112. Bis-allylic Reactivity of the Funicolides, 5,8(17)-Diunsaturated Briarane Diterpenes of the Sea Pen *Funiculina quadrangularis* from the Tuscan Archipelago, Leading to 16-Nortaxane Derivatives[1])

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Funicolides A–C (**1**–**3**), D (**5**), and E (**7**) and 7-epifunicolide A (**4**), new 5,8(17)-diunsaturated briarane diterpenes, as well as the known analogue brianthein W (**6**), were isolated from the pennatulacean coral *Funiculina quadrangularis* (PALLAS, 1766) collected in the Tuscan archipelago. Easy degradation under oxidative and/or basic conditions served to assign the ester groups at C(2) or C(14), while revealing bis-allylic reactivity at C(7) with formation of 16-nortaxane derivatives.

1. Introduction. – Briarane diterpenes, which conceivably arise biogenetically *via* C(3)–C(8) cyclization of cembranoid precursors [1], were first isolated from the gorgonacean coral *Briareum asbestinum* (PALLAS) (suborder Scleraxonia, family Briareidae) from the Caribbeans [2a]. Briaranes were later also isolated from *a*) other tropical gorgonians, mostly in the same suborder, like *Erythropodium caribaeorum* (DUCHASSAING and MICHELOTTI) (Anthotelidae) [2b,c], *Solenopodium* spp. (Briareidae) [2d] and *Junceella* spp. (Ellisellidae) [2e], but also in the suborder Holaxonia, like *Plexaureides*[2]) *praelonga* [2g], *b*) pennatulacean corals from several areas, like *Stylatula* sp. [3a], *Ptilosarcus gurneyi* [3b], *Scytalium tentaculatum* [3c], *Renilla reniformis* [3d], *Pteroeides laboutei* [3e], *Cavernulina grandiflora* [3f], *Veretillum cynomorium* [1, 3g–h], *c*) a single alcyonacean coral, *Minabea* sp. [4], *d*) the stoloniferan corals *Pachyclavularia* sp. [5a] and *Tubipora* sp. [5b], and *e*) as dietary products, from the nudibranch mollusc *Armina maculata* that feeds on *V. cynomorium* [1].

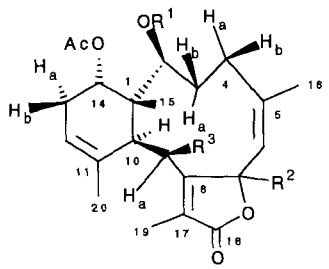
We report here on new briaranes, (called funicolides) isolated from the pennatulacean coral *Funiculina quadrangularis* (PALLAS, 1766). This luminescent sea pen, which belongs to the single-genus family Funiculinidae, suborder Sessiliflorae, is characterized by pale-yellow colonies on a unusually square-crossed, corneous skeleton that may surpass 1 m in length[3]). It is commonly encountered, albeit sparsely, on muddy and sandy bottoms at

[1]) Presented in part by *A.G.* at 'Giornate di Chimica delle Sostanze Naturali', Amalfi, 29 May–1 June 1994.

[2]) In an authoritative taxonomic guide, this genus does not appear, while *Plexauroides* is listed [2f].

[3]) Except for *Lituaria* [6], briaranes were reported for representative species of all the above genera of pennatulacean corals, including some in the primitive suborder Sessiliflorae (*Cavernulina* [3f], *Renilla* [3d], *Veretillum* [1] and, here, *Funiculina*). Therefore, briarane diterpenes must be an ancient acquisition by pennatulaceans. Interestingly, however, we were unable to detect these or related terpenoids in sea pens of the genera *Pteroeides* and *Pennatula* (Subsessiliflorae) collected in western Mediterranean Sea, around Banyuls-sur-Mer in the same area as *V. cynomorium*. It would be interesting to know if species of the sessilifloran *Lituaria* [6] contain briaranes.

Scheme 1 [a])



a) **1** R^1 = EtCO, $R^2 = H_\beta$, R^3 = H
2 R^1 = EtCO, R^2 = α-OH, R^3 = H
3 R^1 = EtCO, $R^2 = H_\beta$, R^3 = AcO
4 R^1 = EtCO, $R^2 = H_\alpha$, R^3 = H
5 R^1 = PrCO, $R^2 = H_\beta$, R^3 = H

b) **6** R^1 = Ac, $R^2 = H_\beta$, R^3 = H
7 R^1 = Ac, R^2 = α-OH, R^3 = H
11 R^1 = Ac, $R^2 = H_\alpha$, R^3 = H

a) Enzyme or K_2CO_3, $(CD_3)_2SO$, 60°, 180 min.
b) K_2CO_3, $(CD_3)_2SO$, 60°, 180 min.

[a]) Briarane numbering is used throughout, except for retrieval purposes (*Exper. Part*, where IUPAC numbering is used). Briarane/IUPAC equivalence is C(1)/C(8a), C(2)/C(8), C(3)/C(7), C(4)/C(6), C(6)/C(4), C(7)/C(3a), C(8)/C(13a), C(9)/C(13), C(10)/C(12a), C(11)/C(12), C(12)/C(11), C(13)/C(10), C(14)/C(9), C(17)/C(1), and C(18)/C(2), while in the other cases there is identical numbering.

depths below 100 m throughout the Mediterranean basin. After a long search, we finally found abundant populations of this coral between Vada and Capraia island in the Tuscan archipelago, Ligurian Sea. The new butenolidic briaranes **1**–**7** (*Scheme 1*) isolated from this coral revealed interesting chemical features that, along with elucidation of their conformational behavior in the accompanying paper [7], place the natural product chemistry of the briaranes on a more rational basis than heretofore.

2. Results and Discussion. – 2.1. *Structural Elucidation of the Funicolides.* Funicolide A (**1**), being the most abundant briarane of *F. quadrangularis*, could be investigated in detail, thus serving as a basis for structural definition of the other funicolides reported below. The composition $C_{25}H_{34}O_6$ was based on MS data in combination with ^{13}C- (*Table*

Table 1. *^{13}C-NMR Data* (in $CDCl_3$ at 20°, unless otherwise stated) *for Funicolides A–C* (**1–3**), *7-Epifunicolide A* (**4**), *Funicolide D* (**5**), *Brianthein W* (**6**), *and Funicolide E* (**7**)

	1	**2**	**3**[a])	**4**[a])	**5**[b])	**6**	**7**
C(1)	41.44 (*s*)	42.93 (*s*)	42.47 (*s*)	43.66 (*s*)	41.68 (*s*)	41.39 (*s*)	42.66 (*s*)
C(2)	74.24 (*d*)	76.38 (*d*)	73.20 (*d*)	78.11 (*d*)	74.3 (br. *d*)	74.49 (*d*)	76.32 (*d*)
C(3)	33.66 (*t*)	30.46 (*t*)	30.35 (*t*)	30.61 (*t*)	[c])	33.62 (*t*)	30.34 (*t*)
C(4)	29.57 (*t*)	28.08 (*t*)	26.26 (*t*)	30.23 (*t*)	29.5 (br. *t*)	29.50 (*t*)	27.98 (*t*)
C(5)	143.75 (*s*)	146.14 (*s*)	145.51 (*s*)	141.02 (*s*)	143.48 (*s*)	143.70 (*s*)	146.36 (*s*)
C(6)	122.68 (*d*)	124.43 (*d*)	121.88 (*d*)	122.32 (*d*)	122.91 (*d*)	122.67 (*d*)	124.31 (*d*)
C(7)	80.95 (*d*)	106.56 (*s*)	79.24 (*s*)	79.29 (*s*)	80.88 (*d*)	80.99 (*d*)	106.59 (*s*)
C(8)	160.03 (*s*)	160.57 (*s*)	157.70 (*s*)	164.02 (*s*)	159.81 (*s*)	160.02 (*s*)	160.53 (*s*)
C(9)	29.57 (*t*)	27.42 (*t*)	67.95 (*d*)	27.57 (*t*)	29.56 (*t*)	29.51 (*t*)	27.38 (*t*)
C(10)	37.53 (*d*)	37.99 (*d*)	45.61 (*d*)	39.67 (*d*)	37.58 (*d*)	37.53 (*d*)	37.95 (*d*)

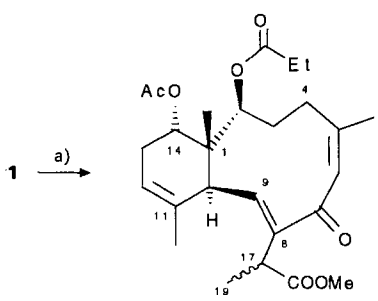
Table 1 (cont.)

	1	2	3[a])	4[a])	5[b])	6	7
C(11)	136.40 (*s*)	136.65 (*s*)	131.38 (*s*)	135.83 (*s*)	136.52 (*s*)	136.36 (*s*)	136.49 (*s*)
C(12)	116.70 (*d*)	117.52 (*d*)	122.58 (*d*)	118.43 (*d*)	116.72 (*d*)	116.69 (*d*)	117.57 (*d*)
C(13)	25.99 (*t*)	26.75 (*t*)	27.61 (*t*)	26.75 (*t*)	26.1 (br. *t*)	26.02 (*t*)	26.70 (*t*)
C(14)	72.64 (*d*)	72.83 (*d*)	74.24 (*d*)	73.96 (*d*)	73.0 (br. *d*)	72.55 (*d*)	72.59 (*d*)
C(15)	14.71 (*q*)	13.72 (*q*)	17.41 (*q*)	15.03 (*q*)	14.76 (*q*)	14.63 (*q*)	13.73 (*q*)
C(16)	27.69 (*q*)	23.14 (*q*)	23.87 (*q*)	22.21 (*q*)	27.3 (br. *q*)	27.56 (*q*)	23.27 (*q*)
C(17)	124.59 (*s*)	126.39 (*s*)	127.60 (*s*)	122.85 (*s*)	124.69 (*s*)	124.57 (*s*)	126.51 (*s*)
C(18)	174.09 (*s*)	171.22 (*s*)	172.79 (*s*)	174.38 (*s*)	173.9 (br. *s*)	174.05 (*s*)	171.46 (*s*)
C(19)	9.68 (*q*)	9.38 (*q*)	9.19 (*q*)	9.38 (*q*)	9.55 (*q*)	9.65 (*q*)	9.59 (*q*)
C(20)	21.49 (*q*)	22.18 (*q*)	21.52 (*q*)	22.01 (*q*)	21.39 (*q*)	21.47 (*q*)	22.42 (*q*)
AcO–C(2) or	8.96 (*q*)	8.80 (*q*)	8.81 (*q*)	8.76 (*q*)	16.60 (*q*)	21.16 (*q*)	21.29 (*q*)[d])
EtCOO–C(2) or	27.58 (*t*)	27.78 (*t*)	27.89 (*t*)	27.74 (*t*)	18.21 (*t*)	170.74 (*s*)	170.95 (*s*)[e])
PrCOO–C(2)	174.09 (*s*)	173.52 (*s*)	172.49 (*s*)	173.03 (*s*)	36.22 (*t*)		
					173.9 (*s*)		
AcO–C(9)	–	–	20.27 (*q*)	–	–	–	–
			169.32 (*s*)				
AcO–C(14)	21.19 (*q*)	21.07 (*q*)	20.66 (*q*)	21.12 (*q*)	21.05 (*q*)	20.99 (*s*)	21.14 (*q*)[d])
	170.68 (*s*)	170.63 (*s*)	170.05 (*s*)	170.15 (*s*)	170.43 (*s*)	170.73 (*s*)	170.41 (*s*)[e])

[a]) At 66°. [b]) At 55°. [c]) Not detected. [d])[e]) These data can be exchanged.

