186. Gilmaniellin and Dechlorogilmaniellin, Two Novel Dimeric Oxaphenalenones

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Dedicated to Prof. *Edgardo Giovannini* on the occasion of his 70th birthday

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Summary

The structure and configuration of gilmaniellin, a metabolite of *Gilmaniella humicola* BARRON, has been shown to be **2** by X-ray analysis. By comparison of spectral data structure **1** has been assigned to dechlorogilmaniellin.

Introduction. – During our investigations [1] on the minor metabolites of *Gilmaniella humicola* BARRON, one fermentation unexpectedly yielded two phenolic compounds $C_{26}H_{20}O_{16}$ and $C_{26}H_{19}ClO_{10}$ along with (–)-6-hydroxy-mellein (**5**) [2]. In this particular fermentation no traces of mikrolin (**6**) and dechloromikrolin (**7**) [3] or related metabolites [1] were observed. All our attempts to repeat this fermentation result have been futile. Fortunately the crystals of $C_{26}H_{19}ClO_{10}$ were suitable for X-ray analysis and the structure of this compound has been elucidated as **2**. By comparison of the ^{1}H-NMR. spectrum and fragmentation pattern in the mass spectrum of $C_{26}H_{20}O_{10}$ with those of **2** structure **1** was assigned to this product. Trivial names gilmaniellin and dechlorogilmaniellin are proposed for **2** and **1** respectively. Details of this work are presented in this communication.

Isolation and structure of the metabolites. – The ethyl acetate extract of the culture filtrate as well as the mycelium of *Gilmaniella humicola* BARRON were concentrated and purified by chromatography on a silica gel column followed by preparative thin layer chromatography on silica gel to yield three crystalline compounds. (–)-6-Hydroxy-mellein [(–)-3,4-dihydro-6,8-dihydroxy-3-methylisocoumarin] (**5**), m.p. 214–215°, $[\alpha]_D^{22} = -64 \pm 2°$ was identified by comparison of its spectral data with the literature values [2].

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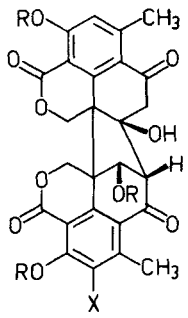
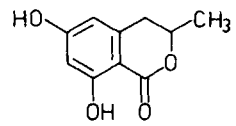
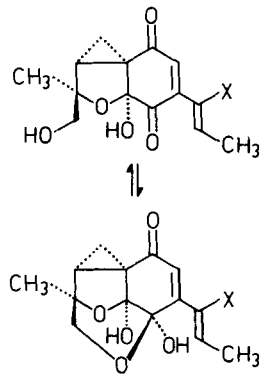
Scheme 1



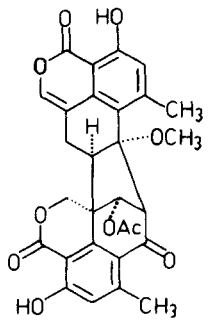
1 R=X=H: Dechloro-gilmaniellin
2 R=H; X=Cl: Gilmaniellin
3 R=Ac; X=Cl
4 R=Ac; X=H



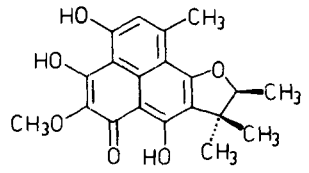
5 6-Hydroxy-mellein



6 X=Cl: Mikrolin
7 X=H: Dechloromikrolin



8 Duclauxin



9 Deoxyherqueinone

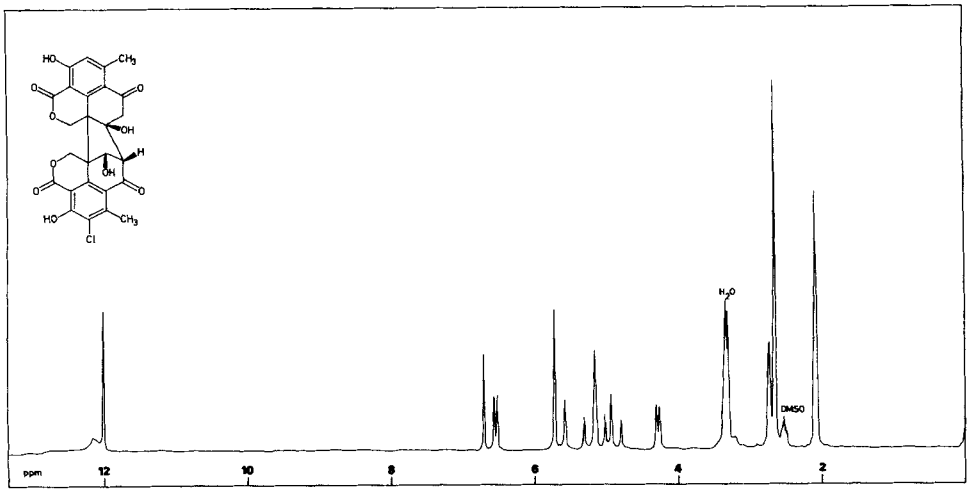


Fig. 1. *^{1}H-NMR. spectrum of gilmaniellin* (**2**) *in (D_6)DMSO* with TMS as an internal standard

Gilmaniellin (**2**) gave a positive Iron (III) chelate colour test indicating the phenolic nature of the molecule. It dissolved in 1 N NaOH and could be recovered after neutralization with hydrochloric acid without any change in spectral or chemical properties.

The molecular formula $C_{26}H_{19}ClO_{10}$ was deduced from accurate mass measurement. The presence of fragments at *m/z* 282, 264 and 245 in the mass spectrum suggested the dimeric nature of the molecule with one half containing a chlorine atom. The mass spectral fragmentation is shown on *Scheme 2.*

The ^{1}H-NMR. spectrum ((D$_6$)DMSO) was rather simple *(Fig. 1)* and the following structural features could be deduced. The signals at 2.07 and 2.62 ppm indicated the presence of aromatic methyl groups. The former exhibited an allylic coupling of 0.6 Hz with the only aromatic proton at 6.67 ppm. This aromatic proton did not show any further coupling thereby suggesting the presence of a penta-substituted benzene ring in the molecule. The presence of 2 phenolic hydroxyl groups at 11.9 and 12.1 ppm, one secondary hydroxyl at 6.4 ppm and a tertiary hydroxyl at 5.7 ppm was also apparent. On treatment with D_2O all four of these signals disappeared and the doublet at 4.25 ppm collapsed to a singlet, the latter confirming the presence of a C*H*–OH unit. The formation of the tri-*O*-acetylderivative **3** upon treatment with acetic anhydride and pyridine also corroborates these conclusions. Signals for the acetyl groups in the ^{1}H-NMR. spectrum of **3** appeared at 2.28, 2.29 and 2.39 ppm. The methine proton at 4.25 ppm in **2** exhibited the expected downfield shift of ~1 ppm (5.24 ppm) in the ^{1}H-NMR. spectrum of the derivative **3**. Two sets of *AB*-systems (methylene groups) at 4.81 and 5.12 ppm (J = 12.6 Hz), and 4.98 and 5.6 ppm (J = 13.2 Hz) were also evident. In addition to these, signals at 2.7 and 3.28 ppm appearing as singlets integrated for two methylene and one methine proton respectively. The former became magnetically non-equivalent in the triacetate **3** and appeared as an *AB*-system at 2.65 and 3.02 ppm (J = 15 Hz) in its ^{1}H-NMR. spectrum.

The IR. spectrum of gilmaniellin (**2**) was not very informative and exhibited absorptions at 3500–3200 cm^{-1} (OH) and 1700–1600 cm^{-1}. However, absorptions at 1750 and 1690 cm^{-1} in the IR. spectrum of the triacetyl derivative **3** suggested the presence of conjugated lactone and conjugated ketone moieties. Considering the small amounts of material available, the complex nature of the molecule, and, most importantly, our inability to repeat this fermentation result it was decided to carry out an X-ray analysis of gilmaniellin (**2**).

Single crystals of gilmaniellin (**2**) could be grown from chloroform/methanol mixtures. Preliminary X-ray photographs displayed monoclinic symmetry and accurate lattice constants of a = 9.385 (6), b = 13.394 (12), c = 9.773 (6) Å and β = 94.10 (5)° were determined by a least-squares fit of 15 moderate 2θ-values measured by a computer controlled diffractometer.

Systematic absences and a density measurement suggested space group $P2_1$ with an asymmetric unit of $C_{26}H_{19}ClO_{10} \cdot 2\,CH_3OH$. All unique diffraction maxima with $2\theta \leq 114.1°$ were measured on an automated fourcircle diffractometer using an ω-scan technique and graphite monochromated CuK_α (1.54178 Å) X-rays. Of the 1700 reflections surveyed in this fashion, 1466 (86%) were judged observed after correction for *Lorentz*, polarization and background effects.

