

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 Criterion¹⁾

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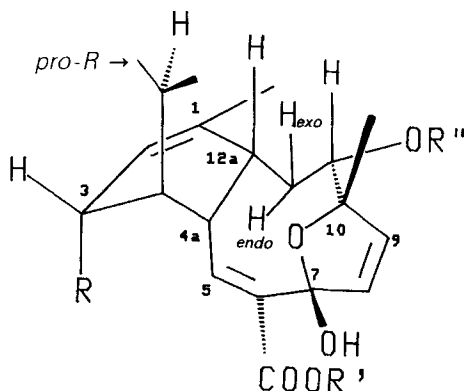
It is shown here that the stoloniferan coral *Sarcodictyon roseum* of east Pyrenean waters contains four novel diterpenoids, sarcodictyin C ((-)-3), D ((-)-4), E ((+)-5), and F ((+)-6), which are related to sarcodictyin A (= (-)-4*R*, 4*aR*, 7*R*, 10*S*, 11*S*, 12*aR*, 1*Z*, 5*E*, 8*Z*)-7,10-epoxy-3,4,4*a*,7,10,11,12,12*a*-octahydro-7-hydroxy-6-(methoxycarbonyl)-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 3*α*-hydroxy and 3*α*-acetoxy derivatives of (-)-1, sarcodictyin E ((+)-5) is the (*Z*)-urocanate isomer of (-)-3, and sarcodictyin F ((+)-6) is the 1*α*-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.

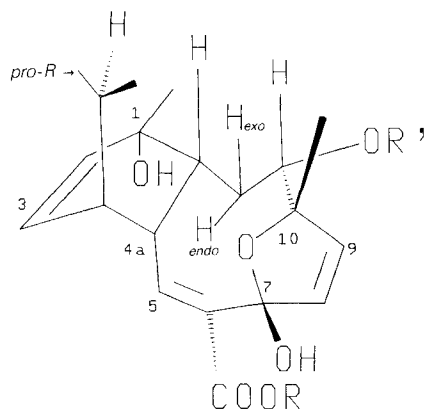
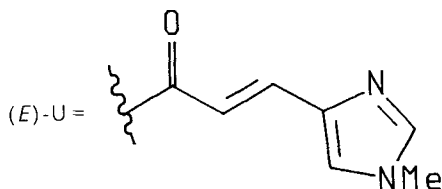
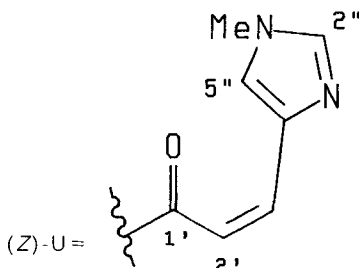
2. Results and Discussion. – The new sarcodictyins are more polar than sarcodictyin A and B [1], the polarity increasing in the order sarcodictyin E ((+)-5), D ((-)-4), F ((+)-6), and C ((-)-3).

2.1. Structures. The ¹³C-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 ¹³C, ¹H 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

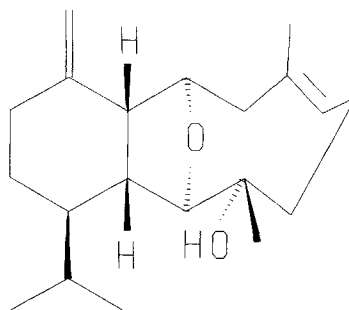
¹⁾ Presented by F.P. as a part of a lecture at the University of Hawaii at Manoa, Honolulu, December 9th, 1987.



- (–)-**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 ^1H -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 ^1H -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 ^1H -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 ($\delta(\text{C})$) in both $\text{C}_5\text{D}_5\text{N}$ and CD_3OD and Long-Range C,H Correlations in $\text{C}_5\text{D}_5\text{N}$ for Sarcodictyin C ((-)-**3**) and ^{13}C -NMR Data ($\delta(\text{C})$) in CD_3OD for Sarcodictyin D ((-)-**4**), E ((+)-**5**), F ((+)-**6**), and for Enone **9**

C-Atom	$\delta(\text{C}; \text{C}_5\text{D}_5\text{N})$ (-)- 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 ₂ CH			
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 ₂ CH	28.83 (d)	H-C(4), Me(<i>pro-S</i>), H-C(3)			
Me(<i>pro-S</i>)	20.66 (q)				
Me(<i>pro-R</i>)	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	$\delta(\text{C}; \text{CD}_3\text{OD})$				
	(-)- 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 ₂ CH	29.84 (d)	29.45 (d)	29.86 (d)	33.25 (d)	28.10 (d)
Me (<i>pro-S</i>)	20.83 (q)	21.37 (q)	20.88 (q)	21.82 (q)	21.73 (q)
Me (<i>pro-R</i>)	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.)

