52. Novel Trinor-eremophilanes (Dendryphiellin B, C, and D), Eremophilanes (Dendryphiellin E, F, and G), and Branched C_9-Carboxylic Acids (Dendryphiellic Acid A and B) from the Marine Deuteromycete *Dendryphiella salina* (SUTHERLAND) PUGH *et* NICOT

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Further investigation of global extracts from cultures of the marine deuteromycete *Dendryphiella salina* leads to the isolation of three novel trinor-eremophilanes esterified by branched C_9-carboxylic acids, dendryphiellin B (=(+)-(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*)-6-hydroxy-6-methylocta-2,4-dienoate; (+)-**2**), dendryphiellin C (=(+)-(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*S*,2*E*,4*E*)-6-methylocta-2,4-dienoate; (+)-**3**), and dendryphiellin D (=(+)-(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*)-6-(hydroxymethyl)octa-2,4-dienoate; (+)-**4**). An intact eremophilane, dendryphiellin E (**5**), and its ethanolysis product dendryphiellin F whose absolute configuration is represented by structural formula (+)-**6** are also isolated from the above extracts. Dendryphiellin E exists as an open form **5a** in equilibrium with a closed form **5b**. A similar equilibrium exists between the open form **8a** and the closed form **8b** of a non-esterified eremophilane, dendryphiellin G (**8**), which is isolated too from the above extracts and proves structurally related to the cyclic portion of **5**. Finally, the free, branched C_9-carboxylic acids dendryphiellic acid A ((+)-**9**) and B ((+)-**10**) which correspond to side chains of the above esterified terpenes are also isolated from the above extracts.

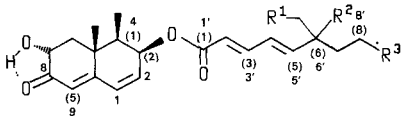
1. Introduction. – From global extracts of cultures of the marine deuteromycete *Dendryphiella salina,* we have recently isolated, in one of the few studies of secondary metabolites of marine fungi[1]), the trinor-eremophilane dendryphiellin A ((+)-**1**)[2]) [1]. Continuing such studies [1], we report here on the isolation of novel trinor-eremophilanes and eremophilanes esterified by branched C_9-carboxylic acids, besides a non-esterified eremophilane and the free carboxylic acids.

2. Trinor-eremophilanes[3]). – The trinor-eremophilanes now isolated from the previous cultures of *Dendryphiella salina,* showing spectral features that closely resemble those of dendryphiellin A ((+)-**1**) [1], are called dendryphiellin B, C, and D.

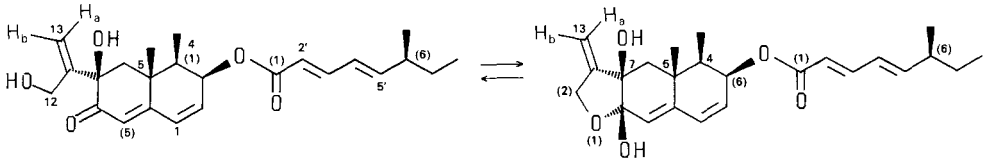
[1]) To be added to the previous list of metabolites isolated from marine fungi [1] are the acetogenin zopfinol from *Zopfiella marina* [2a] and the alkaloids melinacidin III and IV, and gancidin W from *Corollospora pulchella* [2b].

[2]) The configurational prefix (7*R**) was previously inadvertently omitted [1].

[3]) IUPAC numbering (displayed on the structural formulae as arabics within parentheses) is only used for retrieval purposes (see *Exper. Part*); all experimental data are discussed in terms of eremophilane numbering (displayed on the structural formulae as arabics without parentheses). Eremophilane numbering is also used for the hydrofurans **5b**, (+)-**6**, **7**, and **8b**.



(+)-**1** $R^1 = R^2 = H$, $R^3 = OH$
(+)-**2** $R^1 = R^3 = H$, $R^2 = OH$
(+)-**3** $R^1 = R^2 = R^3 = H$, (6′*S*)
(+)-**4** $R^1 = OH$, $R^2 = R^3 = H$



5a **5b**

Dendryphiellin B has the same elemental composition as dendryphiellin A ((+)-**1**) [1], as indicated by MS and NMR data which point to structure (+)-**2**. The presence of the bicyclic moiety and of the estereal side chain is indicated by mass peaks at *m/z* 191 (deriving from C(3)–O breaking, though the acid residue at *m/z* 169 could not be detected), 190, and 170 (from *β*-elimination of the carboxylic acid). A broad UV absorption at 271.5 nm is consistent with the dienone and the diene ester moieties [1]. The ^{13}C- and ^1H-NMR spectra *(Exper. Part)* have a general similarity to those of dendryphiellin A ((+)-**1**). However, (+)-**2** has a ^{13}C-NMR *s* arising from a O-bearing quaternary C-atom and a ^1H-NMR O-deshielded Me *s* in place of the C(6′) *d* and the CH_3–C(6′) *d* for (+)-**1**, respectively. All these data support structure (+)-**2**, where the side-chain OH group is at C(6′) rather than at C(8′) as with dendryphiellin A ((+)-**1**).

With dendryphiellin C, there is no NMR evidence for an OH group at the side chain *(Exper. Part)*; the MS confirms structure (+)-**3** showing peaks at *m/z* 190 and 154 for the bicyclic and the side-chain moiety, respectively. The latter peak must arise from *β*-elimination of the carboxylic acid while no peaks resulting from direct C(3)–O breaking could be observed.

Dendryphiellin D, like the B analogue, is isomeric with dendryphiellin A ((+)-**1**). The MS reveals peaks at *m/z* 190 and 170 for the bicyclic and the side-chain moieties, the latter deriving from *β*-elimination of the carboxylic acid. Moreover, the ^{13}C-NMR spectrum reveals a *t* for a C-atom which must be singly bound to an O-atom, like with (+)-**1**, but at lower field *(Exper. Part)* [1]. These data can be rationalized by placing the OH group of (+)-**4** at *C*–C(6′) rather than at C(8′) as with (+)-**1**. This is confirmed in the ^1H-NMR spectrum *(Exper. Part)* by both a deshielded *AB* part of an *ABX* system for $HOCH_2$-C(6′) and a Me *t* for C(8)H_3 (in place of the Me *d* and the *XY* part of an A_2XY system for (+)-**1** [1]).

The results of NOE experiments *(Exper. Part)* fully confirm the connectivities and the configurational relationships within the bicyclic system, besides confirming the ester side chain, for dendryphiellin B ((+)-**2**), C((+)-**3**), and D ((+)-**4**).

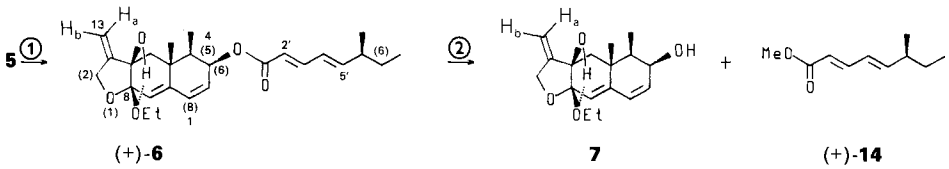
3. Eremophilanes. – Two new natural eremophilanes, dendryphiellin E and G, and an artifact eremophilane of the extraction process, dendryphiellin F, have been now isolated

from cultures of *Dendryphiella salina*. The MS of dendryphiellin E (**5**) reveal peaks for the same ester side chain as that of (+)-**3** (*m/z* 154), besides peaks at *m/z* 230 and 228 which indicate that the cyclic moiety must contain the additional fragment C_3H_4O as for an intact eremophilane. The pattern of NMR data for **5** proves quite complex, however, revealing more than one molecular species; full analysis has to wait that dendryphiellin F ((+)-**6**), an ethyl acetal which must derive from EtOH trapping by dendryphiellin E during the extraction process[4]), is examined.

