′) = 10.8, *J*(4′,2′) and *J*(4′,6′) small, H–C(4′)); 6.09 (*dd*, *J*(5′,4′) = 15.3, *J*(5′,6′) = 7.8, H–C(5′)); 2.19 (br. *dtq*, *J*(6′,5′) = 7.8, *J*(6′,7′) = 7.2, *J*(6′, Me–C(6′)) = 6.6, *J*(6′,4′) small, H–C–(6′)); 1.40 (*dq*, *J*(7′,8′) = 7.5, *J*(7′,6′) = 7.2, 2 H–C(7′)); 0.89 (*t*, *J*(8′,7′) = 7.5, 3 H–C(8′)); 1.05 (*d*, *J*(Me–C(6′),6′) = 6.6, Me–C(6′)). MS: 228 (7, $M^{+\cdot}$), 137 (94), 136 (100, $[M$ – glycerol$]^{+\cdot}$).

4. *Ester (+)-***8** *from (+)-***3** *and (+)-***1** *and Ester (+)-***9** *from (+)-*7. Compound (+)-**2** (0.36 g) in 2.5 ml of pyridine was treated with TsCl (0.52 g) and stirred for 14 h at 0° [13]. Et_2O was added and the mixture washed with aq. 1M HCl until acid reaction, then with sat. $NaHCO_3$, and finally dried (Na_2SO_4): (+)-**3** (82%).

A mixture of dry MeCN (1 ml), **5** (15 mg, 0.078 mmol), and 6 mg of [18]crown-6 (*Fluka*) was stirred for 10 min. After addition of (+)-**3** (70 mg, 0.24 mmol) [14] stirring was continued for 12 h. FC (hexane/Et_2O 3:2) gave (+)-**8** (20 mg, 96%; data, see below) which was practically identical with the acetonization product of (+)-**1** ($[\alpha]_{20}$ = +31.6 (589), +37.4 (577), +41.3 (546), +79.8 (435), +135.9 (365; *c* = 0.09, EtOH)).

An identical procedure with (+)-7 in place of (+)-**3** led to (+)-**9** (98%).

*((4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-Methylbenzenesulfonate* ((+)-**3**). ^{1}H-NMR ($CDCl_3$): 1.31, 1.34 (2 br. *s*, 2 Me–C(2)); 4.27 (*m*, H–C(4)); 3.76, 4.01 (*2dd*, *J* = 8.8, 5.1 and 8.8, 6.3, resp., 2 H–C(5)); 4.00, 3.97 (*AB* of *ABC*, *J*(*AB*) = 10.5, *J*(*AC*) = 6.5, *J*(*BC*) = 5.5, CH_2–C(4)); Ts: 7.79 (*d*, 2 H); 7.35 (br. *d*, 2 H); 2.45 (br. *s*, 3 H). ^{13}C-NMR ($CDCl_3$): 110.07 (*s*, C(2)); 25.16, 26.65 (2*q*, 2 CH_3–C(2)); 72.90 (*d*, C(4)); 66.19 (*t*, C(5)); 72.90 (*t*, CH_2–C(4)); Ts: 145.10 (*s*), 128.02 (*d*), 129.94 (*d*), 132.60 (*s*), 21.89 (*q*).