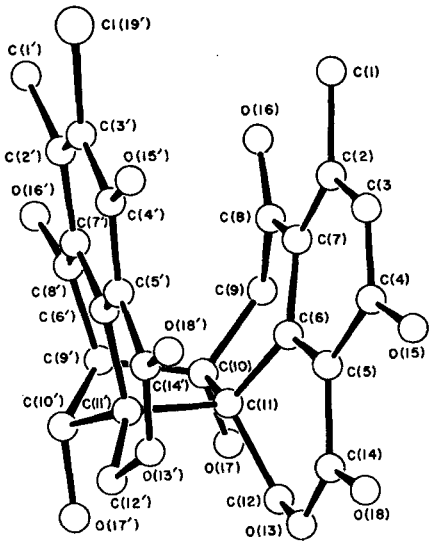


Fig. 2. *Stereoscopic projection of gilmaniellin* (**2**)

A phasing model was achieved by a weighted multi-solution tangent formula approach[2]). A plausible fragment from this was used in the tangent formula recycling procedure to reveal all non hydrogen atoms of gilmaniellin. One of the carbon atoms from one of the CH_3OH of crystallization could not be located even on difference syntheses and is believed to be totally disordered. All of the hydrogen atoms

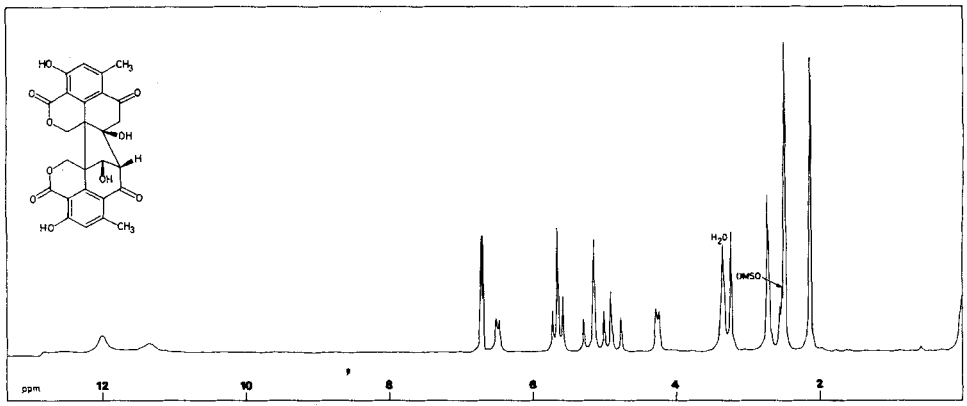


Fig. 3. *^{1}H-NMR. spectrum of dechlorogilmaniellin* (**1**) *in (D_6)DMSO* with TMS as an internal standard

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[2]) All crystallographic calculations were done on a *Prime* 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were: REDUCE and UNIQUE, data reduction programs, *M.E. Leonowicz*, Cornell University, 1978; BLS, block diagonal least-squares refinement, *K. Hirotsu*, Cornell University, 1978; ORFLS (modified), full-matrix least-squares, *W.R. Busing, K.O. Martin & H.S. Levy*, Oak Ridge, ORNL-TM-305; ORTEP, crystallographic illustration program, *C. Johnson*, Oak Ridge, ORNL-3794, BOND, structural parameters and errors, *K. Hirotsu*, Cornell University, 1978; MULTAN-76, direct methods and fast *Fourier* transform, *G. Germain, P. Main & M. Woolfson*, University of York.

of gilmaniellin were located on a difference synthesis and included in the refinement. Full matrix least-squares refinements with anisotropic non hydrogens and isotropic hydrogens have converged to a standard crystallographic residual of 0.057 for the observed reflections. The absolute configuration was not determined by the X-ray experiment. *Table 1* contains the final fractional coordinates and thermal parameters, *Table 2* the bond distances, and *Table 3* the bond angles. Observed and calculated structure factors may be obtained from the authors *[J. C.]*.

Figure 2 is a computer-generated drawing of the final X-ray model of gilmaniellin (**2**) without hydrogen atoms. In general all bond distances and angles agree well with accepted values. There is a long bond between C(11) and C(11′) of 1.598 Å. Such long bonds have been noted before between fully substituted sp^3 carbon atoms. There are three intramolecular hydrogen bonds: O(15)H · · · O(18) of 2.60 Å, O(15)H · · · O(18′) of 2.58 Å and O(17)H · · · O(17′) of 2.85 Å. There are three intermolecular hydrogen bonds and all other contacts correspond to normal *Van der Waals'* contacts.

Dechlorogilmaniellin (**1**) has the molecular formula $C_{26}H_{20}O_{10}$ determined by high resolution mass spectrometry. On treatment with acetic anhydride/pyridine it yielded the tri-*O*-acetylderivative **4**. IR., UV. and ^{1}H-NMR. spectra of **1** and **4** were very similar to those of **2** and **3** respectively. The only difference in the ^{1}H-NMR. spectra of **1** and **2** (see *Fig. 1* and *3*) was the appearance of a new aromatic proton at 6.61 ppm in the former. This proton showed an allylic coupling of 0.6 Hz with the methyl group at 2.45 ppm, thus suggesting that chlorine atom present in **2** has been replaced by a hydrogen atom, a fact also supported by the mass spectral fragmentation pattern *(Scheme 2)*. Based on above evidence structure **1** is proposed for dechlorogilmaniellin.

Scheme 2

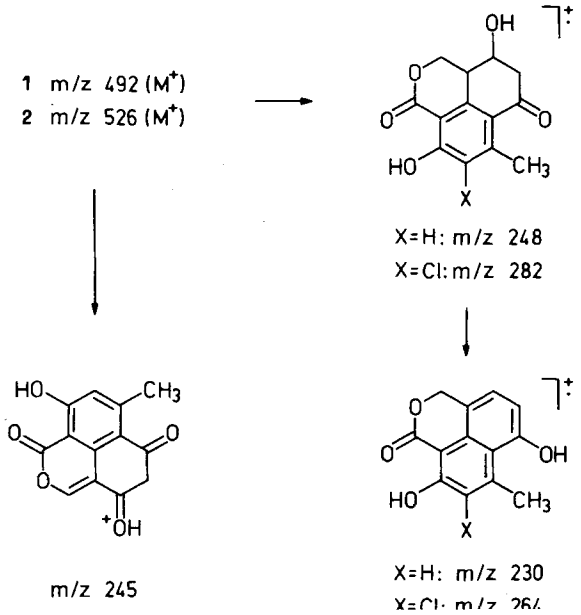


Table 1. *Fractional coordinates and temperature factors for gilmaniellin.* Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded.