1) and ^{1}H-NMR data[4]). C,C Connectivities and heteroatom positions in **1** are fully supported by chemical-shift data, ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY maps, and ^nJ heterocorrelation data (*Table 2*). The relative positions of the ester substituents could not be deduced from spectra, however, because of the superimposition of the signals for H–C(2) and H–C(14). However, the propanoate group at C(2) and the acetate group at C(14) could be assigned by ^{13}C-NMR (*Table 3*) and heterocorrelations (*Table 2*) for the major product **8** or **9** (we do not know which is which) obtained by treatment of **1** with K_2CO_3 in MeOH under air (*Scheme 2*).

Scheme 2



8 (17*S**)[a])
9 (17*R**)[a])

a) K_2CO_3, MeOH, air, r.t., 90 min.

[a]) Configuration at C(17) can be interchanged.

[4]) Difficulties in interpretation for these and other funicolides due to broad ^{13}C- and ^{1}H-NMR signals could be overcome by recording the spectra above the coalescence temperature.

Table 2. *Key Multiple-Bond ^1H, ^{13}C-Heteronuclear Correlations for Funicolide A* (**1**) *and Its Major Transformation Product* **8** (or **9**), *Funicolide B* (**2**), *Funicolide C* (**3**), *and 7-Epifunicolide A* (**4**)

	1[a])	**2**[b])	**3**[b])	**4**[b])	**8** (or **9**)[a])
H–C(2)		*C*OO–C(2)	*C*OO–C(2), C(3), C(14),	C(4), C(10), *C*OO–C(2)	C(1), C(15), *C*OO–C(2)
H_b–C(4)		C(5)	C(2), C(5), C(16)	C(2), C(16)	
H–C(6)		C(7)	C(4), C(16)	C(4), C(16)	C(4), C(16)
H–C(7)			C(5), C(6), C(8), C(17)	C(5), C(6), C(8)	
H–C(9)	C(10), C(17)	C(8)		C(8), C(10), C(11), C(17)	C(7), C(17)
H_a–C(9)	C(7), C(8), C(11)	C(7)	C(1), C(7), C(8), *C*OO–C(9), C(11), C(17)	C(1), C(8), C(10), C(11)	
H–C(10)			C(1), C(2), C(8), C(9), C(11), C(12), C(14)	C(1), C(8), C(11)	C(8), C(11), C(12), C(15)
H–C(14)			C(2), *C*OO–C(14), C(15)	C(10), C(12), *C*OO–C(14)	C(10), C(12), *C*OO–C(14)
3 *H*–C(15)	C(1), C(10), C(14)	C(1), C(2), C(10), C(14)	C(1), C(10), C(14)	C(1), C(2), C(10), C(14)	C(2), C(10), C(14)
3 *H*–C(16)	C(5), C(6)	C(4), C(5), C(6)	C(4), C(5), C(6)	C(4), C(5), C(6)	C(5), C(6)
3 *H*–C(19)	C(8), C(17), C(18)	C(8), C(17), C(18)	C(8), C(17), C(18)	C(8), C(17), C(18)	C(8), C(17), C(18)
3 *H*–C(20)	C(10), C(11), C(12)	C(11), C(12)	C(10), C(11), C(12)	C(10), C(11), C(12)	C(10), C(11), C(12)
CH_3CH_2COO–C(2)	*C*OO–C(2)	*C*OO–C(2)	*C*OO–C(2)		*C*OO–C(2)
CH_3COO–C(9)			*C*OO–C(9)		
CH_3COO–C(14)	*C*OO–C(14)	*C*OO–C(14)	*C*OO–C(14)	*C*OO–C(14)	*C*OO–C(14)
CH_3O–C(18)					C(18)

[a]) From ^1H,^{13}C COSY [10].

[b]) From HMBC [11].

Table 3. *^{13}C-NMR Data* (in $CDCl_3$ at 20°, unless otherwise stated) *of the Transformation Products* **8** (or **9**), **12**, *and* **13** *of Funicolide A* (**1**), **10** *of Funicolide B* (**2**), *and* **11** *and* **14** *of Brianthein W* (**6**)

	8 (or **9**)	**10**[a])	**11**	**12**	**13**[b])	**14**[b])
C(1)	43.37 (*s*)	43.17 (*s*)	43.50 (*s*)	47.06 (*s*)	44.28 (br. *s*)	47.00 (*s*)
C(2)	74.77 (*d*)	75.39 (*d*)	78.34 (*d*)	72.72 (*d*)	72.00 (br. *d*)	72.94 (*d*)
C(3)	28.60 (*t*)[d])	29.12 (*t*)[d])	30.53 (*t*)	38.03 (*t*)	32.22 (*t*)	37.95 (*t*)
C(4)	28.10 (*t*)[d])	29.29 (*t*)[d])	30.17 (*d*)	54.88 (*d*)	126.09 (*d*)	54.83 (*d*)
C(5)	156.20 (*s*)	153.95 (*s*)	141.07 (*s*)	166.96 (*s*)	132.81 (br. *s*)	166.95 (*s*)
C(6)	130.79 (*d*)	130.18 (*d*)	122.22 (*d*)	125.52 (*d*)	45.93 (br. *t*)	125.52 (*d*)
C(7)	196.82 (*s*)	199.21 (*s*)	79.36 (*s*)	193.36 (*s*)	207.19 (*s*)	193.37 (*s*)
C(8)	142.10 (*s*)	153.49 (*s*)	164.20 (*s*)	145.64 (*s*)	122.01 (*s*)	145.65 (*s*)
C(9)	135.04 (*d*)	30.46 (*t*)	27.62 (*d*)	135.07 (*d*)	30.24 (br. *t*)	135.04 (*d*)
C(10)	42.91 (*d*)	36.77 (*d*)	39.62 (*d*)	38.03 (*d*)	40.56 (br. *d*)	38.00 (*d*)
C(11)	133.01 (*s*)	135.69 (*s*)	135.77 (*s*)	133.61 (*s*)	134.45 (br, *s*)	133.61 (*s*)
C(12)	118.05 (*d*)	117.10 (*d*)	118.44 (*d*)	116.52 (*d*)	120.33 (br. *d*)	116.51 (*d*)
C(13)	27.03 (*t*)	27.41 (*t*)	26.70 (*t*)	28.77 (*t*)	27.62 (*t*)	28.81 (*t*)
C(14)	72.42 (*d*)	72.79 (*d*)	73.95 (*d*)	71.58 (*d*)	74.30 (*d*)	71.48 (*d*)
C(15)	14.11 (*q*)	13.56 (*q*)	15.07 (*q*)	11.48 (*q*)	14.87 (*q*)	11.45 (*q*)
C(16)	25.45 (*q*)	25.27 (*q*)	22.23 (*q*)	23.35 (*q*)	25.18 (*q*)	23.32 (*q*)
C(17)	43.28 (*d*)	125.52 (*s*)	122.85 (*s*)	79.90 (*s*)	158.90 (br. *s*)	79.90 (*s*)
C(18)	173.61 (*s*)	168.16 (*s*)	174.59 (*s*)	28.45 (*q*)	167.58 (br. *s*)	28.46 (*q*)
C(19)	15.87 (*q*)	14.79 (*q*)	9.49 (*q*)	22.21 (*q*)	14.13 (*q*)	22.21 (*q*)
C(20)	22.65 (*q*)	21.44 (*q*)	22.13 (*q*)	–	21.11 (*q*)	–
*Ac*O–C(2) or	8.80 (*q*)	8.87 (*q*)	21.25 (*q*)[c])	8.88 (*q*)	9.06 (*q*)	21.31 (*q*)[c])
*EtC*OO–C(2)	27.66 (*t*)	27.70 (*t*)	170.32 (*s*)[d])	27.82 (*t*)	28.09 (*t*)	170.86 (*s*)[d])
	174.10 (*s*)	173.46 (*s*)		174.06 (*s*)	173.50 (*s*)	
*Ac*O–C(14)	21.14 (*q*)	21.26 (*q*)	20.97 (*q*)[c])	21.15 (*q*)	21.32 (*q*)	21.17 (*q*)[c])
	170.76 (*s*)	170.91 (*s*)	169.77 (*s*)[d])	170.72 (*s*)	170.97 (*s*)	170.82 (*s*)[d])
CH_3O–C(18)	51.86 (*q*)	52.09 (*q*)	–	–	52.24 (*q*)	–

[a]) At 55°. [b]) At 25°; recording the spectrum at 45°, the signals of C(1), C(2), C(5), C(6), C(9), C(10), C(11), C(12), C(17), and C(18) sharpened. [c])[d]) Data exchangeable within the same column.

The relative configurations at both the ring junctions and the heteroatom-bearing centres, as shown in **1**, were based on NOE enhancements between the couples of protons H_b–C(4)/H–C(7), H–C(6)/H–C(10), H–C(10)/H–C(2), H–C(14)/3 H–C(15), and 3 H–C(15)/H–C(9) (*Table 4*). (*Z*)-Configuration at C(5)=C(6) was assigned on both NOE enhancement between H–C(6) and 3 H–C(16) (*Table 4*) and low-field resonance for C(16). NOE Data for **8** (*Exper. Part*) supported the α-position for AcO–C(14).