The structure of (+)-**6** is, therefore, described first. High-resolution MS experiments prove the composition $C_{26}H_{36}O_5$, with five C-atoms more than the above trinor-eremophilanes. The mass fragmentation showing loss of EtOH (*m/z* 382), of the side chain as a carboxylic acid (*m/z* 274), and of both (*m/z* 228) suggests a sesquiterpene unit. All NMR signals can be assigned on the basis of decoupling, $^1H,^1H$-COSY [3], $^1H,^{13}C$-COSY [4], and NOE experiments. The latter in particular *(Exper. Part)* support nearly all internal relationships among the elements of both the bicyclic and the side-chain moieties and between them. NOE enhancements among CH_2O and both H–C(9) and CH_3–C(5) indicate that EtO is at C(8). A small coupling between H_α–C(6) and OH suggests a W relationship, which is compatible with the H-bonding of structural formula (+)-**6**.

The absolute configuration at the tricyclic moiety of dendryphiellin F is established as in structural formula (+)-**6** on the basis that internal exciton coupling of the enone with the unsaturated-ester chromophore gives rise to a positive band at 257 nm and a negative band at 234 nm [5]. Moreover, dendryphiellin F ((+)-**6**), on treatment with MeONa/MeOH, gives eremophilane **7** and a dienic methyl ester *(Scheme 1)* which will later prove to be identical with the synthetic compound (+)-**14**, thus establishing the (6′*S*) configuration.

Scheme 1



(+)-**6** **7** (+)-**14**

① Hexane, EtOH, AcOH, r.t., 20 h. ② 0.5M MeONa in MeOH, r.t., 8 h.

Continuing with dendryphiellin E (**5**), the NMR data of the *Exper. Part* can now be rationalized with the aid of $^1H,^1H$-COSY data [3], thus revealing an equilibrium mixture (1:1 in C_6D_6 or 3:2 in CD_3CN) between the open form **5a** and the hemiacetal form **5b**.

It becomes now straightforward to appreciate from the spectral data in the *Exper. Part* that also dendryphiellin G is an intact eremophilane which exists in two equilibrium forms. Mass and NMR spectra show that there is no side chain, and NMR data can be analyzed in terms of the open form **8a** and the hemiacetal form **8b** in equilibrium (1:6 at 20° and 1:3 at 55° in CD_3OD).

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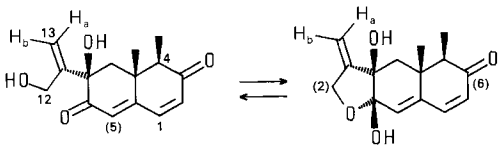
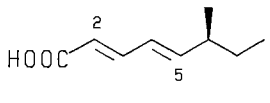
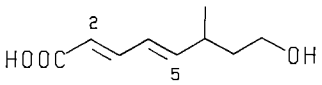
[4]) This is supported by the finding that on treatment with EtOH in the presence of traces of AcOH in hexane at r.t. for some h, dendryphiellin E (**5**) gives (+)-**6**.



8a **8b**



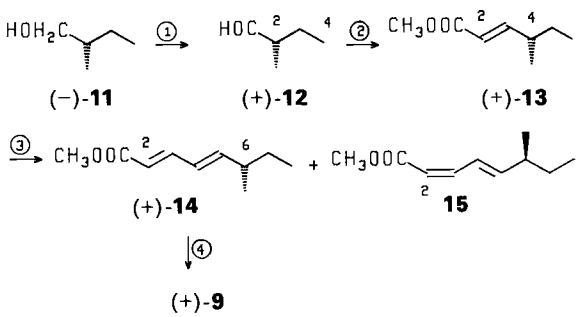
(+)-**9**



(+)-**10**

4. Free Carboxylic Acids. – Two of the side chains of the above terpenoids exist also as free acids (dendryphiellic acid A ((+)-**9**) and B ((+)-**10**)) in the global extracts from the cultures of *D. salina*. Acid (+)-**9** shows the same spectral data as the side chain of dendryphiellin C ((+)-**3**), E (**5**), and F ((+)-**6**), whilst spectral data for acid (+)-**10** match those for the side chain of dendryphiellin A ((+)-**1**) [1]. In fact, (+)-**10** was already described as the product of hydrolysis of dendryphiellin A ((+)-**1**) [1]. Full assignment of NMR data is given in the *Exper. Part.*

Scheme 2



(−)-**11** (+)-**12** (+)-**13**

(+)-**14** **15**

(+)-**9**

① CrO_3, pyridine, CH_2Cl_2, r.t., 30 min. ② $Ph_3P{=}CHCO_2CH_3$, toluene, 95°, 15 h. ③ a) $((CH_3)_2CHCH_2)_2AlH$, toluene, −40 to −10°, 4 h; b) CrO_3, pyridine, CH_2Cl_2, r.t., 30 min; c) $Ph_3P{=}CHCO_2CH_3$, toluene, 95°, 15 h. ④ a) HPLC purification; b) 3% KOH in MeOH; c) AcOH; d) flash chromatography.

In order to establish the absolute configuration of dendryphiellic acid A ((+)-**9**), the synthesis of *Scheme 2* is carried out. Commercial (−)-(2*S*)-2-methylbutan-1-ol ((−)-**11**) is subjected to *Collins* oxidation [6] to afford aldehyde (+)-**12** which is then elongated to the ester (+)-**13** *via* a *Wittig* reaction [7]. Reduction of (+)-**13** to give an allylic alcohol with diisobutylaluminium hydride [8] followed by *Collins* oxidation gives an aldehyde which is then subjected to *in situ Wittig* elongation [7] to give a 5:95 mixture of the undesired **15** and the desired ester (+)-**14**. The latter is chromatographically separated and subjected to saponification to give (+)-**9** whose absolute configuration is thus established to be *S*. It has also to be mentioned that (+)-**14** arises in the treatment of dendryphiellin C ((+)-**3**) and F ((+)-**6**) with MeONa/MeOH which is the basis of the configurational assignment at the ester chain of (+)-**3**, **5**, and (+)-**6**.

We thank Mr. *N. Demattè* for skilled technical aid in the isolation of the metabolites, Dr. *A. Fissi* (Istituto di Biofisica, *C.N.R.*, Pisa) for the CD spectra, Mr. *A. Sterni* for recording the mass spectra, and for financial support of the work in Trento, both *M.P.I.* (Progetti di Interesse Nazionale) and *C.N.R.*, Roma.

Experimental Part

1. *General.* Flash chromatography (FC): *Merck RP-18 LiChroprep* 40-65 μm. HPLC: *Merck-LiChrosorb Si-60* (7 μm), *Merck-LiChrosorb CN* (7 μm); reverse-phase, *Merck-LiChrosorb RP18* (7 μm) on 25 × 1 cm colums with solvent flux 5 ml/min, monitoring by UV at 245 nm. TLC: *Merck* silica gel *60* F_{254}. Polarimetric data: *JASCO-DP-181* digital polarimeter. UV (λ_{max} in nm, ε in mol^{-1} l cm^{-1}): *Perkin-Elmer-Lambda-3*. CD: *JASCO J-500 A*. NMR: *Varian-XL-300*; δ's (ppm) relative to internal Me_4Si (= 0 ppm); probe temp. 21°, unless otherwise stated; ^{1}H-NMR at 300 MHz, J in Hz, couplings obtained from double irradiations and (for (+)-**4**, **5**, (+)-**6**, **8** and (+)-**9**) ^{1}H,^{1}H COSY [3] experiments; NOE always means differential NOE (8 sec of preirradiation), irradiated proton(s) $\delta \rightarrow$ %NOE on the observed proton(s). ^{13}C-NMR at 75.43 MHz with multiplicities from DEPT [9] and chemical shift assignments (for (+)-**3**, (+)-**6**, **8**, and (+)-**9**) from ^{13}C,^{1}H correlations [4]. EI-MS (*m/z* (%)): low resolution, home-built spectrometer based on the *ELFS-4-162-8-Extranuclear* quadrupole [10]; high resolution, *VG ZAB2*.