*((4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methyl (6*S*,2*E*,4*E*)-6-Methylocta-2,4-dienoate* ((+)-**8**). $[\alpha]_{20}$ = +33.4 (589), +38.1 (577), +43.3 (546), +82.4 (435), +149.2 (365; *c* = 0.19, EtOH). UV (EtOH): 260 (16800). ^{1}H-NMR ($CDCl_3$): 1.44, 1.38 (2*q*, *J* = 0.6, 2 Me–C(2)); 4.35 (*m*, H–C(4)); 4.09, 3.77 (*2dd*, *J* = 8.4, 6.3, 2 H–C(5)); 4.23, 4.17 (*AB* of *ABC*, *J*(*AB*) = 11.4, *J*(*AC*) = 4.8, *J*(*BC*) = 5.7, CH_2–C(4)); 5.83 (br. *d*, *J* = 15.4, H–C(2′)); 7.29 (br. *dd*, *J* = 15.4, 10.4, H–C(3′)); 6.13 (*dddd*, *J* = 15.3, 10.5, 0.6, 0.6, H–C(4′)); 6.04 (br. *dd*, *J* = 15.3, 7.5, H–C(5′)); 2.17 (*m*, H–C(6′)); 1.03 (*d*, *J* = 6.9, Me–C(6′)); 1.37 (*dq*, *J* = 7.5, 7.0, 2 H–C(7′)); 0.87 (*t*, *J* = 7.0, 3 H–C(8′)). ^{13}C-NMR ($CDCl_3$): 109.80 (*s*, C(2)); 26.71, 25.43 (2*q*, 2 CH_3–C(2)); 73.79 (*d*, C(4)); 64.52 (*t*, C(5)); 66.55 (*t*, CH_2–C(4)); 166.95 (*s*, C(1′)); 118.48 (*d*, C(2′)); 146.12 (*d*, C(3′)); 126.64 (*d*, C(4′)); 150.76 (*d*, C(5′)); 38.80 (*d*, C(6′)); 19.44 (*q*, CH_3–C(6′)); 29.29 (*t*, C(7′)); 11.64 (*q*, C(8′)). MS: 268 (2, M^+), 253 (100, $[M - Me]^+$), 210 (12, $[M - Me_2CO]^{+\cdot}$), 137 (20), 115 (10), 114 (8, $[M$ – carboxylate moiety – H$]^{+\cdot}$), 101 (34).

*((4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methyl (6*S*,2*E*,4*E*)-6-Methylocta-2,4-dienoate* ((+)-**9**). $[\alpha]_{20}$ = +20.8 (589), +26.1 (577), +28.2 (546), +53.6 (435), +92.8 (365; *c* = 0.28, EtOH). The only spectral difference with respect to (+)-**8** is in the ^{1}H-NMR: 1.1-Hz low-field shift of the 4.17 signal (*B* of *ABC*).

5. *Dendryphiellin A1* (= *(+)-(3*R**,4*E*,6*E*)-7-{[(1*R**,2*S**,7*R**,8a*R**)-1,2,6,7,8,8a-Hexahydro-7-hydroxy-1,8a-dimethyl-6-oxonaphthalen-2-yl]oxycarbonyl}-3-methylhepta-4,6-dienoic Acid;* (+)-**11**). $[\alpha]^{20}_{589}$ = +444.8 (*c* = 0.17, EtOH). UV (EtOH): 273 (53700). ^{1}H-NMR (CD_3OD): 6.47 (br. *d*, *J*(1,2) = 10.0, *J*(1,9) small, H–C(1)); 6.13–6.37 (overlapping signals, H–C(2), H–C(4′), H–C(5′)); 5.42 (br. *dd*, *J*(3,2) = *J*(3,4) = 5.0, H–C(3)); 2.02 (*dq*, *J*(4, Me–C(4)) = 7.0, *J*(4,3) = 5.0, H–C(4)); 1.67 (*dd*, *J*(6ax,7) = J_{gem} = 13.0, H_{ax}–C(6)); 2.25–2.40 (overlapping signals, H_{eq}–C(6), 2 H–C(7′)); 4.41 (*dd*, *J*(7,6ax) = 13.0, *J*(7,6eq) = 5.5, H–C(7)); 5.85 (br. *s*, *J*(9,1) small, H–C(9)); 1.40 (*s*, Me–C(5)); 1.06 (*d*, *J*(Me–C(4),4) = 7.0, Me–C(4)); 5.89 (*d*, *J*(2′,3′) = 15.0, H–C(2′)); 7.27 (*dd*, *J*(3′,2′) = 15.0, *J*(3′,4′) = 10.2, H–C(3′)); 2.78 (*m*, H–C(6′)); 1.11 (*d*, *J*(Me–C(6′),6′) = 6.5, Me–C(6′)).