Table 4. *Key Differential NOE for Funicolides A–C* (**1**–**3**) *and 7-Epifunicolide A* (**4**)

Irradiated proton	Relaxed proton(s) (% increase)			
	1[a])	**2**	**3**	**4**
H–C(2)	H–C(10) (12), 3 H–C(15) (1), 3 H–C(16) (2)	H–C(10) (4), H_a–C(4) (3)	H–C(10) (3), H_a–C(13) (10)	H_a–C(4) (3), H–C(10) (5)
H_a–C(4)		H–C(2) (7)		H–C(2) (4), H–C(7) (13), H–C(10) (4)

Table 4 (cont.)

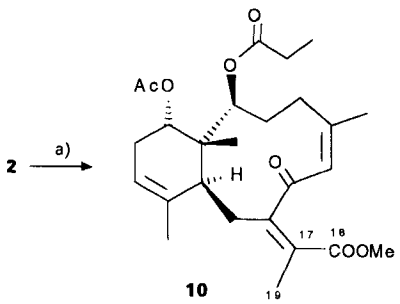
Irradiated proton	Relaxed proton(s) (% increase)			
	1[a])	2	3	4
H_b–C(4)	H–C(7) (7)		H–C(6) (13), H–C(7) (13)	
H–C(6)	H–C(10) (6), 3 H–C(16) (2)	3 H–C(16) (3)	H–C(10) (2), 3 H–C(16) (3)	3 H–C(16) (3)
H–C(7)	H_b–C(4) (4)		H_b–C(4) (10), 3 H–C(15) (4)	H_a–C(4) (9), H–C(10) (7)
H_a–C(9)	3 H–C(19) (2)		H–C(10) (6), 3 H–C(19) (2), 3 H–C(20) (5)	3 H–C(15) (3)
H–C(9)	H_b–C(4) (3), 3 H–C(15) (2)	3 H–C(15) (2), H–C(6) (2)		
H–C(10)	H–C(2) (10), H–C(6) (5)	H–C(2) (8), 3 H–C(20) (2)	H_a–C(9) (9), 3 H–C(20) (3)	H–C(2) (5), H–C(7) (11)
H–C(12)	3 H–C(20) (3)	3 H–C(20) (3)	3 H–C(20) (3)	3 H–C(20) (3)
H–C(14)	H–C(10) (12) 3 H–C(15) (1), 3 H–C(16) (2)	3 H–C(15) (2)	3 H–C(15) (2)	
3 H–C(15)	H–C(9) (7), H–C(10) (3), H_b–C(13) (4), H–C(14) (10)	H_a–C(9) (3), H–C(6) (2), H–C(14) (12)	H_b–C(3) (18), H_b–C(4) (4), H–C(7) (11), H–C(10) (3), H–C(14) (13)	H–C(2) (2), H–C(9) (7), H_a–C(9) (10), H–C(14) (9)
3 H–C(16)	H–C(2) (7), H–C(6) (10)	H–C(6) (18)	H–C(6) (16)	H–C(6) (12)
3 H-C (19)	H_a–C(9) (5), 3 H–C(20) (2)		H_a–C(9) (13)	H_a–C(9) (9)
3 H–C(20)	H_a–C(9) (4), H–C(10) (6), H–C(12) (11), 3 H–C(19) (3)	H–C(12) (17)		H_a–C(9) (5), H–C(10), (4), H–C(12) (10)

[a]) Because of signal superimposition, the irradiation affected H–C(2) and H–C(14) simultaneously.

Comparison of the spectral data of funicolide B (**2**) with those of funicolide A (**1**) indicated OH–C(7) in place of H–C(7) and the connectivities and relative configurations shown in *Scheme 1*. The heterocorrelation *H*–C(2)/Et*C*OO (*Table 2*) confirmed the position of EtCOO at C(2). Low-field shifts for H–C(10) and H_a–C(4) suggested the α-position for OH–C(7). NOE Enhancements between 3 H–C(15) and both H–C(6) and H–C(9) indicated that the C(5)=C(6) bond points upwards and OH–C(7) downwards. As above for **1**, the relative configurations for **2** were based on NOE data (*Table 4*). Further support for the structure of **2** was provided by the spectral data of product **10** (see *Table 3* and *Exper. Part*) obtained by treatment of **2** with KOH in DMSO, followed by MeI (*Scheme 3*).

The closest literature analogues of funicolide B (**2**) are *i*) a briarane isolated from the stoloniferan coral *Pachyclavularia* sp., which, however, is epimeric at C(7) and bears an epoxide group at C(11)–C(12) and an ester group at C(4) rather than at C(2) [5a], and *ii*) an analogue of the latter briarane, isolated from *Briareum asbestinum*, albeit of uncertain configuration [5b].

Scheme 3



a) 1. KOH, DMSO, r.t., 10 min;
2. MeI, 30 min.

Structure **3** for funicolide C (*Scheme 1*) was based on both the NMR (*Tables 1* and *2*) and MS data. NOE Enhancements (*Table 4*) supported the configuration in three areas: those at the ring junctions (H–C(7)/3 H–C(15) and H–C(6)/H–C(10), at the ester-bearing positions (H–C(2)/H–C(10), H–C(2)/H_a–C(13), 3 H–C(15)/H_b–C(3), 3 H–C(19)/H_a–C(9), and H_a–C(9)/3 H–C(20)), and at the C(5)=C(6) bond (H–C(7)/H_b–C(4) and H–C(6)/3 H–C(16)).

For 7-epifunicolide A (**4**), the same connectivities as in **1** were established by NMR (*Tables 1* and *2*), though δ values at the ten-membered ring differ in the two compounds. NOE Enhancements (H–C(10)/H–C(7), H–C(7)/H_a–C(4), H_a–C(4)/H–C(2), H–C(2)/H–C(10); see *Table 4*) suggested inverted configuration at C(7) with respect to **1**.

Structure **5** for funicolide D was based on NMR evidence (*Table 1* and *Exper. Part*) that relates it to **1**, except for the signals of a butanoate in place of those of a propanoate at C(2).

Comparison of the spectral data of the second more abundant terpenoid of *F. quadrangularis i.e.*, of **6** (see *Table 1* and the *Exper. Part*), with those of **1** straightforwardly disclosed replacement of EtCOO by MeCOO and the connectivities and relative configurations indicated in *Scheme 1*. The spectral data of **6** match those reported for brianthein W, previously isolated from the gorgonian *Briareum polyanthes* [2h].

Structure **7** for funicolide E could be readily assigned from close spectral similarity with funicolide B (**2**), structural differences being limited to MeCOO group in place of an EtCOO group at C(2).

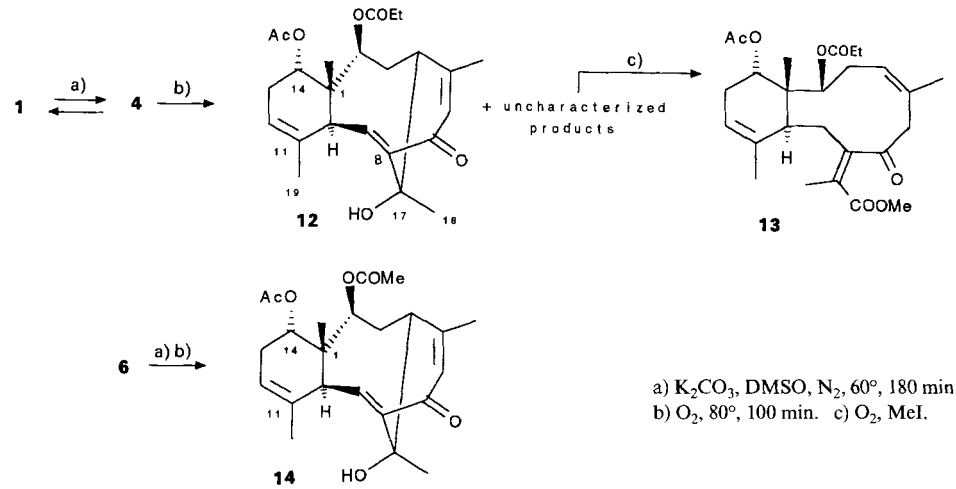
Finally, base-induced epimerization of **6** gave the unnatural epimer 7-epibrianthein W (**11**; *Scheme 1*), which served to confirm structural assignments.

2.2. *On the Bis-allylic Reactivity of the Funicolides.* The transformation **2** → **10** see *Scheme 3*) represents a straightforward nucleophilic opening of the butenolide ring by OH^-, which is made irreversible by subsequent reaction of the carboxylate group with MeI. This interconversion between the butenolide and open forms is probably reversible though the equilibrium is strongly displaced towards the former. Our expectation is that similar processes will be found with close analogues [5].

For briaranes bearing a H-atom at C(7), simple processes under basic conditions only occur under inert atmosphere. Thus, **1** was transformed into epimer **4** (*Scheme 1*), *via*, conceivably, a bis-allylically stabilized carbanion at C(7)[5]). In the presence of K_2CO_3, **1** in

[5]) Epimerization at C(7) of **1** is favored by the acidity of H–C(7), as evidenced by its low-field resonance (δ_H 5.48) and rapid H/D exchange in the presence of K_2CO_3 in CD_3OD at room temperature under N_2.

Scheme 4



a) K_2CO_3, DMSO, N_2, 60°, 180 min.
b) O_2, 80°, 100 min. c) O_2, MeI.

DMSO at 60° under N_2 underwent epimerization at C(7) with pseudo-first-order kinetics, resulting, after 3 h, in a *ca.* 1:4 mixture **1**/**4** in quantitative yield (*Scheme 4*). In the presence of O_2 under otherwise similar conditions, a more complex pattern of reactivity emerged. Thus, in oxygenated DMSO at 80°, **1**/**4** disappeared within 100 min to give more polar material from which the 16-nortaxane derivative **12**[6]) and another, less stable product were isolated by reversed-phase HPLC. The latter was reacted with MeI in K_2CO_3/DMSO to give **13**[7]). Compound **13** was also obtained directly, besides **12**, on treatment of **1** with K_2CO_3/DMSO/MeI. A similar behavior was noticed for brianthein W (**6**) (→ **14**[6]) (*Scheme 4*). Without exclusion of air, **1** reacted with K_2CO_3 in MeOH to give **8**/**9** (see above *Scheme 2*)[8]).

