105. Isolation from the Mediterranean Stoloniferan Coral *Sarcodictyon roseum* of Sarcodictyin C, D, E, and F, Novel Diterpenoidic Alcohols Esterified by (*E*)- or (*Z*)-*N*(1)-Methylurocanic Acid. Failure of the Carbon-Skeleton Type as a Classification Criterion[1])

by **Michele D'Ambrosio, Antonio Guerriero,** and **Francesco Pietra***

Istituto di Chimica, Università di Trento, I-38050 Povo-Trento

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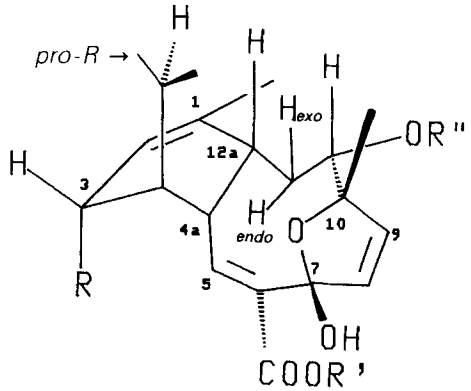
It is shown here that the stoloniferan coral *Sarcodictyon roseum* of east Pyrenean waters contains four novel diterpenoids, sarcodictyin C ((−)-**3**), D ((−)-**4**), E ((+)-**5**), and F ((+)-**6**), which are related to sarcodictyin A (= (−)-(4*R*,4a*R*,7*R*,10*S*,11*S*,12a*R*,1*Z*,5*E*,8*Z*)-7,10-epoxy-3,4,4a,7,10,11,12,12a-octahydro-7-hydroxy-6-(methoxycarbonyl)-1,10-dimethyl-4-(1-methylethyl)-benzocyclodecen-11-yl (*E*)-*N*[1]-methylurocanate; (−)-**1**), previously isolated from the same coral. Sarcodictyin C ((−)-**3**) and D ((−)-**4**) are the 3α-hydroxy and 3α-acetoxy derivatives of (−)-**1**, sarcodictyin E ((+)-**5**) is the (*Z*)-urocanate isomer of (−)-**3**, and sarcodictyin F ((+)-**6**) is the 1α-hydroxy-2-ene isomer of (−)-**3**. In all cases, the nine-membered ring is locked, and the molecule stabilized, by the urocanic appendage; when this is removed in MeOH/KOH, the C(11)–O^- function is free to attack at C(5), and *retro*-condensations then lead to the ring-contracted butenolides **11** (from (−)-**3**) or **10** (from (−)-**1**) with extrusion of the hydroxyfuran nucleus *(Scheme 3)*. Under the same conditions, with (−)-**3**, the C(3)–O^- group competitively attacks at C(5), the hydroxyfuran nucleus is expelled, and aldehyde **14** is formed. Peculiarly, in the reaction of (−)-**3** with MeOD/KOD, the ring-contracted butenolide **17** contains D at the 4′-ax position. The sarcodictyins are unique in these chemical properties, not shared by the cladiellanes which have the same C-skeleton.

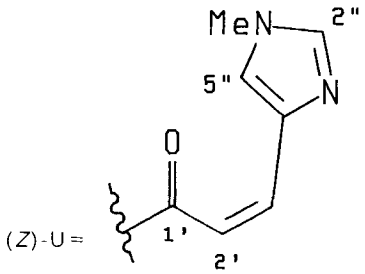
1. Introduction. – We have recently isolated from the Mediterranean stolonifer *Sarcodictyon roseum* two novel diterpenoidic alcohols esterified by (*E*)-*N*[1]-methylurocanic acid, sarcodictyin A ((−)-**1**) and B ((−)-**2**) [1]. We report now on the isolation from the same coral of four novel sarcodictyins. Their chemistry is not shared by the cladiellanes (see *e.g.* **7**) [2] in spite of the same C-skeleton.

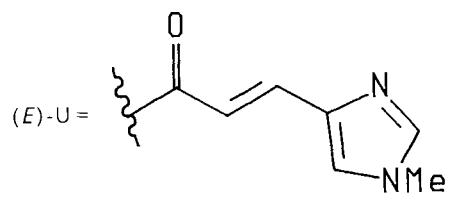
2. Results and Discussion. – The new sarcodictyins are more polar than sarcodictyin A and B [1], the polarity increasing in the order sarcodictyin E ((+)-**5**), D ((−)-**4**), F ((+)-**6**), and C ((−)-**3**).

2.1. *Structures.* The ^{13}C-NMR spectrum of sarcodictyin C ((−)-**3**) bears much resemblance to that of sarcodictyin A ((−)**1**) [1] except for a *d* at 67.05 ppm *(Table 1)* replacing the *t* at 24.58 ppm (C(3)) of (−)-**1**. Such a deshielding is attributable to an OH group at C(3) of (−)-**3**, which is also indicated in the MS by the M^+ at 16 mass units higher than that of (−)-**1** and by an intense $(M - 18)^+$ peak *(Exper. Part)*. In accordance, the 2 high-field br. *d* for the geminally coupled protons at C(3) of (−)-**1** are replaced in (−)-**3** by a deshielded br. *d* for a proton which shows small couplings with H–C(2), H–C(4), and Me–C(1) *(Table 2)*. The long-range ^{13}C, ^{1}H correlations in *Table 1* confirm the same C-skeleton as for (−)-**1**. In analogy with (−)-**1**, NOESY data for (−)-**3** *(Exper. Part)* indicate that the isopropyl group is locked in the axial position. The OH group at C(3) must occupy the α position to account for 1-ppm deshielding of H–C(5) *(Table 2)* with respect to (−)-**1**. In accordance, H–C(3) has a small

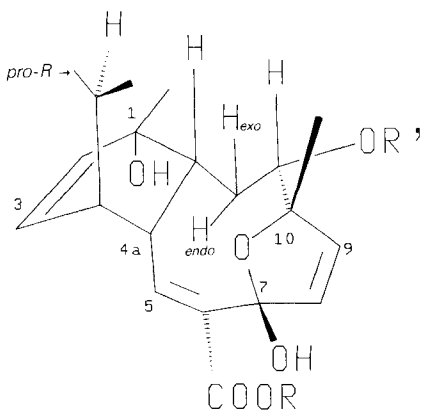
[1]) Presented by *F.P.* as a part of a lecture at the University of Hawaii at Manoa, Honolulu, December 9th, 1987.



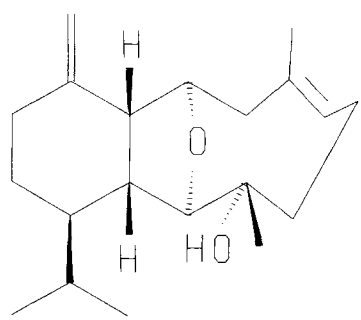




(−)-**1** R = H, R′ = Me, R″ = (*E*)-U
(−)-**2** R = H, R′ = Et, R″ = (*E*)-U
(−)-**3** R = OH, R′ = Me, R″ = (*E*)-U
(−)-**4** R = OAc, R′ = Me, R″ = (*E*)-U
(+)-**5** R = OH, R′ = Me, R″ = (*Z*)-U



(+)-**6** R = Me, R′ = (*E*)-U



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coupling with H–C(4), which is compatible with a *ca.* 90° H–C(3)–C(4)–H dihedral angle. Should OH–C(3) occupy the *β* position, the dihedral angle would be smaller and the coupling constant larger.

The ^{1}H-NMR spectra of sarcodictyin D ((−)-**4**) are similar to those of (−)-**3** except for deshielding of H–C(3) by more than 1 ppm, as expected for OAc in place of OH at C(3).

Also the ^{1}H-NMR spectrum of sarcodictyin E ((+)-**5**) resembles much that of (−)-**3**, differences being restricted to the urocanic portion. $J(2',3')$ is 12.5 *vs.* 16.0 Hz for (−)-**3**, which points to the (*Z*) configuration for (+)-**5**. This is confirmed by a *ca.* 1-ppm deshielding of H–C(5″) by the carbonyl group. This is in accordance with data for model compound (*Z*)-**8**, obtained by photoisomerization of (*E*)-**8** *(Scheme 1)*, similarly to the case of urocanic acid [3]. The isomer (*Z*)-**8**, shows the same pattern of chemical shifts and coupling constants as the urocanic-acid portion of (+)-**5**.

