Studies on Fungal Products. Part 10.[1] Isolation and Structures of Novel Bicoumarins, Desertorins A, B, and C, from *Emericella desertorum*

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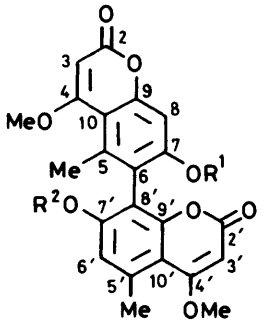
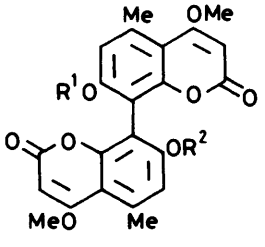
Together with silvaticol (**11**), nidulol (**12**), ergosterol, paxilline (**10**), and mannitol, three new bicoumarins designated as desertorin A (**1**) ($C_{22}H_{18}O_8$), B (**2**) ($C_{23}H_{20}O_8$), and C (**3**) ($C_{24}H_{22}O_8$) have been isolated from *Emericella desertorum*, strain CBS 653.73. The structures of desertorins A (**1**), B (**2**), and C(**3**) were determined on the basis of the spectroscopic and chemical investigations of these compounds and their derivatives *i.e.*, as 7,7'-dihydroxy-4,4'-dimethoxy-5,5'-dimethyl-6,8'-bicoumarin, 5,5'-dimethyl-7-hydroxy-4,4',7'-trimethoxy-6,8'-bicoumarin and 5,5'-dimethyl-4,4',7,7'-tetramethoxy-6,8'-bicoumarin, respectively. It is interesting to note that silvaticol (**11**) and nidulol (**12**), both of the known metabolites of *Aspergillus silvaticus*, were isolated from the same extracts.

Recently we reported the isolation of the antifungal macrocylic epidithiodioxopiperazine, emestrin,[2] and its derivative, dethiosecoemestrin,[1] from *Emericella striata*. In the course of searching for emestrin and related compounds in members of the *Aspergillus nidulans* group (teleomorph genus: *Emericella*), three new bicoumarins (**1**), (**2**), and (**3**) were isolated from the mycelium of *E. desertorum* Samson & Mouchacca, strain CBS 653.73, which originates from desert soils in Egypt. Although no metabolites from this fungus have been reported, the fungal extract is known to possess weak toxicity against chick embryos and mice.[3]

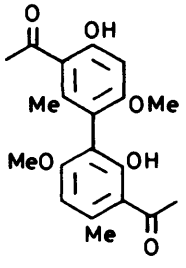
From the mycelial chloroform extract, three bicoumarins (**1**), (**2**), and (**3**), designated desertorin A, B, and C, respectively, were isolated along with ergosterol and a small amount of paxilline (**10**),[4] a tremorgenic indole which was recently found in cultures of *E. striata*.[1] Mannitol and desertorin A (**1**) were isolated from the mycelial acetone extract, whereas compounds (**1**) and (**2**) accompanied by the phthalides, silvaticol (**11**), and nidulol (**12**), known metabolites of *A. silvaticus* Fennell & Raper, strain IFO 8173,[5] were isolated from the acidic dichloromethane extract. According to Fennell and Raper,[6] *A. silvaticus* is a non-ascosporic form which appears to be intermediate between the *A. versicolor* and *A. nidulans* groups. However, the chemotaxonomic profile of *E. desertorum* and *A. silvaticus* is strikingly suggestive of their placements in the same group, *viz. A. nidulans* group. The structural elucidation of desertorins A (**1**), B (**2**), and C (**3**) is described in this paper.