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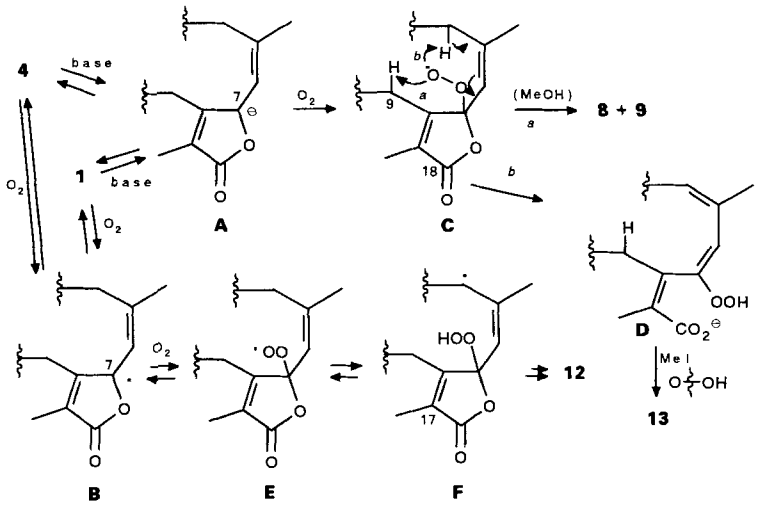
[6]) The composition $C_{24}H_{32}O_6$ for **12** was mainly based on 1D (^1H and ^{13}C) and 2D-NMR ($^1H,^1H$- and $^1H,^{13}C$-COSY). With respect to **1**, 1 C-atom was lost, while spectral changes were observed for the C(4) to C(9) portion, indicating replacement of the lactone C=O by an α,β-unsaturated (λ_{max} 236 and 330 nm) keto group. Moreover, two CH groups appeared instead of CH_2(4) and CH_2(9), while CH(7) had disappeared. The new connectivities in **12** were established by HMBC: the correlations H–C(4)/C(8) and C(17) and 3H–C(18)/C(4), C(8), and C(17) supported C(4)–C(17) bonding and the correlations H–C(6)/C(8) and H–C(9)/C(7), C(8), and C(17) the C=O position. In the MS, no M^+ was detected. The fragment at m/z 373.2009 ($C_{22}H_{29}O_5^+$) was attributed to $[M - Ac]^+$ whose Ac group did not derive from AcO. The latter was lost in the next fragmentation step. The configurations at C(4), C(17), and C(8)=C(9) were supported by NOE data (H–C(10)/H–C(2), H–C(2)/H–C(4), H–C(4)/3 H–C(18), 3 H–C(18)/H–C(6), H–C(9)/3 H–C(15), and 3 H–C(15)/H_b–C(3)) and coupling constants (J(4,3) = 10.0, 6.5 and J(9,10) = 10.6). The structure of the analogue **14** rests on similar evidence (*Exper. Part*).

[7]) Structure **13** was based on the molecular ion (m/z 460) and NMR spectra (*Exper. Part*). In particular, the connectivities C(6)–C(7)–C(8)–C(9), while escaping $^1H,^1H$-COSY capabilities, emerged from HMBC (H_a–C(9)/C(8), C(7), and C(17); H_a–C(6)/C(5) and C(7); H_b–C(6)/C(5), and C(7); 3 H–C(19)/C(8), C(17), and C(18)). The (*Z*)-configuration of C(4)=C(5) was established by NOE enhancement 3 H–C(16)/H–C(4), while the NOE enhancements H–C(4)/H–C(2) and H–C(2)/H–C(10) suggest a preferential conformation with C(4)=C(5)Me positioned below the mean plane of the 10-ring moiety.

[8]) In the presence of O_2, H–C(7) abstraction may be followed by, in the order, hydroperoxide formation, nucleophilic attack by MeO^- at the butenolide carbonyl group, butenolide opening, and hydroperoxide expulsion to give, after C(8)=C(17) bond shift to C(8)=C(9), the diasteroisomer mixture **8**/**9**.

Scheme 5. *Proposed Pathwys for Degradation of Funicolide A* (**1**) *in Oxygenated Basic Media* (brianthein W (**6**) behaves similarly)



As detailed mechanistic studies are lacking, we can only offer a gross, tentative rationalization of the described butenolide openings (*Scheme 5*). Thus, **1** and its epimer **4** are supposed to be in equilibrium *via* either carbanion **A** or free radical **B**. Carbanion **A** could capture aerial O_2 to give a peroxide anion **C** which abstracts either an allylic H–C(9) (route *a*) and is attacked by MeOH at C(18) (→ **8**/**9**) or which abstracts an allylic H–C(4) (route *b*) to give an intermediate *D* that is driven towards **13** on carboxylate trapping by MeI and hydroperoxide reduction by I^- [8]. In parallel, radical **B** could be trapped by aerial O_2 to give hydroxyperoxyl radical **E** that abstracts the proton at C(4). The resulting free radical **E** attacks then C(17) affording **12** *via* butenolide ring opening and decarboxylative hydroxylation at C(17).

These observations disclose fine facets of the chemical behavior of briaranes. Epimerization at C(7) may lead to artifacts, although 7-epifunicolide A (**4**) is unlikely to be such a case since the 5:95 ratio of epimers **4** and **1** in the coral extracts is opposite to that observed under the basic conditions of interconversion (4:1). The bis-allylic reactivity described here concerns not only **1** and **6** but is likely to be a common theme of the chemistry of briaranes bearing 5,8(17)-diunsaturation. That this might also be true under biogenetic conditions is suggested by the co-occurrence of the couples of C(7)-reduced/C(7)-oxidized products **1**/**2** and **6**/**7** in *F. quadrangularis*.

Literature examples of 5,8(17)-diunsaturation comprise also briareolide G [2c], a series of compounds extracted from the gorgonians *Briareum steckei* [9], and a compound extracted from *Briareum* sp. [10].

We thank the *Consorzio Regionale di Idrobiologia e Pesca*, Livorno, and the *Laboratoire Arago*, Banyuls-sur-Mer, for much aid to *F.P.* in collecting the sea pen, Dr. *M. Grasshoff* for the taxonomic identifications, Mr. *S. Gadotti* and Mr. *A. Sterni* for skilled technical contributions in product isolation and mass spectra, respectively, and, for financial support, *MURST* (Progetti di Interesse Nationale) and *CNR*, Roma.

Experimental Part

1. *General.* All evaporations were carried out at reduced pressure. Yields are given on reacted substrates. TLC: *Merck* silica gel *60 PF_{254}*. Reversed-phase flash chromatography (FC): *Merck LiChroprep RP-18*, 40–63 μm. HPLC: *Merck LiChrosorb RP-18*, (7 μm) or *Merck LiChrosorb CN* (7 μm), in both cases with 25 × 1-cm columns. Polarimetric data: *JASCO-DP-181* polarimeter; λ in nm. UV (λ_{max} in nm, ε in mol^{-1} 1 cm^{-1}): *Perkin-Elmer-Lambda-3* spectrophotometer. NMR: *Varian-XL-300* (^{13}C at 75.43 MHz, ^1H at 299.94 MHz); δ in ppm rel. to internal Me_4Si (= 0 ppm) and J and $w_{1/2}$ in Hz; probe temp. 20° and solvent $CDCl_3$, if not otherwise stated; br. (not followed by multiplicity specification) indicates very broad or submerged signals; 6-s preirradiation for differential NOE (irradiated proton (s)→relaxed proton(s) (% increment)); multiplicities and C and H assignments from DEPT [11], $^1H,^1H$-COSY [12], $^1H,^{13}C$-COSY [13], and HMBC [14] (reported as ^1H→correlated ^{13}C). EI-MS (m/z (%)): *Kratos MS80* with home-built acquisition system.

2. *Collection and Isolation. Funiculina quadrangularis* (PALLAS, 1766) was collected (registration number 603M) during the campaign *Survey X* on November 14, 1990, by beam trawling between Vada, south of Livorno, and Capraia island, from 43° 17.20′ north, 10° 10.45′ east, to 43° 11.20′ north, 10° 10.45′ east, at depths 122–135 m. *F. quadrangularis*, which left copious mucous substance on board, was freed from a few accompanying specimens of the sea pen *Kophobelemnon stelliferum* (O.F. MÜLLER, 1776), immediately soaken in 95% EtOH, and tightly packed for a total of 4 l in glass containers. Identifications were done by Dr. *M. Grasshoff, Forschungsinstitut Senckenberg*, Frankfurt am Main, who retains voucher specimens. After storage of these samples for a few weeks in the cold, the solvent was decanted and the sea pen further extracted twice with fresh EtOH. The combined org. phase was evaporated to leave an aq. residue that was extracted 3× with 0.3 l of petroleum ether and then 4× with 0.2 l of AcOEt. Evaporation of the petroleum-ether phase gave a residue that was subjected to reversed-phase FC (H_2O/MeOH gradient) to give, with H_2O/MeOH 1:9, the funicolides. These were separated by HPLC (*RP-18*, MeCN/H_2O 65:35, 4 ml/min, λ_{max} 254 nm), collecting three fractions at t_R 8.5, 10.0, and 11.0 min. The latter gave pure funicolide A (**1**; 55 mg). The fraction with t_R 8.5 min was further subjected to HPLC (*CN*, hexane/AcOEt 4:1, 4 ml/min), to give funicolide B (**2**; 19 mg; t_R 6 min), briantheine W (**6**; 35 mg; t_R 7 min), and funicolide E (**7**; 8.8 mg; t_R 9 min). The fraction with t_R 10.0 min was subjected to HPLC (*RP-18*, MeCN/H_2O 3:2, 4 ml/min), to give funicolide C (**3**; 4.6 mg), 7-epifunicolide A (**4**; 2.9 mg), and funicolide D (**5**; 3.8 mg).

