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The Crystal and Molecular Structure of Emericellin, A Metabolite of *Aspergillus nidulans*

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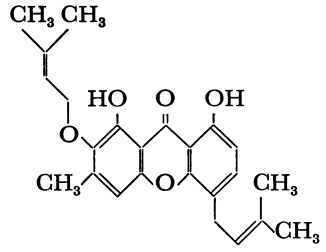
Synopsis. The crystal and molecular structure of emericellin has been determined by the X-ray diffraction method. The compound crystallizes in the space group $P\bar{1}$, with $a=8.667$, $b=14.665$, $c=9.157$ Å, $\alpha=88.29$, $\beta=113.10$, and $\gamma=91.61°$. The structure was refined to an R value of 0.086 for 2151 non-zero reflections. There are two intramolecular hydrogen bonds.

Emericellin was isolated as a new metabolite of *Aspergillus nidulans* (Eidam) Winter.[1] The isolation and the chemical structure (shown below), proposed on the basis of the chemical and spectroscopic data, have been reported previously.[1] In order to confirm this, an X-ray structure analysis has been undertaken as part of the investigation of the metabolites of the genus *Aspergillus*.[2,3]



Emericellin crystallized from an ethanol solution in the form of yellow prisms. Preliminary oscillation and Weissenberg photographs showed that the crystals were triclinic and that there was no significant reflection in the region of $2\theta>110°$ (Cu $K\alpha$ radiation). Measurement was made by manually operating a Toshiba four-circle diffractometer. The cell constants were obtained by least-squares fits of the θ values for 49 reflections. Crystal data: $C_{25}H_{28}O_5$, $M=408.5$, triclinic, $P\bar{1}$, $a=8.667(5)$, $b=14.665(7)$, $c=9.157(5)$ Å, $\alpha=88.29(9)$, $\beta=113.10(9)$, $\gamma=91.61(9)°$, $V=1070$ Å^3, $Z=2$, $D_o=1.28$ g/cm^3, $D_x=1.27$ g/cm^3. The intensities of 2584 independent reflections were measured with Ni-filtered Cu $K\alpha$ radiation up to $\sin\theta/\lambda=0.531$ from a specimen with dimensions of *ca.* $0.21\times0.15\times0.06$ mm. The stationary-crystal stationary-counter method was used, with a counting time of 30 seconds. The background for each reflection was taken from plots of the background as a function of 2θ. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The structure was deduced from an interpretation of the three-dimensional Patterson map, followed by successive Fourier syntheses. The coordinates and isotropic temperature factors of all the non-hydrogen atoms were refined with the carbon scattering factor. Five oxygen atoms were assigned by an inspection of the temperature factors. When an R value reached 0.12 by further refinement with anisotropic temperature factors, the positions of all the hydrogen atoms were derived from a difference Fourier synthesis. The final refinement, made by including the hydrogen atoms, used the following weighting scheme: $w=0.0$ for $F_o=0$, $w=1.0$ for $0<F_o\leqq17$, and $w=1.0/(1.0+0.3(F_o-17))$ for $17<F_o$. The final R value is 0.086 for 2151 non-zero reflections. The final atomic parameters are given in Tables 1 and 2.

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[4] The computations were performed on a TOSBAC-3400 computer at the Tottori University Computing Center and on a NEAC 2200-N700 computer at the Computation Center of Osaka University.