With sarcodictyin F ((+)-**6**), there are marked ^{1}H-NMR spectral differences with respect to (−)-**3**. Whereas the signals for the urocanic portion are identical, in place of the br. *d*'s for H–C(2) and H–C(3) of (−)-**3**, there is with (+)-**6** an *AXY* pattern attributable to a *cis* CH(2)=CH(3)–CH(4) system. Moreover, in place of the Me–C(*1*) br. *s*

Table 1. *^{13}C-NMR Data (δ(C)) in both C_5D_5N and CD_3OD and Long-Range C,H Correlations in C_5D_5N for Sarcodictyin C ((−)-**3**) and ^{13}C-NMR Data (δ(C)) in CD_3OD for Sarcodictyin D ((−)-**4**), E ((+)-**5**), F ((+)-**6**), and for Enone **9***

C-Atom	δ(C; C_5D_5N) (−)-**3**	Correlated protons[a]) (−)-**3**
C(1)	134.98 (*s*)	Me–C(1), H–C(3), H–C(4a), H–C(12a), H_{endo}–C(12)
C(2)	127.79 (*d*)	Me–C(1), H–C(3)
C(3)	67.05 (*d*)	H–C(4), H–C(4a)
C(4)	52.12 (*d*)	Me_2CH
C(4a)	34.12 (*d*)	H_{endo}–C(12), H_{exo}–C(12), H–C(12a), H–C(3)
C(5)	145.67 (*d*)	H–C(4a), H–C(4), H–C(12a)
C(6)	134.20 (*s*)	H–C(4a), H–C(5)
C(7)	112.51 (*s*)	H–C(8), H–C(9), H–C(5)
C(8)	135.10 (*d*)	H–C(9)
C(9)	132.64 (*d*)	H–C(8), Me–C(10), H–C(11)
C(10)	89.65 (*s*)	H–C(9), H–C(8), Me–C(10), H_{exo}–C(12), H–C(11)
C(11)	81.14 (*d*)	H_{exo}–C(12), H–C(12a), Me–C(10)
C(12)	32.50 (*t*)	
C(12a)	39.81 (*d*)	
Me_2CH	28.83 (*d*)	H–C(4), Me(*pro-S*), H–C(3)
Me(*pro-S*)	20.66 (*q*)	
Me(*pro-R*)	22.33 (*q*)	
Me–C(1)	21.60 (*q*)	
Me–C(10)	25.86 (*q*)	
C–C(6)	168.12 (*s*)	H–C(5), MeO, H–C(9)
MeO	51.48 (*q*)	
C(1′)	167.17 (*s*)	H–C(2′), H–C(3′)
C(2′)	115.42 (*d*)	H–C(3′), H–C(5″)
C(3′)	138.10 (*d*)	
C(2″)	140.26 (*d*)	MeN, H–C(5″), H–C(3′)
C(4″)	138.50 (*s*)	H–C(2′), H–C(5″), H–C(3′), H–C(2″)
C(5″)	124.35 (*d*)	MeN, H–C(2″), H–C(3′)
MeN	33.14 (*q*)	H–C(5″)

C-Atom	δ(C; CD_3OD)				
	(−)-**3**	(−)-**4**[b])	(+)-**5**	(+)-**6**	**9**
C(1)	137.09 (*s*)	138.47 (*s*)	137.13 (*s*)	68.55 (*s*)	163.01 (*s*)
C(2)	126.89 (*d*)	121.55 (*d*)	127.01 (*d*)	136.06 (*d*)	127.05 (*d*)
C(3)	68.26 (*d*)	70.99 (*d*)	68.30 (*d*)	129.19 (*d*)	204.02 (*s*)
C(4)	52.72 (*d*)	[c])	52.82 (*d*)	47.82 (*d*)	59.90 (*d*)
C(4a)	34.78 (*d*)	34.55 (*d*)	34.81 (*d*)	34.84 (*d*)	39.18 (*d*)
C(5)	147.89 (*d*)	146.13 (*d*)	147.90 (*d*)	148.31 (*d*)	143.20 (*d*)
C(6)	133.29 (*s*)	134.37 (*s*)	133.32 (*s*)	132.18 (*s*)	135.22 (*s*)
C(7)	112.61 (*s*)	112.59 (*s*)	112.65 (*s*)	112.69 (*s*)	116.74 (*s*)
C(8)	134.50 (*d*)	134.22 (*d*)	134.46 (*d*)	134.89 (*d*)	131.88 (*d*)
C(9)	134.10 (*d*)	134.15 (*d*)	134.13 (*d*)	133.89 (*d*)	136.54 (*d*)
C(10)	90.99 (*s*)	90.96 (*s*)	90.98 (*s*)	91.29 (*s*)	91.20 (*s*)
C(11)	82.04 (*d*)	82.39 (*d*)	81.68 (*d*)	81.72 (*d*)	82.38 (*d*)
C(12)	32.98 (*t*)	32.83 (*t*)	33.01 (*t*)	31.29 (*t*)	32.16 (*t*)
C(12a)	40.64 (*d*)	39.99 (*d*)	40.76 (*d*)	42.29 (*d*)	41.92 (*d*)
Me_2CH	29.84 (*d*)	29.45 (*d*)	29.86 (*d*)	33.25 (*d*)	28.10 (*d*)
Me (*pro-S*)	20.83 (*q*)	21.37 (*q*)	20.88 (*q*)	21.82 (*q*)	21.73 (*q*)
Me (*pro-R*)	22.50 (*q*)	22.43 (*q*)	22.52 (*q*)	22.21 (*q*)	22.28 (*q*)
Me–C(1)	21.56 (*q*)	21.77 (*q*)	21.61 (*q*)	29.17 (*q*)	22.84 (*q*)

Table 1 (cont.)

C-Atom	δ(C; CD_3OD)				
	(−)-**3**	(−)-**4**[b])	(+)-**5**	(+)-**6**	**9**
Me–C(10)	25.94 (*q*)	25.98 (*q*)	25.95 (*q*)	25.81 (*q*)	24.58 (*q*)
C–C(6)	168.69 (*s*)	168.53 (*s*)	168.62 (*s*)	169.43 (*s*)	167.58 (*s*)
MeO	52.18 (*q*)	52.30 (*q*)	52.21 (*q*)	52.12 (*q*)	52.55 (*q*)
C(1′)	168.32 (*s*)	168.39 (*s*)	166.97 (*s*)	169.22 (*s*)	168.38 (*s*)
C(2′)	115.91 (*d*)	115.83 (*d*)	114.54 (*d*)	116.06 (*d*)	115.59 (*d*)
C(3′)	138.13 (*d*)	138.20 (*d*)	139.16 (*d*)	137.97 (*d*)	138.45 (*d*)
C(2″)	141.27 (*d*)	141.30 (*d*)	139.43 (*d*)	141.27 (*d*)	141.36 (*d*)
C(4″)	138.47 (*s*)	140.83 (*s*)	137.52 (*s*)	138.51 (*s*)	138.45 (*s*)
C(5″)	125.50 (*d*)	125.57 (*d*)	127.78 (*d*)	125.45 (*d*)	125.66 (*d*)
MeN	33.95 (*q*)	33.95 (*q*)	34.09 (*q*)	33.95 (*q*)	33.95 (*q*)

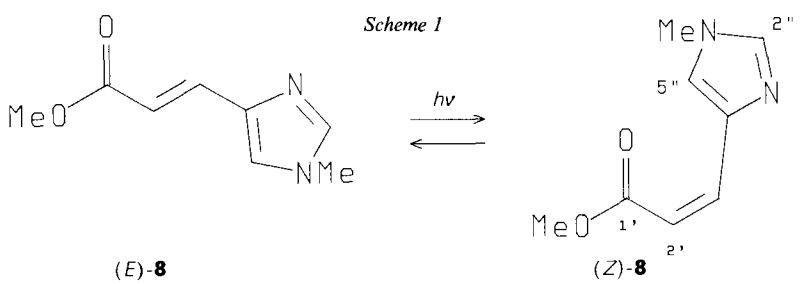
[a]) These protons are correlated with the C-atoms in the first columns. [b]) Ac 172.10 (*s*), 22.11 (*q*). [c]) Submerged by the solvent-residue signals.

Table 2. *^{1}H-NMR Data for Sarcodictyin C ((−)-**3**) in CD_3OD and, within Brackets, in C_5D_5N*[a])

H–C(2)	5.55 (br. *d*, $J(2,3) \approx 3$, $J(2, Me–C(1))$ small) [5.87]
H–C(3)	4.08 (br. *d*, $J(3,2) \approx 3$, $J(3,4) \approx J(3, Me–C(1))$ small) [4.34]
H–C(4)	1.49 (*m*, $J(4, Me_2CH) \approx 8$, $J(4,4a) = 2.0$, $J(4,3)$ small) [1.81]
H–C(4a)	4.34 (*ddd*, $J(4a,5) = 9.7$, $J(4a,12a) = 4.8$, $J(4a,4) = 2.0$) [4.73]
H–C(5)	7.21 (*d*, $J(5,4a) = 9.7$) [7.90]
H–C(8)	6.55 (*d*, $J(8,9) = 5.9$) [7.14]
H–C(9)	6.22 (*d*, $J(9,8) = 5.9$) [6.29]
H–C(11)	4.76 (br. *d*, $J(11,12endo) = 7.3$) [5.20]
H_{exo}–C(12)	1.65 (br. *d*, $J_{gem} = 15.0$, $J(12exo,12a) \approx 2$) [2.00]
H_{endo}–C(12)	1.48 (*ddd*, $J_{gem} = 15.0$, $J(12endo,12a) = 12.0$, $J(12endo,11) = 7.3$) [1.91]
H–C(12a)	2.62 (br. *d*, $J(12a,12endo) = 12.0$, $J(12a,4a) = 4.8$, $J(12a,12exo) \approx 2$) [2.93]
Me_2CH	1.63 (*m*, $J(Me_2CH, 4) \approx 8$, $J(Me_2CH, Me(pro\text{-}S)) = J(Me_2CH, Me(pro\text{-}R)) = 7.0$) [1.58]
Me(*pro-S*)	1.05 (*d*, $J(Me(pro\text{-}S), Me_2CH) = 7.0$) [0.99][b])
Me(*pro-R*)	1.08 (*d*, $J(Me(pro\text{-}R), Me_2CH) = 7.0$) [0.98][b])
Me–C(1)	1.56 (br. *s*, $J(Me–C(1), 2) \approx J(Me–C(1), 3)$ small) [1.61]
Me–C(10)	1.47(*s*) [1.54]
MeO	3.69 (*s*) [3.50]
H–C(2′)	6.46 (*d*, $J(2',3') = 16.0$) [7.10]
H–C(3′)	7.58 (*d*, $J(3',2') = 16.0$) [8.04]
H–C(2″)	7.70 (br. *s*, $J(2'',5'')$ small) [7.73]
H–C(5″)	7.47 (br. *s*, $J(5'',2'')$ small) [7.40]
Me–N(1″)	3.75 (*s*) [3.46]