2. *Isolation.* The previous FC fractions from extracts of the culture of *D. salina* [1] were further investigated. Thus, the 6th and 7th fractions gave *dendryphiellin G* (**8**) and *dendryphiellic acid B* ((+)-**10**), the 9th fraction, which has already given *dendryphiellin A* ((+)-**1**) [1], gave *dendryphiellin B* ((+)-**2**), *D* ((+)-**4**) and *dendryphiellic acid A* ((+)-**9**), and finally, the 10th fraction gave *dendryphiellin C* ((+)-**3**), *E*(**5**), and *F*((+)-**6**). Details are as follows. From the 6th and 7th fractions, HPLC *(LiChrosorb CN)* with hexane/AcOEt 4:1 gave **8** (t_R 11 min, 2.2 mg) and (+)-**10** (t_R 25 min, 3.2 mg). Continuing as previously indicated [1] the workup of the 9th FC fraction, we have now obtained (+)-**2** (t_R 23 min, 1.2 mg), (+)-**4** (t_R 27 min, 1.4 mg), and (+)-**1** (t_R 31, 6 mg). Moreover, the previously [1] not investigated 3rd fraction from reverse-phase HPLC gave (+)-**9** (t_R 37 min, 18 mg) on *(LiChrosorb CN)* with hexane/EtOH/AcOH 92:8:2. Of the 10th fraction, 3/4 were separated on HPLC *(LiChrosorb CN)* with hexane/EtOH/AcOH 20:1:0.1 giving (+)-**3** (t_R 11 min, 4.2 mg), **5** (t_R 13 min, 0.3 mg), and (+)-**6** (t_R 4.5 min, 9.8 mg). From the remaining 1/4 of the 10th fraction, HPLC with hexane/AcOEt 3:2 further gave (+)-**3** (t_R 7.5 min, 0.8 mg) and **5** (t_R 13.5 min, 1.4 mg).

3. *Dendryphiellin B* (= *(+)-(1*R*,*2*S*,*7*R*,*8a*R*)*-1,2,6,7,8,8a-Hexahydro-7-hydroxy-1,8a-dimethyl-6-oxo-naphthalen-2-yl (6*R*,*2*E,*4*E)*-6-Hydroxy-6-methylocta-2,4-dienoate;* (+)-**2**). Colourless oil. $[\alpha]^{20}$ (λ): +280.0 (589), +296.0 (577), +352.0 (546), +752.0 (435), +1740.0 (365; *c* = 0.05, abs. EtOH). UV (EtOH): 271.5 (17300). ^{1}H-NMR (CD_3OD): 6.47 (br. *d*, *J*(1,2) = 9.9, *J*(1,3) and *J*(1,9) small, H–C(1)); 6.27 (br. *dd*, *J*(2,1) = 9,9, *J*(2,3) = 5.1, H–C(2)); 5.44 (br. *dd*, *J*(3,4) = 4.9, *J*(3,2) = 5.1, *J*(3,1) small, H–C(3)); 2.03 (*dq*, *J*(4, CH_3–C(4)) = 7.0, *J*(4,3) = 4.9, H–C(4)); 1.68 (br. *dd*, J_{gem} = 12.5, *J*(6α,7) = 13.3, *J*(6α,CH_3–C(5)) small, H_α–C(6)); 2.37 (*dd*, J_{gem} = 12.5, *J*(6β,7) = 5.4, H_β–C(6)); 4.41 (*dd*, *J*(7,6α) = 13.3, *J*(7,6β) = 5.4, H–C(7)); 5.86 (br. *s*, *J*(9,1) small, H–C(9)); 1.07 (*d*, *J*(CH_3–C(4),4) = 7.0, CH_3–C(4)); 1.41 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 5.93 (br. *d*, *J*(2′,3′) = 15.2, *J*(2′,4′) small, H–C(2′)); 7.32 (br. *dd*, *J*(3′,2′) = 15.2, *J*(3′,4′) = 10.8, H–C(3′)); 6.43 (br. *dd*, *J*(4′,5′) = 15.1, *J*(4′,3′) = 10.8, *J*(4′,2′) small, H–C(4′)); 6.23 (br. *d*, *J*(5′,4′) = 15.1, H–C(5′)); 1.59 (*q*, *J*(7′,8′) = 7.5, 2 H–C(7′)); 0.89 (*t*, *J*(8′,7′) = 7.5, 3 H–C(8′)); 1.28 (*s*, CH_3–C(6′)); NOE (CD_3OD): 6.47→12% on H–C(9); 1.68→5% on H–C(4); 1.41→15% on H–C(7), 6% on H_β–C(6), and 2% on CH_3–C(4); 1.07→3% on H–C(2′). ^{13}C-NMR (CD_3OD): 131.55 (*d*, C(1)); 134.05 (*d*, C(2)); 70.03 (*d*, C(3)); 42.44 (*d*, C(4)); 38.84 (*s*, C(5)); 44.57 (*t*, C(6)); 70.95 (*d*, C(7)); 120.96 (*d*, C(9)); 163.93 (*s*, C(10)); 10.42 (*q*, CH_3–C(4)); 19.45 (*q*, CH_3–C(5)); 124.69 (*d*, C(2′)); 146.76 (*d*, C(3′)); 126.45 (*d*, C(4′)); 151.87 (*d*, C(5′)); 73.92 (*s*, C(6′)); 35.82 (*t*, C(7′)); 8.51 (*q*, C(8′)); 27.25 (*q*, *C*–C(6′)); signals for neither C(8) nor C(1′) could be detected. MS: 191 (8), 190 (38), 175 (85), 170 (5), 152 (5), 147 (100).

4. *Dendryphiellin C* (= *(+)-(1*R*,*2*S*,*7*R*,*8a*R*)*-1,2,6,7,8,8a-Hexahydro-7-hydroxy-1,8a-dimethyl-6-oxo-naphthalen-2-yl (6*S,*2*E,*4*E)*-6-Methylocta-2,4-dienoate;* (+)-**3**). Colourless oil $[\alpha]^{20}$ (λ): +506.9 (589), +535.8 (577), +635.0 (546), +1429.0 (435; *c* = 0.41, MeOH). UV (MeOH): 273 (30100). ^{1}H-NMR (CD_3OD): 6.47 (br. *d*, *J*(1,2) = 9.7, *J*(1,3) and *J*(1,9) small, H–C(1)); 6.26 (br. *dd*, *J*(2,1) = 9.7, *J*(2,3) = 5.0, H–C(2)); 5.43 (br. *dd*, *J*(3,4) = 4.9, *J*(3,2) = 5.0, *J*(3,1) small, H–C(3)); 2.03 (*dq*, *J*(4, CH_3–C(4)) = 7.1, *J*(4,3) = 4.9, H–C(4)); 1.68 (br. *dd*, J_{gem} = 12.5, *J*(6α,7) = 13.1, *J*(6α, CH_3–C(5) small, H_α–C(6)); 2.37 (*dd*, J_{gem} = 12.5, *J*(6β,7) = 5.5, H_β–C(6)); 4.41 (*dd*, *J*(7,6α) = 13.1, *J*(7,6β) = 5.5, H–C(7)); 5.86 (br. *s*, *J*(9,1) small, H–C(9)); 1.07 (*d*, *J*(CH_3–C(4),4) = 7.1, CH_3–C(4)); 1.41 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 5.87 (br. *d*, *J*(2′,3′) = 15.2, *J*(2′,4′) small, H–C(2′)); 7.28 (br. *dd*, *J*(3′,2′) = 15.1, *J*(3′,4′) = 10.7, H–C(3′)); 6.26 (br. *dd*, *J*(4′,5′) = 15.0, *J*(4′,3′) = 10.7, *J*(4′,2′) and *J*(4′,6′) small, H–C(4′)); 6.08 (br. *d*, *J*(5′,4′) = 15.0, *J*(5′,6′) = 7.9, H–C(5′)); 2.20 (br. *dtq*, *J*(6′,5′) = 7.9, *J*(6′,7′) = *J*(6′, CH_3–C(6′)) = 7.0, *J*(6′,4′) small, H–C(6′)); 1.40 (*dq*, *J*(7′,8′) = 7.4, *J*(7′,6′) = 7.0, 2 H–C(7′)); 0.89 (*t*, *J*(8′,7′) = 7.4, 3 H–C(8′)); 1.05 (*d*, *J*(CH_3–C(6′),6′) = 7.0, CH_3–C(6′)); NOE (CD_3OD): 6.47→16% on H–C(9); 1.41→16% on H–C(7), 7% on H_β–C(6), 3% on CH_3–C(4), and 2% on

