Studies on Fungal Products. Part 15.[1] Isolation and Structure Determination of Arugosin E from *Aspergillus silvaticus* and Cycloisoemericellin from *Emericella striata*

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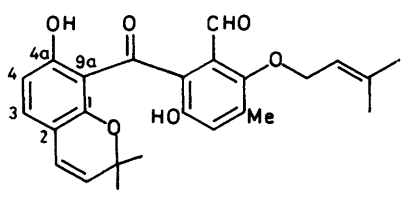
Together with arugosins A (**3**), B (**4**), and C (**5**), a novel compound related to the arugosins, designated arugosin E (**1**), was isolated from the mycelial extract of *Aspergillus silvaticus*. A new compound designated cycloisoemericellin (**2**) was also isolated along with arugosins A (**3**) and B (**4**) from the mycelial extract of *Emericella striata*. The structures of compounds (**1**) and (**2**) were determined on the basis of spectroscopic investigation and chemical correlation with the known compounds (**3**), (**4**), and (**6**). An *X*-ray crystal analysis of arugosin E (**1**) was carried out.

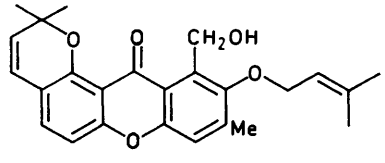
In the previous paper,[2] we reported the isolation of two novel dioxopiperazine derivatives, dithiosilvatin and silvathione, from *Aspergillus silvaticus* Fennell & Raper, strain IFO 8173. In the search for other metabolites from the above fungus, a new compound designated arugosin E (**1**) was isolated along with dithiosilvatin and arugosins A (**3**), B (**4**), and C (**5**) from the mycelial extract. Compounds (**3**), (**4**), and (**5**) are metabolites of *Emericella rugulosa* (Thom & Raper) C. R. Benjamin (anamorph: *A. rugulosus* Thom & Raper)[3,4] and *Emericella variecolor* Berkley & Broome (anamorph: *A. variecolor* Thom & Raper).[5,6] Cycloisoemericellin (**2**) was isolated with arugosins A (**3**) and B (**4**) from the non-polar fraction of the acetone extract of *Emericella striata* (Rai, Tewari & Mukerji) Malloch & Cain (anamorph: *A. striatus* Rai, Tewari & Mukerji), strain 80-NE-22. The structural elucidation of compounds (**1**) and (**2**) is reported in this paper.

Results and Discussion

Arugosin E (**1**), m.p. 159—161 °C, gave a molecular ion at *m/z* 422 by electron impact (e.i.) mass spectrometry, and elemental analysis confirmed the molecular formula as $C_{25}H_{26}O_6$. The ^1H



(**1**)



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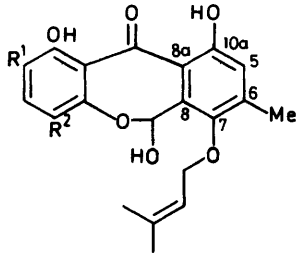
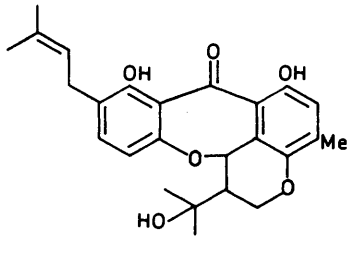
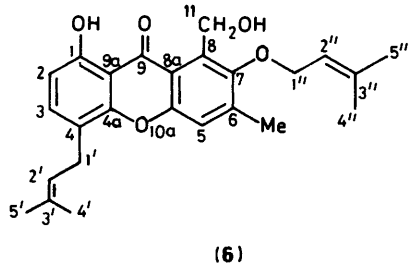




(**5**)

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

(**4**) R^1=H, R^2=



(**6**)

Table 1. ^{1}H. N.m.r. chemical shifts of arugosin E (**1**), cycloisoemericellin (**2**), and their derivatives in $CDCl_3$