[a]) *J* values in C_5D_5N are similar to those in CD_3OD. [b]) Data can be interchanged.

Scheme 1

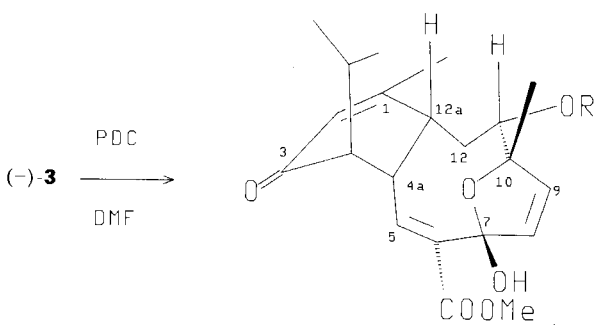


(*E*)-**8** (*Z*)-**8**

of (−)-**3**, there is a *s* at higher field which indicates sp^3 hybridization at C(1) of (+)-**6**. The ^{13}C-NMR spectrum of (+)-**6** shows, in place of a O-deshielded *d* for (−)-**3**, a O-deshielded *s*, besides an additional olefinic *d*. This supports the fragment Me–C(1) (OH)–CH(2)=CH(3)–CH(4). The α position for OH–C(1) is indicated by the NOESY correlation H–C(12a)/Me–C(1) and by a 0.5-ppm deshielding of H_{endo}–C(12).

2.2. *Reactivity.* As expected from its structure, sarcodictyin C ((−)-**3**) undergoes oxidation at C(3) by chromium reagents to give **9** *(Scheme 2)*. The enone system of **9** is indicated by the ^{13}C-NMR signal of C(3) at 204 ppm and by the low-field resonance of C(1) (26 ppm downfield *(Table 1)* as compared to (−)-**3** [1]).

Scheme 2



9 R = (*E*)-U

Treatment of (−)-**3** with MeOH/KOH at r.t. leads to mainly the butenolide **11** (35%), besides the two lactones **13a** (6%) and **13b** (29%) and the aldehyde **14** (12%; *Scheme 3*). Similarly, (−)-**1** gives **10** (50%) and **12** (33%).

The ^{1}H-NMR spectra of **11**, **13a**, and **13b** are similar to one another *(Table 4)*. The acetylation of **13b** to **13c** is accompanied by a low-field shift of H–C(7′), which shows that the OH–C(7′) group has remained intact. The pyranose ring is indicated by a typical *ddd* at 4.48–4.50 ppm for H–C(1′) of **11**, **13a**, and **13b**, by the disappearance of the C(5)=C(6) bond of (−)-**3**, and by the appearance of a (methoxycarbonyl)methylene group with both **11** and **13**. The methylbutenolide group is supported by the NMR data (*Tables 3* and *4*), and the C(3′)–C(4) bonding is indicated by the 1.20 (Me–C(4))/2.95 (H–C(3′)) NOESY correlation. The configurations at C(3) are supported by the coupling data in *Table 2* in combination with molecular mechanics calculations [4]. With **13a**, such calculations indicate that the less strained conformer has H_β–C(2)–C(3)–H and H_α–C(2)–C(3)–H dihedral angles of 35° and 160°. This suggest coupling constants of H–C(3) with H_α and H_β of *ca.* 7–8 Hz, which is in accordance with ^{1}H-NMR spectral data *(Table 4)*. With **13b**, less accurate molecular mechanics calculations indicate that the less strained conformer has H_β–C(2)–C(3)–H and H_α–C(2)–C(3)–H dihedral angles of *ca.* 100° and 20°. This suggests coupling constants of H–C(3) with H_α and H_β of *ca.* 2 and 7 Hz, in accordance with ^{1}H-NMR spectra *(Table 4)* [5].

^{1}H-NMR monitoring of the reaction of sarcodictyin C ((−)-**3**) with MeOH/KOH shows that the signals for the protons around C(11) of (−)-**3** are the first to change. This suggests *(Scheme 4)* that the transformation of (−)-**3** starts with base attack at C(1′), followed by conjugate attack by C(11)–O^- at C(5)[2]) to give intermediate **15**. *Retro-Claisen* decomposition of **15** gives butenolide **11**. Compound **11** can add the solvent to give

[2]) According to *Dreiding* molecular models, the C(11)–O and C(5) portions of sarcodictyin C ((−)-**3**) are rigidly disposed, and can not approach to one another. In contrast, when the urocanic portion has been removed, the system can be easily bent and C(11)–O^- can approach C(5) at bonding distance.