H–C(2'). ^{13}C-NMR (CD_3OD): 131.54 (*d*, C(1)); 134.13 (*d*, C(2)); 69.95 (*d*, C(3)); 42.46 (*d*, C(4)); 38.85 (*s*, C(5)); 44.56 (*t*, C(6)); 70.97 (*d*, C(7)); 201.35 (*s*, C(8)); 119.72 (*d*, C(9)); 163.97 (*s*, C(10)); 10.43 (*q*, CH_3–C(4)); 19.47 (*q*, CH_3–C(5)); 168.23 (*s*, C(1')); 124.69 (*d*, C(2')); 147.43 (*d*, C(3')); 128.14 (*d*, C(4')); 152.10 (*d*, C(5')); 40.24 (*d*, C(6')); 30.37 (*t*, C(7')); 12.09 (*q*, C(8')); 19.96 (*q*, CH_3–C(6')). MS: 190 (43), 175 (100), 154 (6), 147 (97). On treatment of (+)-**3** (3.1 mg) with 1 ml of 0.5M MeONa in MeOH for 2 h at r.t. followed by TLC (with petroleum ether/Et_2O 2:1), (+)-**14** (1.0 mg, 65%) was obtained at R_f 0.85, while none of the accompanying products was investigated.

5. *Dendryphiellin D* (= *(+)-(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)*-6-(Hydroxymethyl)octa-2,4-dienoate;* (+)-**4**). Colourless oil. $[\alpha]^{20}$ (λ): +349.1 (589), +378.5 (577), +445.1 (546), +991.6 (435), +2146.9 (365; *c* = 0.092, abs. EtOH). UV (EtOH): 272.5 (21650). ^{1}H-NMR (CD_3OD): 6.46 (br. *dd*, *J*(1,2) = 9.8, *J*(1,3) = 0.5, *J*(1,9) small, H–C(1)); 6.27 (*dd*, *J*(2,1) = 9.8, *J*(2,3) = 5.0, H–C(2)); 5.43 (*ddd*, *J*(3,4) = 4.8, *J*(3,2) = 5.0, *J*(3,1) = 0.5, H–C(3)); 2.03 (*dq*, *J*(4, CH_3–C(4)) = 7.1, *J*(4,3) = 4.8, H–C(4)); 1.68 (br. *dd*, J_{gem} = 12.6, *J*(6α,7) = 13.2, *J*(6α, CH_3–C(5)) small, H_α–C(6)); 2.37 (*dd*, J_{gem} = 12.6, *J*(6β,7) = 5.5, H_β–C(6)); 4.41 (*dd*, *J*(7,6α) = 13.2, *J*(7,6β) = 5.5, H–C(7)); 5.86 (br. *s*, *J*(9,1) small, H–C(9)); 1.07 (*d*, *J*(CH_3–C(4),4) = 7.1, CH_3–C(4)); 1.41 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 5.89 (br. *d*, *J*(2',3') = 15.3, *J*(2',4') small, H–C(2')); 7.30 (*ddd*, *J*(3',2') = 15.3, *J*(3',4') = 10.9, *J*(3',5') = 0.7, H–C(3')); 6.34 (br. *dd*, *J*(4',5') = 15.2, *J*(4',3') = 10.9, *J*(4',2') and *J*(4',6') small, H–C(4')); 6.05 (*ddd*, *J*(5',4') = 15.2, *J*(5',6') = 8.8, *J*(5',3') = 0.7, H–C(5')); 2.23 (*m*, H–C(6')); 1.35, 1.58 (2 *m*, 2 H–C(7')); 0.90 (*t*, *J*(8',7') = 7.4, 3 H–C(8')); 3.54, 3.51 (*AB* of *ABX*, *J*(*AB*) = 10.8, *J*(*AX*) = 5.7, *J*(*BX*) = 6.6, CH_2–C(6')); NOE (CD_3OD): 6.46→+15% on H–C(9); 1.68→7% on H–C(4); 1.41→20% on H–C(7), 8% on H_β–C(6), 3% on CH_3–C(4), and 3% on H–C(2'). ^{13}C-NMR (CD_3OD): 131.55 (*d*, C(1)); 134.11 (*d*, C(2)); 69.95 (*d*, C(3)); 42.44 (*d*, C(4)); 38.84 (*s*, C(5)); 44.55 (*t*, C(6)); 70.98 (*d*, C(7)); 201.35 (*s*, C(8)); 120.09 (*d*, C(9)); 163.95 (*s*, C(10)); 10.43 (*q*, CH_3–C(4)); 19.16 (*q*, CH_3–C(5)); 168.14 (*s*, C(1')); 124.71 (*d*, C(2')); 147.09 (*d*, C(3')); 130.92 (*d*, C(4')); 147.87 (*d*, C(5')); 24.76 (*t*, C(7')); 12.00 (*q*, C(8')); 65.86 (*t*, CH_2–C(6')); the signal for C(6') was hidden by the solvent signal. MS: 190 (42), 175 (87), 170 (19), 152 (5), 147 (100).

6. *Dendryphiellin E* (**5**). Colourless oil. $[\alpha]^{20}$ (λ): +166.7 (589), +180.9 (577), +214.7 (546), +535.6 (435), +717.3 (365; *c* = 0.22, abs. EtOH). UV (EtOH): 266.0 (11500). MS: 230 (10), 228 (7), 214 (15), 197 (50), 185 (20), 169 (40), 154 (25), 153 (23), 137 (80), 109 (95), 79 (100).

Open Form **5a** (= *(1*R,*2*S,*7*R,*8a*R)*-1,2,6,7,8,8a-Hexahydro-7-hydroxy-7-[1-(hydroxymethyl)ethenyl]-1,8a-dimethyl-6-oxonaphthalen-2-yl (6*S,*2*E,*4*E)*-6-Methylocta-2,4-dienoate*). ^{1}H-NMR (C_6D_6): 5.85 (superimposed, H–C(1)); 6.00 (superimposed, H–C(2)); 5.57 (superimposed, H–C(3)); 1.50 (*dq*, *J*(4, CH_3–C(4)) = 7.0, *J*(4,3) = 5.0, H–C(4)); 1.43 (br. *d*, J_{gem} = 14.0, *J*(6α, CH_3–C(5)) small, H_α–C(6)); 2.02 (*d*, J_{gem} = 14.0, H_β–C(6)); 5.28 (br. *s*, *J*(9,1) small, H–C(9)); 4.02, 4.12 (*AB* of *ABXY*, *J*(*A*, *X*), *J*(*B*, *X*), *J*(*A*, *Y*), and *J*(*B*, *Y*) small, *J*(*A*, *B*) = 13.3, H_x–C(12), H_β–C(12)); 5.10, 5.14 (2 br. *s*, *XY* of *ABXY*, *J*(*A*, *X*), *J*(*A*, *Y*), *J*(*B*, *Y*), and *J*(*X*, *Y*) small, H_a–C(13), H_b–C(13)); 0.89 (*d*, *J*(CH_3–C(4),4) = 7.0, CH_3–C(4)); 1.75 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 5.79 (superimposed, H–C(2')); 7.45 (*ddd*, *J*(3',2') = 15.3, *J*(3',4') = 10.7, *J*(3',5') = 0.7, H–C(3')); 5.85 (superimposed, H–C(4'), H–C(5')); 1.81 (superimposed, H–C(6')); 1.96 (superimposed, 2 H–C(7')); 0.70 (*t*, *J*(8',7') = 7.4, 3 H–C(8')); 0.80 (*d*, *J*(CH_3–C(6'),6') = 6.8, CH_3–C(6')). ^{13}C-NMR (C_6D_6): 130.98 (*d*, C(1)); 133.22 (*d*, C(2)); 68.95 (*d*, C(3) of **5a** or **5b**); 41.18 (*d*, C(4)); 36.51 (*s*, C(5) of **5a** or **5b**); 45.86 (*t*, C(6)); 77.23 (*s*, C(7)); 200.00 (in $CDCl_3$, *s*, C(8)); 120.09 (*d*, C(9)); 162.41 (*s*, C(10)); 152.79 (*s*, C(11)); 64.16 (*t*, C(12)); 112.39 (*t*, C(13)); 10.23 (*q*, CH_3–C(4)); 22.53 (*q*, CH_3–C(5)); 166.50 (*s*, C(1') of **5a** or **5b**); 119.48 (*d*, C(2')); 145.50 (*d*, C(3') of **5a** or **5b**); 123.72 (*d*, C(4') of **5a** or **5b**); 149.63 (*d*, C(5') of **5a** or **5b**); 38.97 (*d*, C(6')); 29.38 (*t*, C(7')); 11.78 (*q*, C(8')); 19.53 (*q*, CH_3–C(6') of **5b** or **5a**).