Carbon[a] No.	(1)	(2)	(3) and (4)	(5)	(6)
1-OH	—	—	(13.44, 12.83)	13.87	12.50
2-H	—	—	(—, 6.66)	—	6.70
3-H	7.01	7.25	(7.27, 7.36)	7.28	7.40
4-H	6.49	6.86	(6.44, —)	6.40	—
4a-OH	12.43	—	—	—	—
5-H	6.99	7.21	6.88	6.81	7.24
5a-OH	5.40	—	(10.88, 11.15)	10.70	—
6-Me	2.36	2.42	2.35	2.24	2.42
11-H	10.19	5.02	6.54	5.08	5.04
11-OH	—	4.98	5.00	—	4.45
1′-H	6.12[b]	6.33[b]	3.31	3.49	3.46
2′-H	5.26[b]	5.64[b]	5.28	5.30	5.30
4′-H	0.94	1.57	1.72	1.76[b]	1.73[b]
5′-H	0.94	1.57	1.72	1.73[b]	1.68[b]
1″-H	4.39	4.45	4.41	4.27 4.38	4.42
2″-H	5.51	5.61	5.53	2.35	5.60
3″-OH	—	—	—	1.55	—
4″-H	1.77	1.81[c]	1.82[b]	1.26[c]	1.85[b]
5″-H	1.63	1.73[c]	1.72[b]	1.32[c]	1.81[b]

[a] Numberings of the related compounds correspond to those of compound (**6**). [b,c] Assignments may be reversed.

Table 2. Final atomic positional parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	0.983 3(4)	0.203 5(2)	0.290 1(3)
O(2)	0.830 3(5)	0.430 9(2)	0.445 1(3)
O(3)	0.644 4(4)	0.337 6(2)	0.376 1(3)
O(4)	0.558 9(5)	0.030 9(2)	0.298 1(3)
O(5)	0.718 6(5)	0.315 1(2)	0.162 4(3)
O(6)	0.728 4(5)	0.186 9(3)	0.473 3(3)
C(2)	1.086 3(7)	0.172 0(4)	0.244 2(5)
C(3)	1.243 8(8)	0.183 4(5)	0.264 0(6)
C(4)	1.279 0(7)	0.240 6(5)	0.319 0(6)
C(4a)	1.164 5(7)	0.292 5(4)	0.349 1(4)
C(5)	1.197 2(7)	0.361 7(4)	0.397 5(4)
C(6)	1.084 5(7)	0.407 6(4)	0.430 0(4)
C(7)	0.936 9(7)	0.384 8(3)	0.412 4(4)
C(8)	0.900 5(6)	0.316 2(3)	0.363 5(4)
C(8a)	1.016 8(6)	0.272 0(3)	0.331 6(4)
C(9)	1.040 8(9)	0.087 9(4)	0.213 4(7)
C(10)	1.061 0(10)	0.220 1(6)	0.132 9(5)
C(11)	0.744 2(6)	0.297 1(3)	0.346 3(3)
C(1′)	0.659 6(6)	0.157 2(3)	0.320 1(4)
C(2′)	0.605 3(6)	0.099 6(3)	0.261 5(4)
C(3′)	0.586 4(6)	0.113 9(3)	0.165 5(4)
C(4′)	0.624 3(7)	0.185 9(4)	0.133 4(4)
C(5′)	0.679 0(6)	0.243 9(3)	0.192 0(4)
C(6′)	0.694 3(5)	0.230 3(3)	0.286 6(3)
C(7′)	0.681 6(7)	0.140 1(4)	0.418 8(4)
C(8′)	0.514 9(9)	0.053 8(4)	0.101 6(5)
C(9′)	0.644 7(11)	−0.039 2(4)	0.280 2(6)
C(10′)	0.772 2(13)	−0.049 0(5)	0.347 3(7)
C(11′)	0.767 0(11)	−0.086 3(5)	0.427 6(6)
C(12′)	0.901 2(14)	−0.097 4(7)	0.493 8(9)
C(13′)	0.634 1(15)	−0.122 6(11)	0.462 1(10)