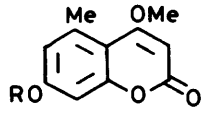
(**1**) $R^1 = R^2 = H$
(**2**) $R^1 = H$, $R^2 = Me$
(**3**) $R^1 = R^2 = Me$



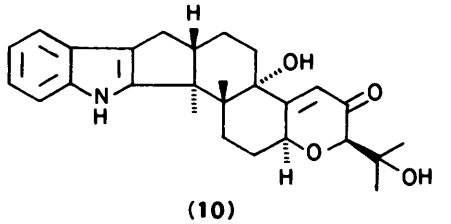
(**5**) $R^1 = R^2 = H$
(**6**) $R^1 = H$, $R^2 = Me$
(**7**) $R^1 = R^2 = Me$



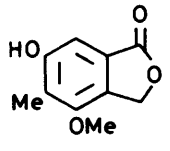
(**4**)



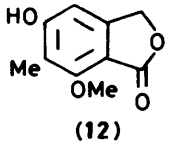
(**8**) R = H
(**9**) R = Me



(**10**)



(**11**)



(**12**)

Results and Discussion

Desertorin A (**1**), m.p. >300 °C, $C_{22}H_{18}O_8$, showed ^1H n.m.r. signals at δ_H 3.93 assigned to the methyl protons of two methoxy groups; desertorin B (**2**), m.p. >300 °C, $C_{23}H_{20}O_8$, showed three signals at δ_H 3.77, 3.92, and 3.96 assigned to the methyl protons of three methoxy groups; desertorin C (**3**), m.p. 235—237 °C, $[\alpha]_D$ +16.8°, $C_{24}H_{22}O_8$, showed signals at δ_H 3.70, 3.77, 3.94, and 3.95 assigned to the methyl protons of four methoxy groups. Other ^1H n.m.r. signals of the compounds are similar and are listed in Table 1. Compounds (**1**) and (**2**) gave the same methylated derivative (**3**), including the absolute stereochemistry, by methylation with diazomethane. These results confirm that the desertorins (**1**), (**2**), and (**3**) have the same carbon skeletons and that (**2**) and (**3**) are mono- and di-methylated derivatives of (**1**).

Table 1. ^{1}H N.m.r. chemical shifts of desertorins (**1**), (**2**), and (**3**) and related compounds in $(CD_3)_2SO$

Proton	(1)	(2)	(3)	(5)[a]	(6)[b]	(7)[c]	(9)[d]
3-H	5.62[e]	5.63	5.62[e]	5.53	5.53[e]	5.51	
3′-H	5.56[e]	5.63	5.69[e]	5.53	5.48[e]	5.51	5.53
4-OMe	3.93	3.92[e]	3.94[f]	3.93	3.90	3.93	
4′-OMe	3.93	3.96[e]	3.95[f]	3.93	3.90	3.93	3.94
5-Me	2.25	2.20	2.23	2.62	2.35	2.70	
5′-Me	2.59	2.70	2.70	2.62	2.68	2.70	2.60
6-H				6.68	6.67[f]	6.72	
6′-H	6.72[f]	6.98	6.97[g]	6.68	6.63[f]	6.72	6.64
7-OMe			3.70			3.80	
7′-OMe		3.77	3.77		3.77	3.80	3.84
7-OH	10.25[g]	10.29		—	7.55		
7′-OH	10.13[g]			—			
8-H	6.70[f]	6.70	6.98[g]				
8′-H							6.64

[a] See ref. 9. [b] See ref. 7. Compound (**6**) was measured in $CDCl_3$. [c] See ref. 9. Compound (7) was measured in $CDCl_3$. [d] See ref. 10. Compound (9) was measured in $CDCl_3$. [e,f, and g] The assignments may be reversed.

On alkaline hydrolysis, desertorin C (**3**) afforded compound (**4**), m.p. 149—150 °C, $C_{20}H_{22}O_6$, which gave ^{1}H n.m.r. signals at δ_H 2.25 (3 H), 2.63 (3 H), and 2.67 (6 H) corresponding to two aromatic methyl protons [which also appeared in the ^{1}H n.m.r. spectra of (**1**), (**2**), and (**3**)], and to the methyl protons of two acetyl groups.