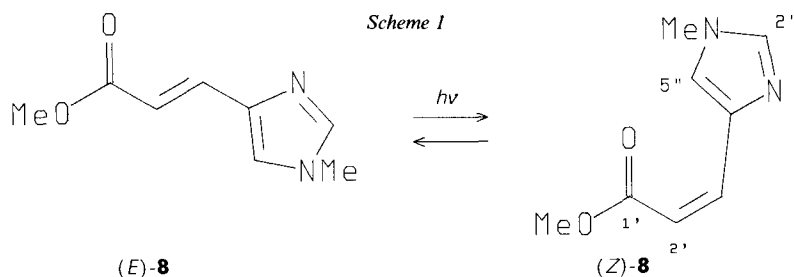
C-Atom	$\delta(\text{C}; \text{CD}_3\text{OD})$				
	(-)-3	(-)-4 ^b	(+)-5	(+)-6	9
Me-C(10)	25.94 (q)	25.98 (q)	25.95 (q)	25.81 (q)	24.58 (q)
C-C(6)	168.69 (s)	168.53 (s)	168.62 (s)	169.43 (s)	167.58 (s)
MeO	52.18 (q)	52.30 (q)	52.21 (q)	52.12 (q)	52.55 (q)
C(1')	168.32 (s)	168.39 (s)	166.97 (s)	169.22 (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. ¹H-NMR Data for Sarcodictyin C ((-)-3) in CD₃OD and, within Brackets, in C₅D₅N^a

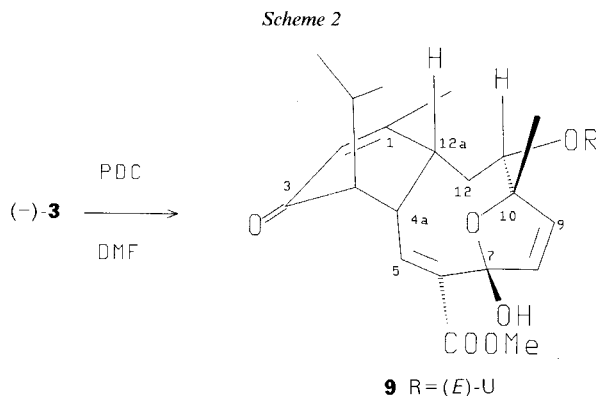
H-C(2)	5.55 (br. d, $J(2,3) \approx 3$, $J(2, \text{Me-C}(1))$ small) [5.87]
H-C(3)	4.08 (br. d, $J(3,2) \approx 3$, $J(3,4) \approx J(3, \text{Me-C}(1))$ small) [4.34]
H-C(4)	1.49 (m, $J(4, \text{Me}_2\text{CH}) \approx 8$, $J(4,4a) = 2.0$, $J(4,3)$ small) [1.81]
H-C(4a)	4.34 (ddd, $J(4a,5) = 9.7$, $J(4a,12a) = 4.8$, $J(4a,4) = 2.0$) [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, $J(11,12\text{endo}) = 7.3$) [5.20]
H _{exo} -C(12)	1.65 (br. d, $J_{\text{gem}} = 15.0$, $J(12\text{exo}, 12a) \approx 2$) [2.00]
H _{endo} -C(12)	1.48 (ddd, $J_{\text{gem}} = 15.0$, $J(12\text{endo}, 12a) = 12.0$, $J(12\text{endo}, 11) = 7.3$) [1.91]
H-C(12a)	2.62 (br. d, $J(12a,12\text{endo}) = 12.0$, $J(12a,4a) = 4.8$, $J(12a,12\text{exo}) \approx 2$) [2.93]
Me ₂ CH	1.63 (m, $J(\text{Me}_2\text{CH}, 4) \approx 8$, $J(\text{Me}_2\text{CH}, \text{Me}(\text{pro-S})) = J(\text{Me}_2\text{CH}, \text{Me}(\text{pro-R})) = 7.0$) [1.58]
Me(pro-S)	1.05 (d, $J(\text{Me}(\text{pro-S}), \text{Me}_2\text{CH}) = 7.0$) [0.99] ^b)
Me(pro-R)	1.08 (d, $J(\text{Me}(\text{pro-R}), \text{Me}_2\text{CH}) = 7.0$) [0.98] ^b)
Me-C(1)	1.56 (br. s, $J(\text{Me-C}(1), 2) \approx J(\text{Me-C}(1), 3)$ 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, $J(2'',5'') \text{ small}$) [7.73]
H-C(5'')	7.47 (br. s, $J(5'',2'') \text{ small}$) [7.40]
Me-N(1'')	3.75 (s) [3.46]