n.m.r. signals of compound (**1**) were similar to those of (**3**) or (**4**), with the exception of (i) the appearance of the aldehyde proton at δ 10.19 in (**1**) instead of the hemiacetal proton at δ 6.54 in (**3**) and (**4**), and (ii) the disappearance of the signals assigned to one of the 3-methylbut-2-enyl groups in (**3**) and (**4**) (Table 1). The signals observed at δ 5.26 (1 H, d) and 6.12 (1 H, d) in (**1**) were assigned as the vicinal olefinic protons, and those at δ 0.94 (6 H, s) in (**1**) as the two aliphatic methyl groups. The above results suggested that the 3-methylbut-2-enyl group in (**3**) or (**4**) was converted into a 2,2-dimethylchromene skeleton in (**1**). 3-Methylbut-2-enyl groups usually undergo cyclisation with a hydroxy group at the *ortho*-position of a benzene ring on treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[7] to give a 2,2-dimethylchlromene skeleton. When arugosins A (**3**) and B (**4**) were treated with DDQ, their hemiacetal bonds were cleaved and oxidative cyclization gave compound (**1**). The structure of arugosin E was therefore assumed to be that in (**1**).

Table 3. Bond lengths (Å) for arugosin E (**1**) with estimated standard deviations in parentheses

O(1)–C(2)	1.477(9)	O(1)–C(8a)	1.358(7)
O(2)–C(7)	1.355(8)	O(3)–C(11)	1.239(7)
O(4)–C(2′)	1.376(7)	O(4)–C(9′)	1.470(11)
O(5)–C(5′)	1.358(8)	O(6)–C(7′)	1.198(8)
C(2)–C(3)	1.524(12)	C(2)–C(9)	1.517(13)
C(2)–C(10)	1.579(13)	C(3)–C(4)	1.304(12)
C(4)–C(4a)	1.454(11)	C(4a)–C(5)	1.413(9)
C(4a)–C(8a)	1.393(9)	C(5)–C(6)	1.394(10)
C(6)–C(7)	1.404(9)	C(7)–C(8)	1.415(8)
C(8)–C(8a)	1.398(8)	C(8)–C(11)	1.461(8)
C(11)–C(6′)	1.503(8)	C(1′)–C(2′)	1.386(8)
C(1′)–C(6′)	1.395(8)	C(1′)–C(7′)	1.476(8)
C(2′)–C(3′)	1.426(8)	C(3′)–C(4′)	1.378(9)
C(3′)–C(8′)	1.520(10)	C(4′)–C(5′)	1.392(9)
C(5′)–C(6′)	1.402(8)	C(9′)–C(10′)	1.485(15)
C(10′)–C(11′)	1.341(16)	C(11′)–C(12′)	1.526(17)
C(11′)–C(13′)	1.467(23)		

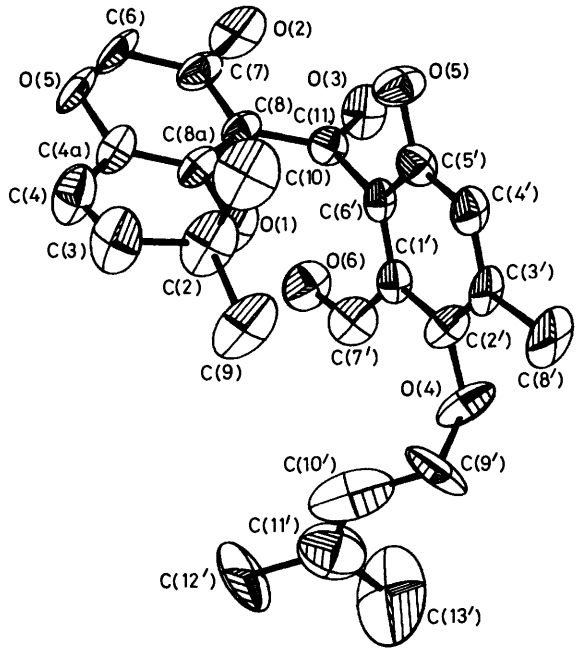


Figure. Perspective view of the crystal structure of arugosin E (**1**) with thermal ellipsoids at 50% probability

In order to determine the exact structure of arugosin E (**1**), an *X*-ray structure analysis was undertaken (see Figure). Most of the bond lengths and angles were as expected (Tables 3 and 4). An intermolecular hydrogen bond of 2.769 Å was apparent between O(5) and O(6). The molecules of (**1**) are packed closely together in the *c* direction through hydrogen bonding. An intramolecular hydrogen bond of 2.504 Å was

Table 4. Bond angles (°) for arugosin E (**1**) with estimated standard deviations in parentheses