The structural formula of emericellin has been confirmed by the present X-ray analysis. A stereo-

Table 1. Final atomic parameters and their estimated standard deviations ($\times10^4$) for carbon and oxygen atoms

The anisotropic temperature factors are of the form;
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	259(6)	638(3)	2647(6)	209(10)	46(3)	147(8)	28(8)	159(15)	11(7)
C(2)	-919(6)	-11(3)	1838(5)	170(9)	52(3)	134(8)	32(8)	151(14)	18(7)
C(3)	-362(6)	-816(3)	1358(5)	152(9)	57(3)	135(8)	5(8)	115(13)	4(8)
C(4)	-1441(6)	-1593(4)	569(6)	168(9)	64(3)	134(8)	-8(9)	105(14)	10(8)
C(5)	-678(6)	-2347(3)	146(6)	182(10)	49(3)	139(8)	14(8)	114(14)	-5(7)
C(6)	-1601(6)	-3112(4)	-618(6)	191(10)	54(3)	176(9)	-10(9)	117(16)	-5(8)
C(7)	-830(7)	-3822(4)	-995(7)	247(12)	57(3)	184(10)	-10(10)	116(18)	-38(9)
C(8)	891(7)	-3767(4)	-606(7)	238(12)	66(3)	175(10)	31(10)	135(17)	-18(9)
C(9)	1874(6)	-3035(4)	159(6)	181(10)	60(2)	147(8)	11(9)	95(15)	4(8)
C(10)	1037(6)	-2324(3)	528(6)	189(10)	48(3)	151(8)	19(8)	126(15)	-8(8)
C(11)	1359(6)	-881(3)	1726(6)	184(10)	48(3)	147(8)	9(8)	147(15)	0(7)
C(12)	2522(6)	-219(3)	2521(6)	169(9)	55(3)	143(8)	-1(8)	122(14)	-7(8)
C(13)	1993(6)	547(3)	3019(6)	201(10)	54(3)	136(8)	-5(8)	131(15)	3(8)
C(14)	3239(7)	1272(4)	3904(7)	240(12)	60(3)	181(10)	-29(10)	124(18)	-32(9)
C(15)	-237(8)	1350(4)	4697(6)	287(13)	55(3)	172(9)	30(10)	208(18)	-7(9)
C(16)	43(7)	2260(4)	5440(6)	207(11)	61(3)	179(9)	18(9)	152(16)	-30(9)
C(17)	-1146(7)	2859(4)	5240(7)	245(12)	59(3)	197(10)	22(10)	182(18)	-13(9)
C(18)	-704(10)	3755(4)	6108(9)	402(19)	63(4)	316(15)	19(13)	395(28)	-23(12)
C(19)	-2933(9)	2717(5)	4164(11)	234(15)	98(5)	489(23)	53(14)	114(30)	-44(18)
C(20)	-2761(7)	158(4)	1424(6)	179(10)	72(3)	166(9)	37(9)	125(16)	14(9)
C(21)	3753(7)	-2982(4)	566(7)	215(11)	71(3)	190(10)	54(10)	141(17)	-9(10)
C(22)	4756(7)	-3122(4)	2324(7)	188(11)	70(3)	208(10)	31(10)	132(17)	-42(10)
C(23)	5605(7)	-3860(4)	3068(7)	195(11)	62(3)	192(10)	6(9)	134(17)	-28(9)
C(24)	5774(11)	-4666(5)	2192(8)	509(23)	73(4)	219(13)	132(16)	118(27)	-62(12)
C(25)	6550(8)	-3914(5)	4835(7)	260(14)	84(4)	210(11)	34(12)	70(20)	-15(11)
O(1)	-3465(4)	-417(3)	2292(4)	195(7)	87(3)	209(7)	25(7)	215(12)	21(7)
O(2)	-2998(4)	-1606(3)	262(5)	160(7)	74(2)	249(8)	-14(6)	156(11)	-51(7)
O(3)	-3294(5)	-3178(3)	-1012(5)	192(7)	72(2)	263(8)	-40(7)	155(12)	-68(7)
O(4)	2043(4)	-1611(2)	1294(4)	158(6)	51(2)	179(6)	10(5)	125(10)	-29(5)
O(5)	-221(5)	1433(2)	3114(4)	259(8)	52(2)	159(6)	47(6)	171(11)	10(5)