Atom	X	Y	Z	B11 or B	B22	B33	B12	B13	B23
C(1)	0.5354 (12)	0.3270 (9)	0.1772 (9)	0.0182 (15)	0.0100 (8)	0.0126 (10)	0.0020 (10)	0.0028 (10)	−0.0010 (7)
C(2)	0.5218 (8)	0.3110 (6)	0.3288 (7)	0.0114 (10)	0.0078 (6)	0.0125 (9)	0.0009 (6)	0.0005 (8)	0.0005 (6)
C(3)	0.3934 (9)	0.3157 (7)	0.3782 (8)	0.0105 (11)	0.0092 (6)	0.0141 (10)	0.0008 (7)	−0.0022 (9)	0.0014 (7)
C(4)	0.3696 (8)	0.3110 (6)	0.5179 (8)	0.0121 (10)	0.0066 (5)	0.0143 (10)	−0.0010 (6)	0.0029 (8)	0.0009 (6)
C(5)	0.4871 (8)	0.2930 (6)	0.6089 (7)	0.0113 (10)	0.0070 (5)	0.0130 (9)	−0.0007 (6)	0.0026 (8)	0.0004 (6)
C(6)	0.6242 (8)	0.2788 (6)	0.5624 (7)	0.0119 (10)	0.0071 (5)	0.0091 (8)	−0.0003 (6)	0.0008 (7)	−0.0008 (5)
C(7)	0.6445 (8)	0.2978 (6)	0.4253 (8)	0.0131 (11)	0.0059 (5)	0.0164 (11)	0.0016 (6)	0.0057 (9)	0.0005 (6)
C(8)	0.7918 (8)	0.3052 (6)	0.3839 (7)	0.0116 (10)	0.0085 (6)	0.0138 (9)	0.0002 (6)	0.0034 (8)	0.0036 (6)
C(9)	0.9011 (9)	0.3222 (9)	0.4989 (10)	0.0086 (11)	0.0108 (8)	0.0187 (13)	−0.0017 (7)	0.0047 (10)	0.0023 (8)
C(10)	0.8977 (8)	0.2508 (6)	0.6190 (8)	0.0125 (11)	0.0078 (6)	0.0147 (11)	0.0008 (6)	0.0034 (9)	0.0003 (6)
C(11)	0.7396 (9)	0.2351 (6)	0.6623 (8)	0.0112 (10)	0.0069 (5)	0.0137 (10)	0.0000 (6)	0.0035 (8)	0.0007 (6)
C(12)	0.7207 (8)	0.2838 (7)	0.8010 (8)	0.0112 (11)	0.0093 (7)	0.0112 (9)	−0.0009 (7)	0.0007 (8)	0.0003 (7)
O(13)	0.5787 (6)	0.2733 (5)	0.8477 (5)	0.0150 (8)	0.0092 (4)	0.0119 (6)	0.0007 (5)	0.0042 (6)	−0.0009 (4)
C(14)	0.4657 (9)	0.2850 (7)	0.7585 (8)	0.0163 (12)	0.0079 (6)	0.0143 (10)	0.0001 (7)	0.0064 (9)	−0.0008 (7)
O(15)	0.2371 (6)	0.3236 (6)	0.5533 (8)	0.0109 (8)	0.0115 (6)	0.0169 (10)	0.0002 (5)	0.0030 (7)	0.0000 (6)
O(16)	0.8212 (6)	0.3070 (5)	0.2648 (6)	0.0169 (9)	0.0130 (6)	0.0164 (8)	−0.0006 (6)	0.0075 (7)	0.0031 (6)
O(17)	0.9842 (5)	0.2943 (5)	0.7270 (5)	0.0128 (7)	0.0093 (4)	0.0165 (7)	−0.0012 (4)	−0.0005 (5)	−0.0016 (5)
O(18)	0.3465 (6)	0.2897 (5)	0.8006 (5)	0.0129 (7)	0.0115 (5)	0.0150 (7)	0.0002 (5)	0.0049 (6)	−0.0011 (5)
C(1′)	0.8094 (14)	0.0380 (12)	0.1645 (10)	0.0231 (19)	0.0131 (12)	0.0098 (10)	−0.0008 (13)	0.0046 (11)	−0.0006 (9)
C(2′)	0.7114 (8)	0.0515 (6)	0.2791 (7)	0.0141 (11)	0.0068 (5)	0.0138 (9)	0.0015 (6)	0.0044 (8)	0.0011 (5)
C(3′)	0.5674 (9)	0.0393 (6)	0.2551 (7)	0.0180 (13)	0.0071 (5)	0.0132 (9)	−0.0004 (7)	0.0051 (8)	−0.0008 (6)
C(4′)	0.4719 (8)	0.0426 (5)	0.3599 (7)	0.0158 (10)	0.0062 (5)	0.0141 (9)	−0.0002 (6)	0.0009 (8)	0.0005 (5)
C(5′)	0.5279 (8)	0.0614 (5)	0.4943 (7)	0.0158 (11)	0.0062 (5)	0.0106 (8)	−0.0004 (6)	0.0030 (7)	0.0001 (5)
C(6′)	0.6732 (7)	0.0810 (5)	0.5214 (6)	0.0128 (9)	0.0062 (4)	0.0104 (7)	0.0007 (5)	0.0015 (7)	0.0009 (5)
C(7′)	0.7685 (7)	0.0763 (6)	0.4158 (7)	0.0106 (9)	0.0071 (5)	0.0132 (8)	0.0012 (6)	0.0024 (7)	0.0000 (5)
C(8′)	0.9202 (8)	0.1034 (6)	0.4490 (7)	0.0139 (10)	0.0085 (6)	0.0138 (9)	0.0022 (7)	0.0038 (8)	0.0014 (6)
C(9′)	0.9552 (9)	0.1452 (6)	0.5961 (8)	0.0135 (11)	0.0097 (7)	0.0137 (10)	0.0003 (7)	0.0031 (8)	0.0001 (6)
C(10′)	0.8796 (8)	0.0827 (7)	0.6946 (8)	0.0154 (11)	0.0067 (6)	0.0168 (11)	0.0014 (7)	0.0049 (8)	−0.0008 (6)
C(11′)	0.7216 (7)	0.1164 (6)	0.6628 (7)	0.0122 (9)	0.0073 (5)	0.0136 (9)	−0.0009 (6)	0.0046 (7)	−0.0003 (5)
C(12′)	0.6341 (9)	0.0689 (7)	0.7645 (8)	0.0199 (13)	0.0069 (6)	0.0100 (9)	0.0015 (7)	0.0020 (9)	−0.0004 (6)
O(13′)	0.4803 (5)	0.0770 (4)	0.7336 (4)	0.0138 (6)	0.0085 (4)	0.0109 (6)	−0.0001 (4)	0.0029 (5)	0.0004 (4)
C(14′)	0.4281 (7)	0.0643 (6)	0.6047 (8)	0.0099 (8)	0.0073 (5)	0.0153 (10)	0.0003 (6)	0.0022 (7)	0.0003 (6)
O(15′)	0.3344 (7)	0.0307 (6)	0.3246 (7)	0.0154 (9)	0.0099 (5)	0.0151 (8)	−0.0032 (5)	0.0025 (7)	−0.0012 (6)
O(16′)	1.0126 (5)	0.0916 (6)	0.3730 (5)	0.0135 (7)	0.0154 (6)	0.0158 (7)	0.0009 (6)	0.0064 (6)	−0.0030 (6)
O(17′)	0.9269 (6)	0.1004 (5)	0.8312 (5)	0.0158 (8)	0.0098 (5)	0.0117 (6)	0.0014 (5)	−0.0006 (6)	−0.0007 (5)
O(18′)	0.2995 (5)	0.0582 (5)	0.5813 (5)	0.0117 (6)	0.0102 (5)	0.0163 (7)	−0.0008 (5)	0.0040 (6)	0.0006 (5)
Cl(19′)	0.4892 (2)	0.0177 (2)	0.0903 (2)	0.0214 (3)	0.0113 (2)	0.0125 (2)	−0.0016 (2)	0.0018 (2)	−0.0012 (2)
C(50)	0.1649 (17)	0.1895 (12)	0.0857 (13)	0.0405 (31)	0.0137 (11)	0.0216 (18)	−0.0047 (16)	0.0007 (18)	0.0037 (13)
O(51)	0.1559 (9)	0.2694 (9)	0.0016 (9)	0.0248 (14)	0.0206 (10)	0.0311 (14)	0.0030 (10)	0.0142 (11)	0.0076 (11)
O(52)	0.9817 (10)	0.4220 (6)	0.0864 (9)	0.0391 (19)	0.0120 (7)	0.0315 (15)	−0.0091 (9)	0.0176 (14)	−0.0070 (8)

H1A	0.609 (10)	0.393 (8)	0.205 (10)	9.7 (27)
H1B	0.585 (8)	0.279 (6)	0.162 (7)	3.9 (19)
H1C	0.451 (10)	0.289 (13)	0.171 (13)	13.1 (40)
H3	0.325 (7)	0.322 (5)	0.335 (7)	3.2 (16)
H9A	0.875 (9)	0.401 (8)	0.513 (9)	8.2 (24)
H9B	0.965 (9)	0.318 (6)	0.459 (7)	4.4 (18)
H12A	0.778 (7)	0.357 (5)	0.822 (6)	5.0 (15)
H12B	0.795 (5)	0.259 (4)	0.875 (5)	1.4 (10)
H15	0.249 (12)	0.322 (10)	0.620 (10)	8.8 (38)
H17	0.998 (11)	0.225 (8)	0.798 (11)	7.2 (30)
H1'A	0.792 (8)	0.080 (7)	0.098 (9)	5.8 (20)
H1'B	0.889 (10)	0.068 (7)	0.173 (8)	6.1 (26)
H1'C	0.802 (11)	−0.017 (9)	0.119 (11)	10.2 (30)
H9'	1.063 (7)	0.148 (4)	0.621 (6)	4.0 (14)
H10'	0.896 (6)	0.018 (5)	0.688 (5)	2.8 (13)
H12'A	0.646 (5)	0.097 (4)	0.852 (6)	2.2 (12)
H12'B	0.668 (7)	0.002 (5)	0.770 (6)	3.3 (14)
H15'	0.305 (12)	0.032 (10)	0.386 (10)	8.4 (37)
H17'	0.988 (10)	0.051 (8)	0.876 (10)	6.2 (28)

Table 2. *Bond distances of gilmaniellin.* The standard deviation of the least significant figure of each distance is given in parenthesis