C(2)–O(1)–C(8a)	118.6(5)	C(2′)–O(4)–C(9′)	118.0(6)
O(1)–C(2)–C(3)	108.1(6)	O(1)–C(2)–C(9)	104.1(6)
O(1)–C(2)–C(10)	106.7(6)	C(3)–C(2)–C(9)	114.0(7)
C(3)–C(2)–C(10)	110.4(7)	C(9)–C(2)–C(10)	113.0(7)
C(2)–C(3)–C(4)	121.9(8)	C(3)–C(4)–C(4a)	119.9(8)
C(4)–C(4a)–C(5)	122.5(6)	C(4)–C(4a)–C(8a)	118.6(6)
C(5)–C(4a)–C(8a)	118.8(6)	C(4a)–C(5)–C(6)	120.9(6)
C(5)–C(6)–C(7)	118.9(6)	O(2)–C(7)–C(6)	117.2(6)
O(2)–C(7)–C(8)	121.2(5)	C(6)–C(7)–C(8)	121.6(6)
C(7)–C(8)–C(8a)	117.7(5)	C(7)–C(8)–C(11)	118.4(5)
C(8a)–C(8)–C(11)	123.9(5)	O(1)–C(8a)–C(4a)	119.6(5)
O(1)–C(8a)–C(8)	118.0(5)	C(4a)–C(8a)–C(8)	122.1(5)
O(3)–C(11)–C(8)	121.8(5)	O(3)–C(11)–C(6′)	115.8(5)
C(8)–C(11)–C(6′)	122.2(5)	C(2′)–C(1′)–C(6′)	120.8(5)
C(2′)–C(1′)–C(7′)	119.0(5)	C(6′)–C(1′)–C(7′)	120.1(5)
O(4)–C(2′)–C(1′)	119.1(5)	O(4)–C(2′)–C(3′)	120.5(5)
C(1′)–C(2′)–C(3′)	120.2(5)	C(2′)–C(3′)–C(4′)	118.1(5)
C(2′)–C(3′)–C(8′)	120.8(6)	C(4′)–C(3′)–C(8′)	120.9(6)
C(3′)–C(4′)–C(5′)	121.8(6)	O(5)–C(5′)–C(4′)	123.2(5)
O(5)–C(5′)–C(6′)	116.8(5)	C(4′)–C(5′)–C(6′)	120.0(5)
C(11)–C(6′)–C(1′)	123.9(5)	C(11)–C(6′)–C(5′)	117.1(5)
C(1′)–C(6′)–C(5′)	119.0(5)	O(6)–C(7′)–C(1′)	122.7(6)
O(4)–C(9′)–C(10′)	112.1(8)	C(9′)–C(10′)–C(11′)	124.9(10)
C(10′)–C(11′)–C(12′)	123.6(10)	C(10′)–C(11′)–C(13′)	124.8(12)
C(12′)–C(11′)–C(13′)	111.6(12)		

Table 5. Selected torsion angles (°) with estimated standard deviations in parentheses

O(3)–C(11)–C(8)–C(7)	−2.7(0.8)
O(3)–C(11)–C(8)–C(8a)	179.8(0.5)
O(3)–C(11)–C(6′)–C(5′)	91.1(0.6)
O(3)–C(11)–C(6′)–C(1′)	−87.3(0.7)
O(6)–C(7′)–C(1′)–C(6′)	0.4(0.9)
O(6)–C(7′)–C(1′)–C(2′)	179.8(0.6)

apparent between O(2) and O(3), whereas the distance of 3.248 Å found between O(3) and O(5) suggested no hydrogen bonding. The torsion angles around the ketones are given in Table 5. The dihedral angles between the least-squares planes formed by the chromane ring and the ketone, and by the benzene ring and the ketone are 4.5° and 93.0°, respectively. All the above results confirmed that the planes formed by the chromanylketone and the benzene ring in compound (**1**) were almost perpendicular. This was also shown in the ^{1}H n.m.r. spectra—the signal at δ 12.43 being assigned as the phenolic hydroxy which was hydrogen-bonded to the ketone, and the signal at δ 5.40 being assigned as the non hydrogen-bonded phenolic hydroxy of the benzene ring. The ketone signal observed at δ_C 200.44 also indicated that there was no conjugation between chromanylketone and the benzene ring in (**1**). The assignments of ^{13}C n.m.r. signals of arugosin E (**1**) are given in Table 6.