The ^{13}C n.m.r. signals at δ_C 204.10 and 204.54 were assigned to the carbonyl carbons of the two acetyl ketones, and the signals at δ_C 32.33 and 32.64 were assigned to the methyl carbons of the same acetyl groups. The ^{1}H n.m.r. signals which appeared at δ_H 13.18 and 13.22 in compound (**4**) were assigned to the protons of the two hydroxyl groups strongly chelated with the above acetyl ketones. Other ^{1}H n.m.r. signals were assigned to the methyl protons of two aromatic methoxy groups (δ_H 3.71 and 3.78) and two aromatic protons (δ_H 6.41). These signals show that the functional groups of (**3**) are also present in (**4**), with the exception of two methoxy groups and two olefinic protons. The ^{13}C n.m.r. spectrum of (**4**) was similar to that of the symmetrical biphenyl derivative derived from kotanin (**7**) by alkaline hydrolysis.[7] Thus it is clear that compound (**4**) is a non-symmetrical dimer of the *o*-hydroxyacetophenone derivative. Desertorins A (**1**), B (**2**), and C (**3**) could, therefore, be 4-methoxycoumarin or 1-methoxychromone derivatives. The absence of ^{13}C n.m.r. signals in the region lower than δ_C 180 in compounds (**1**), (**2**), (**3**), suggests that the carbonyl groups in these compounds are esters, not ketones.[8] The u.v. spectra of desertorins A (1) and C (**3**) showed absorption maxima at 312 and 321 nm, and at 295 and 310 nm, respectively, whereas those of orlandin (**5**)[9] and kotanin (**7**)[7], which are bicoumarin derivatives isolated from fungi, showed maxima at 311 and 321 nm, at 250, 290, 307, and 316 nm, respectively. Thus it was confirmed that the carbon skeletons of desertorins A (1), B (**2**), and C (**3**) are non-symmetrical dimers of coumarin.

The ^{1}H and ^{13}C n.m.r. signals of desertorins A (1), B (**2**), and C (**3**) were closely similar as were those of (**5**), (**6**), and (**7**), except that the former had twice the number of signals due to its asymmetrical structure; the signals were also similar to those of a coumarin monomer, siderin (**8**)[10,11] (Tables 1 and 2). Thus desertorin C (**3**) is presumed to be the dimer of 4-methoxycoumarin, bearing two methoxy groups, two methyl groups, and two aromatic protons in its aromatic ring. Heteronuclear ^{13}C-{^{1}H} long-range selective decoupling experiments of (**3**) were undertaken in order to determine the positions of the above functional groups. The results are listed in Table 3. The carbon signals at δ_C 107.36, 119.35, and 136.69 were observed to be changed by selective irradiation of the protons of the two aromatic methyl groups (δ_H 2.227). This result and the values of ^{13}C n.m.r. chemical shifts confirm that the structure of one of the coumarin moieties in (**3**) is 4,7-dimethoxy-5-methylcoumarin and that it is connected to the other common ring at its C-6 position. The carbon signals at δ_C 107.71, 111.37, and 137.93 were altered by selective irradiation of the two aromatic methyl protons at δ_H 2.227 and 2.701, these data and the values of carbon chemical shifts confirm that the structure of the other coumarin moiety in (**3**) is 4,7-dimethoxy-5-methylcoumarin, and that this is connected to the other coumarin ring at its C-8 position. Thus the structure of desertorin C (**3**) was determined as 4,4′,7,7′-tetramethoxy-5,5′-dimethyl-6,8′-bicoumarin as shown.