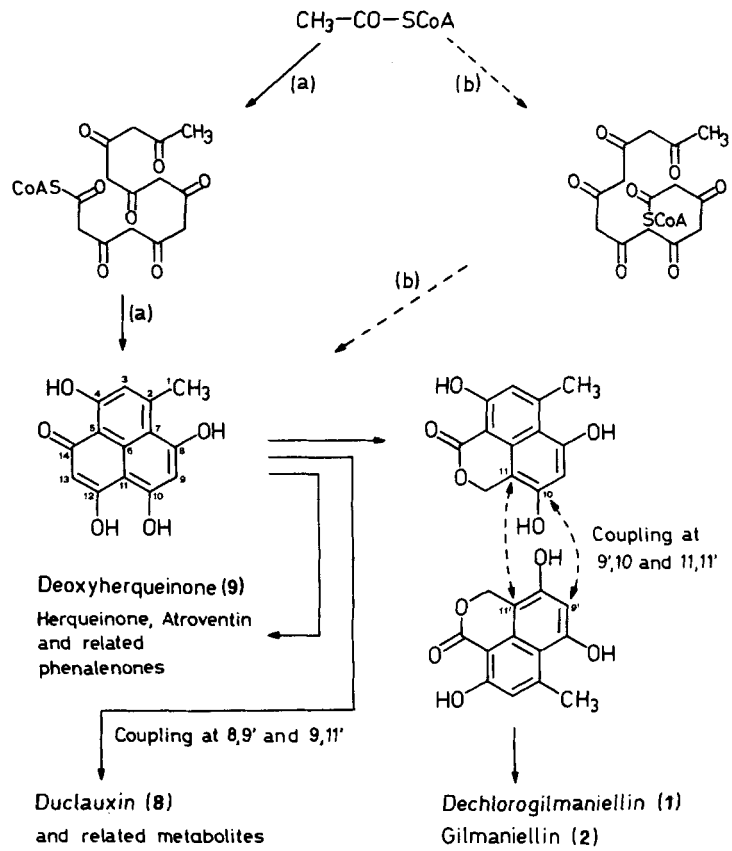
C(1) -C(2)	1.512 (11)	C(1') -C(2')	1.510 (14)
C(2) -C(3)	1.332 (11)	C(2') -C(3')	1.365 (11)
C(2) -C(7)	1.446 (10)	C(2') -C(7')	1.442 (10)
C(3) -C(4)	1.400 (11)	C(3') -C(4')	1.409 (11)
C(4) -C(5)	1.387 (10)	C(3') -Cl(19')	1.746 (7)
C(4) -O(15)	1.325 (10)	C(4') -C(5')	1.402 (10)
C(5) -C(6)	1.408 (11)	C(4') -O(15')	1.321 (10)
C(5) -C(14)	1.494 (11)	C(5') -C(6')	1.395 (10)
C(6) -C(7)	1.390 (11)	C(5') -C(14')	1.480 (11)
C(6) -C(11)	1.522 (11)	C(6') -C(7')	1.415 (9)
C(7) -C(8)	1.471 (11)	C(6') -C(11')	1.500 (9)
C(8) -C(9)	1.484 (11)	C(7') -C(8')	1.483 (10)
C(8) -O(16)	1.215 (9)	C(8') -C(9')	1.556 (10)
C(9) -C(10)	1.516 (13)	C(8') -O(16')	1.192 (9)
C(10)-C(11)	1.586 (12)	C(9') -C(10')	1.493 (12)
C(10)-O(17)	1.410 (9)	C(10')-C(11')	1.560 (10)
C(10)-C(9')	1.536 (11)	C(10')-O(17')	1.397 (9)
C(11)-C(12)	1.526 (11)	C(11')-C(12')	1.479 (11)
C(11)-C(11')	1.598 (11)	C(12')-O(13')	1.458 (10)
C(12)-O(13)	1.446 (10)	O(13')-C(14')	1.329 (9)
O(13)-C(14)	1.333 (9)	C(14')-O(18')	1.215 (8)
C(14)-O(18)	1.221 (10)	C(50) -O(51)	1.349 (18)

Table 3. *Bond angles of gilmaniellin.* The standard deviation of the least significant figure of each angle is given in parenthesis

C(1) -C(2) -C(3)	119.4 (7)	C(1′) -C(2′) -C(7′)	120.6 (7)
C(1) -C(2) -C(7)	122.5 (7)	C(3′) -C(2′) -C(7′)	119.0 (7)
C(3) -C(2) -C(7)	117.9 (7)	C(2′) -C(3′) -C(4′)	123.0 (6)
C(2) -C(3) -C(4)	124.2 (7)	C(2′) -C(3′) -Cl(19′)	121.6 (6)
C(3) -C(4) -C(5)	117.3 (7)	C(4′) -C(3′) -Cl(19′)	115.4 (6)
C(3) -C(4) -O(15)	117.8 (7)	C(3′) -C(4′) -C(5′)	118.1 (7)
C(5) -C(4) -O(15)	124.9 (7)	C(3′) -C(4′) -O(15′)	117.8 (6)
C(4) -C(5) -C(6)	121.3 (7)	C(5′) -C(4′) -O(15′)	124.1 (7)
C(4) -C(5) -C(14)	118.9 (7)	C(4′) -C(5′) -C(6′)	120.5 (7)
C(6) -C(5) -C(14)	119.7 (6)	C(4′) -C(5′) -C(14′)	118.3 (7)
C(5) -C(6) -C(7)	118.6 (7)	C(6′) -C(5′) -C(14′)	121.2 (6)
C(5) -C(6) -C(11)	118.0 (6)	C(5′) -C(6′) -C(7′)	120.8 (6)
C(7) -C(6) -C(11)	123.2 (7)	C(5′) -C(6′) -C(11′)	117.5 (6)
C(2) -C(7) -C(6)	119.5 (7)	C(7′) -C(6′) -C(11′)	121.4 (6)
C(2) -C(7) -C(8)	122.1 (7)	C(2′) -C(7′) -C(6′)	118.3 (6)
C(6) -C(7) -C(8)	118.3 (6)	C(2′) -C(7′) -C(8′)	123.1 (6)
C(7) -C(8) -C(9)	114.5 (7)	C(6′) -C(7′) -C(8′)	118.5 (6)
C(7) -C(8) -O(16)	123.2 (7)	C(7′) -C(8′) -C(9′)	115.2 (6)
C(9) -C(8) -O(16)	122.0 (7)	C(7′) -C(8′) -O(16′)	124.2 (7)
C(8) -C(9) -C(10)	116.0 (8)	C(9′) -C(8′) -O(16′)	120.6 (7)
C(9) -C(10) -C(11)	111.3 (6)	C(10) -C(9′) -C(8′)	114.4 (6)
C(9) -C(10) -O(17)	106.0 (7)	C(10) -C(9′) -C(10′)	103.5 (7)
C(9) -C(10) -C(9′)	116.2 (7)	C(8′) -C(9′) -C(10′)	108.4 (7)
C(11) -C(10) -O(17)	110.7 (6)	C(9′) -C(10′) -C(11′)	101.4 (6)
C(11) -C(10) -C(9′)	105.2 (6)	C(9′) -C(10′) -O(17′)	112.8 (7)
O(17) -C(10) -C(9′)	107.4 (6)	C(11′) -C(10′) -O(17′)	112.0 (6)
C(6) -C(11) -C(10)	114.5 (6)	C(11) -C(11′) -C(6′)	109.7 (6)
C(6) -C(11) -C(12)	106.4 (6)	C(11) -C(11′) -C(10′)	100.9 (6)
C(6) -C(11) -C(11′)	108.3 (6)	C(11) -C(11′) -C(12′)	119.6 (7)
C(10) -C(11) -C(12)	110.5 (6)	C(6′) -C(11′) -C(10′)	108.3 (6)
C(10) -C(11) -C(11′)	103.5 (6)	C(6′) -C(11′) -C(12′)	109.7 (6)
C(12) -C(11) -C(11′)	113.8 (7)	C(10′) -C(11′) -C(12′)	107.9 (6)
C(11) -C(12) -O(13)	114.0 (6)	C(11′) -C(12′) -O(13′)	114.7 (6)
C(12) -O(13) -C(14)	119.4 (6)	C(12′) -O(13′) -C(14′)	118.7 (5)
C(5) -C(14) -O(13)	119.5 (7)	C(5′) -C(14′) -O(13′)	119.0 (6)
C(5) -C(14) -O(18)	121.1 (7)	C(5′) -C(14′) -O(18′)	122.2 (7)
O(13) -C(14) -O(18)	119.4 (7)	O(13′) -C(14′) -O(18′)	118.8 (7)
C(1′) -C(2′) -C(3′)	120.4 (7)		

Discussion. – Gilmaniellin (**2**) and dechlorogilmaniellin (**1**) show a close resemblance to duclauxin (**8**) [4] and related metabolites [5] isolated from *Penicilium duclauxi*, and bear an obvious structural relationship to the known methylphenalenones [6]. Tracer experiments [7] have shown that duclauxin (**8**) is derived from a polyketide precursor through the intermediacy of a hypothetical phenalenone intermediate. The origin of this intermediate from a single heptaketide chain instead of multi-chain condensations was also confirmed and folding (**a**) of the heptaketide chain over the alternate folding (**b**) was favoured. *Barton et al.* [8] proposed a similar polyketide pathway for the biosynthesis of phenalenone skeletons in atroventin, herqueinone, norherqueinone and other related metabolites (folding (**a**) again being favoured over the alternate (**b**); see *Scheme 3*). Biosynthetic studies on

Scheme 3



norherqueinone by *Thomas* [9] substantiated these proposals. However, recent biosynthetic studies by *Simpson* [10] on deoxyherqueinone (**9**) using ^{13}C-NMR. techniques have revealed beyond doubt that the phenalenone skeleton is derived through the alternate folding (**b**). Probably this conclusion is also true for all the compounds with the phenalenone skeleton. At present there is no indication as to the stage at which the coupling of the monomer units takes place. This could involve either coupling of two independent methylphenalenones followed by independent oxidative ring cleavage or alternatively the coupling of two oxaphenalenones. While duclauxin (**8**) and related metabolites are derived through dimerization at 9,11′ and 8,9′ (numbering based on the intermediate polyketide chain), gilmaniellin (**2**) and dechlorogilmaniellin (**1**) are formed through couplings at 9,10′ and 11,11′. The gilmaniellins constitute the first example of oxaphenalenone dimers derived through this mode of coupling.