Hemiacetal Form **5b** (= *(3a*R,*4a*R,*5*R,*6*S,*9a*S)*-2,3,3a,4,4a,5,6,9a-Octahydro-3a,9a-dihydroxy-4a,5-dimethyl-3-methylidenenaphtho[2,3-*b*]furan-6-yl (6*S,*2*E,*4*E)*-6-Methylocta-2,4-dienoate*). ^{1}H-NMR (C_6D_6): 5.81 (superimposed, H–C(1)); 6.02 (*dd*, *J*(2,1) = 9.6, *J*(2,3) = 5.0, H–C(2)); 5.42 (br. *dd*, *J*(3,2) = *J*(3,4) = 5.0, *J*(3,1) small, H–C(3)); 1.35 (superimposed, H–C(4)); 1.74 (br. *d*, J_{gem} = 14.0, *J*(6α, CH_3–C(5)) small, H_α–C(6)); 2.17 (*d*, J_{gem} = 14.0, H_β–C(6)); 5.99 (br. *s*, *J*(9,1) small, H–C(9)); 4.40, 4.26 (*AB* of *ABXY*, *J*(*A*, *B*) = 13.3, *J*(*A*, *X*) = *J*(*A*, *Y*) = *J*(*B*, *X*) = *J*(*B*, *Y*) = 2.3, H_α–C(12), H_β–C(12)); 5.31, 4.76 (*XY* of *ABXY*, *J*(*X*, *Y*) ≈ 0, *J*(*A*, *X*) = *J*(*A*, *Y*) = *J*(*B*, *Y*) = *J*(*B*, *X*) = 2.3, H_a–C(13), H_b–C(13)); 0.78 (*d*, *J*(CH_3–C(4),4) = 7.0, CH_3–C(4)); 1.65 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 5.78 (superimposed, H–C(2')); 7.47 (*ddd*, *J*(3',2') = 15.3, *J*(3',4') = 10.6, *J*(3',5') = 0.7, H–C(3')); 5.85 (superimposed, H–C(4'), H–C(5')); 1.81 (superimposed, H–C(6')); 1.96 (superimposed, 2 H–C(7')); 0.71 (*t*, *J*(8',7') = 7.4, 3 H–C(8')); 0.78 (*d*, *J*(CH_3(6'),6') = 6.8, CH_3–C(6')). ^{13}C-NMR (C_6D_6): 131.51 (*d*, C(1)); 126.65 (in $CDCl_3$, *d*, C(2)); 70.07 (*d*, C(3) of **5b** or **5a**); 42.46 (*d*, C(4)); 36.56 (*s*, C(5) of **5a** or **5b**); 43.90 (*t*, C(6)); 78.51 (*s*, C(7)); 99.61 (*s*, C(8)); 120.09 (*d*, C(9)); 143.86 (*s*, C(10)); 154.62 (*s*, C(11)); 67.52 (*t*,

C(12)); 105.61 (*t*, C(13)); 10.23 (*q*, CH_3–C(4)); 20.96 (*q*, CH_3–C(5)); 166.71 (*s*, C(1') of **5a** or **5b**); 119.48 (*d*, C(2')); 145.98 (*d*, C(3') of **5a** or **5b**); 124.42 (*d*, C(4') of **5a** or **5b**); 150.23 (*d*, C(5') of **5a** or **5b**); 38.97 (*d*, C(6')); 29.38 (*t*, C(7')); 11.78 (*q*, C(8')); 19.61 (*q*, *C*–C(6') of **5b** or **5a**).