Scheme 3

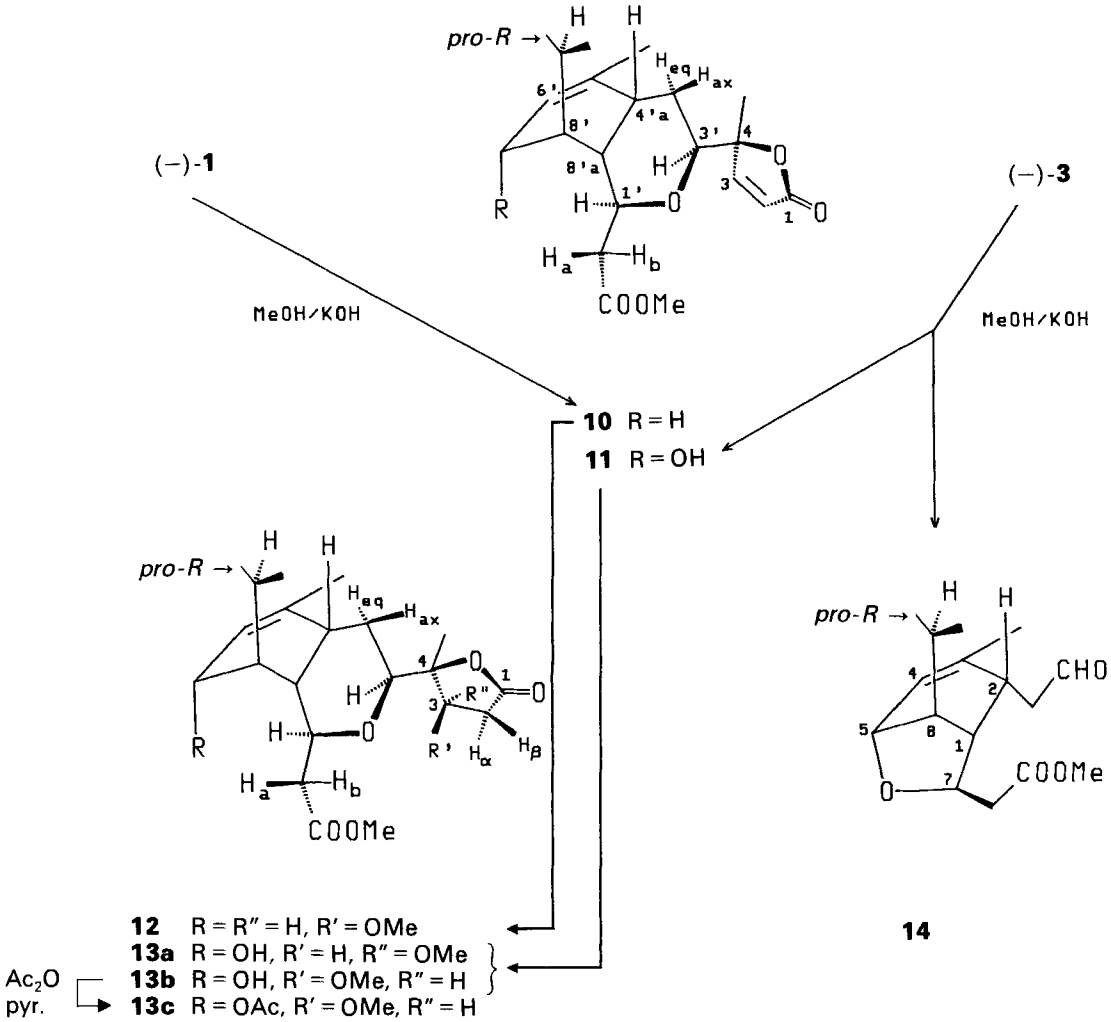


Table 3. *^{13}C-NMR Data in C_6D_6 for Compounds* **10–12** *and* **13b**

C-Atom	**10**	**11**	**12**	**13b**
C(1)[a])	171.48 (*s*)	171.53 (*s*)	174.51 (*s*)	174.60 (*s*)
C(2)	121.16 (*d*)	121.18 (*d*)	36.06 (*t*)	36.10 (*t*)
C(3)	157.91 (*d*)	157.99 (*d*)	80.33 (*d*)	80.31 (*d*)
C(4)	88.05 (*s*)	88.14 (*s*)	88.94 (*s*)	88.92 (*s*)
Me–C(4)	21.83 (*q*)	22.00 (*q*)	16.78 (*q*)	16.80 (*q*)
C(1′)	75.13 (*d*)	75.12 (*d*)	75.28 (*d*)	75.10 (*d*)
C(3′)	76.87 (*d*)	77.29 (*d*)	78.51 (*d*)	78.76 (*d*)
C(4′)	27.43 (*t*)	27.11 (*t*)	26.97 (*t*)	26.65 (*t*)
C(4′a)	32.14 (*d*)	32.49 (*d*)	32.12 (*d*)	32.51 (*d*)
C(5′)	132.90 (*s*)	136.45 (*s*)	133.00 (*s*)	136.42 (*s*)

Table 3 (cont.)

C-Atom	**10**	**11**	**12**	**13b**
C(6′)	122.95 (*d*)	125.49 (*d*)	123.16 (*d*)	126.74 (*d*)
C(7′)	24.36 (*t*)	66.56 (*d*)	24.35 (*t*)	66.60 (*d*)
C(8′)	40.03 (*d*)	47.30 (*d*)	40.02 (*d*)	47.44 (*d*)
C(8′a)	39.99 (*d*)	39.80 (*d*)	39.42 (*d*)	39.28 (*d*)
Me–C(5′)	21.29 (*q*)	21.16 (*q*)	21.41 (*q*)	21.26 (*q*)
Me_2CH	27.33 (*d*)	26.87 (*d*)	27.37 (*d*)	26.98 (*d*)
Me(*pro-S*)	20.54 (*q*)	21.50 (*q*)	20.69 (*q*)	21.68 (*q*)
Me(*pro-R*)	21.83 (*q*)	22.17 (*q*)	21.85 (*q*)	22.18 (*q*)
CH_2–C(1′)	39.17 (*t*)	38.92 (*t*)	38.63 (*t*)	38.40 (*t*)
*C*OOMe[a])	171.48 (*s*)	171.76 (*s*)	172.00 (*s*)	172.17 (*s*)
COO*Me*	51.10 (*q*)	50.99 (*q*)	51.12 (*q*)	51.01 (*q*)
OMe	–	–	56.69 (*q*)	56.70 (*q*)

[a]) The C(1) and *C*OOMe signals can be interchanged.

Table 4. *^{1}H-NMR Data (C_6D_6) for Compounds* **10–12**, **13a**, *and* **13b**

	10	**11**
H–C(2)	5.61 (*d*, *J*(2,3) = 5.8)	5.61 (*d*, *J*(2,3) = 5.5)
H–C(3)	6.73 (*d*, *J*(3,2) = 5.8)	6.78 (*d*, *J*(3,2) = 5.5)
Me–C(4)	1.16 (*s*)	1.20 (*s*)
H–C(1′)	3.91 (*ddd*, *J*(1′,8′a) = 10.0, *J*(1′, H_b) = 9.5, *J*(1′, H_a) = 3.1)	4.50 (*ddd*, *J*(1′,8′a) = *J*(1′, H_b) = 9.5, *J*(1′, H_a) = 3.0)
H–C(3′)	3.27 (*dd*, *J*(3′, H_{ax}) = 11.5, *J*(3′, H_{eq}) = 1.5)	3.32 (*dd*, *J*(3′, H_{ax}) = 11.5, *J*(3′, H_{eq}) = 1.5)
H_{ax}–C(4′)	0.92 (*ddd*, J_{gem} = 14.0, *J*(H_{ax}, 3′) = 11.5, *J*(H_{ax}, 4′a) = 5.0)	0.94 (*ddd*, J_{gem} = 14.0, *J*(H_{ax}, 3′) = 11.5, *J*(H_{ax}, 4′a) = 5.5)
H_{eq}–C(4′)	1.79 (*ddd*, J_{gem} = 14.0, *J*(H_{eq}, 4′a) = 2.8, *J*(H_{eq}, 3′) = 1.5)	1.77 (*ddd*, J_{gem} = 14.0, *J*(H_{eq}, 3′) = 1.5, *J*(H_{eq}, 4′a) = 2.5)
H–C(4′a)	2.09 (br. *s*, *J*(4′a,8′a) = 4.5, *J*(4′a, H_{ax}) ≈ 5.0, *J*(4′a, H_{eq}) = 2.8, *J*(4′a, Me–C(5′), small)	2.01 (br. *s*, *J*(4′a, H_{ax}) = 5.5, *J*(4′a,8′a) = 4.5, *J*(4′a, H_{eq}) = 2.5, *J*(4′a,6′) = 2.0, *J*(4′a, Me–C(5′)) = 1.0)
H–C(6′)	5.20 (br. *s*)	5.19 (br. *s*, *J*(6′,7′) = 5.1, *J*(6′,4′a) = 2.0, *J*(6′, Me–C(5′)) = 1.0)
H–C(7′)	1.76 (br. *s*, 2H)	3.67 (br. *d*, *J*(7′,6′) = 5.1, *J*(7′, Me–C(5′)) = 1.0, *J*(7′,8′) small)
H–C(8′)	0.80 (*m*, submerged)	1.19 (submerged)
H–C(8′a)	1.49 (*ddd*, *J*(8′a,1′) = 10.0, *J*(8′a,4′a) = 4.5, *J*(8′a,8) = 2.8)	1.66 (br. *d*, *J*(8′a,1′) = 9.5, *J*(8′a,4′a) = 4.5, *J*(8′a,8′) = 2.4)
Me–C(5′)	1.45 (br. *s*)	1.42 (br. *s*, *J*(Me–C(5′), 4′a) = *J*(Me–C(5′),6′) = *J*(Me–C(5′), 7′) = 1.0)
Me_2CH	1.30 (*m*)	1.04 (*dqq*, *J*(Me_2CH, 8′) = 10.0, *J*(Me_2CH, Me(*pro-S*)) = *J*(Me_2CH, Me(*pro-R*)) = 6.5)
Me(*pro-S*)	0.67 (*d*, *J*(Me(*pro-S*), Me_2CH) = 6.5)	0.68 (*d*, *J*(Me(*pro-S*), Me_2CH) = 6.5)
Me(*pro-R*)	0.78 (*d*, *J*(Me(*pro-R*), Me_2CH) = 6.5)	0.81 (*d*, *J*(Me(*pro-R*), Me_2CH) = 6.5)
H_aCH–C(1′)	2.33 (*dd*, J_{gem} = 14.5, *J*(H_a, 1′) = 3.1)	2.97 (*dd*, J_{gem} = 14.5, *J*(H_a, 1′) = 3.0)
H_bCH–C(1′)	2.20 (*dd*, J_{gem} = 14.5, *J*(H_b, 1′) = 9.5)	2.33 (*dd*, J_{gem} = 14.5, *J*(H_b, 1′) = 9.5)
COOMe	3.40 (*s*)	3.40 (*s*)
	12	**13a**
H–C(2)	2.93 (*dd*, J_{gem} = 17.8, *J*(H_α, 3) = 6.8, H_α); 2.37 (*dd*, J_{gem} = 17.8, *J*(H_β, 3) = 1.8, H_β)	2.24 (*dd*, J_{gem} = 16.5, *J*(H_α, 3) = 7.8, H_α); 2.85 (*dd*, J_{gem} = 16.5, *J*(H_β, 3) = 7.8, H_β)
H–C(3)	3.74 (*dd*, *J*(3, H_α) = 6.8, *J*(3, H_β) = 1.8)	3.16 (*dd*, *J*(3, H_α) = *J*(3, H_β) = 7.8)
Me–C(4)	1.20 (*s*)	1.06 (*s*)

Table 4 (cont.)