Cycloisoemericellin (**2**), m.p. 136—138 °C, gave a molecular ion at *m/z* 406 by e.i. m.s. and elemental analysis confirmed the molecular formula as $C_{25}H_{26}O_5$. The u.v. maxima at 238, 280, 317, and 380 nm in (**2**) suggested the presence of a xanthone nucleus as in emericellin (**6**) (u.v. maxima at 237, 271, 294, and 384 nm). The ^{1}H n.m.r. signals observed at δ 1.73 (3 H), 1.81 (3 H), 5.61 (1 H, br t), and 4.45 (2 H, br d) were assigned to the 3-methylbut-2-enyloxy group in (**2**). The ^{1}H (Table 1) and ^{13}C (Table 6) n.m.r. signals of (**2**) were similar to those of (**6**), with the exception of signals observed at δ 1.57 (6 H, s), 5.64 (1 H, d), and 6.33 (1 H, d) in the ^{1}H n.m.r. spectrum and at δ_C 28.01 (Qm), 77.88 (Sm), 129.42 (Dm), and 121.61 (Dd) in the ^{13}C n.m.r.

Table 6. ^{13}C N.m.r. chemical shifts of arugosin E (**1**), cycloisoemericellin (**2**), and emericellin (**6**) in $CDCl_3$

Carbon[a] No.	(1)	(2)	(3)
1	154.42 (Sdd)	154.39 (Sdd)	154.08 (S)
2	112.72 (Sddd)	116.91 (Sddd)	110.14 (D)
3	133.83 (Dd)	131.77 (Dd)	136.97 (D)
4	109.70 (Dd)	108.33 (D)	109.20 (S)
4a	163.62 (Sm)	156.42 (Sdd)	160.09 (S)
5	125.06 (Sq)	118.84 (Dq)	118.94 (D)
6	134.49 (Sq)	140.50 (Sq)	142.68 (S)
6-Me	15.88 (Qd)	17.47 (Qd)	17.82 (Q)[b]
7	154.27 (Sm)	152.38 (Sm)	152.79 (S)[c]
8	128.75 (Sd)	134.58 (S br,t)	134.45 (S)
8a	128.45 (Sm)	120.73 (Sm)	121.81 (S)
9	200.44 (S)	179.10 (S)	184.75 (S)
9a	112.05 (S br,dd)	112.86 (Sd)	118.11 (S)
10a	148.15 (Sd)	152.84 (Sd)	152.95 (S)[c]
11	189.43 (D)	57.20 (Td)	57.23 (T)
1′	121.92 (Dd)	121.61 (Dd)	27.58 (T)
2′	126.43 (Dm)	129.42 (Dm)	119.47 (D)[d]
3′	77.50 (Sm)	77.88 (Sm)	133.36 (S)
4′	27.41 (Qm)	28.01 (Qm)	18.20 (Q)[b]
5′	27.41 (Qm)	28.01 (Qm)	25.92 (Q)[e]
1″	72.81 (T)	72.06 (T)	72.37 (T)
2″	119.13 (Dm)	119.99 (Dm)	119.84 (D)[d]
3″	139.95 (Sm)	138.52 (Sm)	138.95 (S)
4″	18.05 (Qm)	18.11 (Qm)	18.02 (Q)[b]
5″	25.74 (Qm)	25.82 (Qm)	25.85 (Q)[e]

[a] Numberings of the above compounds correspond to those of compound (**6**). [b–e] Assignments may be reversed.

spectrum of (**2**). This suggested that compound (**2**) contains a 2,2-dimethylchromene skeleton [*cf.* arugosin E (**1**)], instead of the 3-methylbut-2-enyl group present in (**6**). All the above results and the consideration of the co-occurrence of emericellin (**6**)[8] support the structure of cycloisoemericellin as that given in (**2**).