6. *Dendryphiellin A1 Methyl Ester* (= *(+)-(1*R**,2*S**,7*R**,8a*R**)-1,2,6,7,8,8a-Hexahydro-7-hydroxy-1,8a-dimethyl-6-oxonaphthalen-2-yl (6*R**,2*E*,4*E*)-7-(Methoxycarbonyl)-6-Methylhepta-2,4-dienoate;* (+)-**12**). $[\alpha]_{20}$ = +390.0 (589), +453.0 (577), +527.4 (546), +1157 (435; *c* = 0.17, abs. EtOH). UV (EtOH): 273 (48100). ^{1}H-NMR ($CDCl_3$): 6.37 (br. *d*, *J*(1,2) = 9.6, *J*(1,9) small, H–C(1)); 6.27 (*dd*, *J*(2,1) = 9.6, *J*(2,3) = 4.9, H–C(2)); 5.41 (br. *dd*, *J*(3,4) = *J*(3,2) = 4.9, *J*(3,1) small, H–C(3)); 1.98 (*dq*, *J*(4,Me–C(4)) = 7.1, *J*(4,3) = 4.9, H–C(4)); 1.63 (br. *dd*, *J*(6ax,7) = J_{gem} = 12.9, *J*(6ax,Mc–C(5)) small, H_{ax}–C(6)); 2.45 (*dd*, J_{gem} = 12.9, *J*(6eq,7) = 5.7, H_{eq}–C(6)); 4.37 (*dd*, *J*(7,6ax) = 12.9, *J*(7,6eq) = 5.7, H–C(7)); 5.89 (br. *s*, *J*(9,1) small, H–C(9)); 1.38 (br. *s*, *J*(Me–C(5),6ax) small, Me–C(5)); 1.05 (*d*, *J*(Me–C(4),4) = 7.1, Me–C(4)); 5.84 (br. *d*, *J*(2′3′) = 15.3, *J*(2′,4′) small, H–C(2′)); 7.22 (*dd*, *J*(3′,2′) = 15.3, *J*(3′,4′) = 10.5, H–C(3′)); 6.19 (br. *dd*, *J*(4′,5′) = 15.5, *J*(4′,3′) = 10.5, *J*(4′,2′) and *J*(4′,6′) small, H–C(4′)); 6.08 (*dd*, *J*(5′,4′) = 15.5, *J*(5′,6′) = 7.2, H–C(5′)); 2.82 (br. *dddq*, *J*(6′,5′) = 7.2, *J*(6′,7′) = 7.1, *J*(6′,Me–C(6′)) = 6.8, H–C(6′)); 1.11 (*d*, *J*(Me–C(6′),6′) = 6.8, Me–C(6′)); 2.37, 2.35 (*AB* of *ABX*, *J*(*AB*) = 15.5, *J*(*AX*) = *J*(*BX*) = 7.1, 2 H–C(7′)); 3.67 (*s*, MeOOC). ^{13}C-NMR ($CDCl_3$): 130.38 (*d*, C(1)); 133.42 (*d*, C(2)); 68.33 (*d*, C(3)); 41.07 (*d*, C(4)); 37.55 (*s*, C(5)); 42.83 (*t*, C(6)); 69.97 (*d*, C(7)); 199.40

(*s*, C(8)); 119.80 (*d*, C(9)); 162.93 (*s*, C(10)); 19.02 (*q*, CH_3–C(5)); 10.04 (*q*, CH_3–C(4)); 166.31 (*s*, C(1′)); 122.73 (*d*, C(2′)); 145.33 (*d*, C(3′)); 127.19 (*d*, C(4′)); 147.75 (*d*, C(5′)); 33.82 (*d*, C(6′)); 19.68 (*q*, CH_3–C(6′)); 40.71 (*t*, C(7′)); 172.24 (*s*, C(8′)); 51.62 (*q*, CH_3OOC).