Table 2. Positional parameters ($\times10^3$) and isotropic temperature factors (Å^2) for hydrogen atoms

	x	y	z	B		x	y	z	B
H(1)	-146(7)	-442(4)	156(7)	5.2(15)	H(2)	147(7)	-432(4)	-79(7)	5.1(14)
H(3)	379(6)	-30(3)	266(6)	3.3(11)	H(4)	465(7)	118(4)	404(7)	5.6(15)
H(5)	353(8)	129(4)	512(7)	6.7(16)	H(6)	531(8)	174(4)	328(7)	6.8(16)
H(7)	63(7)	90(4)	534(7)	4.6(14)	H(8)	-139(7)	106(4)	455(7)	4.7(14)
H(9)	124(7)	246(4)	614(7)	5.1(14)	H(10)	-154(8)	373(5)	639(8)	7.0(18)
H(11)	-96(8)	430(5)	529(8)	7.0(18)	H(12)	48(9)	387(5)	684(8)	7.8(19)
H(13)	-361(10)	331(6)	335(10)	10.7(24)	H(14)	-349(10)	215(6)	468(10)	10.7(24)
H(15)	-343(10)	211(5)	332(9)	9.8(22)	H(16)	-350(6)	8(4)	18(6)	3.9(12)
H(17)	-286(7)	89(4)	177(7)	4.7(14)	H(18)	-372(8)	-106(4)	195(7)	6.2(16)
H(19)	-351(8)	-267(4)	-62(8)	6.8(17)	H(20)	408(7)	-235(4)	26(6)	4.2(13)
H(21)	404(7)	-346(4)	-8(6)	4.0(13)	H(22)	486(7)	-258(4)	309(7)	4.8(14)
H(23)	613(10)	-510(5)	272(9)	9.7(22)	H(24)	473(10)	-490(6)	134(10)	9.9(23)
H(25)	584(10)	-455(5)	112(9)	9.7(22)	H(26)	630(9)	-331(5)	503(8)	8.2(19)
H(27)	766(8)	-384(5)	506(8)	6.9(17)	H(28)	627(7)	-450(4)	529(7)	5.8(16)

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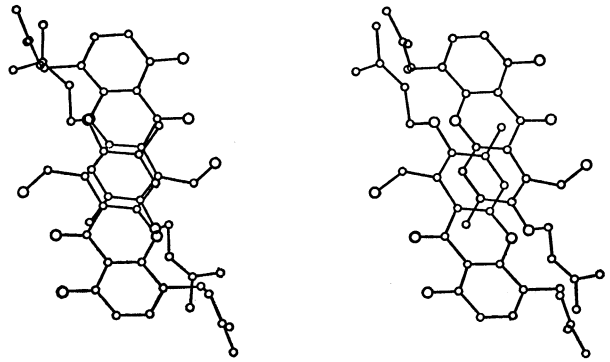
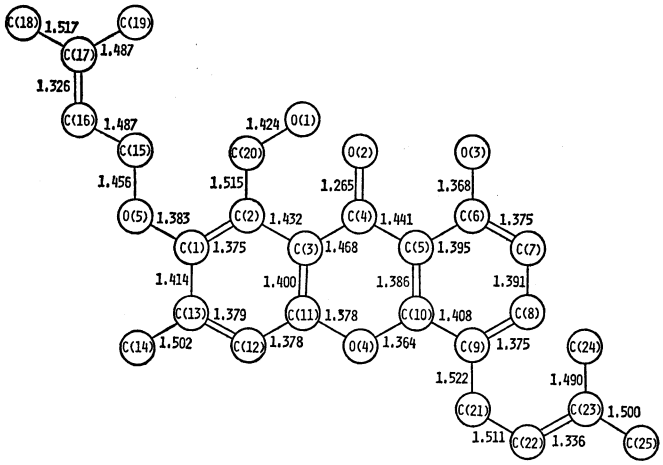


Fig. 1. Stereoscopic view of a pair of melecules.