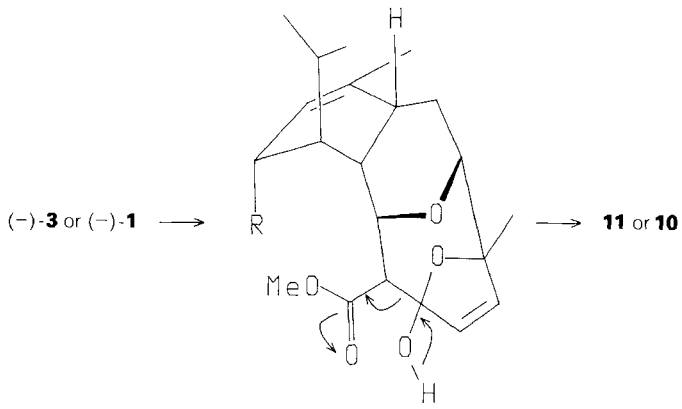
	12	**13a**
H–C(1′)	3.86 (*ddd*, J(1′,8′a) = 10.0, J(1′, H_b) = 9.5, J(1′, H_a) = 3.1)	4.49 (*ddd*, J(1′,8′a) = 10.5, J(1′,H_b) = 8.5, J(1′, H_a) = 3.0)
H–C(3′)	2.92 (*dd*, J(3′, H_{ax}) = 11.7, J(3′, H_{eq}) = 1.6)	3.59 (*dd*, J(3′, H_{ax}) = 10.0, J(3′, H_{eq}) = 3.0)
H_{ax}–C(4′)	1.60 (*ddd*, J_{gem} = 14.0, J(H_{ax}, 3′) = 11.7, J(H_{ax}, 4′a) = 5.0)	1.5–1.6 (superimposed)
H_{eq}–C(4′)	1.77 (*ddd*, J_{gem} = 14.0, J(H_{eq}, 4′a) = 2.6, J(H_{eq}, 3′) = 1.6)	
H–C(4′a)	2.14 (br. *s*, J(4′a, H_{ax}) = 5.0, J(4′a,8′a) = 4.7, J(4′a, H_{eq}) = 2.6, J(4′a, Me–C(5′)) small)	2.19 (br. *s*)
H–C(6′)	5.24 (br. *s*)	5.19 (br. *s*, J(6′,7′) = 5.0, J(6′, Me–C(5′)) = 1.0)
H–C(7′)	1.76 (br. *s*, 2 H)	3.73 (br. *d*, J(7′,6′) = 5.0, J(7′, Me–C(5′)) = 1.0, J(7′,8′) small)
H–C(8′)	0.80 (*m*, submerged)	1.3 (*m*)
H–C(8′a)	1.55 (*dd*, J(8′a,1′) = 10.0, J(8′a,4′a) = 4.7, J(8′a,8′) = 3.0)	1.88 (br. *d*, J(8′a,1′) = 10.5)
Me–C(5′)	1.42 (br. *s*)	1.43 (br. *s*, J(Me–C(5′), 6′) = J(Me–C(5′),7′) = 1.0)
Me_2CH	1.30 (*m*)	1.07 (*m*)
Me(*pro-S*)	0.69 (*d*, J(Me(*pro-S*), Me_2CH) = 6.6)	0.76 (*d*, J(Me(*pro-S*), Me_2CH) = 6.5)
Me(*pro-R*)	0.80 (*d*, J(Me(*pro-R*), Me_2CH) = 6.6)	0.84 (*d*, J(Me(*pro-R*), Me_2CH) = 6.5)
H_a–CH–C(1′)	2.25 (*dd*, J_{gem} = 14.5, J(H_a, 1′) = 3.1)	2.90 (*dd*, J_{gem} = 13.5, J(H_a, 1′) = 3.0)
H_bCH–C(1′)	2.33 (*dd*, J_{gem} = 14.5, J(H_b, 1′) = 9.5)	2.44 (*dd*, J_{gem} = 13.5, J(H_b, 1′) = 8.5)
COOMe	3.39 (*s*)	3.50 (*s*)
OMe	2.86 (*s*)	2.82 (*s*)

	13b
H–C(2)	2.96 (*dd*, J_{gem} = 17.5, J(H_α, 3) = 6.5, H_α); 2.36 (*dd*, J_{gem} = 17.5, J(H_β, 3) = 1.8, H_β)
H–C(3)	3.80 (*dd*, J(3, H_β) = 1.8, J(3, H_α) = 6.5)
Me–C(4)	1.20 (*s*)
H–C(1′)	4.48 (*ddd*, J(1′,8′a) = J(1′,H_b) = 9.5, J(1′, H_a) = 3.0)
H–C(3′)	2.95 (*dd*, J(3′, H_{ax}) = 11.0, J(3′, H_{eq}) = 2.3)
H_{ax}–C(4′)	1.68 (*ddd*, J_{gem} = 14.0, J(H_{ax}, 3′) = 11.0, J(H_{ax}, 4′a) = 5.0)
H_{eq}–C(4′)	1.73 (superimposed to H–C(8′a))
H–C(4′a)	2.09 (br. *s*, J(4′a, H_{ax}) = 5.0, J(4′a, 6′) = 2.0, J(4′a, Me–C(5′)) = 1.0)
H–C(6′)	5.24 (br. *s*, J(6′,7′) = 5.0, J(6′,4′a) = 2.0, J(6′, Me–C(5′)) = 1.0)
H–C(7′)	3.68 (br. *d*, J(7′,6′) = 5.0, J(7′, Me–C(5′)) = 1.0, J(7′,8′) small)
H–C(8′)	1.19 (submerged by Me–C(4))
H–C(8′a)	1.73 (superimposed to H_{eq}–C(4′))
Me–C(5′)	1.39 (br. *s*, J(Me–C(5′),4′a) = J(Me–C(5′),6′) = J(Me–C(5′),7′) = 1.0)
Me_2CH	1.06 (*dqq*, J(Me_2CH, 8′) = 10.0, J(Me_2CH, Me(*pro-S*)) = J(Me_2CH, Me(*pro-R*)) = 6.0)
Me(*pro-S*)	0.69 (*d*, J(Me(*pro-S*), Me_2CH) = 6.0)
Me(*pro-R*)	0.82 (*d*, J(Me(*pro-R*), Me_2CH) = 6.0)
H_aCH–C(1′)	2.86 (*dd*, J_{gem} = 14.5, J(H_a, 1′) = 3.0)
H_bCH–C(1′)	2.30 (*dd*, J_{gem} = 14.5, J(H_b, 1′) = 9.5)
COOMe	3.40 (*s*)
OMe	2.88 (*s*)

the lactones **13a** and **13b** (see above, *Scheme 3*). Similarly, (–)-**1** gives **10** and **12** through the intermediate **16**[3]).

[3]) Isolation of the minor stereoisomeric lactone with R″ = OMe was not attempted.

Scheme 4



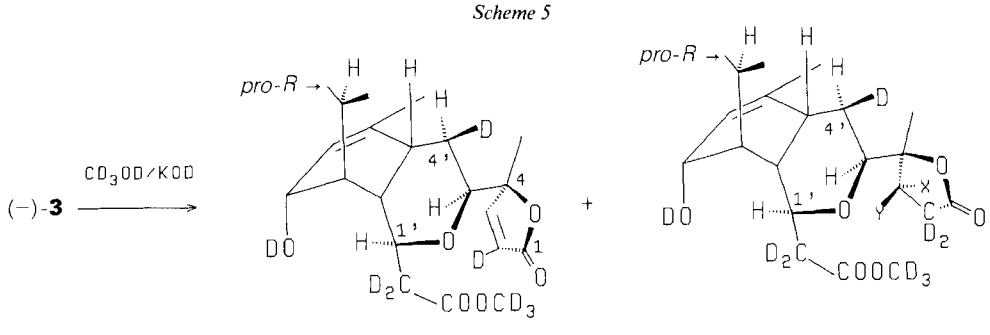
15 R = OH
16 R = H

When (−)-**3** is allowed to react in CD_3OD/KOD, butenolide **17** is isolated, to our surprise stereospecifically deuteriated at the 4′-axial position *(Scheme 5)*[4]). Incorporation of D at the 4-axial position does not occur at the level of a type-**17** compound; this is proved by the fact that compound **11** in CD_3OD/KOD in a week at r.t. does not incorporate D at C(4), whereas the protons $-C(H_2)-C(1')$ and C(2)H are exchanged.

Addition of MeOH at the butenolide double bond accounts for formation of **13a** and **13b**. The reaction is reversible, as shown by incorporation of D at C(2) in **11** to give **17** when CD_3OD is used.