In order to determine the positions of the phenolic hydroxy groups in desertorin B (**2**), we applied the rule of *O*-methylation shifts of the *ortho*- monosubstituted phenols possessing *para*-conjugated systems.[11] The assignments of the ^{13}C n.m.r. chemical shifts of (**1**)—(**3**) are summarized in Table 2. The *O*-methylation shift values (Δ) on corresponding carbons C-5 to C-10 and C-5′ to C-10′ were calculated and are listed in Table 4. One of the protonated aromatic carbon atoms (C-6′) was observed at 4.79 p.p.m. upfield after methylation of (**1**) to (**2**), and another one (C-8) was observed at 2.70 p.p.m. upfield after methylation of (**2**) to (**3**). The shift values (Δ) for other aromatic carbons were comparable to those of simple *ortho*-monosubstituted phenols.[12] Considering these results on the *O*-methylation effects of *ortho*-monosubstituted phenols, the methylated coumarin moiety is sure to connect with the other coumarin ring at the C-8 position in the first example, *i.e.* (**1**) to (**2**), and the other one is connected at the C-6 position in the second example, *i.e.* (**2**) to (**3**). From this, the structures of desertorin A and B were determined as 7,7′-dihydroxy-4,4′-dimethoxy-5,5′-dimethyl-6,8′-bicoumarin (**1**) and 5,5′-dimethyl-7-hydroxy-4,4′-7′-trimethoxy-6,8′-bicoumarin (**2**) respectively.

There are few reports of the isolation of symmetrical dimers of 4-methoxycoumarins: orlandin (**5**) from *A. niger* van Tieghem (ATCC 36626),[9] demethylkotanin (6) and kotanin (**7**) from *A. glaucus* (KOTA AG),[7] and kotanin (**7**) from *A. clavatus* Desmazieres (MIT-M-18)[13] have been reported and a monomer: siderin (4,7-dimethoxy-5-methylcoumarin) (**9**) from *A. stellatus* Curzi (Teleomorph: *E. variecolor* Berkeley & Broome) (IMI 53749)[11] is also known. This is the first report of non-symmetrical dimers of (**9**) being isolated. Compound (**9**) has also been isolated from some higher plants (*Sideritis* sp.[10] and *Cedrela* sp.[14]). All the compounds described [(**1**—**3**), (**5**—**7**) and (**9**)] were obtained only from *Aspergillus* species in the case of fungi, the six dimers being composed from (**8**) and/or (**9**).

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-181 spectrometer. Electron impact (e.i.) mass spectra were taken with a JEOL JMS-D 300 spectrometer. U.v. spectra and i.r. spectra were recorded on a Hitachi 124 spectrophotometer and a Hitachi 215 spectrophotometer, respectively. ^{1}H-(99.60 MHz) and ^{13}C-(25.05 MHz) N.m.r. spectra were recorded on a JEOL JNM-FX 100 spectrometer, while ^{1}H-(399.78 MHz) and ^{13}C-(100.43 MHz) n.m.r. spectra were taken with a JEOL JNM-GX 400 spectrometer, using tetramethylsilane as internal standard. The coupling patterns are indicated as follows: singlet = S or s, doublet = D or d, triplet = T or t, quarter = Q or q, multiplet = m, and broad = br. Capital letters refer to the pattern resulting from directly bonded coupling ($^1H_{C,H}$). C.d. curves were determined on a JASCO J-40 spectrophotometer. Column chromatography was performed using Kieselgel 60 (Art. 7734; Merck). Low pressure

Table 2. ^{13}C N.m.r. chemical shifts of desertorins (**1**), (**2**), and (**3**) and related compounds in $(CD_3)_2SO$