^a) J values in C₅D₅N are similar to those in CD₃OD. ^b) Data can be interchanged.



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-desielded *d* for (–)-**3**, a O-desielded *s*, besides an additional olefinic *d*. This supports the fragment $\text{Me}-\text{C}(1)(\text{OH})-\text{CH}(2)=\text{CH}(3)-\text{CH}(4)$. The α position for $\text{OH}-\text{C}(1)$ is indicated by the NOESY correlation $\text{H}-\text{C}(12\text{a})/\text{Me}-\text{C}(1)$ and by a 0.5-ppm deshielding of $\text{H}_{\text{endo}}-\text{C}(12)$.

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]).



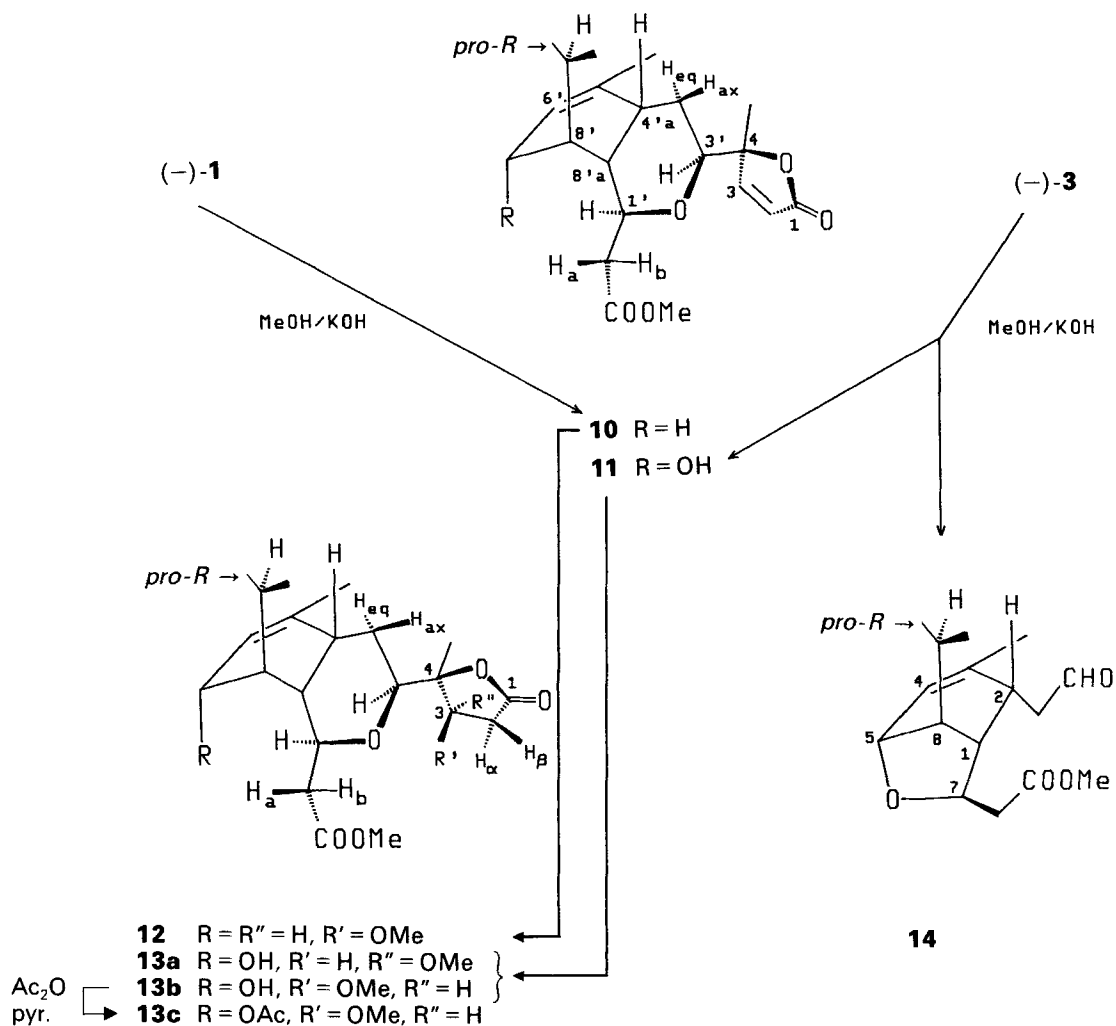
Treatment of (–)-**3** with MeOH/KOH at r.t. leads to mainly the butenolide **11** (35%), besides the two lactones **13a** (6%) and **13b** (29%) and the aldehyde **14** (12%; Scheme 3). Similarly, (–)-**1** gives **10** (50%) and **12** (33%).