7. *Dendryphiellin F* (= *(+)-(3a*R,*4a*R,*5*R,*6*S,*9a*S*)-9a-Ethoxy-2,3,3a,4,4a,5,6,9a-octahydro-3a-hydroxy-4a,5-dimethyl-3-methylidenenaphtho[2,3-*b*]furan-6-yl (6*S,*2*E,*4*E*)-6-Methylocta-2,4-dienoate;* (+)-**6**). Colourless oil. $[\alpha]^{20}$ (λ): +364.5 (589), +380.7 (577), +443.8 (546), +888.1 (435), +1789.4 (365; *c* = 0.70, abs. EtOH). UV (EtOH): 240 (26500), 259 (32800). CD (EtOH, 4.06×10^{-5} M; cell, optical path 1 cm; sensitivity 5; λ in nm (elongation in cm, $\Delta\varepsilon$ in mol^{-1} 1 cm^{-1})): 257 (+9.9, +36.9), 234 (−5.1, −19.0). ^{1}H-NMR ($CDCl_3$; within brackets, CD_3OD): 6.20 [6.27] (br. *d*, *J*(1,2) = 9.7, *J*(1,3) and *J*(1,9) small, H–C(1)); 5.91 [5.87] (*dd*, *J*(2,1) = 9.7, *J*(2,3) = 4.8, H–C(2)); 5.37 [5.34] (br. *dd*, *J*(3,4) = *J*(3,2) = 4.8, *J*(3,1) small, H–C(3)); 1.81 [1.79] (*dq*, *J*(4, CH_3–C(4)) = 7.2, *J*(4,3) = 4.8, H–C(4)); 1.49 [1.50] (br. *dd*, J_{gem} = 14.0, *J*(6α, OH) = 2.2, *J*(6α, CH_3–C(5) small; decoupling at 2.83→br. *d* with J_{gem} = 14.0, H_α–C(6)); 1.98 [1.90] (*d*, J_{gem} = 14.0, H_β–C(6)); 5.80 [5.86] (br. *s*, *J*(9,1) small, H–C(9)); 4.46 [4.44], 4.41 [4.41] (*AB* of *ABXY*, *J*(*A*, *B*) = 13.2, *J*(*A*, *X*) = *J*(*A*, *Y*) = *J*(*B*, *X*) = *J*(*B*, *Y*) = 2.1, H_α–C(12), H_β–C(12)); 5.31 [5.25], 5.01 [5.01] (*XY* of *ABXY*, *J*(*A*, *X*) = *J*(*A*, *Y*) = *J*(*B*, *Y*) = *J*(*B*, *X*) = 2.1, *J*(*X*, *Y*) ≈ 0, H_a–C(13), H_b–C(13)); 0.98 [0.98] (*d*, *J*(CH_3–C(4), 4) = 7.2, CH_3–C(4)); 1.42 [1.41] (br. *s*, *J*(CH_3–C(5), 6α) small, CH_3–C(5)); 5.82 [5.83] (*dd*, *J*(2',3') = 15.3, *J*(2',4') = 0.7, H–C(2')); 7.24 [7.24] (br. *dd*, *J*(3',2') = 15.3, *J*(3',4') = 10.7, *J*(3',5') small, H–C(3')); 6.15 [6.24] (*dddd*, *J*(4',5') = 15.2, *J*(4',3') = 10.7, *J*(4',2') = *J*(4',6') = 0.7, H–C(4')); 5.99 [6.06] (br. *dd*, *J*(5',4') = 15.2, *J*(5', 6') = 7.7, *J*(5',3') small, H–C(5')); 2.17 [2.19] (br. *dtq*, *J*(6',5') = 7.7, *J*(6'7') = 7.4, *J*(6', CH_3–C(6')) = 7.1, H–C(6')); 1.36 [1.40] (*dq*, *J*(7',6') = *J*(7',8') = 7.4, 2 H–C(7')); 0.86 [0.89] (*t*, *J*(8',7') = 7.4, 3 H–C(8')); 1.02 [1.04] (*d*, *J*(CH_3–C(6'),6') = 7.1, CH_3–C(6')); 1.21 [1.20], 3.73 [3.73], 3.78 [3.74] (A_3, *Y*, and *X*, resp. of A_3XY, *J*(*A*, *X*) = *J*(*A*, *Y*) = 7.0, *J*(*X*, *Y*) = 9.2, CH_3CH_2O); 2.83 (*d*, *J*(OH, 6α) = 2.2, OH; shifted upfield on raising the temp., $\Delta\delta$ = 0.3 Hz/°; *J* typical for a W relationship, *i.e.* H–bonding); NOE ($CDCl_3$): 0.98→+8% on H–C(4), +5% on H_β–C(6), 4% on H–C(3), and 1.5% on CH_3–C(5); 1.42→+1% on H–C(2'), +6% on H_β–C(6), and +3% on CH_3–C(4); 1.81→+14% on H–C(3) and 6% on H_α–C(6); 5.91→3% on H–C(3); 6.20→14% on H–C(2) and 17% on H–C(9); 5.80→20% on H–C(1) and 6% on CH_3CH_2O; 3.73 and 3.78→7% on H–C(9) and 1% on CH_3–C(5); 5.01→+29% on H_a–C(13), +2% on both H_α- and H_β–C(12); 5.31→+24% on H_b–C(13); 5.82 +10% on H–C(4') and + 5 and −4% on H–C(3')[5]; 6.15→5% on H–C(6'), +3 and −2% on H–C(3'), and +2 and −4% on H–C(5'). ^{13}C-NMR (CD_3OD; within brackets, $CDCl_3$): 132.99 [131.54] (*d*, C(1)); 127.32 [126.75 or 126.92] (*d*, C(2)); 71.62 [69.96] (*d*, C(3)); 43.79 [42.33] (*d*, C(4)); 37.42 [36.26] (*s*, C(5)); 45.41 [43.43] (*t*, C(6)); 80.06 [78.83] (*s*, C(7)); 102.85 [101.22] (*s*, C(8)); 120.69 [119.37] (*d*, C(9)); 145.74 [144.98] (*s*, C(10)); 155.87 [154.16] (*s*, C(11)); 68.37 [67.58] (*t*, C(12)); 105.26 [105.27] (*t*, C(13)); 10.56 [10.10] (*q*, CH_3–C(4)); 21.08 [20.51] (*q*, CH_3–C(5)); 168.63 [167.00] (*s*, C(1')); 120.16 [118.53] (*d*, C(2')); 147.01 [145.41] (*d*, C(3')); 128.17 [126.92 or 126.75] (*d*, C(4')); 151.73 [150.23] (*d*, C(5')); 40.21 [38.77] (*d*, C(6')); 30.40 [29.29] (*t*, C(7')); 12.12 [11.62] (*q*, C(8')); 19.98 [19.47] (*q*, *C*–C(6')); 57.84, 16.06 [56.86, 15.70] (*t*, *q*, CH_3CH_2O). HR-MS: 428.25607 ± 0.01 ($C_{26}H_{36}O_5$, calc. 428.25628). MS: 428 (32, $M^{+\cdot}$), 383 (19, $M^{+\cdot} - CH_3CH_2O$), 382 (6, $M^{+\cdot}$ − EtOH), 275 (9), 274 (19), 228 (97), 191 (66), 137 (100), 109 (84).

Transesterification of (+)-**6** (4.4 mg) in 2 ml of 0.5M MeONa in MeOH for 8 h at r.t., followed by TLC purification with petroleum ether/Et_2O 2:1, gave (+)-**14** (1.0 mg, 58%; R_f 0.85; see below) and *(3a*R,*4a*R,*5*R,*6*S,*9a*S*)-9a-ethoxy-2,3,3a,4,4a,5,6,9a-octahydro-4a,5-dimethyl-3-methylidenenaphtho[2,3-*b*]furan-3a,6-diol* (**7**; 2.2 mg, 73%). ^{1}H-NMR ($CDCl_3$): 6.14 (br. *d*, *J*(1,2) = 9.5, *J*(1,9) and *J*(1,3) small, H–C(1)); 5.98 (*dd*, *J*(2,1) = 9.5, *J*(2,3) = 4.8, H–C(2)); 4.07 (br. *dd*, *J*(3,2) = *J*(3,4) = 4.8, *J*(3,1) small, H–C(3)); 1.60 (*dq*, *J*(4, CH_3–C(4)) = 7.1, *J*(4,3) = 4.8, H–C(4)); 1.46 (br. *d*, J_{gem} = 14.2, *J*(6α, CH_3–C(5)) small, H_α–C(6)); 1.99 (br. *d*, J_{gem} = 14.2, *J*(6β,9) small, H_β–C(6)); 5.00, 5.31 (*XY* of *ABXY*, *J*(*X*, *Y*) ≈ 0, *J*(*A*, *X*) = *J*(*B*, *X*) = 2.5, *J*(*A*, *Y*) = *J*(*B*, *Y*) = 2.1, 2 H–C(13)); 4.41, 4.45 (*AB* of *ABXY*, *J*(*A*, *B*) = 13.3, *J*(*A*, *X*) = *J*(*B*, *X*) = 2.5, *J*(*A*, *Y*) = *J*(*B*, *Y*) = 2.1, 2 H–C(12)); 5.78 (br. *s*, *J*(9,1) and *J*(9,6β) small, H–C(9)); 1.11 (*d*, *J*(CH_3–C(4),4) = 7.1, CH_3–C(4)); 1.40 (br. *s*, *J*(CH_3–C(5),6α) small, CH_3–C(5)); 3.73, 3.77 (*XY* of A_3XY, *J*(*X*,*Y*) = 9.2, *J*(*A*, *X*) = *J*(*B*,*X*) = 7.0, CH_3CH_2O); 1.20 (A_3 of A_3XY, *J*(*A*, *X*) = *J*(*B*, *X*) = 7.0, CH_3CH_2O); 4.23 (br. *s*, OH).

8. *Dendryphiellin G* (**8**). Colourless oil. $[\alpha]^{20}$ (λ): −11.2 (589), −11.3 (577), −19.2 (546), −241.6 (435), −1868.0 (365; *c* = 0.12, abs. EtOH). UV (EtOH): 279.0 (13.800). MS: 247 (4, $M^{+\cdot}$ − Me), 245 (7, $M^{+\cdot}$ − 17), 244 (13, $M^{+\cdot} - H_2O$), 228 (99), 213 (100), 190 (44), 198 (40), 185 (73), 162 (83), 134 (95), 91 (86).

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[5]) These and the following sometimes positive and sometimes negative NOE are typical of strongly coupled three-spin systems [1] [11].