3. *Funicolide A* (= *(+)-(1R*,2R*,7R*,10R*,14R*,5Z)-14-Acetoxy-18-oxobriara-5,8(17),11-trien-2-yl Propanoate* = *(+)-(3aR*,8R*,8aR*,9R*,12aR*,4Z)-9-Acetoxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8-yl Propanoate*; **1**). $[\alpha]^{20}$ (λ) = +33.2 (589), +42.7 (546), +82.3 (435), +155.5 (365; c = 0.6, EtOH). UV (EtOH): 206 (18500). ^{1}H-NMR: 4.87 (br. *s*, $w_{1/2}$ = 7.5, H–C(2)); 1.73 (br., H_b–C(3)); 2.29 (br., H_a–C(3)); 2.23 (br., H_a–C(4)); 2.57 (br., H_b–C(4)); 5.17 (br. *d*, J(6,7) = 9.5, H–C(6)); 5.48 (br. *d*, J(7,6) = 9.5, H–C(7)); 2.87 (br. *d*, J_{gem} = 16.0, H–C(9)); 2.53 (br. *dd*, J_{gem} = 16.0, J(9,10) = 7.0, H_a–C(9)); 2.71 (br. *s*, H–C(10)); 5.22 (br. *d*, J(12,13a) = 6.0, H–C(12)); 2.06 (br., H_a–C(13)); 2.27 (br., H_b–C(13)); 4.88 (br. *s*, $w_{1/2}$ = 8, H–C(14)); 1.01 (br. *s*, 3 H–C(15)); 2.08 (br. *s*, 3 H–C(16)); 1.85 (br. *s*, 3 H–C(19)); 1.60 (br. *s*, 3 H–C(20)); 1.95 (*s*, AcO); 2.33 (*q*, J = 7.5, MeCH_2CO); 1.13 (*t*, J = 7.5, *Me*CH_2CO). MS: 430 (0.6, M^+), 374 (1.5, $[M - MeCH{=}CO]^+$), 370 (2.0, $[M - AcOH]^+$), 356 (1.5, $[M - EtCOOH]^+$), 314 (15.5), 296 (36), 281 (23), 216 (43), 208 (22), 190 (23), 185 (25), 171 (36), 157 (33), 119 (53), 107 (31), 105 (36), 91 (57), 84 (54), 57 (100), 43 (96).

4. *Funicolide B* (= *(−)-(1R*,2R*,7S*,10R*,14R*,5Z)-14-Acetoxy-7-hydroxy-18-oxobriara-5,8(17),11-trien-2-yl Propanoate* = *(−)-(3aR*,8S*,8aS*,9S*,12aS*,4Z)-9-Acetoxy-3a-hydroxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8-yl Propanoate*; **2**). $[\alpha]^{20}$ (λ) = −45.7 (589), −46.4 (577), −99.3 (435), −203.6 (365; c = 0.14, EtOH). UV (EtOH): 225 (6000). ^{1}H-NMR: 4.89 (*dd*, J = 7.8, 2.7, H–C(2)); 1.85 (br., 2 H–C(3)); 2.25 (br., H_b–C(4)); 3.42 (br. *dd*, J_{gem} = 14.1, H_a–C(4)); 5.26 (br. *s*, H–C(6)); 7.9 (br. *s*, in $(CD_3)_2SO$, OH–C(7)); 2.33 (*dd*, J_{gem} = 15, J(9,10) = 10, H_a–C(9)); 2.75 (br. *d*, J_{gem} = 15, H–C(9)); 3.33 (br. *d*, J(10,9a) = 10, H–C(10)); 5.24 (br. *d*, J(12,13a) = 6, H–C(12)); 2.28 (br., H_b–C(13)); 2.05 (br., H_a–C(13)); 4.87 (br. *s*, $w_{1/2}$ = 6, H–C(14)); 1.01 (*s*, 3 H–C(15)); 1.73 (*d*, J(16,6) = 1.2, 3 H–C(16)); 1.84 (*d*, J(19,9) = 1.5, 3 H–C(19)); 1.60 (br. *s*, 3 H–C(20)); 2.01 (*s*, AcO); 2.28, 2.31 (ABX_3, $J(A,B)$ = 16, $J(A,X) = J(B,X)$ = 7.5, MeCH_2CO); 1.11 (*t*, J = 7.5, *Me*CH_2CO). MS: 428 (0.5, $[M - H_2O]^+$), 386 (0.3, $[M - AcOH]^+$), 372 (1.5, $[M - EtCOOH]^+$), 330 (2, $[372 - CH_2CO]^+$), 312 (21), 294 (16), 279 (16), 268 (23), 119 (45), 107 (33), 105 (35), 91 (52), 57 (82), 43 (100).

5. *Funicolide C* (= *(+)-(1R*,2R*,7R*,9R*,10R*,14R*,5Z)-9,14-Diacetoxy-18-oxobriara-5,8(17),11-trien-2-yl Propanoate* = *(+)-(3aR*,8R*,8aR*,12aR*,13R*,4Z)-9,13-Diacetoxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8-yl Propanoate*; **3**). $[\alpha]^{20}$ (λ) = +69.4 (589), +84.1 (546), +135.2 (435; c = 0.31, EtOH). UV (EtOH): 211 (19700). ^{1}H-NMR (66°): 5.35 (br. *s*, $w_{1/2}$ = 9.5,

H–C(2)); 2.30, 1.65 (br., 2 H–C(3)); 2.10 (br., H_a–C(4)); 2.90 (br. *d*, J_{gem} = 14.0, H_b–C(4)); 5.15 (br. *d*, *J*(6,7) = 9.6, H–C(6)); 6.10 (br. *d*, *J*(7,6) = 9.5, *J*(7,19) = 1.8, H–C(7)); 6.42 (br. *s*, H_a–C(9)); 3.41 (br. *s*, H–C(10)); 5.42 (br. *s*, $w_{1/2}$ = 9.0, H–C(12)); 2.38, 2.15 (br., 2 H–C(13)); 5.02 (br. *dd*, *J* = 8.4, 6.3, H–C(14)); 1.41 (br. *s*, 3 H–C(15)); 1.86 (br. *d*, *J*(16,6) = 1.2, 3 H–C(16)); 1.83 (*dd*, *J*(19,7) = *J*(19,9a) = 1.8, 3 H–C(19)); 1.69 (br. *s*, 3 H–C(20)); 1.97 (*s*, AcO); 2.35 (*q*, *J* = 7.5, MeCH_2CO); 1.18 (*t*, *J* = 7.5, *Me*CH_2CO). MS: 488 (3.3, $M^{+\cdot}$), 446 (1.9, $[M - CH_2CO]^{+\cdot}$), 428 (1.8, $[M - AcOH]^{+\cdot}$), 414 (5.5, $[M - EtCOOH]^{+\cdot}$), 372 (8.4, $[M - CH_2CO]^{+\cdot}$), 354 (5.1, $[414 - AcOH]^{+\cdot}$), 312 (21), 294 (31), 266 (62), 206 (40), 119 (13), 91 (16), 57 (51), 43 (100). HR-MS: 488.2410 ($C_{27}H_{36}O_8^+$; calc. 488.2401), 466.2304 ($C_{25}H_{34}O_7^+$; calc. 446.2299).

6. *7-Epifunicolide A* (= *(–)-(1*R*,*2*R*,*7*S*,*10*R*,*14*R*,*5*Z*)-14-Acetoxy-18-oxobriara-5,8(17),11-trien-2-yl Propanoate* = *(–)-(3a*R*,*8*S*,*8a*S*,*9*S*,*12a*S*,*4*Z*)-9-Acetoxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8-yl Propanoate*; **4**). $[\alpha]^{20}$ (λ) = –43.4 (589), –45.5 (546), –81.4 (435), –150.3 (365; *c* = 0.14, EtOH). UV (EtOH): 222 (16500). ^{1}H-NMR (66°): 4.95 (*dd*, *J* = 6.8, 2.5, H–C(2)); 1.90, 2.05 (br., 2 H–C(3)); 2.25 (br., H_b–C(4)); 2.65 (br., H_a–C(4)); 4.86 (br. *d*, *J*(6,7) = 7.0, H–C(6)); 5.78 (br. *d*, *J*(7,6) = 7.0, H–C(7)); 2.96 (br., H–C(9)); 2.39 (*dd*, J_{gem} = 15.0, *J*(9,10) = 11.0, H_a–C(9)); 2.98 (br., H–C(10)); 5.29 (br. *d*, *J*(12,13a) ≈ 5, H–C(12)); 2.12 (br. *d*, *J*(13a,12) ≈ 5, H_a–C(13)); 2.30 (br., H_b–C(13)); 4.85 (br. *s*, $w_{1/2}$ = 7, H–C(14)); 0.97 (br. *s*, 3 H–C(15)); 1.72 (br. *s*, 3 H–C(16)); 1.86 (br. *s*, 3 H–C(19)); 1.57 (br. *s*, 3 H–C(20)); 2.01 (*s*, AcO); 2.28 (br., MeCH_2CO); 1.13 (*t*, *J* = 7.5, *Me*CH_2CO). MS: 430 (0.1, $M^{+\cdot}$), 374 (1.8, $[M - MeCH{=}CO]^{+\cdot}$), 370 (2.5, $[M - AcOH]^{+\cdot}$), 356 (0.5, $[M - EtCOOH]^{+\cdot}$), 314 (9.3), 296 (40), 281 (6), 216 (23), 208 (24), 190 (15), 119 (22), 57 (100), 43 (65).

7. *Funiculide D* (= *(+)-(1*R*,*2*R*,*7*R*,*10*R*,*14*R*,*5*Z*)-14-Acetoxy-18-oxobriara-5,8(17),11-trien-2-yl Butanoate* = *(+)-(3a*R*,*8*R*,*8a*R*,*9*R*,*12a*R*,*4*Z*)-9-Acetoxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8-yl Butanoate*; **5**). $[\alpha]^{20}$ (λ) = +33.2 (589), +43.8 (546), +88.8 (435), +169.3 (365; *c* = 0.25, EtOH). UV (EtOH): 207 (15000). ^{1}H-NMR (45°): 4.90 (br. *s*, $w_{1/2}$ = 8, H–C(2)); 1.7–2.3 (br., 2 H–C(3)); 2.2 (br., H_a–C(4)); 2.58 (br., H_b–C(4)); 5.17 (br. *d*, *J*(6,7) = 9.5, H–C(6)); 5.49 (br. *d*, *J*(7,6) = 9.5, *J*(7,18) = 1.5, H–C(7)); 2.89 (br. *d*, J_{gem} = 16.0, H–C(9)); 2.53 (br. *dd*, J_{gem} = 16.1, *J*(9,10) = 7.5, H_a–C(9)); 2.79 (br. *d*, *J*(10,9) = 7.5, H–C(10)); 5.22 (br. *d*, *J*(12,13a) = 6.1, H–C(12)); 2.05 (br., H_a–C(13)); 2.25 (br., H_b–C(13)); 4.85 (br. *s*, $w_{1/2}$ = 8, H–C(14)); 1.01 (br. *s*, 3 H–C(15)) 2.06 (br. *s*, 3 H–C(16)); 1.89 (*dd*, *J*(19,7) = *J*(19,9) = 1.5, 3 H–C(19)); 1.61 (br. *s*, 3 H–C(20)); 1.94 (*s*, AcO); 2.28 (*t*, *J* = 7.5, CH_2CO); 1.66 (*quint.*, *J* = 7.5, MeCH_2); 0.96 (*t*, *J* = 7.5, *Me*CH_2). MS: 444 (0.5, $M^{+\cdot}$), 384 (2.1, $[M - AcOH]^{+\cdot}$), 374 (1.5), 356 (1.2, $[M - PrCOOH]^{+\cdot}$), 341 (0.2), 314 (6.7), 296 (36, $[356 - AcOH]^{+\cdot}$), 286 (3.9), 281 (4.4), 228 (7.8), 216 (15), 208 (15), 119 (22), 107 (14), 105 (12), 91 (16), 71 (55), 43 (100).