The ^1H -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 $\text{H}-\text{C}(7')$, which shows that the $\text{OH}-\text{C}(7')$ group has remained intact. The pyranose ring is indicated by a typical *ddd* at 4.48–4.50 ppm for $\text{H}-\text{C}(1')$ of **11**, **13a**, and **13b**, by the disappearance of the $\text{C}(5)=\text{C}(6)$ 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 $\text{C}(3')-\text{C}(4)$ bonding is indicated by the 1.20 ($\text{Me}-\text{C}(4)$)/2.95 ($\text{H}-\text{C}(3')$) 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 $\text{H}_\beta-\text{C}(2)-\text{C}(3)-\text{H}$ and $\text{H}_\alpha-\text{C}(2)-\text{C}(3)-\text{H}$ dihedral angles of 35° and 160° . This suggests coupling constants of $\text{H}-\text{C}(3)$ with H_α and H_β of ca. 7–8 Hz, which is in accordance with ^1H -NMR spectral data (Table 4). With **13b**, less accurate molecular mechanics calculations indicate that the less strained conformer has $\text{H}_\beta-\text{C}(2)-\text{C}(3)-\text{H}$ and $\text{H}_\alpha-\text{C}(2)-\text{C}(3)-\text{H}$ dihedral angles of ca. 100° and 20° . This suggests coupling constants of $\text{H}-\text{C}(3)$ with H_α and H_β of ca. 2 and 7 Hz, in accordance with ^1H -NMR spectra (Table 4) [5].

^1H -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 $\text{C}(11)-\text{O}^-$ at $\text{C}(5)^2$ 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 $\text{C}(11)-\text{O}$ and $\text{C}(5)$ 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 $\text{C}(11)-\text{O}^-$ can approach $\text{C}(5)$ 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 ⁶)	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 (<i>d</i>)	125.49 (<i>d</i>)	123.16 (<i>d</i>)	126.74 (<i>d</i>)
C(7')	24.36 (<i>t</i>)	66.56 (<i>d</i>)	24.35 (<i>t</i>)	66.60 (<i>d</i>)
C(8')	40.03 (<i>d</i>)	47.30 (<i>d</i>)	40.02 (<i>d</i>)	47.44 (<i>d</i>)
C(8'a)	39.99 (<i>d</i>)	39.80 (<i>d</i>)	39.42 (<i>d</i>)	39.28 (<i>d</i>)
Me–C(5')	21.29 (<i>q</i>)	21.16 (<i>q</i>)	21.41 (<i>q</i>)	21.26 (<i>q</i>)
Me ₂ CH	27.33 (<i>d</i>)	26.87 (<i>d</i>)	27.37 (<i>d</i>)	26.98 (<i>d</i>)
Me(<i>pro-S</i>)	20.54 (<i>q</i>)	21.50 (<i>q</i>)	20.69 (<i>q</i>)	21.68 (<i>q</i>)
Me(<i>pro-R</i>)	21.83 (<i>q</i>)	22.17 (<i>q</i>)	21.85 (<i>q</i>)	22.18 (<i>q</i>)
CH ₂ –C(1')	39.17 (<i>t</i>)	38.92 (<i>t</i>)	38.63 (<i>t</i>)	38.40 (<i>t</i>)
COOMe ^a	171.48 (<i>s</i>)	171.76 (<i>s</i>)	172.00 (<i>s</i>)	172.17 (<i>s</i>)
COOMe	51.10 (<i>q</i>)	50.99 (<i>q</i>)	51.12 (<i>q</i>)	51.01 (<i>q</i>)
OMe	–	–	56.69 (<i>q</i>)	56.70 (<i>q</i>)