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Table 4. *Observed and calculated structure factors for gilmaniellin*

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H,K=	0	0	6	34	31	5	33	34	6	11	11
1	476	461	7	26	24	6	24	22	8	34	34
2	125	119	8	16	15	7	18	21	9	22	21
3	39	35	9	30	32	8	12	11	10	11	14
4	109	97	10	10	7	H,K=	0	10	H,K=	1	1
5	14	14	H,K=	0	5	0	47	50	−9	22	23
6	42	46	−3	43	44	1	11	9	−8	38	38
7	9	7	−2	181	166	2	18	17	−7	15	16
9	27	27	−1	237	221	3	31	33	−6	45	45
H,K=	0	1	1	231	221	4	31	31	−5	42	40
1	213	208	2	176	166	5	34	33	−4	113	116
2	80	75	3	43	44	6	14	14	−3	170	167
3	119	114	4	62	64	7	21	20	−2	245	232
4	167	156	5	32	34	H,K=	0	11	−1	156	145
5	23	19	6	39	40	1	56	60	0	252	265
6	20	21	8	25	26	2	20	22	1	183	142
7	24	25	9	15	14	3	40	43	2	267	233
8	42	43	H,K=	0	6	5	12	10	3	47	45
9	13	14	0	176	176	H,K=	0	12	4	164	157
10	18	14	1	70	65	0	22	22	5	63	60
H,K=	0	2	2	45	44	1	50	54	6	14	18
0	232	214	3	40	40	2	24	21	7	23	26
1	145	135	4	19	21	3	16	13	8	31	28
2	40	39	5	84	85	4	11	14	9	34	36
3	100	87	6	23	25	5	10	12	10	18	17
4	75	77	7	25	27	H,K=	0	13	H,K=	1	2
5	141	134	8	10	15	1	23	22	−10	17	18
6	57	56	H,K=	0	7	2	11	6	−9	16	13
7	22	21	1	175	174	3	16	15	−8	86	91
9	11	8	2	11	13	4	17	13	−7	55	56
10	11	11	3	34	35	H,K=	0	14	−6	85	91
H,K=	0	3	4	96	95	0	17	17	−5	167	180
1	247	221	5	52	54	1	11	6	−4	122	114
2	52	48	6	21	20	H,K=	1	0	−3	200	203
3	109	102	7	15	13	−10	12	6	−2	88	92
4	142	131	8	21	19	−8	60	57	−1	81	79
5	88	89	9	9	3	−7	86	83	0	127	125
6	18	19	H,K=	0	8	−6	64	62	1	165	152
7	19	20	0	201	210	−5	104	104	3	38	40
8	16	19	1	126	124	−4	170	157	4	199	178
9	18	15	2	31	31	−3	37	38	5	141	134
10	16	13	4	56	57	−2	171	162	6	99	100
H,K=	0	4	6	40	41	−1	91	68	7	20	21
0	995	991	8	16	13	0	304	318	9	10	9
1	416	386	H,K=	0	9	1	50	41	10	20	16
2	149	138	1	54	53	2	51	50	H,K=	1	3
3	60	61	2	41	42	3	101	104	−10	11	9
4	59	55	3	53	58	4	138	137	−9	10	9
5	35	38	4	29	33	5	167	151	−8	55	55

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
−7	36	38	4	92	93	−3	59	58	2	45	46
−6	33	33	5	62	66	−2	73	71	3	13	15
−5	18	16	6	15	16	−1	22	19	4	14	15
−4	165	162	7	47	45	0	121	118	5	17	21
−3	112	109	8	27	28	1	155	163	6	15	11
−2	157	157	9	10	6	2	51	51	H,K=	1	12
−1	68	65	H,K=	1	6	3	30	32	−5	15	16
0	83	89	−9	28	28	4	49	51	−4	12	11
1	210	205	−8	52	49	5	40	38	−3	13	15
2	134	136	−6	37	36	6	24	22	0	26	28
3	91	82	−5	60	60	H,K=	1	9	1	43	49
4	191	177	−4	109	108	−8	19	17	2	12	12
5	67	62	−3	58	58	−7	24	27	3	20	21
6	52	48	−2	24	26	−5	27	27	4	21	21
7	24	25	−1	125	122	−4	23	23	H,K=	1	13
8	27	28	0	107	111	−3	50	47	−1	20	19
9	35	37	1	21	25	−2	36	33	0	11	10
10	11	8	2	29	32	−1	49	51	1	20	21
H,K=	1	4	3	62	64	0	19	22	2	12	11
−9	15	18	4	80	82	1	76	80	3	18	19
−8	36	37	5	28	29	2	38	39	H,K=	1	14
−7	65	65	6	31	33	3	48	51	0	12	10
−6	60	59	7	40	43	4	34	37	1	16	11
−5	72	65	H,K=	1	7	5	28	32	2	12	14
−4	153	146	−9	19	20	6	15	22	H,K=	2	0
−3	116	114	−8	39	35	7	38	37	−9	59	56
−2	111	101	−7	50	49	H,K=	1	10	−8	74	77
−1	57	52	−6	17	14	−7	11	11	−7	54	60
0	443	426	−5	10	7	−6	12	10	−6	26	27
1	151	140	−4	70	68	−4	51	49	−5	54	56
2	84	86	−3	41	40	−3	28	28	−4	92	93
3	92	89	−2	57	56	−2	21	22	−3	46	43
4	93	91	−1	38	39	−1	21	21	−2	49	47
5	59	60	0	93	91	0	16	15	−1	139	128
6	36	37	1	144	141	1	19	23	0	232	229
8	26	24	2	56	57	2	40	45	1	66	70
H,K=	1	5	3	26	27	3	35	39	2	41	43
−8	47	46	4	79	81	4	11	11	3	27	18
−7	27	28	5	42	40	5	32	36	4	30	31
−6	10	12	6	42	41	6	18	20	5	76	76
−5	33	31	7	21	20	7	18	16	6	64	65
−4	87	86	8	14	11	H,K=	1	11	7	13	16
−3	62	64	9	16	17	−6	11	9	10	15	14
−2	73	65	H,K=	1	8	−4	33	33	H,K=	2	1
−1	44	46	−8	31	27	−3	19	19	−10	28	26
0	157	157	−7	16	15	−2	12	11	−9	35	39
1	135	128	−6	10	8	−1	25	25	−8	104	112
2	23	24	−5	45	44	0	18	18	−7	41	41
3	85	78	−4	33	33	1	49	49	−6	37	39

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
−5	70	67	1	76	74	−9	32	31	7	27	24
−4	68	69	2	154	145	−8	39	39	H,K =	2	9
−3	143	146	3	120	119	−7	53	55	−7	40	34
−2	99	86	4	108	103	−6	30	34	−5	25	21
−1	218	205	5	46	44	−5	19	19	−4	39	40
0	132	143	7	85	91	−4	53	54	−2	16	18
1	129	123	8	55	56	−3	27	29	−1	61	63
2	94	81	9	18	19	−2	71	69	0	39	39
3	81	78	H,K =	2	4	−1	39	37	1	60	64
4	173	164	−10	10	6	0	32	34	2	36	37
5	52	46	−9	33	32	1	68	69	3	41	41
6	16	15	−8	49	49	2	67	67	4	38	39
7	112	114	−7	43	45	3	32	36	5	19	18
8	70	75	−6	42	44	5	52	55	6	13	11
9	14	14	−5	36	36	7	30	33	7	23	22
10	10	7	−4	17	19	9	13	8	H,K =	2	10
H,K =	2	2	−3	9	9	H,K =	2	7	−7	28	25
−10	13	13	−2	90	86	−9	31	27	−6	21	20
−9	30	32	−1	25	24	−7	42	41	−5	24	24
−8	63	72	0	64	65	−6	27	28	−4	38	38
−7	83	86	1	79	82	−5	17	14	−3	21	20
−6	74	76	2	111	109	−4	82	82	−2	43	44
−5	51	49	3	54	60	−3	45	41	−1	22	22
−4	58	53	4	11	9	−2	84	87	0	22	22
−3	10	13	5	97	103	−1	27	28	1	42	47
−2	47	47	6	52	51	0	52	51	2	38	40
−1	77	76	7	30	32	1	26	27	3	13	17
0	122	124	8	21	19	2	100	102	H,K =	2	11
1	181	160	H,K =	2	5	3	21	20	−6	10	10
2	134	136	−9	18	17	4	16	15	−5	12	8
3	49	49	−8	51	50	5	31	33	−4	34	33
4	15	18	−7	69	67	6	18	18	−3	11	11
5	66	68	−6	21	24	7	32	33	−2	19	18
6	32	29	−5	51	50	8	37	34	0	21	20
7	46	45	−4	53	57	H,K =	2	8	1	30	33
8	31	31	−3	134	124	−8	15	11	2	36	36
10	13	14	−2	119	113	−7	27	25	3	22	22
H,K =	2	3	−1	123	123	−6	31	31	4	10	8
−10	17	15	0	72	73	−4	40	40	5	11	11
−9	49	48	1	72	68	−3	43	44	6	13	12
−8	73	80	2	47	50	−2	34	37	H,K =	2	12
−7	43	44	3	16	16	−1	19	20	−5	22	21
−6	34	35	4	113	115	0	47	51	−3	21	19
−5	48	50	5	33	38	1	20	20	−2	16	18
−4	78	77	6	28	32	2	52	53	−1	16	18
−3	201	200	7	67	71	3	30	29	0	15	15
−2	101	100	8	30	32	4	15	18	1	17	19
−1	84	88	9	21	23	5	56	62	2	10	6
0	176	175	H,K =	2	6	6	55	59	3	13	14