Carbon	(1)	(2)	(3)	(5)[a]	(7)[b]	(9)[c]
2	163.63 (S)[d]	161.43 (S)[d]	161.46 (S)[d]	161.43[i]	162.82[i]	
2′	161.69 (S)[d]	161.55 (S)[d]	161.34 (S)[d]	161.43[i]	162.82[i]	162.7[d]
3	86.48 (D)[e]	87.34 (D)[e]	87.42 (D)[e]	86.28	87.67	
3′	86.84 (D)[e]	86.93 (D)[e]	87.69 (D)[e]	86.28	87.67	87.4
4	169.57 (Sdq)	169.44 (Sdq)[f]	169.29 (Sdq)[f]	169.38[i]	169.64[i]	
4′	169.57 (Sdq)	169.28 (Sdq)[f]	169.25 (Sdq)[f]	169.38[i]	169.64[i]	169.3
5	136.78 (Sq)[f]	137.08 (Sq)[g]	136.69 (Sq)	136.82	138.34	
5′	137.34 (Sq)[f]	137.67 (Sq)[g]	137.93 (Sq)	136.82	138.34	138.2
6	118.96 (Sm)	118.59 (Sm)	119.35 (Sm)	115.26	111.30	
6′	115.51 (Dq)	110.72 (Dq)	111.37 (Dq)	115.26	111.30	115.4
7	158.85 (Sbrs)	158.62 (Sbrs)	160.00 (Sqd)	158.26	159.37	
7′	158.03 (Sbrs)	158.89 (Sm)	158.83 (Sm)	158.26	159.37	161.6[d]
8	100.24 (D)	100.26 (D)	97.56 (D)	105.91	108.36	
8′	109.32 (St)	111.29 (Sbrd)	110.35 (Sd)	105.91	108.36	98.6
9	155.33 (Sd)	155.31 (Sd)	155.86 (Sd)	153.68[i]	153.32[i]	
9′	153.69 (S)	152.73 (S)	152.64 (S)	153.68[i]	153.32[i]	156.3
10	106.24 (Sm)	106.25 (Sm)	107.36 (Sm)	105.52	107.35	
10′	106.24 (Sm)	107.62 (Sm)	107.71 (Sm)	105.52	107.35	107.6
4-OMe	56.39 (O)	56.41 (Q)[h]	56.51 (Q)	56.36	56.05	
4′-OMe	56.39 (Q)	56.53 (Q)[h]	56.51 (Q)	56.36	56.05	55.8
5-Me	18.82 (Q)	18.82 (Q)	18.75 (Q)	23.11	24.10	
5′-Me	23.09 (Qd)	23.36 (Qd)	23.39 (Qd)	23.11	24.10	23.4
7-OMe			56.07 (Q)[g]		55.84	
7′-OMe		55.92 (Q)	55.98 (Q)[g]		55.84	55.4

[a] See ref. 9. [b] See ref. 9. Compound (**7**) was measured in $CDCl_3$. [c] See ref. 11. Compound (9) was measured in $CDCl_3$. [d, e, f, g, and h] The assignments may be reversed. [i] The assignments were revised.

Table 3. Changes of ^{13}C n.m.r. coupling patterns of desertorin C (**3**) by selective irradiation of methyl protons

			Irradiated at	
	δ_C		δ 2.227	δ 2.227 & 2.701
5	136.69	Sq	S	S
5′	137.93	Sq	Sq	S
6	119.35	Sm	Sd	Sd
6′	111.37	Dq	Dq	D
10	107.36	Sm	Sdd	Sdd
10′	107.71	Sm	Sm	Sdd

Table 4. *O*-Methylation effect on ^{13}C n.m.r. chemical shifts of aromatic rings in desertorins A (**1**), B (**2**), and C (**3**)

	Δ[(3)—(2)][a]		Δ[(2)—(1)]	
Carbon	Observed[b]	Calculated[c]	Observed	Calculated
5	−0.39	−1.1	+0.30	
6	+0.76	+1.0	−0.37	
7	+1.38	+1.1	−0.23	
8	−2.70	−4.5	−0.02	
9	+0.55	−0.6	−0.02	
10	+1.11	+0.8	+0.01	
5′	+0.26		+0.33	−0.6
6′	+0.65		−4.79	−4.5
7′	−0.06		+0.86	+1.1
8′	−0.94		+1.93	+1.0
9′	−0.09		−0.96	−1.1
10′	+0.09		+1.38	+0.8

[a] *O*-Methylation shift values [Δ(A − B)] are calculated by subtracting ^{13}C n.m.r. chemical shifts of phenols (B) from the corresponding shifts of their methyl ethers (A). [b] The values are calculated from the carbon chemical shifts in Table 2. [c] Mean *O*-methylation shift values from ref. 12 are used.

liquid chromatography (l.p.l.c.) was performed on a Chemco Low-Prep pump 81-M-2 and glass column (200 × 10- or 20-mm) packed with silica gel CQ-3 (30—50 μ; Wako). T.l.c. was conducted on pre-coated Kieselgel 60 F_{254} (Art. 5715; Merck). Spots on t.l.c. were detected by their absorption under u.v. light, and/or with iodine vapour.