^a The C(1) and COOMe signals can be interchanged.Table 4. ¹H-NMR Data (C₆D₆) for Compounds 10–12, 13a, and 13b

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

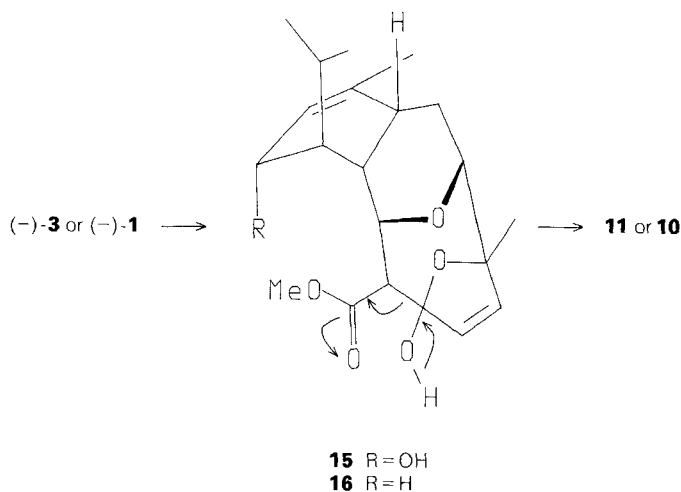
Table 4 (cont.)