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
4	16	19	H,K =	3	2	3	95	95	−1	98	98
5	16	12	−9	31	31	4	45	51	0	17	15
H,K =	2	13	−8	26	28	5	36	33	1	51	55
−1	15	13	−7	41	42	6	34	34	2	47	46
8	18	21	−6	54	58	7	29	27	3	34	35
1	24	27	−5	38	42	8	26	26	4	45	47
2	16	16	−4	58	59	9	14	13	5	16	16
3	16	14	−3	70	71	H,K =	3	5	6	22	20
H,K =	2	14	−2	73	78	−8	47	45	7	21	22
1	10	6	−1	54	50	−7	15	18	8	13	10
H,K =	3	0	0	35	36	−6	31	31	H,K =	3	8
−10	15	14	1	144	145	−5	36	34	−8	29	24
−9	12	13	2	93	96	−4	59	57	−7	35	33
−7	24	24	3	142	138	−3	48	49	−6	30	29
−5	35	35	4	22	18	−2	61	62	−5	10	12
−4	67	67	5	73	77	−1	57	54	−4	32	31
−3	95	91	6	17	19	0	51	53	−3	26	29
−2	62	63	8	32	29	1	44	45	−2	39	39
−1	106	108	9	23	23	2	35	31	−1	40	40
0	33	32	H,K =	3	3	3	127	133	1	21	22
1	273	263	−9	23	23	4	46	50	2	63	63
2	17	14	−7	27	26	5	22	23	3	27	31
3	145	132	−6	22	25	6	14	15	5	16	16
4	69	69	−5	53	55	7	63	63	6	17	16
5	74	76	−4	139	142	8	17	20	7	16	19
6	35	39	−3	134	133	9	15	13	H,K =	3	9
7	34	34	−2	93	92	H,K =	3	6	−7	26	22
8	52	52	−1	188	192	−7	36	35	−6	25	27
9	18	16	0	29	28	−6	13	21	−5	30	31
H,K =	3	1	1	70	72	−5	46	52	−4	21	21
−9	16	16	2	116	116	−4	68	70	−3	33	33
−8	40	40	3	66	64	−3	73	74	−1	16	15
−7	36	39	4	44	43	−2	56	55	1	20	18
−6	12	11	6	28	29	−1	52	51	3	36	40
−5	31	31	7	27	28	0	86	90	4	27	27
−4	101	95	8	31	32	1	25	26	5	18	19
−3	259	252	9	15	10	2	33	31	6	14	12
−2	181	184	H,K =	3	4	3	51	53	7	22	19
−1	166	166	−9	17	18	5	15	17	H,K =	3	10
0	82	78	−8	30	31	6	15	14	−7	11	8
1	90	86	−7	29	29	7	26	23	−6	33	30
2	156	150	−5	10	18	8	35	31	−4	22	20
3	197	193	−4	77	77	H,K =	3	7	−3	41	40
4	19	15	−3	35	35	−8	13	7	−2	21	23
5	45	42	−2	75	74	−7	32	33	−1	22	22
6	14	11	−1	67	69	−5	25	23	0	12	9
7	62	67	0	100	98	−4	65	65	2	13	10
8	33	39	1	145	137	−3	51	53	3	21	22
9	13	14	2	71	73	−2	30	29	4	11	8

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
6	11	14	0	74	75	−7	26	29	−8	31	28
H,K=	3	11	1	54	51	−6	33	37	−6	45	40
−6	22	18	2	34	33	−5	31	28	−5	18	16
−5	10	11	3	74	73	−4	27	25	−4	22	21
−4	26	27	4	38	37	−3	54	56	−3	38	37
−2	32	32	5	32	32	−2	64	63	−2	108	109
−1	27	25	6	21	20	−1	88	85	−1	34	33
0	10	16	7	34	33	0	57	54	0	46	47
1	22	18	8	10	16	1	128	127	1	19	23
2	21	25	H,K=	4	2	2	33	31	2	26	27
3	15	15	−8	32	33	3	74	74	3	24	22
4	29	30	−7	22	22	4	34	30	4	32	35
5	13	9	−6	48	54	5	59	57	5	13	11
H,K=	3	12	−5	59	64	6	32	31	6	17	18
−5	11	13	−4	73	71	7	14	15	7	12	10
−4	15	10	−3	60	61	H,K=	4	5	H,K=	4	8
−1	19	16	−2	204	203	−9	14	12	−7	32	30
0	12	12	−1	54	55	−7	55	58	−6	18	19
1	15	13	0	109	113	−6	26	28	−5	26	29
2	22	24	1	101	101	−5	47	48	−3	22	25
H,K=	3	13	2	70	68	−4	14	11	−2	23	25
−2	20	17	3	32	34	−3	118	117	−1	20	19
0	11	14	4	11	15	−2	29	29	0	12	16
1	14	9	5	32	30	−1	92	92	1	43	47
H,K=	4	0	6	24	26	0	44	41	3	27	29
−8	20	23	7	29	33	1	18	18	4	15	10
−7	33	35	9	17	17	2	25	25	5	27	27
−6	51	50	H,K=	4	3	3	28	31	6	13	17
−5	61	62	−9	18	14	4	50	52	7	21	18
−4	87	91	−8	24	24	5	40	40	H,K=	4	9
−3	10	12	−7	24	24	6	17	12	−7	34	31
−2	153	151	−6	32	34	7	23	25	−6	19	18
−1	182	175	−5	37	38	H,K=	4	6	−5	32	29
0	153	145	−4	60	60	−7	32	33	−4	16	14
1	172	164	−3	57	56	−6	24	26	−3	47	46
2	45	43	−2	138	145	−5	15	19	−2	42	41
3	139	138	−1	108	106	−4	25	24	−1	10	5
4	47	50	0	100	100	−3	46	48	0	26	27
5	18	20	1	55	53	−2	95	88	2	17	14
6	51	57	2	26	28	−1	49	49	3	16	18
7	17	19	3	68	67	0	32	32	4	20	22
H,K=	4	1	4	32	35	1	45	48	5	12	10
−9	17	15	5	17	14	2	34	35	6	13	10
−7	37	37	6	15	17	3	39	39	H,K=	4	10
−5	35	37	7	23	23	4	19	15	−5	28	25
−4	11	15	8	37	36	5	11	7	−4	20	17
−3	79	80	9	14	14	7	13	12	−2	13	15
−2	143	144	H,K=	4	4	8	20	18	−1	44	44
−1	119	109	−8	17	15	H,K=	4	7	0	20	21