When there is a 3α-OH group in the sarcodictyin, such as with (−)-**3**, aldehyde **14** is formed competitively with ring contraction (see above, *Scheme 3*). We suggest *(Scheme*

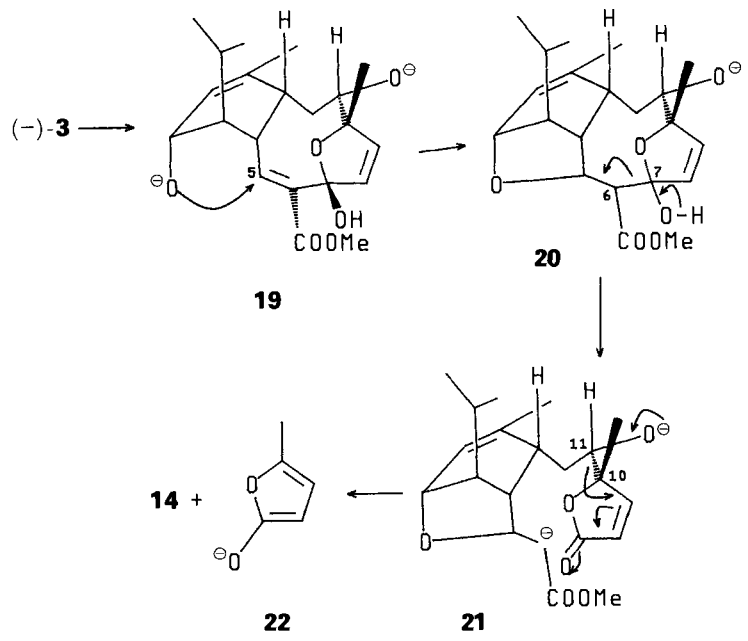
Scheme 5



17 **18** Y = OCD_3, X = H

[4]) Deuteriations at CH_2–C(1′) and C(2) are attributable to enolization and addition/removal of the solvent at the butenolide *via* deuteriated lactones of type **13**. Deuteriated lactones of type **13a** and **14** were present in small amounts, and the isolation was not attempted.

Scheme 6



6) that the first intermediate of the hydrolysis (**19**) undergoes intramolecular conjugate attack by C(3)–O^- to C(5) to give **20**, followed by consecutive C(6)–C(7) *retro-Claisen* bond breaking to give **21** and C(10)–C(11) *retro*-aldol bond breaking, with expulsion of hydroxyfuran **22** to give aldehyde **14** [6].

3. Conclusions. – Formation of the butenolide moiety of **10** and **11**, or of hydroxyfuran **22**, from the dihydrohydroxyfuran nucleus of the sarcodictyins governs the chemistry of these terpenoids in basic media. Extrusion to form the butenolide, or expulsion of **22**, are delineated in *Scheme 3* and rationalized in *Schemes 4* and *6*. The primary act of the rearrangements is hydrolysis at the ester function at C(11); in fact, the sarcodictyins are stable only as long as their C(11)–OH function is esterified by the bulky methylurocanic acid.

Regrettably, no chemical transformations have been reported for either cladiellin (**7**) or structurally related terpenoids [2], which are the only known compounds possessing the C-skeleton of the sarcodictyins. However, the cladiellans, lacking stable removable groups, are not expected to give any of the transformations which have been described here for the sarcodictyins.

This is a case of failure of the C-skeleton as a criterion of classification of terpenoids. To be chemically meaningful, separate classes are thus required for the sarcodictyins and the cladiellanes.

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Experimental Part

1. *General.* TLC: *Merck Kieselgel 60 PF_{254}* plates. HPLC: *Merck-LiChrosorb-CN* (7 μm) 25 × 1 cm column, hexane/EtOH/(*i*-Pr)NH_2 80:18:2, 5 ml/min. All evaporations were carried out at reduced pressure at r.t. Reaction yields are calculated on reacted materials. Polarimetric data: *JASCO-DIP-181* digital polarimeter. UV and IR spectra: *Perkin-Elmer Lambda-3* (λ_{max} in nm, ε in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) and *Pye-Unicam SP3-100* ($\tilde{\nu}_{max}$ in cm^{-1}) spectrophotometers, resp. ^{1}H-NMR and ^{13}C-NMR spectra: *Varian XL300* (300 or 75.43 MHz, resp.); δ (ppm) relative to internal Me_4Si (= 0 ppm) and J in Hz, the notation 'small' indicates $J < 0.5$ Hz; J's are derived from homonuclear decoupling; ^{13}C multiplicities: APT [7] or DEPT [8] techniques; all assignments are supported by ^{13}C, ^{1}H-NMR shift correlation experiments (HETCOR) [9] as in [1]. Low-resolution MS: home-built quadrupole mass spectrometer based on the *ELFS-4-162-8 Extranuclear* quadrupole [10]. High-resolution MS and linked scans [11]: *VG-ZAB2F* ((−)-**3**) or *VG 70–70* ((+)-**6**) spectrometers. Molecular-mechanics calculations were carried out with the MMPMI program by *Serena Software*, Blomington, Indiana.

2. *Isolations.* Continuing the HPLC elution of extracts of *S. roseum* on the *CN* column as before [1], sarcodictyin E ((+)-**5**; 0.058 g, t_R 13.8), D ((−)-**4**; 0.017 g, t_R 16.2), F ((+)-**6**; 0.038 g, t_R 18.8), and C ((−)-**3**; 0.27 g, t_R 21.3 min) were obtained.

3. *Sarcodictyin C (= (−)-(3R*,4S*,4aS*,7S*,10R*,11R*,12aS*,1Z,5E,8Z)-7,10-Epoxy-3,4,4a,7,10,11,12,12a-octahydro-3,7-dihydroxy-6-(methoxycarbonyl)-1,10-dimethyl-4-(1-methylethyl)benzocyclodecen-11-yl (E)-3-(1-Methyl-1H-imidazol-4-yl)acrylate*[6]); (−)-**3**). Colourless microcrystalline powder. M.p. 225–227° (from $(CH_3)_2O$). $[\alpha]^{20} = -16.5$ (589), −20.0 (577), −22.4 (546), −57.6 (435) ($c = 0.085$, EtOH). UV (EtOH): 290 (15300), 202 (13800). IR (nujol): 3400*s* (OH), 1700*s* (C=O), 1690*s* (C=O), 1630*m*, 1170*s*, 1150*s*, 1050*s*. NOESY (C_5D_5N): 1.81 (H–C(4))/7.90 (H–C(5)); 6.29 (H–C(9))/1.54 (Me–C(10)); 5.20 (H–C(11))/1.54 (Me–C(10)); 2.93 (H–C(12a))/1.58 (Me_2CH); 7.40 (H–C(5″))/3.46 (MeN). MS: 512 (0.4, M^+), 494 (2, $M^+ - 18$), 451 (2), 342 (2), 310 (1), 195 (3), 179 (3), 166 (4), 153 (20), 135 (100), 107 (7), 65 (10). HR-MS: found 494.2415 ± 0.05 ($C_{28}H_{34}N_2O_6$, calc. 494.2417). Linked scans (B/E [11]): working on $M^+ - 18$, peaks at 476 (494 – H_2O), 462 (494 – MeOH), 451 (494 – C_3H_7), 341 (494 – $C_7H_9N_2O_2$); working on *m/z* 451, peaks at 433 (451 – H_2O), 419 (451 – MeOH); working on *m/z* 342, peaks at *m/z* 324 (342 – H_2O), 310 (342 – MeOH).

4. *Oxidation of* (−)-**3**. A soln. of (−)-**3** (0.012 g, 0.023 mmol) and 1.5 mol-equiv. of pyridinium dichromate in 1 ml of dry DMF was stirred overnight at r.t., then eluted over silica gel and evaporated. The residue was subjected to HPLC obtaining **9** (t_R 17.2 min; 0.0082 g, 70%). ^{1}H-NMR (CD_3OD): 5.81 (*m*, J(2,12a) = 2.8, J(2, Me–C(1)) = 1.2, J(2,4) = 0.5, H–C(2)); 1.94 (br. *dd*, J(4, Me_2CH) = 10.5, J(4,4a) = 2.5, J(4,2) = 0.5, H–C(4)); 4.58 (*ddd*, J(4a,5) = 9.7, J(4a,12a) = 4.6, J(4a,4) = 2.5, H–C(4a)); 6.45 (*d*, J(5,4a) = 9.7, H–C(5)); 6.49 (*d*, J(8,9) = 6.0, H–C(8)); 6.41 (*d*, J(9,8) = 6.0, H–C(9)); 4.79 (br. *d*, J(11,12*endo*) = 7.0, J(11,12*exo*) small, H–C(11)); 1.84 (br. *d*, J_{gem} = 15.0, J(12*exo*,12a) = 2.0, J(12*exo*,11) small, H_{exo}–C(12)); 1.52 (*ddd*, J_{gem} = 15.0, J(12*endo*, 12a) = 12.0, J(12*endo*, 11) = 7.0, H_{endo}–C(12)); 3.31 (submerged by the solvent signal, H–C(12a)); 2.05 (*dqq*, $J(Me_2CH, 4) = 10.5$, $J(Me_2CH, Me(pro\text{-}S)) = J(Me_2CH, Me(pro\text{-}R)) = 6.5$, Me_2CH); 1.15, 0.93 (2 *d*, J = 6.5, Me(*pro-S*), Me(*pro-R*)); 1.83 (br. *s*, Me–C(1)); 1.52 (*s*, Me–C(10)); 3.69 (*s*, MeO); 6.48 (*d*, J(2′,3′) = 15.5, H–C(2′)); 7.62 (*d*, J(3′,2′) = 15.5, H–C(3′)); 7.72 (br. *s*, J(2″,5″) small, H–C(2″)); 7.49 (br. *s*, J(5″,2″) small, H–C(5″)); 3.76 (*s*, MeN).