	12	13a
H—C(1')	3.86 (<i>ddd</i> , $J(1', 8'a) = 10.0$, $J(1', H_b) = 9.5$, $J(1', H_a) = 3.1$)	4.49 (<i>ddd</i> , $J(1', 8'a) = 10.5$, $J(1', H_b) = 8.5$, $J(1', H_a) = 3.0$)
H—C(3')	2.92 (<i>dd</i> , $J(3', H_{ax}) = 11.7$, $J(3', H_{eq}) = 1.6$)	3.59 (<i>dd</i> , $J(3', H_{ax}) = 10.0$, $J(3', H_{eq}) = 3.0$)
H _{ax} —C(4')	1.60 (<i>ddd</i> , $J_{gem} = 14.0$, $J(H_{ax}, 3') = 11.7$, $J(H_{ax}, 4'a) = 5.0$)	1.5–1.6 (superimposed)
H _{eq} —C(4')	1.77 (<i>ddd</i> , $J_{gem} = 14.0$, $J(H_{eq}, 4'a) = 2.6$, $J(H_{eq}, 3') = 1.6$)	
H—C(4'a)	2.14 (br. <i>s</i> , $J(4'a, H_{ax}) = 5.0$, $J(4'a, 8'a) = 4.7$, $J(4'a, H_{eq}) = 2.6$, $J(4'a, Me-C(5'))$ small)	2.19 (br. <i>s</i>)
H—C(6')	5.24 (br. <i>s</i>)	5.19 (br. <i>s</i> , $J(6', 7') = 5.0$, $J(6', Me-C(5')) = 1.0$)
H—C(7')	1.76 (br. <i>s</i> , 2 H)	3.73 (br. <i>d</i> , $J(7', 6') = 5.0$, $J(7', Me-C(5')) = 1.0$, $J(7', 8')$ small)
H—C(8')	0.80 (<i>m</i> , submerged)	1.3 (<i>m</i>)
H—C(8'a)	1.55 (<i>dd</i> , $J(8'a, 1') = 10.0$, $J(8'a, 4'a) = 4.7$, $J(8'a, 8') = 3.0$)	1.88 (br. <i>d</i> , $J(8'a, 1') = 10.5$)
Me—C(5')	1.42 (br. <i>s</i>)	1.43 (br. <i>s</i> , $J(Me-C(5'), 6') = J(Me-C(5'), 7') = 1.0$)
Me ₂ CH	1.30 (<i>m</i>)	1.07 (<i>m</i>)
Me(<i>pro-S</i>)	0.69 (<i>d</i> , $J(Me(pro-S), Me_2CH) = 6.6$)	0.76 (<i>d</i> , $J(Me(pro-S), Me_2CH) = 6.5$)
Me(<i>pro-R</i>)	0.80 (<i>d</i> , $J(Me(pro-R), Me_2CH) = 6.6$)	0.84 (<i>d</i> , $J(Me(pro-R), Me_2CH) = 6.5$)
H _a —CH—C(1')	2.25 (<i>dd</i> , $J_{gem} = 14.5$, $J(H_a, 1') = 3.1$)	2.90 (<i>dd</i> , $J_{gem} = 13.5$, $J(H_a, 1') = 3.0$)
H _b CH—C(1')	2.33 (<i>dd</i> , $J_{gem} = 14.5$, $J(H_b, 1') = 9.5$)	2.44 (<i>dd</i> , $J_{gem} = 13.5$, $J(H_b, 1') = 8.5$)
COOMe	3.39 (<i>s</i>)	3.50 (<i>s</i>)
OMe	2.86 (<i>s</i>)	2.82 (<i>s</i>)
13b		
H—C(2)	2.96 (<i>dd</i> , $J_{gem} = 17.5$, $J(H_x, 3) = 6.5$, H_x); 2.36 (<i>dd</i> , $J_{gem} = 17.5$, $J(H_\beta, 3) = 1.8$, H_β)	
H—C(3)	3.80 (<i>dd</i> , $J(3, H_\beta) = 1.8$, $J(3, H_x) = 6.5$)	
Me—C(4)	1.20 (<i>s</i>)	
H—C(1')	4.48 (<i>ddd</i> , $J(1', 8'a) = J(1', H_b) = 9.5$, $J(1', H_a) = 3.0$)	
H—C(3')	2.95 (<i>dd</i> , $J(3', H_{ax}) = 11.0$, $J(3', H_{eq}) = 2.3$)	
H _{ax} —C(4')	1.68 (<i>ddd</i> , $J_{gem} = 14.0$, $J(H_{ax}, 3') = 11.0$, $J(H_{ax}, 4'a) = 5.0$)	
H _{eq} —C(4')	1.73 (superimposed to H—C(8'a))	
H—C(4'a)	2.09 (br. <i>s</i> , $J(4'a, H_{ax}) = 5.0$, $J(4'a, 6') = 2.0$, $J(4'a, Me-C(5')) = 1.0$)	
H—C(6')	5.24 (br. <i>s</i> , $J(6', 7') = 5.0$, $J(6', 4'a) = 2.0$, $J(6', Me-C(5')) = 1.0$)	
H—C(7')	3.68 (br. <i>d</i> , $J(7', 6') = 5.0$, $J(7', Me-C(5')) = 1.0$, $J(7', 8')$ 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. <i>s</i> , $J(Me-C(5'), 4'a) = J(Me-C(5'), 6') = J(Me-C(5'), 7') = 1.0$)	
Me ₂ CH	1.06 (<i>dq</i> , $J(Me_2CH, 8') = 10.0$, $J(Me_2CH, Me(pro-S)) = J(Me_2CH, Me(pro-R)) = 6.0$)	
Me(<i>pro-S</i>)	0.69 (<i>d</i> , $J(Me(pro-S), Me_2CH) = 6.0$)	
Me(<i>pro-R</i>)	0.82 (<i>d</i> , $J(Me(pro-R), Me_2CH) = 6.0$)	
H _a CH—C(1')	2.86 (<i>dd</i> , $J_{gem} = 14.5$, $J(H_a, 1') = 3.0$)	
H _b CH—C(1')	2.30 (<i>dd</i> , $J_{gem} = 14.5$, $J(H_b, 1') = 9.5$)	
COOMe	3.40 (<i>s</i>)	
OMe	2.88 (<i>s</i>)	