Open Form **8a** (= *(1R*,7R*,8aR*)-8,8a-Dihydro-7-hydroxy-7-[1-(hydroxymethyl)ethenyl]-1,8a-dimethylnaphthalene-2,6(1H,7H)-dione*). ^{1}H-NMR (CD_3OD): 7.22 (br. *d*, $J(1,2) = 9.6$, $J(1,9)$ small, H–C(1)); 6.21 (br. *d*, $J(2,1) = 9.6$, $J(2,9)$ small, H–C(2)); 2.70 (*q*, $J(4, CH_3–C(4)) = 6.8$, H–C(4)); 2.38 (br. *d*, $J_{gem} = 14.5$, $J(6\alpha, CH_3–C(5))$ small, H_α–C(6)); 2.01 (*d*, $J_{gem} = 14.5$, H_β–C(6)); 6.20 (br. *s*, $J(9,1)$ and $J(9,2)$ small, H–C(9)); 4.06, 4.11 (*AB* of *ABXY*, $J(A, B) = 13.2$, $J(A, X) = J(B, X) = J(A, Y) = J(B, Y) \approx 1.1$, H_α–C(12), H_β–C(12)); 5.35, 5.42 (*XY* of *ABXY*, $J(A, X) = J(A, Y) = J(B, Y) = J(B, X) = 1.1$, $J(X, Y) \approx 0$, H_a–C(13), H_b–C(13)); 1.12 (*d*, $J(CH_3–C(4),4) = 6.8$, CH_3–C(4)); 1.35 (br. *s*, $J(CH_3–C(5), 6\alpha)$ small, CH_3–C(5)). ^{13}C-NMR (CD_3OD): 145.43 (*d*, C(1)); 134.57 (*d*, C(2)); 55.47 (*d*, C(4)); 43.37 (*s*, C(5)); 48.77 (*t*, C(6)); 130.26 (*d*, C(9)); 162.10 (*s*, C(10)); 154.89 (*s*, C(11)); 64.90 (*t*, C(12)); 114.00 (*t*, C(13)); 9.01 (*q*, CH_3–C(4)); 24.13 (*q*, CH_3–C(5)); signals for C(3), C(7), and C(8) could not be detected.

Hemiacetal Form **8b** (= *(3aR*,4aR*,5R*,9aS*)-3,3a,4,4a,5,9a-Hexahydro-3a,9a-dihydroxy-4a,5-dimethyl-3-methylidenenaphtho[2,3-b]furan-6(2H)-one*). ^{1}H-NMR (CD_3OD): 7.07 (br. *d*, $J(1,2) = 9.8$, $J(1,9)$ small, H–C(1)); 5.97 (br. *d*, $J(2,1) = 9.8$, $J(2,9)$ small, H–C(2)); 2.42 (*q*, $J(4, CH_3–C(4)) = 6.9$, H–C(4)); 1.76 (br. *d*, $J_{gem} = 14.1$, $J(6\alpha, CH_3–C(5))$ small, H_α–C(6)); 1.95 (*d*, $J_{gem} = 14.1$, H_β–C(6)); 6.01 (br. *s*, $J(9,1)$ and $J(9,2)$ small, H–C(9)); 4.55, 4.44 (*AB* of *ABXY*, $J(A, B) = 13.1$, $J(A, X) = J(B, X) = J(A, Y) = J(B, Y) = 2.4$, H_α–C(12), H_β–C(12)); 5.29, 5.06 (*XY* of *ABXY*, $J(A, X) = J(A, Y) = J(B, Y) = J(B,X) = 2.4$, $J(X, Y) \approx 0$; H_a–C(13), H_b–C(13)); 1.06 (*d*, $J(CH_3–C(4),4) = 6.9$, CH_3–C(4)); 1.23 (br. *s*, $J(CH_3–C(5),6\alpha)$ small, CH_3–C(5)); 4.62 (*m*, OH; upfield shift on raising temp. suggested intramolecular H–bonding). ^{13}C-NMR (CD_3OD): 147.50 (*d*, C(1)); 130.28 (*d*, C(2)); 204.80 (*s*, C(3)); 55.79 (*d*, C(4)); 42.54 (*s*, C(5)); 47.38 (*t*, C(6)); 79.39 (*s*, C(7)); 101.80 (*s*, C(8)); 132.74 (*d*, C(9)); 145.14 (*s*, C(10)); 156.86 (*s*, C(11)); 69.72 (*t*, C(12)); 107.59 (*t*, C(13)); 8.96 (*q*, CH_3–C(4)); 22.27 (*q*, CH_3–C(5)).

9. *Dendryphiellic Acid A* (= *(6S,2E,4E)-6-Methylocta-2,4-dienoic Acid;* (+)-**9**). Colourless oil. $[\alpha]^{20}$ (λ): +52.2 (589), +71.3 (546), +134.5 (435), +246.9 (365; $c = 0.17$, 95% EtOH). UV (95% EtOH): 252 (30200). ^{1}H-NMR (CD_3OD; within brackets, $CDCl_3$): 5.80 [5.79] (br. *d*, $J(2,3) = 15.2$, $J(2,4)$ small, H–C(2)); 7.25 [7.31] (br. *dd*, $J(3,2) = 15.2$, $J(3,4) = 10.7$, $J(3,5)$ small, H–C(3)); 6.22 [6.15] (br. *ddd*, $J(4,3) = 10.7$, $J(4,5) = 15.2$, $J(4,6) = 0.9$, $J(4,2)$ small, H–C(4)); 6.05 [6.06] (br. *dd*, $J(5,4) = 15.2$, $J(5,6) = 7.8$, $J(5,3)$ small, H–C(5)); 2.19 [2.17] (*ddtq* (br. *'sept.'*), $J(6,5) = 7.8$, $J(6, CH_3–C(6)) = 6.8$, $J(6,7) = 7.1$, $J(6,4) = 0.9$, H–C(6)); 1.40 [1.37] (*m*, 2 H–C(7)); 0.89 [0.87] (*t*, $J(8,7) = 7.4$, 3 H–C(8)); 1.04 [1.02] (*d*, $J(CH_3–C(6),6) = 6.8$, CH_3–C(6)). ^{13}C-NMR (CD_3OD): 170.81 (*s*, C(1)); 120.52 (*d*, C(2)); 147.08 (*d*, C(3)); 128.21 (*d*, C(4)); 151.29 (*d*, C(5)); 40.19 (*d*, C(6)); 30.41 (*t*, C(7)); 12.10 (*q*, C(8)); 20.01 (*q*, CH_3–C(6)). MS: 154 (9, $M^{+\cdot}$), 139 (3, $M^{+\cdot} - CH_3$), 125 (32), 109 (15), 97 (100), 79 (77).

10. *Dendryphiellic Acid B* (= *(6R*,2E,4E)-8-Hydroxy-6-methylocta-2,4-dienoic Acid;* (+)-**10**). ^{1}H-NMR ($CDCl_3$): 5.82 (br. *d*, $J(2,3) = 15.3$, $J(2,4)$ small, H–C(2)); 7.31 (br. *dd*, $J(3,2) = 15.3$, $J(3,4) = 10.6$, $J(3,5)$ small, H–C(3)); 6.21 (br. *dd*, $J(4,3) = 10.6$, $J(4,5) = 15.0$, $J(4,2)$ and $J(4,6)$ = small, H–C(4)); 6.07 (br. *dd*, $J(5,4) = 15.0$, $J(5,6) = 7.9$, $J(5,3)$ small, H–C(5)); 2.49 (br. *dtq*, $J(6,5) = 7.9$, $J(6, CH_3–C(6)) = 7.0$, $J(6,7) = 7.0$, $J(6,4)$ small, H–C(6)); 1.63 (*dt* as A_2 of A_2XY, $J(7,6) = 7.0$, $J(7,8) = 6.8$, 2 H–C(7)); 3.67, 3.64 (*XY* of A_2XY, $J(X, Y) = 10.9$, $J(X, A_2) = J(Y, A_2) = 6.8$, 2 H–C(8)); 1.08 (*d*, $J(CH_3–C(6),6) = 7.0$, CH_3–C(6)). ^{13}C-NMR ($CDCl_3$): 170.26 (*s*, C(1)); 118.77 (*d*, C(2)); 146.81 (*d*, C(3)); 127.00 (*d*, C(4)); 150.23 (*d*, C(5)); 39.13 (*d*, C(6)); 33.98 (*t*, C(7)); 60.82 (*t*, C(8)); 20.02 (*q*, CH_3–C(6)). For other spectroscopic data, see [1].