7. *Dendryphiellin E1* (= *(+)-(1*R*,2S*,7S*,8a*R*)-1,2,6,7,8,8a-Hexahydro-1,8a-dimethyl-7-(1-methylethenyl)-6-oxonaphthalen-2-yl (6*S,2*E,4*E)-6-Methylocta-2,4-dienoate;* (+)-**13**). $[\alpha]^{20}$ = +725.8 (589), +776.1 (577), +919.3 (546), +2203 (435), +4498 (365; *c* = 0.10, abs. EtOH). UV (EtOH): 275 (42000). ^{1}H-NMR ($CDCl_3$): 6.33 (br. *d*, *J*(1,2) = 9.8, *J*(1,3), *J*(1,6eq), and *J*(1,9) small, H–C(1)); 6.25 (br. *dd*, *J*(2,1) = 9.8, *J*(2,3) = 5.0, *J*(2,9) small, H–C(2)); 5.46 (br. *dd*, *J*(3,2) = *J*(3,4) = 5.0, *J*(3,1) and *J*(3,15) small, H–C(3)); 1.98 (br. *dq*, *J*(4,15) = 7.1, *J*(4,3) = 5.0, *J*(4,14) small, H–C(4)); 2.03 (*A* of *ABX*, *J*(*AB*) = 13.3, *J*(*AX*) = 5.1), *J*(6eq,1) small, H_{eq}–C(6)); 1.90 (*B* of *ABX*, *J*(*BA*) = *J*(*BX*) = 13.3, *J*(6ax,14) small, H_{ax}–C(6)); 3.27 (*X* of *ABX*, *J*(*XA*) = 5.1, *J*(*XB*) = 13.3, *J*(7,9) and *J*(7,12*B*) small, H–C(7)); 5.84 (br. *s*, *J*(9,7), *J*(9,2) and *J*(9,1) small, H–C(9)); 5.00 (*dq*, J_{gem} = *J*(12*A*,13) = 1.5, H_A–C(12)); 4.89 (br. *dq*, J_{gem} = 1.5, *J*(12*B*,13) = 0.8, *J*(12*B*,7) small, H_B–C(12)); 1.05 (br. *d*, *J*(15,4) = 7.1, *J*(15,3) small, 3H–C(15)); 1.36 (br. *s*, *J*(14,6ax) and *J*(14,4) small, 3H–C(14)); 1.74 (*dd*, *J*(13,12*A*) = 1.5, *J*(13,12*B*) = 0.8, 3H–C(13)); 5.83 (br. *d*, *J*(2′,3′) = 15.3, *J*(2′,4′) and *J*(2′,5′) small, H–C(2′)); 7.26 (br. *dd*, *J*(3′,2′) = 15.3, *J*(3′,4′) = 10.5, *J*(3′,5′) small, H–C(3′)); 6.16 (br. *dd*, *J*(4′,5′) = 15.3, *J*(4′,3′) = 10.5, *J*(4′,2′) and *J*(4′,6′) small, H–C(4′)); 6.04 (br. *dd*, *J*(5′,4′) = 15.3, *J*(5′,6′) = 7.5, *J*(5′,3′) and *J*(5′,2′) small, H–C(5′)); 2.19 (br. *sept.*, *J* ≈ 7.0, H–C(6′)); 1.02 (*d*, *J*(Me–C(6′),6′) = 6.8, Me–C(6′)); 1.38 (*m*, 2 H–C(7′)); 0.87 (*t*, *J* = 7.3, 3 H–C(8)). Differential NOE ($CDCl_3$): 1.36→22% on 3.27, 16% on 1.98, 10% on 1.05, and 2% on 5.83; 1.74→6% on 5.00 and −1% on 4.89; 5.00→18% on 4.89 and 3% on 1.74; 4.89→24% on 5.00 and 11% on 3.27; 5.84→15% on 6.33. MS: 368 (30, M^+), 353 (3, $[M - Me]^+$), 231 (5), 216 (24), 214 (22, $[M$ − carboxylate moiety − H$]^+$), 199 (78), 173 (**14**), 171 (14), 159 (22), 146 (43), 137 (100), 119 (61), 109 (96).