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

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

Scheme 4

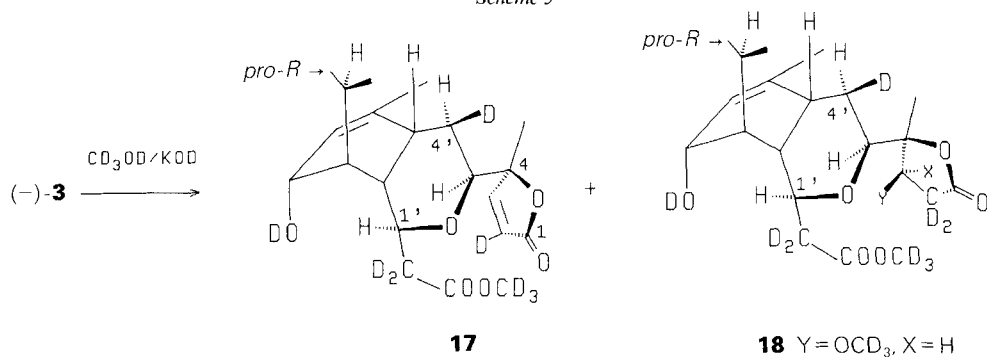


When $(-)\text{-3}$ is allowed to react in $\text{CD}_3\text{OD}/\text{KOD}$, butenolide **17** is isolated, to our surprise stereospecifically deuteriated at the 4'-axial position (Scheme 5)⁴. Incorporation of D at the 4-axial position does not occur at the level of a type-**17** compound; this is proved by the fact that compound **11** in $\text{CD}_3\text{OD}/\text{KOD}$ in a week at r.t. does not incorporate D at C(4), whereas the protons $-\text{C}(\text{H}_2)-\text{C}(1')$ 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.

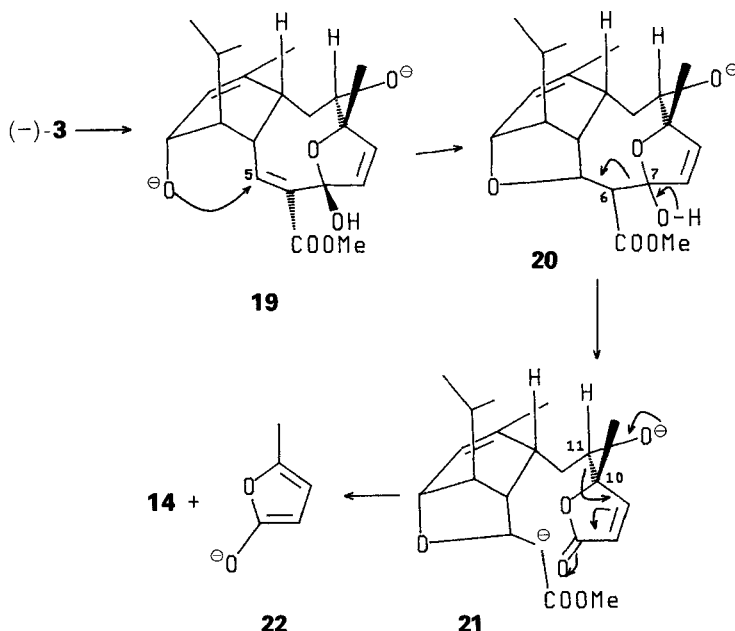
When there is a $3\alpha\text{-OH}$ group in the sarcodictyin, such as with $(-)\text{-3}$, aldehyde **14** is formed competitively with ring contraction (see above, Scheme 3). We suggest (Scheme

Scheme 5



⁴) Deuteriations at $\text{CH}_2-\text{C}(1')$ 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.

We thank Mr. J. Mabit and Mr. G. Boyer for aid in the collection of *S. roseum*, the *Laboratoire Arago* for laboratory facilities, and both the *M. P. I.* (Progetti di Interesse Nazionale) and the *C. N. R.* (Roma) for financial support.