8. *Brianthein W* (= *(+)-(1*R*,*2*R*,*7*R*,*10*R*,*14*R*,*5*Z*)-18-Oxobriara-5,8(17),11-triene-2,14-diyl Diacetate* = *(+)-(3a*R*,*8*R*,*8a*R*,*9*R*,*12a*R*,*4*Z*)-2,3a,6,7,8,8a,9,10,12a,13-Decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8,9-diyl Diacetate*; **6**). $[\alpha]^{20}$ (λ) = +32.2 (589), +42.2 (546), +81.1 (435), +155.5 (365; *c* = 0.18, EtOH). ^{1}H-NMR: 4.83 (br. *s*, H–C(2)); 1.75, 2.34 (br., 2 H–C(3)); 2.22 (br., H_a–C(4)); 2.57 (br., H_b–C(4)); 5.16 (br. *d*, H–C(6)); 5.47 (br. *d*, H–C(7)); 2.52, 2.86 (br., 2 H–C(9)); 2.69 (br. *s*, H–C(10)); 5.21 (br. *d*, H–C(12)); 2.04, 2.26 (br., 2 H–C(13)); 4.88 (br. *s*, H–C(14)); 1.00 (br. *s*, 3 H–C(15)); 2.05 (br. *s*, 3 H–C(16)); 1.88 (br. *s*, 3 H–C(19)); 1.59 (br. *s*, 3 H–C(20)); 1.94, 2.02 (2*s*, 2 AcO).

9. *Funicolide E* (= *(–)-(1*R*,*2*R*,*7*S*,*10*R*,*14*R*,*5*Z*)-7-Hydroxy-18-oxobriara-5,8(17),11-triene-2,14-diyl Diacetate* = *(–)-(3a*R*,*8*S*,*8a*S,*9*S*,*12a*S*,*4*Z*)-3a-Hydroxy-2,3a,6,7,8,8a,9,10,12a,13-decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8,9-diyl Diacetate*; **7**). $[\alpha]^{20}$ (λ) = –61.7 (589), –73.6 (546), –144.7 (435), –268.8 (365; *c* = 0.59, EtOH). UV (EtOH): 222 (8600). ^{1}H-NMR: 4.87 (*dd*, *J* = 8.5, 1.8, H–C(2)); 1.83–1.95 (br., 2 H–C(3)); 2.33 (br., H_b–C(4)); 3.39 (br., H_a–C(4)); 5.27 (br. *s*, H–C(6)); 3.82 (br. *s*, OH–C(7)); 2.34 (*dd*, J_{gem} = 15.0, *J*(9,10) = 11.5, H_a–C(9)); 2.77 (br. *d*, J_{gem} = 15.0, H–C(9)); 3.31 (br. *d*, *J*(10,9a) = 11.5, H–C(10)); 5.25 (br. *d*, *J*(12,13a) = 6, H–C(12)); 2.29 (br., H_b–C(13)); 2.04 (br., H_a–C(13)); 4.90 (br. *s*, $w_{1/2}$ = 6, H–C(14)); 1.02 (*s*, 3 H–C(15)); 1.74 (br. *s*, 3 H–C(16)); 1.86 (*d*, *J*(19,9) = 1.2, 3 H–C(19)); 1.61 (br. *s*, 3 H–C(20)); 2.02 (*s*, AcO–C(2), AcO–C(14)). NOE: H–C(2) → H_a–C(4) (6), H–C(10) (3); H–C(6) → 3 H–C(16) (3); H_a–C(9) → 3 H–C(19) (2); H–C(9) → 3 H–C(15) (3); H–C(10) → H–C(2) (9); H–C(12) → 3 H–C(20) (3); 3 H–C(15) → H–C(14) (10); 3 H–C(16) → H–C(6) (13); 3 H–C(19) → H_a–C(9) (4); 3 H–C(20) → H–C(12) (11). HMBC: *H*–C(6) → C(4), C(16); H_a–C(9) → C(7), C(8), C(10), C(17); *H*–C(2) and/or *H*–C(14) → C(2), C(10), C(12); 3 *H*–C(15) → C(1), C(2), C(10), C(14); 3 *H*–C(16) → C(4), C(5), C(6); 3 *H*–C(19) → C(8), C(17), C(18); 3 *H*–C(20) → C(10), C(11), C(12). MS: 414 (0.2, $[M - H_2O]^{+\cdot}$), 372 (1.7, $[M - AcOH]^{+\cdot}$), 354 (0.6), 312 (17, $[M - 2\,AcOH]^{+\cdot}$), 294 (5), 268 (15), 231 (9), 119 (18), 107 (18), 91 (19), 43 (100).

10. *Treatment of* **1** *with* K_2CO_3 *in MeOH*. Solid K_2CO_3 (*ca.* 20 mg) was added to a soln. of **1** (8.2 mg) in MeOH (2 ml), and the mixture was stirred at r.t. for 90 min. The solvent was evaporated and the residue subjected to FC and then HPLC (*CN*, hexane/AcOEt 97.5:2.5): **8** (3.4 mg; t_R 8 min) and **9** (1.2 mg; t_R 9 min).

Methyl (αR or αS*,1R*,4aR*,12R*,12aR*,5E,8Z)-1-Acetoxy-1,2,4a,7,10,11,12,12a-octahydro-α,4,9,12a-tetramethyl-7-oxo-12-(propanoyloxy)benzocyclodecene-6-acetate* (**8**; major product): $[\alpha]^{20}$ (λ) = +13.5 (589), +17.9 (546), +42.2 (435; *c* = 0.59, EtOH). UV (EtOH): 246 (12600). ^{1}H-NMR[9]): 4.78 (br. *dd*, *J* = 9.9, 3.0, H–C(2)); 1.8–2.0 (br., 2 H–C(3), H_a–C(4)); 3.56 (*m*, H_b–C(4)); 6.20 (*q*, *J*(6,16) = 1.2, H–C(6)); 5.63 (*dd*, *J*(9,10) = 12.1, *J*(9,17) = 1.0, H–C(9)); 3.45 (br. *d*, *J*(10,9) = 12.1, H–C(10)); 5.34 (br. *d*, H–C(12)); 2.14, 2.27 (br., 2 H–C(13)); 4.98 (br. *t*, *J*(14,13) = 2.7, H–C(14)); 1.03 (br. *s*, 3 H–C(15)); 2.14 (*d*, *J*(16,6) = 1.2, 3 H–C(16)); 3.66 (*dq*, *J*(17,19) = 7.2, *J*(17,9) = 1.0, H–C(17)); 1.38 (*d*, *J*(19,17) = 7.2, 3 H–C(19)); 1.45 (br. *s*, 3 H–C(20)); 1.93 (*s*, AcO); 2.26, 2.29 (*AB* of ABX_3, *J*(*A*,*B*) = 16.8, *J*(*A*,*X*) = *J*(*B*,*X*) ≈ 7.7, MeCH_2CO); 1.09 (*X* of ABX_3, *Me*CH_2CO); 3.66 (*s*, MeO). NOE[9]): H–C(2) → H–C(10) (17), 3 H–C(16) (5); H–C(9) → 3 H–C(15) (2); H–C(10) → H–C(2) (11), H–C(6) (2); 3 H–C(15) → H–C(9) (15), H–C(14) (13); 3 H–C(16) → H–C(6) (16); H–C(17) → H–C(9) (3); 3 H–C(19) → H–C(9) (5). MS: 460 (3.2, $M^{+\cdot}$), 445 (1.0, $[M - Me]^+$), 429 (1.6, $[M - MeO]^+$), 428 (1.0, $[M - MeOH]^+$), 404 (2.2, $[M - MeCH{=}CO]^{+\cdot}$), 400 (1.9, $[M - AcOH]^{+\cdot}$), 386 (1.8, $[M - EtCOOH]^{+\cdot}$), 344 (4), 326 (9), 311 (8), 294 (6), 285 (6), 279 (6), 239 (19), 157 (19), 119 (23), 69 (36), 57 (100), 43 (93).

Methyl (αS or αR*,1R*,4aR*,12R*,5E,8Z)-1-Acetoxy-1,2,4a,7,10,11,12,12a-octahydro-α,4,9,12a-tetramethyl-7-oxo-12-(propanoyloxy)benzocyclodecene-6-acetate* (**9**; minor product): $[\alpha]^{20}$ (λ) = +9.8 (589 *c* = 0.16, EtOH). UV (EtOH): 245 (11800). ^{1}H-NMR[9]): 4.78 (br. *dd*, *J* = 10.0, 2.5, H–C(2)); 3.55 (*m*, H_b–C(4)); 6.19 (*q*, *J*(6,16) = 1.2, H–C(6)); 5.59 (*dd*, *J*(9,10) = 12.3, *J*(9,17) = 0.9, H–C(9)); 3.42 (br. *d*, *J*(10,9) = 12.3, H–C(10)); 5.33 (br. *d*, H–C(12)); 4.97 (br. *t*, H–C(14)); 1.03 (br. *s*, 3 H–C(15)); 2.14 (*d*, *J*(16.6) = 1.2, 3 H–C(16)); 3.54 (*dq*, *J*(17,19) = 7.2, *J*(17,9) = 0.9, H–C(17)); 1.44 (*d*, *J*(19,17) = 7.2, 3 H–C(19)); 1.47 (br. *s*, 3 H–C(20)); 1.93 (*s*, AcO); 2.26, 2.29 (*AB* of ABX_3, MeCH_2CO); 1.09 (*X* of ABX_3, *Me*CH_2CO). MS: practically superimposable to that of **8**.