Isolation of Metabolites from Emericella desertorum.—*Emericella desertorum*, strain CBS 653.73, was cultivated at 28 °C for 15 days in Czapek-Dox medium, using 200 Roux flasks containing 250 ml of the above medium in each flask. The culture filtrate (50 l) was extracted with dichloromethane at pH 2, and the organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The residue (4.0 g) was chromatographed on silica gel with chloroform–methanol (100:1—50:1, v/v) followed by l.p.l.c. using the solvent system of benzene–acetone (10:1, v/v) to give silvaticol (**11**) (6 mg) and nidulol (**12**) (12 mg), with chloroform–methanol (30:1, v/v) followed by l.p.l.c. using the solvent system of chloroform–methanol (100:1, v/v) or hexane–ethyl acetate–acetic acid (90:20:0.1, v/v) to obtain desertorin B (**2**) (35 mg), and with chloroform–methanol (20:1, v/v) to give desertorin A (**1**) (120 mg). The dried mycelia (395 g) were pulverized and extracted with hexane, chloroform, ether, and acetone at room temperature successively. From the mycelial chloroform extract (15.0 g), ergosterol (2.2 g), desertorin B (**2**) (280 mg), and desertorin A (**1**) (70 mg) were isolated by column chromatography with the solvent systems of chloroform–methanol (50:1, v/v), (10:1, v/v), and (5:1, v/v), respectively. The eluate from the solvent system of chloroform–methanol (50:1, v/v) of the above chromatography was further purified by l.p.l.c. Paxilline (**10**) (50 mg) was isolated from the fraction by benzene–ethyl acetate (2:1, v/v) and then desertorin C (**3**) (160 mg) was isolated from the fraction of benzene–ethyl acetate (1:1, v/v). The mycelial ether extract (3.7 g) contained almost the same metabolites as the mycelial chloroform extract. Desertorin A (**1**) (750 mg) was also isolated from the water insoluble part of the mycelial acetone extract (4.8 g), and mannitol (210 mg) was isolated from the water soluble part.

Desertorin A (**1**) was obtained as needles with violet fluorescence (from methanol), m.p. >300 °C (Found: C, 64.05;

H, 4.4. $C_{22}H_{18}O_8$ requires C, 64.39; H, 4.42%); *m/z* 410 (M^+, 100%, e.i.), 395 [$(M - Me)^+$, 27], 393 [$(M - OH)^+$, 23], and 378 (24); $\lambda_{max.}$(EtOH) 211 (log ε 4.81), 312 (4.51), and 321sh nm (4.48); $\nu_{max.}$(KBr) 3 200 (OH) and 1 680 cm^{-1} (CO_2). ^1H and ^{13}C N.m.r. signals are summarized in Tables 1 and 2, respectively.

Desertorin B (**2**) was obtained as a crystalline powder (from dichloromethane), m.p. >300 °C; *m/z* 424.1163 (M^+, 100%, e.i., $C_{23}H_{20}O_8$ requires 424.1158), 409 [$(M - Me)^+$, 12], and 393 [$(M - OMe)^+$, 31]; $\nu_{max.}$(KBr) 3 100 (OH), 1 700, and 1 680 cm^{-1} (CO_2). ^1H and ^{13}C N.m.r. signals are summarized in Tables 1 and 2, respectively.