Experimental Part

1. *General.* TLC: Merck Kieselgel 60 PF₂₅₄ plates. HPLC: Merck-LiChrosorb-CN (7 μ m) 25 $\times$ 1 cm column, hexane/EtOH/(*i*-Pr)NH₂ 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 ($\lambda_{\max}$ in nm, ϵ in dm³ · mol⁻¹ · cm⁻¹) and Pye-Unicam SP3-100 ($\tilde{\nu}_{\max}$ in cm⁻¹) spectrophotometers, resp. ¹H-NMR and ¹³C-NMR spectra: Varian XL300 (300 or 75.43 MHz, resp.); δ (ppm) relative to internal Me₄Si (= 0 ppm) and *J* in Hz, the notation 'small' indicates *J* < 0.5 Hz; *J*'s are derived from homonuclear decoupling; ¹³C multiplicities: APT [7] or DEPT [8] techniques; all assignments are supported by ¹³C, ¹H-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)acrylate⁶); (-)-3). Colourless microcrystalline powder. M.p. 225–227° (from (CH₃)₂O). [α]_D²⁰ = -16.5 (589), -20.0 (577), -22.4 (546), -57.6 (435) (*c* = 0.085, EtOH). UV (EtOH): 290 (15300), 202 (13800). IR (nujol): 3400s (OH), 1700s (C=O), 1690s (C=O), 1630m, 1170s, 1150s, 1050s. NOESY (C₆D₆N): 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 (Me₂CH); 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 $\pm$ 0.05 (C₂₈H₃₄N₂O₆, calc. 494.2417). Linked scans (B/E [11]): working on *M*⁺ - 18, peaks at 476 (494 - H₂O), 462 (494 - MeOH), 451 (494 - C₃H₇), 341 (494 - C₇H₅N₂O₂); working on *m/z* 451, peaks at 433 (451 - H₂O), 419 (451 - MeOH); working on *m/z* 342, peaks at *m/z* 324 (342 - H₂O), 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%). ¹H-NMR (CD₃OD): 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, Me₂CH) = 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*(11,12endo) = 7.0, *J*(11,12exo) small, H-C(11)); 1.84 (*br. d*, *J*_{gem} = 15.0, *J*(12exo,12a) = 2.0, *J*(12exo,11) small, H_{exo}-C(12)); 1.52 (*ddd*, *J*_{gem} = 15.0, *J*(12endo,12a) = 12.0, *J*(12endo,11) = 7.0, H_{endo}-C(12)); 3.31 (submerged by the solvent signal, H-C(12a)); 2.05 (*dq*, *J*(Me₂CH, 4) = 10.5, *J*(Me₂CH, Me(*pro-S*)) = *J*(Me₂CH, Me(*pro-R*)) = 6.5, Me₂CH); 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 Et₂O, 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 CD₃OD/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*,4aS*,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): 3500s (OH); 1740s, 1750s, 1780s (C=O); 1440s, 1110s. NOESY (key data only; C₆D₆): 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).

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'-[(methoxycarbonylmethyl]-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'-[(methoxycarbonylmethyl]-5'-methyl-8'-(1-methylethyl)-1'H-2'-benzopyran-3'-yl]-3-methoxy-4-methylbutan-4-olide (13b). IR (film): 3500s (OH); 1740s, 1780s (C=O); 1100s. NOESY (key data only, C_6D_6): 2.96 ($H_2-C(2)$)/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): 2710w (CHO), 1730s (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 ($s, COOMe$); 50.96 ($q, COOMe$); 25.31 (d, Me_2CH); 20.23, 22.24 (2 $q, Me(pro-S), Me(pro-R)$). 1H -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). 1H -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 $COOC$ 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). 1H -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. $s, J(H-C(4'), 4'a) \approx 2, J(H-C(4'), 3') = 2.3, H-C(4')$), while signals for protons at $C-C(1')$, $C(2)$, $CO-C(3)$, and $COOC$ 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)acrylate⁶); (-)-4). Colourless microcrystalline powder. M.p. 130–132° (from MeOH). $[\alpha]_{589}^{20} = -27.2$ ($c = 0.25, MeOH$). 1H -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)acrylate⁶); (+)-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). 1H -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-1H-imidazol-4-yl)acrylate ((E)-8)*. A 0.04 M soln. of (E)-8 in CD₃OD was irradiated with a 4-W low-pressure Hg lamp in a 5 mm Pyrex NMR tube at r.t. during 13 h. The ¹H-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* (= (+)-(1R*,4R*,4aR,7R*,10S*,11S*,12aR*,2Z,5E,8Z)-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-1H-imidazol-4-yl)acrylate; (+)-6). Colourless microcrystalline powder. M.p. 228–229° (from MeOH). [α]_D²⁰ = +2.7 (c = 0.15, MeOH). ¹H-NMR (C₅D₅N): 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, Me₂CH) = 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, Me₂CH); 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; C₅D₅N): 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⁺), 494 (0.6, M⁺ – 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 (C₂₈H₃₆N₂O₇, 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 0.1 M KOH/MeOH was allowed to stand at r.t. for 4 days and then subjected to TLC with petroleum ether/Et₂O 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)-N¹-methylurocanic acid (R_f 0.006; 0.0029 g, 95%).

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