8. *Dendryphiellin E2* (= *(+)-(1*R*,2S*,8aR*)-1,2,6,7,8,8a-Hexahydro-7-isopropylidene-1,8a-dimethyl-6-oxonaphthalen-2-yl (6*S,2*E,4*E)-6-Methylocta-2,4-dienoate;* (+)-**14**). $[\alpha]^{20}$ = +617.6 (589), +653.5 (577), +779.1 (546), +1963 (435; *c* = 0.18 abs. EtOH). UV (EtOH): 271 (34000). ^{1}H-NMR ($CDCl_3$): 6.31 (br. *d*, *J*(1,2) = 9.8, *J*(1,3), *J*(1,6eq), and *J*(1,9) small, H–C(1)); 6.22 (br. *dd*, *J*(2,1) = 9.8, *J*(2,3) = 5.0, *J*(2,9) small, H–C(2)); 5.45 (br. *dd*, *J*(3,2) = *J*(3,4) = 5.0, *J*(3,1) and *J*(3,15) small, H–C(3)); 2.01 (br. *dq*, *J*(4,15) = 7.2, *J*(4,3) = 5.0, *J*(4,14) small, H–C(4)); 2.95 (br. *d*, J_{gem} = 13.5, *J*(6eq,13), *J*(6eq,12), and *J*(6eq,1) small, H_{eq}–C(6)); 2.16 (br. *d*, J_{gem} = 13.5, *J*(6ax,14) and *J*(6ax,12) small, H_{ax}–C(6)); 5.81 (br. *s*, *J*(9,1) and *J*(9,2) small, H–C(9)); 1.08 (br. *d*, *J*(15,4) = 7.2, *J*(15,3) small, 3H–C(15)); 1.16 (br. *s*, *J*(14,4) and *J*(14,6ax) small, 3H–C(14)); 1.90 (br. *s*, *J*(12,6ax), *J*(12,6eq), and *J*(12,13) small, 3H–C(12)); 2.19 (br. *s*, *J*(13,12) and *J*(13,6eq) small, 3H–C(13)); 5.81 (br. *d*, *J*(2′,3′) = 15.5, *J*(2′,4′) and *J*(2′,5′) small, H–C(2′)); 7.24 (br. *dd*, *J*(3′,2′) = 15.5, *J*(3′,4′) = 10.5, *J*(3′,5) small, H–C(3′)); 6.14 (br. *dd*, *J*(4′,5′) = 15.2, *J*(4′,3′) = 10.5, *J*(4′,2′) and *J*(4′,6′) small, H–C(4′)); 6.02 (br. *dd*, *J*(5′,4′) = 15.2, *J*(5′,6′) = 7.6, *J*(5′,3′) small, H–C(5′)); *ca.* 2.2 (submerged by H_{ax}–C(6) and 3 H–C(13), H–C(6′)); 1.02 (*d*, *J*(Me–C(6′),6′) = 6.6, Me–C(6′)); 1.37 (*dq*, *J* = 7.8, 7.2, 2H–C(7′)); 0.86 (*t*, *J* = 7.2, 3H–C(8)). Differential NOE ($CDCl_3$): 2.95→12% on 2.19, and 3% on 1.08, 1.90, and 1.16; 1.08→8% on 2.95 and 11% on 2.01; 2.19→27% on 2.95 and 10% on 1.90; 1.90→9% on 2.95; 5.81→10% on 6.31. MS: 368 (28, M^+), 231 (2), 216 (28), 214 (20), 199 (100), 173 (25), 171 (23), 159 (30), 137 (40), 119 (47), 109 (59).

9. *Transesterification of (+)-***13** *and (+)-***14**. Dendryphiellin E1 ((+)-**13**,1.2 mg) in 0.5M NaOMe/MeOH (1 ml) was stirred at 0° for 4 h. The pH was then adjusted to 7 with AcOH, and prep. TLC gave the known *methyl dendryphiellate A* ((+)-**16**) [1] and *(+)-(1*R*,2S*,8aR*)-1,2,6,7,8,8a-hexahydro-7-isopropylidene-1,8a-dimethyl-6-oxonaphthalen-2-ol* ((+)-**17**). By the same procedure, (+)-**16** and (+)-**17** were obtained from (+)-**14** (2.2 mg). In both cases yields were quantitative.

*(+)-***17**: $[\alpha]_D^{20}$ = +225.0 (*c* = 0.10, $CHCl_3$). UV (EtOH): 281 (8000). ^{1}H-NMR ($CDCl_3$): 6.25 (br. *d*, *J*(1,2) = 11.5, H–C(1)); 6.26 (*dd*, *J*(2,1) = 11.5, *J*(2,3) = 2.9, H–C(2)); 4.19 (br. *dd*, *J*(3,2) = 2.9, *J*(3,4) = 4.4, H–C(3)); 1.80 (*dq*, *J*(4,3) = 4.4, *J*(4,15) = 6.9, H–C(4)); 2.15 (*dqq*, J_{gem} = 13.2, *J*(6ax,12) = 1.5, *J*(6ax,14) = 0.5, H_{ax}–C(6)); 2.94 (*d*, J_{gem} = 13.2, H_{eq}–C(6)); 5.79 (*s*, H–C(9)); 1.89 (*d*, *J*(12,6ax) = 1.5, 3H–C(12)); 2.17 (*s*, 3H–C(13)); 1.12 (*d*, *J*(14,6ax) = 0.5, 3H–C(14)); 1.18 (*d*, *J*(15,4) = 6.9, 3H–C(15)); 2.1 (br. *s*, OH). MS: 232 (100, M^+), 214 (9, $[M - H_2O]^+$), 199 (70), 161 (70).

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