In order to determine the structure of cycloisoemericellin (**2**) conclusively, long-range proton selective decoupling experiments in the ^{13}C n.m.r. spectrum were performed. The carbon signals at δ_C 118.84 (Dq, C-5) and 140.50 (Sq, C-6) were changed into a simple doublet and singlet, respectively, by selective irradiation of the protons at δ 2.42 assigned to the aromatic methyl group. The multiplicity of the carbon at δ_C 152.38 (Sm) was also changed in the above conditions. On the other hand, when the protons at δ 7.25 and 6.86, which were assigned to the aromatic protons coupled with each other, were irradiated at the same time, the five carbon signals at δ_C 154.39 (Sdd, C-1), 116.91 (Sddd, C-2), 156.42 (Sdd, C-4a), 122.86 (Sd, C-9a), and 121.61 (Dd, C-1′) were changed into a doublet, double-doublet, singlet, singlet, and doublet, respectively. The above results confirmed the structure of cycloisoemericellin as (**2**) and the assignments of the ^{13}C n.m.r. signals in Table 6.

It is interesting that the arugosins, which were originally isolated from the fungi of the *A. nidulans* group: *Emericella variecolor* and *Emericella rugulosa*, were also isolated from *A. silvaticus* and *E. striata*. According to Fennell and Raper,[9] *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 *A. silvaticus*, *E. variecolor*, *E. rugulosa*, and *E. striata* is strikingly suggestive of their placements in the same group, *viz.* the *A. nidulans* group.

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. E.i. m.s. were recorded on 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. ^1H (99.60 MHz) N.m.r. spectra were recorded on a JEOL JNM-FX 100 spectrometer, while ^{13}C (100.43 MHz) n.m.r. spectra were recorded 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, and quartet = Q or q. Capital letters refer to the pattern resulting from directly bonded coupling ($^1J_{C,H}$). Column chromatography was performed using Kieselgel 60 (Art. 7734; Merck). Low pressure 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 precoated Kieselgel 60 F_{254} (Art 5715; Merck). Spots on t.l.c. were detected by their absorption under u.v. light, and/or by iodine vapour.

Isolation of Arugosins from Aspergillus silvaticus.—*Aspergillus silvaticus*, strain IFO 8173, was cultivated at 27 °C for 21 days in Czapek-Dox medium, using 340 Roux flasks containing 250 ml of the above medium in each flask. The dried mycelia (470 g) were extracted with chloroform. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the chloroform extract (37 g). Chromatography on silica gel with benzene, followed by repeated purification by l.p.l.c. with benzene gave anhydroarugosin (40 mg), and arugosins A (**3**) and B (**4**) (4.0 g). Further elution with benzene-acetone (50:1) followed by repeated purification by l.p.l.c. with benzene gave dithiosilvatin [2] and arugosin E (**1**) (30 mg) successively.

Arugosin E (**1**) was obtained as yellow needles or prisms (from benzene), m.p. 159—161 °C (Found: C, 70.8; H, 6.2. $C_{25}H_{26}O_6$ requires C, 71.07; H, 6.20%); *m/z* 422 (M^+, 16%), 354 [$(M - C_5H_8)^+$, 53], 339 (73), 325 (100), 321 (25), 270 (22), 187 (37), 161 (63), and 69 [$(C_5H_9)^+$, 55]; $\lambda_{max.}$(MeOH) 214 (log ε 4.42), 273 (4.26), and 348 nm (3.64); $\nu_{max.}$(KBr) 1 690, 1 640, and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 0.94 (6 H, s, aliphatic Me × 2), 1.63 (3 H, s, olefinic Me), 1.77 (3 H, s, olefinic Me), 2.36 (3 H, s, ArMe), 4.39 (2 H, d, *J* 7.3 Hz, OCH_2CH=), 5.26 (1 H, d, *J* 9.8 Hz, C*H*=CH), 5.40 (1 H, br s, PhOH), 5.51 (1 H, br t, *J* 7.3 Hz, OCH_2CH=), 6.12 (1 H, d, *J* 9.8 Hz, CH=C*H*), 6.49 (1 H, d, *J* 8.6 Hz, ArH), 6.99 (1 H, s, ArH), 7.01 (1 H, d, *J* 8.6 Hz, ArH), 10.19 (1 H, s, CHO), and 12.43 (1 H, s, PhOH). The ^{13}C n.m.r. signals are summarized in Table 6.