5. *Treatment of* (−)-**3** *with Methanolic Base.* a) *With MeOH/KOH.* A soln. of (−)-**3** (0.02 g, 0.04 mmol) in 0.5 ml of 0.1 M KOH/MeOH was allowed to stand at r.t. for 4 days and then subjected to TLC with Et_2O, obtaining **14** (R_f 0.91; 0.0013 g, 12%), **11** (R_f 0.59; 0.0053 g, 35%), **13b** (R_f 0.46; 0.0048 g, 29%), **13a** (R_f 0.31; 0.001 g, 6%), and (*E*)-*N*^{1}-methylurocanic acid (R_f 0.006; 0.0058 g, 95%).

b) *With CD_3OD/KOD.* A soln. of (−)-**3** (0.01 g, 0.02 mmol) in 0.4 ml of 0.1 M MeOD/KOD was handled as in a) to give **17** (0.0031 g, 41%) and **18** (0.0022 g, 26%).

(4R,1′R*,3′R*,4′aS*,7′R*,8′S*,8′aR*,5′Z)-4-{3′,4′,4′a,7′,8′,8′a-Hexahydro-7′-hydroxy-1′-[(methoxycarbonyl)methyl]-5′-methyl-8′-(1-methylethyl)-1′H-2′-benzopyran-3′-yl}-4-methyl-2-buten-4-olide* (**11**). IR (film): 3500*s* (OH); 1740*s*, 1750*s*, 1780*s* (C=O); 1440*s*, 1110*s*. NOESY (key data only; C_6D_6): 4.50 (H–C(1′))/3.32 (H–C(3′)); 1.77 (H_{eq}–C(4′))/1.42 (Me–C(5′)); 2.01 (H–C(4′a))/0.68 (Me(*pro-S*)); 3.67 (H–C(7′))/0.81 (Me(*pro-R*)); 1.19 (H–C(8′))/2.97 (H_aC–C(1′)); 1.66 (H–C(8′a))/0.68 (Me(*pro-S*)). MS: 360 (2, $M^+ - 18$), 328 (1), 317 (2), 285 (5), 243 (13), 219 (20), 189 (61), 187 (22), 161 (37), 159 (33), 147 (56), 145 (54), 119 (81), 91 (100).

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[6]) Numbering according to Footnote 5 in [1].

(3R,4S*,1'R*,3'R*,4'aS*,7'R*,8'S*,8'aR*,5'Z)-4-{3',4',4'a,7',8',8'a-Hexahydro-7'-hydroxy-1'-[(methoxycarbonyl)methyl]-5'-methyl-8'-(1-methylethyl)-1'H-2'-benzopyran-3'-yl}-3-methoxy-4-methylbutan-4-olide* (**13a**). Differential NOE effects (C_6D_6, irradiated proton(s)→NOE effect (%) on the observed proton(s)): 2.24→2.85 (9%), 2.82 (1%); 2.85→2.24 (3%); 1.06→3.16 (5%), 3.59 (2%); 3.16→2.82 (1%).

(3R,4R*,1'S*,3'S*,4'aR*,7'S*,8'R*,8'aS*,5'Z)-4-{3',4',4'a,7',8',8'a-Hexahydro-7'-hydroxy-1'-[(methoxycarbonyl)methyl]-5'-methyl-8'-(1-methylethyl)-1'H-2'-benzopyran-3'-yl]-3-methoxy-4-methylbutan-4-olide* (**13b**). IR (film): 3500*s* (OH); 1740*s*, 1780*s* (C=O); 1100*s*. NOESY (key data only, C_6D_6): 2.96 (H_α–C(2))/3.80 (H–C(3)); 3.80 (H–C(3))/1.20 (Me–C(4)); 4.48 (H–C(1'))/2.95 (H–C(3')); 2.95 (H–C(3'))/1.20 (Me–C(4)); 2.09 (H–C(4'a))/0.69 (Me(*pro-S*)); 2.09 (H–C(4'a))/1.06 (Me_2CH); 3.68 (H–C(7'))/0.82 (Me(*pro-R*)); 1.19 (H–C(8'))/2.86 (H_aC–C(1')). Differential NOE effects (C_6D_6, irradiated proton(s)→NOE (%) effect on the observed proton(s)): 1.20→3.80 (2%), 2.95 (9%), 2.88 (2%), 2.36 (3%). MS: 392 (2, $M^{+}-18$), 333 (7), 285 (3), 219 (15), 189 (31), 159 (31), 143 (19), 119 (73), 43 (100).

Methyl (1R,2S*,5R*,7S*,8S*)-2-(Formylmethyl)-3-methyl-8-(1-methylethyl)-6-oxabicyclo[3.2.1]oct-3-en-7-acetate* (**14**). IR (film): 2710*w* (CHO), 1730*s* (C=O). ^{13}C-NMR (C_6D_6): 35.48 (*d*, C(1)); 44.31 (*d*, C(2)); 138.81 (*s*, C(3)); 123.98 (*d*, C(4)); 73.77 (*d*, C(5)); 75.01 (*d*, C(7)); 51.01 (*d*, C(8)); 43.60 (*t*, CH_2–C(2)); 199.85 (*d*, CHO); 21.84 (*q*, *Me*–C(3)); 40.62 (*t*, CH_2–C(7)); 171.52 (*s*, *C*OOMe); 50.96 (*q*, COO*Me*); 25.31 (*d*, Me_2CH); 20.23, 22.24 (2 *q*, Me(*pro-S*), Me(*pro-R*)). ^{1}H-NMR (C_6D_6): 2.11 (br. *dd*, *J*(1,8) = 4.0, *J*(1,2) = 3.0, *J*(1,5) small, H–C(1)); 2.97 (*m*, *J*(2, CH_2–C(2)) = 9.3 and 4.7, *J*(2,4) = 2.2, *J*(2, Me–C(3)) = 1.0, H–C(2)); 5.43 (*m*, *J*(4,5) = 5.8, *J*(4,2) = 2.2, *J*(4, Me–C(3)) = 1.2, H–C(4)); 4.06 (br. *dd*, *J*(5,4) = 5.8, *J*(5,8) = 3.0, *J*(5,1) small, H–C(5)); 4.38 (*dd*, *J*(7, CH_2–C(7)) = 9.5 and 5.0, H–C(7)); 1.56 (*m*, superimposed to Me_2CH, H–C(8)); 2.45, 2.10 (br. *dd*, J_{gem} = 18.5, *J*(CH_2–C(2), 2) = 9.3 and 4.7, *J*(CH_2–C(2), CHO) = 0.8 and small, CH_2–C(2)); 9.48 (br. *s*, *J*(CHO, CH_2–C(2)) = 0.8 and small, CHO); 1.26 (br. *s*, *J*(Me–C(3), 4) = 1.2, *J*(Me–C(3), 2) = 1.0, Me–C(3)); 2.35, 2.61 (*dd*, J_{gem} = 16.0, *J*(CH_2–C(7), 7) = 9.5 and 5.0, CH_2–C(7)); 3.24 (*s*, MeO); 1.56 (*m*, superimposed to H–C(8), Me_2CH); 0.99 (*d*, *J*(Me(*pro-S*), Me_2CH) = 6.0, Me(*pro-S*)); 0.76 (*d*, *J*(Me(*pro-R*), Me_2CH) = 6.0, Me(*pro-R*)). Differential NOE effects (C_6D_6, irradiated proton(s)→NOE effect (%) on the observed proton(s)): 2.10 and 2.11→2.97 (8%), 4.38 (4%); 4.38→2.45 (7%), 2.61 (3%), 2.11 (2%). NOESY (C_6D_6): 2.11 (H–C(1))/0.99 (Me(*pro-S*)); 4.06 (H–C(5))/0.76 (Me(*pro-R*)). MS: 280 (1, M^{+}), 265 (1), 262 (3), 249 (2), 237 (3), 219 (4), 205 (3), 193 (32), 178 (16), 134 (100), 119 (47), 105 (34), 93 (68).

4-{3',4',4'a,7',8',8'a-Hexahydro-7'-(D)hydroxy-1'-[((D$_3$)methoxycarbonyl)(D$_2$)methyl]-5'-methyl-8'-(1-methylethyl)-(4'β-D)-1'H-2'-benzopyran-3'-yl}-4-methyl-2-(2-D)buten-4-olide (**17**). ^{1}H-NMR (C_6D_6): the only signals that differ from those for **11** are 6.78 (*s*, H–C(3)); 4.50 (*d*, *J*(1',8'a) = 9.5, H–C(1')); 3.31 (*d*, *J*(3', H–C(4')) = 1.5, H–C(3')); 1.76 (br. *s*, *J*(H–C(4'), 4'a) = 2.5, *J*(H–C(4'), 3') = 1.5, H–C(4')), while signals for protons at *C*–C(1'), C(2), and COO*C* are absent.