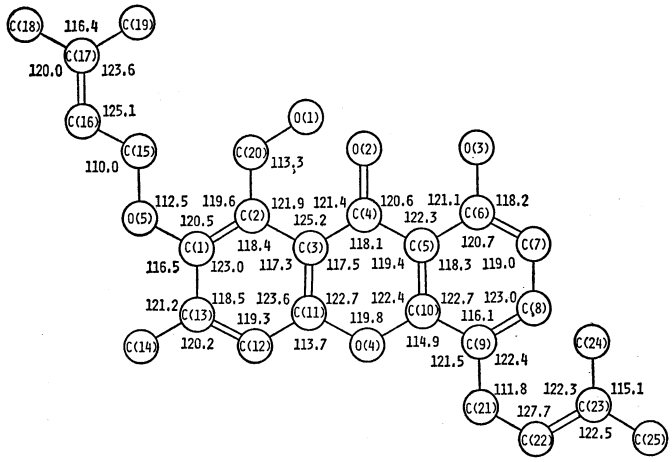


Fig. 2. Bond lengths (Å) and angles (°) for non-hydrogen atoms.
The e. s. d.'s of bond lengths and angles are about 0.008 Å and 0.5° respectively.

scopic view of the pair of molecules is shown in Fig. 1. The bond lengths and angles for non-hydrogen atoms are shown in Fig. 2. The bond lengths and angles in the xanthone skeleton are comparable with those found in sterigmatin.[2] There is a screw-like twist along the longitudinal axis of the skeleton; the twist angle between the two outer benzenoid rings is about

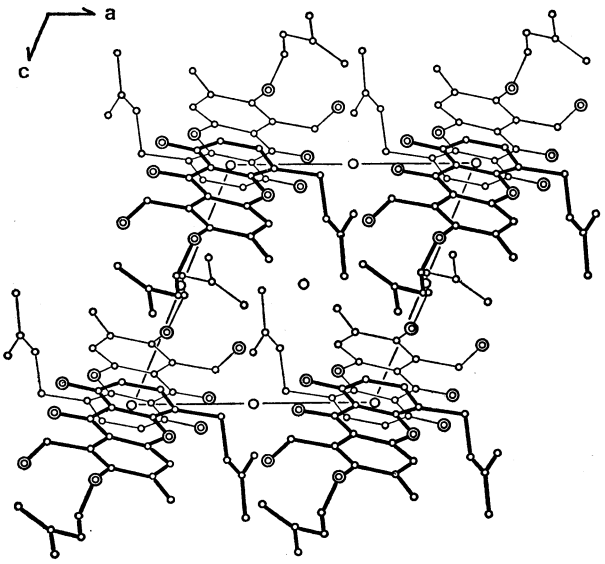


Fig. 3. The crystal structure of emericellin viewed along the b axis. The hydrogen atoms are omitted in the figure.

3°. The C(20) atom is largely displaced from the least-squares plane passing through the 14 ring atoms in the skeleton. The corresponding bond lengths and angles in the two isopentenyl groups are similar to each other. There are two intramolecular hydrogen bonds, O(1)–H(18)·····O(2) and O(3)–H(19)·····O(2). The distances of O(1)·····O(2) and O(3)·····O(2) are 2.736 and 2.575 Å respectively, while the angles of O(1)–H(18)·····O(2) and O(3)–H(19)·····O(2) are 122° and 154° respectively.

The crystal structure viewed along the b axis is shown in Fig. 3. There are only three kinds of close contacts; plane to plane contact of the xanthone skeletons around (0, 0, 0), contact between the isopentenyl group and the xanthone skeleton around (0, 0, 1/2), and head-to-tail contact between the molecules related by unit translation along the a axis. Except for these contacts, the crystal consists of a loose-packed array, and there is no intermolecular hydrogen bond. These are in accordance with the relatively low density of the crystal.

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