Isolation of Cycloisoemericellin (**2**) *from* Emericella striata.—The benzene–acetone (50:1) fraction obtained from column chromatography of the acetone extract (26 g) of the mycelium (660 g) of *Emericella striata*, strain 80-NE-22, was crystallized from acetone to give ergosterol,[8] and the remaining residue was chromatographed on silica gel with hexane–ethyl acetate (20:1, v/v) followed by l.p.l.c. with cyclohexane as solvent to give arugosin A (**3**) and B (**4**) (40 mg) and with hexane–ethyl acetate (10:1, v/v) followed by recrystallization from ether–hexane to give cycloisoemericellin (**2**) (92 mg).

Cycloisoemericellin (**2**) was obtained as yellow needles, m.p. 136—138 °C (Found: C, 74.15; H, 6.75. $C_{25}H_{26}O_5$ requires C, 73.86; H, 6.45%); *m/z* 406 (M^+, 7%), 337 [$(M - C_5H_9)^+$, 100], 319 (32), 305 (78), 295 (31), 267 (20), 255 (38), and 69 [$(C_5H_9)^+$, 26]; $\lambda_{max.}$(MeOH) 238 (log ε 4.35), 280 (4.62), 317sh (3.91), and 380 nm (3.74); $\nu_{max.}$(KBr) 3 450 (OH), 1 640, and 1 610 cm^{-1}; $\delta_H(CDCl_3)$, 1.57 (6 H, s, aliphatic Me × 2), 1.73 (3 H, br s, olefinic Me), 1.81 (3 H, br s, olefinic Me), 2.42 (3 H, d, *J* 0.7 Hz, ArMe), 4.45 (2 H, br d, *J* 7.3 Hz, OCH_2CH=), 4.98 (1 H, s, OH), 5.02 (2 H, br s, CH_2OH), 5.61 (1 H, br t, *J* 7.3 Hz, OCH_2CH=), 5.64 (1 H, d, *J* 9.8 Hz, C*H*=CH), 6.33 (1 H, d, *J* 9.8 Hz, CH=C*H*), 6.86 (1 H, d, *J* 8.3 Hz, ArH), 7.21 (1 H, br s, ArH), and 7.25 (1 H, d, *J* 8.3 Hz, ArH). The ^{13}C n.m.r. signals are summarized in Table 6.

Oxidation of Arugosins A (**3**) *and B* (**4**) *with DDQ.*—DDQ (180 mg) was added to a solution of arugosin A (**3**) [arugosin B (**4**)] (240 mg) in dry benzene (20 ml), and the mixture was heated under reflux for 30 min. The precipitate was filtered off, and the reaction mixture was washed with water several times then evaporated under reduced pressure. The residue was repeatedly purified by l.p.l.c. with benzene to give arugosin E (**1**) (90 mg), which was identified by its i.r. and ^1H n.m.r. spectra and t.l.c. and h.p.l.c. behaviour.

Structure Determination of Arugosin E (**1**) *by X-Ray Diffraction.*—Diffraction intensities were collected from a crystal of dimensions 0.75 × 0.50 × 0.30 mm of arugosin E (**1**) on a Rigaku AFC-5 FOS four-circle diffractometer. Of the total 3 392 reflections (complete for $7° \leq 2\theta \leq 120°$), 2 888 satisfied the criterion $F \geq 3\sigma(F)$ and only these were used in the solution and refinement of the structure.

Crystal Data.—$C_{25}H_{26}O_6$, M = 422.5, monoclinic, a = 9.045(14), b = 17.282(13), c = 14.606(15) Å, β = 92.84(11)°, V = 2 280.3 $Å^3$, Z = 4, D_c = 1.231 g cm^{-3}, $F(000)$ = 896, space group $P2_1/c$, Cu-K_α *X*-radiation (graphite monochromator), λ = 1.5418 Å.

Structure Solution and Refinement.—The structure was solved by direct methods using MULTAN 80 [10] and in the final refinement by block-matrix least-squares method; anisotropic thermal parameters were used for all non-hydrogen atoms. The contribution of hydrogen atoms was ignored. The refinement converged to R 0.092 and R_w 0.102. The data were not corrected for the effects of absorption. Positional parameters are shown in Table 2, and bond lengths and angles are summarized in Tables 3 and 4, respectively. A list of anisotropic and equivalent thermal parameters is available on request from the Cambridge Crystallographic Data Centre.*

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* See para. 5.6.3 in 'Instructions for Authors (1988),' *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1.

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