4-{3',4',4'a,7',8',8'a-Hexahydro-7'-(D)hydroxy-1'-[((D$_3$)methoxycarbonyl)(D$_2$)methyl]-5'-methyl-8'-(1-methylethyl)-(4'β-D)-1'H-2'-benzopyran-3'-yl}-3-(D$_3$)methoxy-4-methyl-(2,2-D$_2$)buten-4-olide (**18**). ^{1}H-NMR (C_6D_6): the only signals that differ from those for **13b** are 3.80 (*s*, H–C(3)); 4.48 (*d*, *J*(1',8'a) = 9.5, H–C(1')); 2.95 (*d*, *J*(3', H–C(4')) = 2.3, H–C(3')); 1.73 (br. *s*, *J*(H–C(4'), 4'a) ≈ 2, *J*(H–C(4'), 3') = 2.3, H–C(4')), while signals for protons at *C*–C(1'), C(2), *C*O–C(3), and COO*C* are absent.

6. *Sarcodictyin D (= (–)-(3R*,4S*,4aS*,7S*,10R*,11R*,12aS*,1Z,5E,8Z)-3-Acetoxy-7,10-epoxy-3,4,4a,7,10,11,12,12a-octahydro-7-hydroxy-6-(methoxycarbonyl)-1,10-dimethyl-4-(1-methylethyl)benzocyclodecen-11-yl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate*[6]); (–)-**4**). Colourless microcrystalline powder. M.p. 130–132° (from MeOH). $[\alpha]_{589}^{20} = -27.2$ (*c* = 0.25, MeOH). ^{1}H-NMR (CD_3OD): 5.48 (br. *s*, H–C(2)); 5.25 (br. *s*, H–C(3)); 1.60 (superimposed, H–C(4)); 4.42 (*ddd*, H–C(4a)); 7.35 (*d*, H–C(5)); 6.56 (*d*, H–C(8)); 6.24 (*d*, H–C(9)); 4.74 (*d*, H–C(11)); 1.71 (br. *d*, H_{exo}–C(12)); 1.46 (superimposed, H_{endo}–C(12)); 2.74 (br. *d*, H–C(12a)); 1.60 (superimposed, Me_2CH); 1.12, 1.08 (2 *d*, Me(*pro-S*), Me(*pro-R*)); 1.62 (br. *s*, Me–C(1)); 1.46 (*s*, Me–C(10)); 3.72 (*s*, MeO); 6.46 (*d*, H–C(2')); 7.58 (*d*, H–C(3')); 7.71 (br. *s*, H–C(2")); 7.47 (br. *s*, H–C(5")); 3.75 (*s*, MeN); coupling constants are practically identical to those for (–)-**3**.

7. *Sarcodictyin E (= (+)-(3R*,4S*,4aS*,7S*,10R*,11R*,12aS*,1Z,5E,8Z)-7,10-Epoxy-3,4,4a,7,10,11,12,12a-octahydro-3,7-dihydroxy-6-(methoxycarbonyl)-1,10-dimethyl-4-(1-methylethyl)benzocyclodecen-11-yl (Z)-3-(1-methyl-1H-imidazol-4-yl)acrylate*[6]); (+)-**5**). Colourless microcrystalline powder. M.p. 212–214° (from MeOH). $[\alpha]_{589}^{20} = +15.6$ (*c* = 0.42, MeOH). UV (MeOH): 272 (14 500), 202 (17 500). ^{1}H-NMR (CD_3OD); 5.57 (br. *s*, H–C(2)); 4.08 (br. *s*, H–C(3)); 1.50 (superimposed, H–C(4)); 4.38 (*ddd*, H–C(4a)); 7.21 (*d*, H–C(5)); 6.55 (*d*, H–C(8)); 6.15 (*d*, H–C(9)); 4.75 (*d*, H–C(11)); 1.64 (superimposed, H_{exo}–C(12)); 1.50 (superimposed, H_{endo}–C(12)); 2.64 (br. *d*, H–C(12a)); 1.64 (superimposed, Me_2CH); 1.10, 1.08 (2 *d*, Me(*pro-S*), Me(*pro-R*)); 1.56 (br. *s*, Me–C(1)); 1.45 (*s*, Me–C(10)); 3.69 (*s*, MeO); 5.83 (*d*, *J*(2',3') = 12.5, H–C(2')); 6.94 (*d*, *J*(3',2') = 12.5,

H–C(3')); 7.65 (br. *s*, H–C(2")); 8.42 (br. *s*, H–C(5")); 3.77 (*s*, MeN); coupling constants not reported are practically identical to those for (–)-**3**.

8. *UV Irradiation of Methyl (*E*)-3-(1-Methyl-1*H*-imidazol-4-yl)acrylate* ((*E*)-**8**). A 0.04M soln. of (*E*)-**8** in CD_3OD was irradiated with a 4-W low-pressure Hg lamp in a 5 mm *Pyrex* NMR tube at r.t. during 13 h. The ^{1}H-NMR spectrum revealed the presence of (*E*)- and (*Z*)-**8** in a 1:1 ratio, with signals identical to the urocanic portion of (–)-**3** and (+)-**5**, respectively.

9. *Sarcodictyin F (= (+)-(1*R*,4*R*,4a*R*,7*R*,10*S*,11*S*,12a*R*,2*Z*,5*E*,8*Z*)-7,10-Epoxy-1,4,4a,7,10,11,12,12a-octahydro-1,7-dihydroxy-6-(methoxycarbonyl)-1,10-dimethyl-4-(1-methylethyl)benzocyclodecen-11-yl (*E*)-3-(1-Methyl-1*H*-imidazol-4-yl)acrylate;* (+)-**6**). Colourless microcrystalline powder. M.p. 228–229° (from MeOH). $[\alpha]_{589}^{20} = +2.7$ ($c = 0.15$, MeOH). ^{1}H-NMR (C_5D_5N): 5.98 (br. *d*, $J(2,3) = 10.0$, $J(2,4)$ small, H–C(2)); 5.76 (*ddd*, $J(3,2) = 10.0$, $J(3,4) = 5.0$, $J(3,4a) = 1.0$, H–C(3)); 1.78 (br. *dd*, $J(4, Me_2CH) = 8.5$, $J(4,3) = 5.0$, $J(4,2)$ small, H–C(4)); 4.81 (*ddd*, $J(4a,5) = 10.0$, $J(4a,12a) = 3.5$, $J(4a,3) = 1.0$, H–C(4a)); 7.24 (*d*, $J(5,4a) = 10.0$, H–C(5)); 7.12 (*d*, $J(8,9) = 6.0$, H–C(8)); 6.26 (*d*, $J(9,8) = 6.0$, H–C(9)); 5.28 (*d*, $J(11,12endo) = 7.0$, H–C(11)); 2.08 (br. *d*, $J_{gem} = 15.0$, $J(12exo,12a)$ small, H_{exo}–C(12)); 2.42 (*ddd*, $J_{gem} = 15.0$, $J(12endo,12a) = 12.0$, $J(12endo,11) = 7.0$, H_{endo}–C(12)); 2.58 (br. *d*, $J(12a,12endo) = 12.0$, $J(12a,4a) = 3.5$, $J(12a,12exo)$ small, H–C(12a)); 1.62 (superimposed, Me_2CH); 0.93, 0.91 (2 *d*, $J = 6.0$, Me(*pro-S*), Me(*pro-R*)); 1.47 (*s*, Me–C(1)); 1.58 (*s*, Me–C(10)); 3.42 (*s*, MeO); 7.11 (*d*, $J(2',3') = 15.0$, H–C(2')); 8.02 (*d*, $J(3',2') = 15.0$, H–C(3')); 7.68 (br. *s*, $J(2",5")$ small, H–C(2")); 7.34 (br. *s*, $J(5",2")$ small, H–C(5")); 3.38 (*s*, MeN). NOESY (key data only; C_5D_5N): 5.98 (H–C(2))/1.47 (Me–C(1)); 1.78 (H–C(4))/4.81 (H–C(4a)); 7.24 (H–C(5))/1.78 (H–C(4)); 6.26 (H–C(9))/1.58 (Me–C(10)); 5.28 (H–C(11))/4.81 (H–C(4a)); 5.28 (H–C(11))/1.58 (Me–C(10)); 5.28 (H–C(11))/2.58 (H–C(12a)); 2.08 (H_{exo}–C(12))/1.47 (Me–C(1)); 2.58 (H–C(12a))/1.47 (Me–C(1)); 7.34 (H–C(5"))/3.38 (MeN). MS: 512 (1, $M^{+\cdot}$), 494 (0.6, $M^{+\cdot} - 18$), 409 (1), 367 (1), 342 (1), 310 (1), 298 (2), 267 (1), 241 (1), 195 (3), 179 (2), 166 (4), 153 (20), 135 (100). HR-MS: 512.25384 ± 0.002 ($C_{28}H_{36}N_2O_7$, calc. 512.25225).

10. *Treatment of* (–)-**1** *with MeOH/KOH*. A soln. of (–)-**1** (0.01 g, 0.02 mmol) in 0.5 ml of 0.1M KOH/MeOH was allowed to stand at r.t. for 4 days and then subjected to TLC with petroleum ether/Et_2O 1:1 to give **10** (R_f 0.72; 0.0036 g, 50%), **12** (R_f 0.66, 0.0028 g, 33%) (NMR data in *Tables 3* and *4*), and (*E*)-N^1-methylurocanic acid (R_f 0.006; 0.0029 g, 95%).

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