11. *Treatment of* **1** *with* K_2CO_3 *in* $(CD_3)_2SO$. Solid K_2CO_3 (*ca.* 10 mg) was added to a soln. of **1** (10.6 mg) in $(CD_3)_2SO$ (0.6 ml) in a NMR tube, and N_2 was bubbled through for 20 min. The tube was then sealed (flame) and heated to 60°, recording ^{1}H-NMR spectra every 10 min. After 180 min, the mixture was subjected in turn to reversed-phase FC and HPLC (*RP-18*, MeCN/H_2O 3:2): **4** (8.1 mg) and **1** (2.0 mg).

12. *Treatment of* **1** *with* K_2CO_3 *in Oxygenated* $(CD_3)_2SO$. Solid K_2CO_3 (*ca.* 12 mg) was added to a soln. of **1** (13.8 mg) in $(CD_3)_2SO$ (1 ml) heating at 60° for 180 min under N_2 to equilibrate **1** with **4**. This mixture was then heated to 80° for 100 min while bubbling O_2 through. The mixture was cooled and subjected in turn to reversed-phase and prep. TLC (hexane/Et_2O 1:4): **12** (4.1 mg, R_f 0.4) and an unstable product (6.5 mg, R_f 0.6). *(+)-(1R*,4aR*,10R*,12R*,12aS*,13R*,5E,8Z)-1-Acetoxy-1,2,4a,7,10,11,12,12a-octahydro-13-hydroxy-4,9,12a,13-tetramethyl-7-oxo-6,10-methanobenzocyclodecen-12-yl Propanoate* (**12**): $[\alpha]^{20}$ (λ) = +43.5 (589), +53.0 (546), +97.2 (435; *c* = 0.4, EtOH). UV (EtOH): 236 (9200), 330 (400). ^{1}H-NMR (25°)[10]): 5.94 (*dd*, *J*(2,3b) = 8.1, *J*(2,3a) = 0.9, H–C(2)); 1.71 (*ddd*, J_{gem} = 15.5, *J*(3a,2) = 0.9, *J*(3a,4) = 6.5, H_a–C(3)); 1.85 (*ddd*, J_{gem} = 15.5, *J*(3b,2) = 8.1, *J*(3b,4) = 10.0, H_b–C(3)); 2.71 (br. *dd*, *J*(4,3b) = 10.0, *J*(4,3a) = 6.5, *J*(4,6) small, H–C(4)); 5.72 (br. *q*, *J*(6,16) = 1.3, *J*(6,4) small, H–C(6)); 6.05 (*d*, *J*(9,10) = 10.6, H–C(9)); 4.85 (br. *s*, *J*(10,9) = 10.6, *J*(10,19) small, H–C(10)); 5.32 (br. *s*, *J*(12,13a), *J*(12,13b), and *J*(12,19) small, H–C(12)); 2.06, 2.37 (2 br. *d*, $J_{gem} \approx 18$, H_a–C(13) and H_b–C(13), resp.); 5.03 (br. *d*, *J*(14,13b) = 3.5, *J*(14,13a) small, H–C(14)); 0.90 (*s*, 3 H–C(15)); 1.97 (*d*, *J*(16,6) = 1.3, 3 H–C(16)); 1.56 (*s*, 3 H–C(18)); 1.75 (br. *s*, *J*(19,10), *J*(19,12), and *J*(19,13b) small, 3 H–C(19)); 1.98 (*s*, AcO); 1.11 (*t*, *J* = 7.5, *Me*CH_2); 2.28, 2.31 (ABX_3, MeCH_2). NOE[10]): H–C(2) → H–C(4) (3), H–C(10) (11); H–C(4) → H–C(2) (4), 3 H–C(16) (2), 3 H–C(18) (2); H–C(6) → 3 H–C(16) (4); H–C(9) → H–C(10) (5), 3 H–C(15) (2), 3 H–C(20) (5); H–C(10) → H–C(2) (10); H–C(14) → 3 H–C(15) (3); 3 H–C(15) → H_b–C(3) (8), H–C(9) (9), H_b–C(13) (7), H–C(14) (8); 3 H–C(16) → H–C(4) (10), H–C(6) (15); 3 H–C(18) → H–C(4) (9), H–C(6) (3); 3 H–C(19) → H–C(9) (11), H–C(12) (8). HMBC: *H*–C(2) → C(1), *C*OO–C(2), C(3), C(4), C(15); *H*–C(4) → C(3), C(5), C(6), C(8), C(16), C(17); *H*–C(6) → C(4), C(8), C(16); H–C(9) → C(7), C(8), C(11), C(17); *H*–C(10) → C(1), C(8), C(9); *H*–C(14) → C(1), C(10), C(12), *C*OO–C(14); 3 *H*–C(15) → C(1), C(2), C(10), C(14); 3 *H*–C(16) → C(4), C(5), C(6); 3 *H*–C(18) → C(4), C(8), C(17); 3 *H*–C(19) → C(11), C(12); *C*H_3CO → COO(14); *C*H_3CH$_2$ → *C*H_3CH$_2$, *C*OO–C(2). MS: 373 (12, $[M - MeCO]^+$), 356 (1, $[M - AcOH]^{+\cdot}$), 342 (3, $[M - EtCOOH]^{+\cdot}$), 283 (10), 282 (31), 267 (16), 264 (34), 240 (35), 239 (81, $[373 - (AcOH + EtCOOH)]^+$), 223 (33), 176 (25), 119 (26), 43 (100). HR-MS: 373.2009 ($C_{22}H_{29}O_5^+$; calc. 373.2015).

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[9]) Numbering in analogy to **1**; briarane-like/IUPAC equivalence is C(1)/C(12a), C(2)/C(12), C(3)/C(11), C(4)/C(10), C(5)/C(9), C(6)/C(8), C(8)/C(6), C(9)/C(5), C(10)/C(4a), C(11)/C(4), C(12)/C(3), C(13)/C(2), C(14)/C(1), C(17)/C(α).

[10]) Numbering in analogy to **1**; briarane-like/IUPAC equivalence is the same as for **8** and **9**, except for C(17)/C(13) in place of C(17)/C(α).

13. *Treatment of* **1** *with K_2CO_3 in Oxygenated DMSO, Followed by MeI.* In a separate run, a mixture identical to that in *Exper. 12* was treated with MeI and then subjected to reversed-phase FC. Workup by HPLC (*RP-18*, MeCN/H_2O 7:3) gave **12** (t_R 6) and **13** (t_R 10). The latter was also obtained as follows: to the unstable product of *Exper. 12* (R_f 0.6) in DMSO were added K_2CO_3 and (after 10 min) MeI. The mixture was worked up to give **13**. *(−)-(4*R*,4a*S*,5*R*,12a*R*,7*Z*)-4-Acetoxy-3,4,4a,5,6,9,10,11,12,12a-decahydro-11-[(*Z*)-1-(methoxycarbonyl)-ethylidene]-1,4a,8-trimethyl-10-oxobenzocyclodecen-5-yl Propanoate* (**13**): $[\alpha]^{20}(\lambda) = -61.5$ (589), −71.8 (546), −121.3 (435; $c = 0.69$, EtOH). UV (EtOH): 206 (14400). ^{1}H-NMR (25°)[11]): 4.98 (br. *dd*, $J(2,3b) = 10.0$, $J(2,3a) = 1.0$, $J(2,15)$ small, H–C(2)); 1.85 (*m*, H_a–C(3)); 2.78 (br. *ddd*, $J_{gem} = 14.5$, $J(3b,2) \approx J(3b,4) = 10.0$, H_b–C(3)); 5.65 (br. *dd*, $J(4,3b) = 10.0$, $J(4,3a) = 7.0$, $J(4,16)$ and $J(4,6)$ small, H–C(4)); 3.25, 3.80 (br. *AB*, $J(A,B) = 13.6$, $J(6,4)$ and $J(6,16)$ small, 2 H–C(6)); 2.32 (br. *d*, $J_{gem} = 15.8$, $J(9,10)$ small, H–C(9)); 2.53 (br. *dd*, $J_{gem} = 15.8$, $J(9a,10) = 9.0$, H_a–C(9)); 2.85 (br. *d*, $J(10,9a) = 9.0$, $J(10,9)$ small, H–C(10)); 5.33 (br. *d*, $J(12,13a) \approx 5$, $J(12,20) = 1.2$, $J(12,13b)$ and $J(12,10)$ small, H–C(12)); 1.95, 2.15 (2*m*, H_b–C(13) and H_a–C(13), resp.); 4.89 (br. *dd*, $J(14,13a) = 10.0$, $J(14,13b) = 5.5$, $J(14,15)$ small, H–C(14)); 1.21 (br. *s*, $J(15,14)$ and $J(15,2)$ small, 3 H–C(15)); 1.97 (br. *s*, $J(16,3a)$, $J(16,4)$, and $J(16,6)$ small, 3 H–C(16)); 1.93 (*d*, $J(19,9) = 1.5$, 3 H–C(19)); 1.46 (br. *s*, $J(20,10)$ and $J(20,12)$ small, 3 H–C(20)); 2.32 (br. *q* = 7.6, MeCH_2CO); 1.15 (*t*, $J = 7.5$, *Me*CH_2CO); 2.04 (*s*, AcO). NOE[11]): H–C(2) → H–C(4) (6), H–C(10) (3); H_b–C(3) → H_b–C(6) (8); H–C(4) → H–C(2) (3), 3 H–C(16) (3); H_b–C(6) → H_b–C(3) (4); H_a–C(6) → 3 H–C(16) (2); H_a–C(9) → 3 H–C(19) (2), H–C(14) (12); H–C(10) → 3 H–C(20) (2); H–C(14) → H_a–C(9) (3), 3 H–C(15) (2); 3 H–C(15) → H_b–C(3) (11), H_b–C(6) (5), H–C(9) (5), H_b–C(9) (4), H–C(14) (10); 3 H–C(16) → H–C(4) (10), H_a–C(6) (6); 3 H–C(19) → H_a–C(9) (10); 3 H–C(20) → H–C(10) (8), H–C(11) (12). HMBC[11]): *H*–C(2) → *C*OO–C(2), C(4), C(15); H_a–C(3) → C(2), C(4), C(5); H_b–C(3) → C(2), C(4), C(5); H_a–C(6) → C(4), C(5), C(7), C(16); H_b–C(6) → C(5), C(7), C(16); H_a–C(9) → C(1), C(7), C(8), C(10), C(17); *H*–C(14) → C(2), C(13), *C*OO–C(14); 3 *H*–C(15) → C(1), C(2), C(10), C(14); 3 *H*–C(16) → C(4), C(5), C(6); 3 *H*–C(19) → C(8), C(17), C(18); 3 *H*–C(20) → C(11), C(12); MeO → C(18). MS: 460 (3.3, $M^{+\cdot}$), 298 (9), 171 (14), 140 (97), 119 (23), 91 (29), 69 (17) 57 (100), 43 (90).