Desertorin C (**3**) was obtained as leaflets (from methanol), m.p. 235—237 °C; $[\alpha]_D^{20}$ +16.8° (*c* 1.00 in $CHCl_3$) (Found: C, 64.45; H, 4.95. $C_{24}H_{22}O_8 \cdot 0.5H_2O$ requires C, 64.43; H, 5.18%); *m/z* 438 (M^+, 100%, e.i.), 423 [$(M - Me)^+$, 6], and 407 [$(M - OMe)^+$, 34]; $\lambda_{max.}$(EtOH) 209 (log ε 4.75), 295sh (4.38), 310 (4.48), and 320sh nm (4.41); $\nu_{max.}$(KBr) 1 705 cm^{-1} (CO_2); c.d. (*c* 4.4×10^{-4} in MeOH) $[\theta]_{241}$ $+3.1 \times 10^4$, $[\theta]_{243}$ -1.4×10^4, $[\theta]_{282}$ -7.1×10^4, and $[\theta]_{301}$ $+8.0 \times 10^3$. ^1H and ^{13}C N.m.r. signals are summarized in Tables 1 and 2, respectively.

Methylation of Desertorin A (**1**) *with Diazomethane.*—Diazomethane in ether was added to the solution of desertorin A (**1**) (100 mg) in dioxane (2 ml) and the mixture left at room temperature for 2 days. The reaction mixture was evaporated and the residue was purified by l.p.l.c. using the solvent system of benzene–acetone (5:1, v/v) to give crystals (120 mg). This compound was identified as desertorin C (**3**) by comparison of t.l.c. behaviour, i.r., ^1H n.m.r., and c.d. spectra, and mixed m.p.

Methylation of Desertorin B (**2**) *with Diazomethane.*—Desertorin B (**2**) (50 mg) was methylated and purified by the same procedure as described above. The crystals obtained (45 mg) were also identified as desertorin C (**3**) by comparison of t.l.c. behaviour, i.r., ^1H n.m.r., and c.d. spectra, and mixed m.p.

Alkaline Hydrolysis of Desertorin C (**3**).—A suspension of desertorin C (**3**) (90 mg) in a mixture of 10% aqueous potassium hydroxide (5 ml) and dioxane (5 ml) was refluxed for 2 h, cooled to 0 °C, and acidified with dilute hydrochloric acid. After being left at room temperature for 3 h, the reaction mixture was extracted with chloroform, dried (Na_2SO_4), and the solvent evaporated. The residue was purified by l.p.l.c. using the solvent system of benzene–ethyl acetate (30:1, v/v) to afford a *biphenyl derivative* (**4**) (40 mg) as leaflets (from methanol), m.p. 149—150 °C (Found: C, 67.15; H, 6.15. $C_{20}H_{22}O_6$ requires C, 67.02; H, 6.19); *m/z* 358 (M^+, 58%, e.i.) and 343 [$(M - Me)^+$, 100]; $\lambda_{max.}$(EtOH) 202 (log ε 4.52), 218sh (4.36), 241 (4.36), and 285 mm (4.25); $\nu_{max.}$(KBr) 1 600 (CO), 1 560 cm^{-1}; $\delta_H(CDCl_3)$ 2.25 (3 H, s), 2.63 (3 H, s), 2.67 (6 H, s), 3.71 (3 H, s), 3.78 (3 H, s), 6.41 (2 H, br s), 13.18 (1 H, s, OH), and 13.22 (1 H, s, OH); $\delta_C[(CD_3)_2SO]$ 16.64 (Q, Me), 22.57 (Qd, Me), 32.33 (Q, $COCH_3$), 32.64 (Q, $COCH_3$), 55.18 (Q, OMe), 55.50 (Q, OMe), 96.91 (D), 106.19 (Dq), 110.91 (St), 113.49 (Sm), 118.81 (Sm), 121.63 (Sm), 136.35 (Sq), 139.24 (Sq), 156.15 (Sm), 158.35 (Sd-like), 158.97 (Sm), 159.97 (Sd-like), 204.10 (Sq, *C*OMe), and 204.54 (Sq, *C*OMe); c.d. (*c* 5.4×10^{-4} in MeOH) $[\theta]_{227}$ $+ 2.54 \times 10^4$ and $[\theta]_{270}$ -2.16×10^4.

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