11. *Synthesis of* (+)-**9**. To a soln. of pyridine (15 ml, 0.18 mol) in CH_2Cl_2 (150 ml) at 0°, CrO_3 (16 g, 0.16 mol) was added slowly and stirred at r.t. for 30 min [6]. Then, (2*S*)-2-methylbutan-1-ol (*Aldrich;* 2.43 g, 0.027 mol) in CH_2Cl_2 (50 ml) was added and further stirred for 30 min. The mixture was filtered over silica gel and washed with CH_2Cl_2 (50 ml). The filtrate, cooled to 0°, was distilled through a short column with the collecting flask immersed in liq. N_2. The tail fraction (40 ml) contained (^{1}H-NMR) (+)-**12**, pyridine, and CH_2Cl_2. The latter was eliminated on a 2nd similar distillation, yielding 9.1 ml of (+)-**12** (40% yield)/pyridine 1:9[6]). A fraction of this soln. (5 ml) was diluted with 35 ml of toluene, methyl (triphenylphosphoranylidene)acetate [7] (*Aldrich*; 4 g, 0.012 mol) added, the flask flushed with N_2 and stoppered, and the mixture stirred at 95° for 15 h. Distillation *in vacuo* (short column) first at r.t. (bath) and then at 40° (bath) with the collecting flask immersed in liq. N_2 yielded 32.3 ml of a 1:7:38 mixture (^{1}H-NMR) of (+)-**13** (68% yield), pyridine, and toluene[7]). This mixture (25 ml, 3.5 mol of (+)-**13**) was flushed with

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[6]) A fraction (3 ml) of this soln., subjected to a 3rd distillation on a more efficient column, gave anal. pure (+)-**12** (78 mg).

[7]) A fraction of this mixture (1 ml) was subjected to HPLC with hexane/AcOEt 98:2 to give anal. pure (+)-**13** (t_R 6 min, 20 mg).

N_2 and cooled to −40°, mixed with 1M diisobutylaluminium hydride/toluene (10 ml) [8], brought to −10°, stirred for 4 h, and then brought to r.t. and neutralized with AcOH (added within 1 h). The mixture was filtered over 20 g of silica gel and washed with a little toluene, the resulting soln. (36 ml) mixed with 25 ml of CrO_3 pyridine soln. in CH_2Cl_2 (see above) and stirred for 30 min [6], the CH_2Cl_2 evaporated *in vacuo*, and the residue filtered over 20 g of silica gel. The filtrate was reacted with 2.0 g of methyl (triphenylphosphoranylidene)acetate as above [7]. The mixture (47 ml) was chromatographed through 100 g of silica gel (95:5 hexane/AcOEt), and the central fractions containing the desired product were concentrated *in vacuo* to 5 ml. A fraction of this mixture (0.5 ml) was subjected to HPLC with hexane/AcOEt 98:2 to give (+)-**14** (t_R 10 min; 26 mg, 44%) and **15** (t_R 7 min; 1.4 mg, 2.3%). A soln. of (+)-**14** (17 mg, 0.1 mmol) in 2 ml of 3% KOH/MeOH was stirred at 40° for 4 h. The mixture was neutralized with AcOH and then subjected to FC with AcOEt/petroleum ether 1:4 to yield (+)-**9** (12 mg, 78%). $[\alpha]_D = +48.6$ ($c = 0.36$, 95% EtOH).

(2S)-2-Methylbutanal ((+)-**12**). $[\alpha]_D^{20} = +28.1$ ($c = 0.55$, $CDCl_3$) [12]: ($[\alpha]_D = +28.5$). ^{1}H-NMR ($CDCl_3$): 9.62 (*d*, $J(1,2) = 1.9$, H–C(1)); 2.28 (*dddq*, $J(2, CH_3–C(2)) = 7.0$, $J(2,3) = 7.0$, 6.3, $J(2,1) = 1.9$, H–C(2)); 1.74, 1.43 ($J_{gem} = 14.2$, $J(3,2) = 7.0$, 6.3, $J(3,4) = 7.0$, 2 H–C(3)); 0.95 (*t*, $J(4,3) = 7.0$, 3 H–C(4)); 1.09 (*d*, $J(CH_3–C(2),2) = 7.0$, $CH_3–C(2)$). MS: 86 (42, $M^{+\cdot}$), 57 (100).

Methyl (4S,2E)-Methylhex-2-enoate ((+)-**13**). $[\alpha]_D^{20} = +39.0$ ($c = 1.7$, toluene). ^{1}H-NMR ($CDCl_3$): 5.70 (*dd*, $J(2,3) = 15.5$, $J(2,4) = 1.2$, H–C(2)); 6.78 (*dd*, $J(3,2) = 15.5$, $J(3,4) = 7.9$, H–C(3)); 2.12 (*dtq*, $J(4,3) = 7.9$, $J(4,5) = 7.0$, $J(4, CH_3–C(4)) = 6.8$, H–C(4)); 1.32 (*m*, 2 H–C(5)); 0.79 (*t*, $J(6,5) = 7.3$, 3 H–C(6)); 0.96 (*d*, $J(CH_3–C(4),4) = 6.8$, $CH_3–C(4)$); 3.63 (*s*, CH_3O). ^{13}C-NMR ($CDCl_3$): 166.96 (*s*, C(1)); 119.30 (*d*, C(2)); 154.31 (*d*, C(3)); 38.00 (*d*, C(4)); 28.68 (*t*, C(5)); 11.27 (*q*, C(6)); 18.67 (*q*, $CH_3–C(4)$); 50.94 (*q*, CH_3O).

Methyl (6S,2E,4E)-6-Methylocta-2,4-dienoate ((+)-**14**). $[\alpha]_D^{20} = +23.6$ ($c = 0.85$, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): 5.80 (br. *d*, $J(2,3) = 15.4$, $J(2,4)$ small, H–C(2)); 7.26 (br. *dd*, $J(3,2) = 15.4$, $J(3,4) = 10.4$, $J(3,5)$ small, H–C(3)); 6.13 (br. *dd*, $J(4,5) = 15.2$, $J(4,3) = 10.4$, $J(4,2)$ and $J(4,6)$ small, H–C(4)); 6.01 (br. *dd*, $J(5,4) = 15.2$, $J(5,6) = 7.7$, $J(5,3)$ small, H–C(5)); 2.16 (*m*, H–C(6)); 1.36 (*dq*, $J(7,8) = 7.4$, $J(7,6) = 7.0$, 2 H–C(7)); 0.86 (*t*, $J(8,7) = 7.4$, 3 H–C(8)); 1.02 (*d*, $J(CH_3–C(6),6) = 6.8$, $CH_3–C(6)$); 3.73 (*s*, CH_3O). ^{13}C-NMR ($CDCl_3$): 167.68 (*s*, C(1)); 118.80 (*s*, C(2)); 145.50 (*d*, C(3)); 126.68 (*d*, C(4)); 150.27 (*d*, C(5)); 38.74 (*d*, C(6)); 29.29 (*t*, C(7)); 11.59 (*q*, C(8)); 19.42 (*q*, $CH_3–C(6)$); 51.35 (*q*, CH_3O).

Methyl (6S,2Z,4E)-Methylocta-2,4-dienoate (**15**). ^{1}H-NMR ($CDCl_3$): 5.58 (*d*, $J(2,3) = 11.3$, H–C(2)); 6.56 (*ddd*, $J(3,2) = J(3,4) = 11.3$, $J(3,5) = 0.6$, H–C(3)); 7.25 (superimposed to residual solvent signal, H–C(4)); 5.96 (*dd*, $J(5,4) = 15.2$, $J(5,6) = 6.9$, H–C(5)); 2.23 (*m*, H–C(6)); 1.38 (*dq*, $J(7,6) = 7.0$, $J(7,8) = 7.3$, 2 H–C(7)); 0.87 (*t*, $J(8,7) = 7.3$, 3 H–C(8)); 1.04 (*d*, $J(CH_3–C(6),6) = 6.8$, $CH_3–C(6)$); 3.72 (*s*, CH_3O).

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