14. *Treatment of* **2** *with KOH in DMSO, Followed by MeI.* To a mixture formed from a KOH pellet in dry DMSO (0.5 ml) with stirring for 10 min under N_2 were added a soln. of **2** in dry DMSO (0.5 ml) and, after 10 min, MeI (100 µl). Stirring was continued for 30 min. The mixture was then subjected in turn to reversed-phase FC and HPLC (*RP-18*, MeCN/H_2O 7:3): **2** (2.3 mg; t_R 6.5), and **10** (3.4 mg; t_R 8.3).

*(−)-(4*R*,4a*R*,5*R*,12a*R*,8*Z*)-4-Acetoxy-3,4,4a,5,6,7,10,11,12,12a-decahydro-11-[(*Z*)-1-(methoxycarbonyl)ethylidene]-1,4a,8-trimethyl-10-oxobenzocyclodecen-5-yl Propanoate* (**10**): $[\alpha]^{20}$ (λ) = −111.8 (589), −133.5 (546), −274.1 (435), −584.7 (365, $c = 0.17$, EtOH). UV (EtOH): 225 (12900). ^{1}H-NMR (25°)[11]): 4.81 (*dd*, $J = 8.7$, 2.7, H–C(2)); 1.84, 2.15 (br. 2 H–C(3)); 2.25, 2.88 (br. 2 H–C(4)); 6.24 (*q*, $J(6,16) = 1.2$, H–C(6)); 2.80 (br. *d*, $J_{gem} = 18$, H–C(9)); 2.43 (*dd*, $J_{gem} = 18$, $J(9a,10) = 7.5$, H–C(9)); 2.60 (br. *d*, $J(10,9a) = 7.5$, H–C(10)); 5.19 (br. *d*, $J(12,13a) \approx 5$, $J(12,20) = 1.2$, $J(12,14)$ small, H–C(12)); 2.0, 2.25 (br. 2 H–C(13)); 4.85 (br. *t*, $J(14,13) = 2.5$, H–C(14)); 0.95 (*s*, 3 H–C(15)); 2.04 (*d*, $J(16,6) = 1.2$, 3 H–C(16)); 1.93 (br. *s*, 3 H–C(19)); 1.63 (br. *s*, 3 H–C(20)); 1.93 (*s*, AcO); 2.29, 2.25 (*AB* of ABX_3, $J(A,B) = 16.0$, $J(A,X) = J(B,X) = 7.5$, MeCH_2CO); 1.09 (*X* of ABX_3, $J = 7.5$, *Me*CH_2CO); 3.67 (*s*, MeO). ^{13}C-NMR[11]): half-intensity line widths at 20° (and 56°) for C(2) 6.1 (2.3), C(7), 4.3 (2.7), C(8), 6.0 (4.6), C(15) 2.6 (1.3), C(17), 4.6 (1.4). MS: 460 (0.9, $M^{+\cdot}$), 445 (0.3, $[M - Me]^+$), 428 (0.2, $[M-MeOH]^{+\cdot}$), 386 (2.4, $[M - EtCOOH]^{+\cdot}$), 368 (0.6), 354 (0.6), 344 (3), 326 (7), 312 (7), 294 (13), 279 (7), 239 (9), 171 (15), 157 (15), 140 (16), 119 (29), 107 (20), 105 (21), 91 (29), 69 (17), 57 (100), 43 (92).

15. *Treatment of* **6** *with K_2CO_3 in DMSO.* Following the procedure described in *Exper. 12*, **6** was equilibrated; **6**/**11** 18:82. *7-Epibrianthein W (= (−)-(1*R*,2*R*,7*S*,10*R*,14*R*,5*Z*)-18-Oxobriara-5,8(17),11-triene-2,14-diyl Diacetate = (−)-(3a*R*,8*S*,8a*S*,9*S*,12a*S*,4*Z*)-2,3a,6,7,8,8a,9,10,12a,13-Decahydro-1,5,8a,12-tetramethyl-2-oxobenzo[4,5]cyclodeca[1,2-b]furan-8,9-diyl Diacetate;* **11**): $[\alpha]^{20}$ (λ) = −43.4 (589), −45.5 (546), −81.4 (435), −150.3 (365; $c = 0.14$, EtOH). UV (EtOH): 222 (16500). ^{1}H-NMR (46°): 4.92 (*dd*, $J = 6.5$, 2.5, H–C(2)); 1.90, 2.05 (br., 2 H–C(3)); 2.25, 2.65 (br., 2 H–C(4)); 4.86 (br. *d*, $J(6,7) = 7.5$, H–C(6)); 5.81 (br. *d*, $J(7,6) = 7.5$, H–C(7)); 2.95 (br. H–C(9)); 2.38 (*dd*, $J_{gem} = 14,8$, $J(9,10) = 11.0$, H_a–C(9)); 2.95 (br. H–C(10)); 5.28 (br. *d*, $J(12,13a) \approx 4.5$, H–C(12)); 2.11 (br. *d*, $J_{gem} \approx 14$, $J(13a,12) \approx 4.5$, H_a–C(13)); 2.28 (br., H_b–C(13)); 4.85 (br. *s*, $w_{1/2} \approx 6.5$, H–C(14)); 0.97 (br. *s*, 3 H–C(15)); 1.72 (br. *s*, 3 H–C(16)); 1.86 *dd*, $J(19,7) \approx J(19,9) = 1.5$, 3 H–C(19)); 1.57 (br. *s*, 3 H–C(20)); 2.02, 2.03 (2*s*, AcO–C(2), AcO–C(14)).

16. *Treatment of* **6** *with K_2CO_3 in Oxygenated DMSO.* Following the procedure in *Exper. 12* above, **6** was converted into both **14** (45%) and a less polar product (50%), the latter was too unstable for spectroscopic

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[11]) Numbering in analogy to **1**; briarane-like/IUPAC equivalence is C(1)/C(4a), C(2)/C(5), C(3)/C(6), C(4)/C(7), C(5)/C(8), C(6)/C(9), C(7)/C(10), C(8)/C(11), C(9)/C(12), C(10)/C(12a), C(11)/C(1), C(12)/C(2), C(13)/C(3), C(14)/C(4).

characterization. *(+)-(1R*,4aR*,10R*,12R*,12aS*,13R*,5E,8Z)-1,2,4a,7,10,11,12,12a-Octahydro-13-hydroxy-4,9,12a,13-tetramethyl-7-oxo-6,10-methanobenzocyclodecene-1,12-diyl Diacetate*; (**14**): $[\alpha]^{20}$ (λ) = +62.1 (589), +77.1 (546), +138.7 (435; *c* = 0.38, EtOH). UV (EtOH): 242 (6500). ^{1}H-NMR (25°)[9]: 5.91 (*dd*, *J*(2,3b) = 8.5, *J*(2,3a) = 1.0, H–C(2)); 1.75 (*ddd*, J_{gem} = 16.0, *J*(3a,2) = 1.0, *J*(3a,4) = 6.6, H_a–C(3)); 1.85 (*ddd*, J_{gem} = 16.0, *J*(3b,2) = 8.5, *J*(3b,4) = 10.0, H_b–C(3)); 2.70 (br. *dd*, *J*(4,3b) = 10.0, *J*(4,3a) = 6.6, *J*(4,6) = 0.6, H–C(4)); 5.72 (*dq*, *J*(6,4) = 0.6, *J*(6,16) = 1.5, H–C(6)); 6.05 (*d*, *J*(9,10) = 10.8, H–C(9)); 4.85 (br. *s*, *J*(10,9a) = 10.8 *J*(10,12) and *J*(10,16), small, H–C(10)); 5.33 (br. *s*, *J*(12,10), *J*(12,13a), and *J*(12,20) small, H–C(12)); 2.05, 2.38 (2 br. *d*, $J_{gem} \approx 18$, H_a–C(13) and H_b–C(13), resp.); 5.06 (br. *d*, *J*(14,13$_b$) = 4.5, *J*(14,13$_a$) small, H–C(14)); 0.90 (*s*, 3 H–C(15)); 1.97 (*d*, *J*(16,6) = 1.5, 3 H–C(16)); 1.56 (*s*, 3 H–C(18)); 1.75 (br. *s*, *J*(20,10), *J*(20,12), *J*(20,13a), and *J*(20,13b) small, 3 H–C(20)); 1.99, 2.01 (2*s*, AcO–C(2), AcO–C(14)). NOE[9]: H–C(2) → H–C(4) (2), H–C(10) (9); H–C(4) → H–C(2) (2); H–C(9) → 3 H–C(15) (6); H–C(10) → H–C(2) (7); H–C(14) → 3 H–C(15 (5); 3 H–C(15) → H_b–C(3) (10), H–C(9) (10), H_b–C(13) (10), H–C(14) (8); 3 H–C(16) → H–C(4) (12), H–C(6) (12); 3 H–C(18) → H–C(4) (9), H–C(6) (4); 3 H–C(19) → H–C((9) (11), H–C(10) (7), H–C(12) (10). HMBC[9]: *H*–C(2) → C(1), *C*OO–C(2), C(3), C(4), C(15); *H*–C(4) → C(3), C(5), C(8), C(16), C(17); *H*–C(6) → C(4), C(8), C(16); *H*–C(9) → C(7), C(8), C(11), C(17); *H*–C(10) → C(1), C(8), C(9), C(11), C(14); *H*–C(12) → C(10), C(14); *H*–C(14) → C(1), C(10), C(12), *C*OO–C(14); 3 *H*–C(15) → C(1), C(2), C(10), C(14); 3 *H*–C(16) → C(4), C(6); 3 *H*–C(18) → C(4), C(8), C(17); 3 *H*–C(19) → C(10), C(11), C(12). MS: 359 (7.4, [*M* – MeCO]$^+$), 299 (2.5, [359 – AcOH]$^+$), 283 (4), 265 (6), 249 (23), 239 (37, [359 – 2AcOH]$^+$), 223 (25), 119 (16), 43 (100). HR-MS: 359.1857 ($C_{21}H_{27}O_5^+$; calc. 359.1858).

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