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
2	12	14	−1	120	125	−2	76	75	−3	15	16
3	23	23	0	77	79	−1	32	32	−2	24	26
4	19	23	1	51	57	0	42	45	−1	39	43
5	12	9	2	53	55	1	34	35	0	33	32
H,K=	4	11	3	42	42	2	81	86	1	35	34
−3	15	12	4	41	43	3	38	40	2	22	20
−2	35	33	5	26	25	4	42	44	3	16	18
−1	17	13	6	13	13	5	44	50	4	44	47
0	14	14	8	30	32	6	33	37	5	23	24
1	18	17	H,K=	5	2	7	20	22	H,K=	5	8
2	12	13	−7	37	39	8	14	15	−7	23	20
3	26	26	−6	55	57	H,K=	5	5	−6	28	27
4	18	17	−5	47	50	−8	14	14	−4	29	32
H,K=	4	12	−4	23	20	−7	48	48	−2	18	16
−4	13	10	−3	75	76	−6	80	81	−1	31	32
−3	18	17	−2	18	10	−4	16	19	0	24	24
1	17	18	−1	79	79	−3	15	17	1	44	45
2	11	14	0	163	160	−2	32	34	2	18	17
3	21	19	1	87	82	−1	96	97	3	35	38
H,K=	4	13	2	29	28	0	12	10	4	40	39
−2	15	14	3	61	63	1	20	19	5	15	15
1	15	9	4	12	12	2	20	22	6	20	18
H,K=	5	0	5	84	84	3	55	56	H,K=	5	9
−9	23	24	6	22	24	4	44	44	−6	15	11
−8	24	24	7	19	21	5	24	24	−2	21	23
−7	44	46	8	12	5	6	11	9	−1	43	46
−5	12	10	H,K=	5	3	7	12	13	0	22	21
−4	26	28	−8	33	34	8	15	9	1	16	20
−3	10	18	−7	48	50	H,K=	5	6	2	13	12
−2	74	71	−6	110	112	−8	21	19	3	39	35
−1	26	23	−5	13	12	−7	13	13	4	20	21
0	83	77	−4	30	29	−6	22	25	5	16	12
1	29	25	−3	31	32	−5	59	61	H,K=	5	10
2	70	74	−2	93	91	−4	33	38	−5	19	18
3	10	5	0	42	45	−3	18	18	−4	26	27
4	16	4	1	78	79	−2	29	34	−2	28	25
5	92	92	2	18	19	−1	56	58	−1	13	10
6	34	37	3	16	17	0	59	56	0	12	11
7	25	22	4	64	64	1	74	75	1	31	31
8	15	14	6	19	18	2	11	10	2	12	11
H,K=	5	1	8	29	29	3	42	46	3	28	26
−9	22	19	H,K=	5	4	4	20	28	4	12	12
−8	22	19	−9	13	15	5	36	35	H,K=	5	11
−7	75	78	−8	18	18	6	22	23	−3	23	21
−6	125	132	−7	48	50	7	28	25	−2	20	18
−5	17	17	−6	25	28	H,K=	5	7	−1	25	23
−4	43	45	−5	25	24	−7	24	22	0	19	14
−3	37	35	−4	34	34	−6	51	48	2	18	16
−2	89	90	−3	32	29	−4	12	13	3	11	12

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
4	21	20	5	49	53	−5	32	32	−1	12	11
H,K=	5	12	7	16	18	−4	42	45	0	21	22
−1	14	11	H,K=	6	3	−3	33	35	1	25	24
0	12	7	−8	13	16	−2	36	34	3	14	13
1	16	15	−7	22	21	−1	25	25	H,K=	6	11
H,K=	6	0	−6	62	66	0	25	26	−2	24	21
−8	41	43	−5	18	16	1	18	20	−1	13	11
−7	53	56	−4	17	16	2	22	24	0	13	11
−6	35	35	−3	77	80	3	13	11	1	11	7
−4	14	13	−1	29	32	4	39	42	2	16	13
−2	52	52	0	27	25	5	32	31	H,K=	7	0
−1	65	69	1	12	8	6	16	14	−7	19	20
0	66	71	2	21	21	H,K=	6	7	−6	13	7
1	23	23	3	18	22	−6	43	42	−5	14	12
3	67	63	4	46	46	−5	36	35	−4	12	4
4	33	32	5	46	46	−4	33	33	−3	101	102
5	59	60	6	20	21	−3	46	47	−2	41	39
6	20	16	H,K=	6	4	−2	38	33	−1	27	26
8	14	13	−8	29	26	0	15	15	0	51	51
H,K=	6	1	−7	31	32	1	19	17	1	67	68
−8	23	24	−6	37	36	3	11	11	2	43	43
−7	50	51	−5	21	21	4	27	26	3	11	6
−6	72	77	−4	36	35	5	23	23	5	12	10
−5	27	29	−3	19	24	H,K=	6	8	6	22	22
−4	15	17	−2	50	49	−6	26	24	H,K=	7	1
−3	58	60	−1	22	24	−5	17	19	−8	31	31
−2	30	31	0	68	67	−4	19	17	−7	15	16
−1	53	56	1	41	40	−3	12	11	−6	31	31
0	43	43	2	36	37	−2	39	39	−4	22	26
1	42	43	3	47	51	−1	13	9	−3	114	118
2	13	6	5	37	37	0	50	51	−2	34	37
3	59	57	H.K=	6	5	1	30	30	−1	23	20
4	55	57	−8	40	34	2	24	27	0	61	62
5	74	74	−7	47	44	3	20	16	2	19	15
6	48	50	−6	41	41	4	16	13	3	16	18
H,K=	6	2	−5	28	31	5	13	14	4	33	32
−8	29	29	−4	15	11	H,K=	6	9	5	17	17
−7	50	54	−3	28	24	−5	18	17	7	13	5
−6	30	32	−2	33	34	−4	21	22	H,K=	7	2
−5	36	37	−1	20	26	−3	20	18	−7	21	19
−4	92	97	0	38	40	−2	14	10	−6	22	21
−3	39	35	1	15	15	−1	53	50	−5	14	9
−2	30	28	3	30	33	0	28	29	−4	27	27
−1	12	9	4	36	35	1	16	17	−3	59	64
0	42	44	5	50	48	2	22	20	−1	33	38
1	29	29	6	39	38	3	16	17	0	20	18
2	48	51	H,K=	6	6	H,K=	6	10	1	117	124
3	18	11	−7	22	21	−4	29	24	2	45	46
4	35	35	−6	20	18	−3	13	9	5	40	42

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
6	19	24	2	19	20	−3	86	86	2	37	38
H,K=	7	3	3	20	16	−2	42	44	4	26	24
−7	30	31	4	12	13	−1	21	20	H,K=	8	6
−6	21	20	5	21	23	0	14	5	−5	13	9
−4	20	19	H,K=	7	7	1	36	37	−4	16	13
−3	83	84	−5	23	22	2	53	54	−3	19	19
−2	57	62	−4	25	25	3	25	19	−2	22	26
−1	47	46	−3	47	44	4	18	17	−1	23	25
0	14	12	−2	41	40	5	22	20	0	17	15
1	24	20	−1	36	37	H,K=	8	2	1	69	68
3	25	28	0	28	31	−6	15	15	2	37	36
4	19	18	1	14	14	−5	18	17	3	26	25
6	14	14	3	20	18	−4	15	16	H,K=	8	7
H,K=	7	4	H,K=	7	8	−3	29	27	−4	17	19
−7	44	40	−5	20	18	−2	32	34	−3	39	37
−6	16	8	−4	56	53	−1	13	13	−2	19	19
−4	60	63	−3	24	26	0	39	39	0	33	35
−3	69	72	−2	21	18	1	107	113	1	10	12
−2	36	32	−1	14	17	2	23	25	2	20	16
−1	19	17	0	15	8	3	13	17	3	13	11
0	37	38	1	24	24	5	18	18	H,K=	8	8
1	49	48	3	12	14	H,K=	8	3	−3	17	20
2	35	38	H,K=	7	9	−6	20	18	−2	31	26
3	11	8	−4	22	22	−5	25	29	1	21	17
4	13	6	−3	13	8	−4	33	35	H,K=	9	0
5	13	13	−2	28	24	−3	85	88	−4	20	23
6	15	13	0	26	23	−2	26	30	−2	22	18
H,K=	7	5	1	15	10	−1	28	26	−1	18	16
−7	20	21	2	17	13	0	23	22	1	26	23
−6	22	19	H,K=	7	10	1	32	32	2	15	20
−5	25	24	−1	11	7	2	35	38	H,K=	9	1
−4	40	41	0	29	28	3	22	20	−5	15	15
−3	71	70	1	19	18	H,K=	8	4	−4	16	17
−2	32	36	H,K=	8	0	−4	33	36	−3	34	39
−1	20	18	−7	14	12	−3	27	24	−2	13	14
0	62	64	−5	18	20	−2	41	41	0	25	18
1	32	30	−4	43	48	−1	11	13	1	29	27
2	28	21	−3	25	23	0	33	27	2	28	31
4	14	17	−1	23	23	1	41	41	4	11	7
5	21	26	0	40	35	2	17	20	H,K=	9	2
6	16	14	1	57	58	4	18	18	−4	25	25
H,K=	7	6	2	33	32	H,K=	8	5	−3	48	51
−5	20	21	3	15	16	−5	31	26	−2	15	17
−4	38	36	4	21	21	−4	18	17	−1	20	16
−3	13	15	5	16	13	−3	30	30	1	44	43
−2	24	21	H,K=	8	1	−2	45	47	2	17	17
−1	29	29	−7	15	16	−1	16	15	3	15	11
0	43	46	−5	31	36	0	13	19	H,K=	9	3
1	59	58	−4	25	27	1	40	39	−3	17	15

Table 4 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
−1	18	18	−2	11	13	−3	40	36	H,K=	9	6
0	17	17	−1	16	18	−2	12	12	0	15	15
1	23	19	0	13	13	−1	27	25	1	34	29
2	14	14	1	16	16	0	13	11	H,K=	10	1
3	13	12	2	20	16	1	23	19	−2	15	10
H,K=	9	4	H,K=	9	5	2	21	21	−1	13	14

Experimental Part

General Methods. The melting points were determined on a *Kofler* block and are uncorrected. IR. (cm^{-1}) and optical rotations were measured on a *Perkin-Elmer* Model 125 grating spectrometer and *Perkin-Elmer* Model 141 polarimeter respectively. The 90 MHz-^{1}H-NMR. spectra (δ ppm, J Hz) were recorded with a *Bruker* WH-90 spectrometer with *Fourier* transform in the spectral laboratory of our institute *(K. Aegerter)*. We thank Dr. *H. Lichti, Sandoz AG*, Basel, for measurements of high resolution MS. on CEC 21-110 H instrument. Preparative thin layer chromatography (TLC.) was carried out on silica gel PF 254 *(Merck)* and for column chromatography silica gel 0.05–0.2 mm *(Merck)* was used.

Isolation of products. The culture medium contained 55 g glucose H_2O, 10 g NH_4NO_3, 5 g KH_2PO_4, 2,5 g $MgSO_4 \cdot 7\ H_2O$, and 30 mg $FeCl_3 \cdot 6\ H_2O$ per liter of demineralised water. Six 500-ml Erlenmeyer flasks containing 160 ml of sterilized medium were innoculated with 1 ml of spore suspension of *Gilmaniella humicola* BARRON under sterile conditions. These flasks were shaken on a rotatory shaker at 200 revolutions/minute at 27° for 6 days. Both the mycelium and the medium were then extracted with ethyl acetate. The organic extracts were washed twice with water, dried (Na_2SO_4) and evaporated *in vacuo* at 40°. The crude extract was chromatographed on silica gel using increasing amounts of methanol in CH_2Cl_2 to yield 48 mg of gilmaniellin (**2**), 31 mg of dechlorogilmaniellin (**1**) and 16 mg of (−)-6-hydroxy-mellein (**5**).

Gilmaniellin (**2**) crystallized from methanol/$CHCl_3$ mixtures as colourless cubes, m.p. > 350°, $[\alpha]_D^{20} = -132 \pm 2°$ ($c = 0.07$, $CHCl_3$/methanol 1:1). – IR. (KBr): 3500–3200, 1700–1600. – ^{1}H-NMR. ((D_6)DMSO): 2.07 (*s*, 3 H); 2.62 (*s*, 3 H); 2.70 (*s*, 2 H); 3.28 (*s*, 1 H); 4.25 (*d*, $J = 4.1$, 1 H); 4.81 (*d*, $J = 12.6$, 1 H); 4.98 (*d*, $J = 13.2$, 1 H); 5.12 (*d*, $J = 12.6$, 1 H); 5.6 (*d*, $J = 13.2$, 1 H); 5.68 (*s*, 1 H, O*H* exchangeable with D_2O); 6.45 (*d*, $J = 4.1$, 1 H, exchangeable with D_2O); 6.67 (*d*, $J = 0.6$, 1 H); 11.95 (*s*, 1 H, exchangeable with D_2O); 12.1 (br., 1 H, exchangeable with D_2O). – MS.: 526.0654 (M^+, calc. for $C_{26}H_{19}ClO_{10}$: 526.0667).

Acetylation of gilmaniellin (**2**) *to the tri-O-acetylderivative* **3**. A solution of 8 mg of gilmaniellin (**2**) in 2 ml of absolute pyridine and 1 ml of acetic anhydride was stirred at RT. for 18 h. The solvent was then removed in high vacuum and the residue purified by preparative TLC. (CH_2Cl_2/methanol 95:5) to give 6 mg of tri-*O*-acetylgilmaniellin (**3**) as white crystals, m.p. 215–217°, $[\alpha]_D^{20} = -114 \pm 2°$ ($c = 0.08$, $CHCl_3$). – IR. ($CHCl_3$): 3400, 1760, 1750, 1742, 1700, 1690, 1605. – ^{1}H-NMR. ($CDCl_3$): 2.2 (*d*, $J = 0.6$, 3 H); 2.28 (*s*, 3 H); 2.29 (*s*, 3 H); 2.39 (*s*, 3 H); 2.65 (*d*, $J = 15$, 1 H); 2.83 (*s*, 3 H); 3.02 (*d*, $J = 15$, 1 H); 3.61 (*s*, 1 H); 4.45 (*d*, $J = 12.6$, 1 H); 5.02 (*d*, $J = 13$, 1 H); 5.25 (*d*, $J = 13$, 1 H); 5.24 (br., 1 H, exchangeable with D_2O); 5.45 (*d*, $J = 12.6$, 1 H); 6.85 (*d*, $J = 0.6$, 1 H). – MS.: 652 (M^+, calc. for $C_{32}H_{25}ClO_{13}$: 652).

Dechlorogilmaniellin (**1**) crystallized from $CHCl_3$/methanol mixtures or from acetone as colourless plates, m.p. > 330° (dec.); $[\alpha]_D^{20} = -130 \pm 2°$ ($c = 0.05$ $CHCl_3$/methanol 1:1), $[\alpha]_D^{20} = -128 \pm 2°$ ($c = 0.267$ acetone). – IR. (KBr): 3500–3400, 1700–1600. – ^{1}H-NMR. ((D_6)DMSO): 2.1 (*d*, $J = 0.8$, 3 H); 2.45 (*d*, $J = 0.8$, 3 H); 2.7 (*s*, 2 H); 3.21 (*s*, 1 H); 4.23 (*d*, $J = 3.7$, 1 H); 4.8 (*d*, $J = 13$, 1 H); 5.06 (*d*, $J = 12.6$, 1 H); 5.18 (*d*, $J = 13$, 1 H); 5.6 (*d*, $J = 12.6$, 1 H); 5.6 (*s*, 1 H, exchangeable with D_2O); 6.45 (*d*, $J = 3.7$, 1 H, exchangeable with D_2O); 6.65 (*d*, $J = 0.8$, 1 H); 6.69 (*d*, $J = 0.8$, 1 H); 11.35 (br., 1 H, exchangeable with D_2O); 11.95 (br., 1 H, exchangeable with D_2O). – MS.: 492.1069 (M^+, calc. for $C_{26}H_{20}O_{10}$: 492.1057).

Acetylation of dechlorogilmaniellin (**1**) *to the tri-O-acetylderivative* **4**. A solution of 7 mg of dechlorogilmaniellin (**1**) in 2 ml of pyridine and 1 ml of acetic anhydride was stirred at RT. for 18 h. The solvent was then evaporated in *vacuo* and the residue purified by preparative TLC. (CH_2Cl_2/methanol 95:5) to yield 4.2 mg of crystalline tri-*O*-acetyldechlorogilmaniellin (**4**), m.p. 198–200°; $[\alpha]_D^{20} = -116 \pm 2°$ ($c = 0.064$ $CHCl_3$). – IR. (KBr): 3450, 1750, 1745, 1700, 1694, 1600. – ^{1}H-NMR. ($CDCl_3$): 2.19 (*d*, $J = 0.8$, 3 H); 2.27 (*s*, 3 H); 2.30 (*s*, 3 H); 2.37 (*s*, 3 H); 2.75 (*d*, $J = 15$, 1H); 2.6 (*d*, $J = 0.8$, 3 H); 2.96 (*d*, $J = 15$, 1H); 3.64 (*s*, 1H); 4.40 (*d*, $J = 12.8$, 1H); 5.0 (*d*, $J = 13$, 1H); 5.2 (*d*, $J = 13$, 1H); 5.26 (*s*, 1H, exchangeable with D_2O); 5.4 (*d*, $J = 12.8$, 1H); 6.8 (*d*, $J = 0.8$, 1H); 6.85 (*d*, $J = 0.8$, 1H). – MS.: 618 (M^+, calc. for $C_{32}H_{26}O_{13}$: 618).

(−)-*6-Hydroxy-mellein* (**5**) crystallized as prisms from acetone/hexane, m.p. 212–213° (lit. [2] 214–215°); sublimed at 139°/0.06 mm (lit. 140°/0.06 mm); $[\alpha]_D^{20} = -64 \pm 2°$ ($c = 0.134$ methanol) (lit. [2] $[\alpha]_D = -63°$ ($c = 0.6$ ethanol)). – UV. (ethanol): 270, 305 (4.11, 3.76). – IR.: 1648. – ^{1}H-NMR. ($CDCl_3$): 1.38 (*d*, $J = 6$, 3 H); 2.9 (*m*, 2 H); 4.7 (*m*, 1 H); 6.19 (*d*, $J = 2.6$, 1 H); 6.22 (*d*, $J = 2.6$, 1 H); 10.59 (1 H, exchangeable with D_2O); 11.12 (1 H, exchangeable with D_2O). – MS.: 194 (M^+, calc. for $C_{10}H_{10}O_4$: 194).

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