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The Crystal and Molecular Structure of Sterigmatin, A Metabolite of *Aspergillus versicolor*

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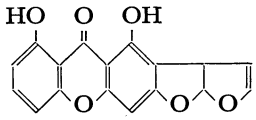
Synopsis. The crystal structure of sterigmatin has been determined by single-crystal X-ray analysis. The crystals are triclinic; space group P1, $Z=2$, with $a=14.392(4)$, $b=14.120(4)$, $c=4.256(2)$ Å, $\alpha=78.22(3)$, $\beta=100.42(3)$, $\gamma=56.90(3)$ °. The structure was refined to an R value of 0.039 for 1961 reflections. There are two intramolecular hydrogen bonds in each of the crystallographically independent molecules.

Sterigmatin was isolated as a metabolite of *Aspergillus versicolor* (Vuillemin) Tiraboschi, and its structural formula was shown to be as follows.[1]



As part of a program of research on the structures of metabolites of this mold,[2,3] the structure of sterigmatin has been studied by means of the X-ray diffraction method.

Sterigmatin was crystallized from acetone in the form of pale yellow needles elongated along the c-axis. The crystals are triclinic; space group P1, $Z=2$, with $a=14.392(4)$, $b=14.120(4)$, $c=4.256(2)$ Å, $\alpha=78.22(3)$, $\beta=100.42(3)$, $\gamma=56.90(3)$ °. The intensities were collected on a Rigaku Denki computer-controlled four-circle diffractometer using Ni-filtered Cu-$K\alpha$ radiation. The ω-2θ scan technique was employed, with a scan speed of 2 ° min^{-1} in ω. The background was measured for 5 s at both the start and end points of the scan range. A total of 1968 intensities were collected, with $\sin\theta/\lambda<0.562$. The crystal used was so small (*ca.* $0.06\times0.07\times0.25$ mm) that the intensities were corrected only for the Lorentz and polarization factors.

The orientations of the xanthone skeletons of the crystallographically independent molecules were easily determined by the application of the convolution molecule method.[4] Since the origin could be arbitrarily chosen for the P1 space group, the Fourier synthesis based on the phases due to one of the xanthone skeletons revealed the other xanthone skeleton. The structure obtained by successive Fourier syntheses was refined by a block-diagonal least-squares method. Seven intense reflections with low-order indices were omitted from the refinement and difference Fourier synthesis because of the extinction effect. The difference electron density map revealed all the hydrogen atoms. The refinement was continued by including the hydrogen atoms until the R value of 0.039 for 1961 reflections. The unit weight was applied for all reflections. The final atomic parameters of the two molecules (A and B) are listed in Tables 1 and 2. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5] 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.

Since the corresponding bond lengths and angles of the two crystallographically independent molecules do not differ significantly, we may use the mean values given in Fig. 1 and Table 3 for the discussion of the

TABLE 1. FINAL ATOMIC PARAMETERS AND e.s.d.'s ($\times10^4$) FOR NON-HYDROGEN 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(A1)	2959(3)	3202(3)	-2639(10)	46(3)	51(3)	392(27)	-57(6)	80(15)	-79(16)
C(A2)	2454(4)	4380(4)	-2987(10)	57(3)	64(4)	445(29)	-83(6)	104(16)	-95(17)
C(A3)	1454(4)	5018(4)	-2026(10)	52(3)	50(3)	442(28)	-68(6)	60(16)	-80(16)
C(A4)	910(4)	6254(4)	-2194(10)	63(4)	53(4)	426(29)	-73(7)	58(17)	-76(17)
C(A5)	-83(4)	6795(4)	-1070(10)	68(4)	56(4)	410(29)	-64(7)	61(17)	-100(17)
C(A6)	-697(4)	7991(4)	-1142(12)	89(5)	56(4)	575(34)	-71(7)	106(20)	-131(19)
C(A7)	-1675(4)	8496(4)	-146(13)	81(5)	59(4)	663(38)	-40(7)	114(22)	-182(21)
C(A8)	-2067(4)	7816(4)	867(13)	67(4)	82(5)	722(39)	-57(8)	139(21)	-225(22)
C(A9)	-1494(4)	6634(4)	985(12)	57(4)	81(5)	685(38)	-67(7)	127(20)	-210(22)
C(A10)	-507(4)	6143(4)	12(11)	53(3)	50(3)	484(30)	-47(6)	75(16)	-139(17)
C(A11)	1016(3)	4409(4)	-773(10)	45(3)	65(4)	441(28)	-65(6)	95(16)	-147(17)
C(A12)	1519(4)	3204(4)	-358(11)	57(4)	56(4)	568(31)	-77(6)	140(17)	-125(17)
C(A13)	2502(4)	2639(3)	-1295(10)	55(3)	50(3)	432(28)	-65(6)	65(16)	-95(16)
C(A14)	4113(4)	1141(4)	-2157(12)	65(4)	68(4)	640(35)	-66(7)	199(19)	-193(19)
C(A15)	5712(4)	774(5)	1479(14)	49(4)	127(6)	752(42)	-51(8)	125(21)	-270(27)
C(A16)	5186(4)	1876(5)	-577(13)	50(4)	91(5)	828(41)	-62(7)	143(20)	-287(24)
C(A17)	4067(4)	2285(4)	-3201(11)	66(4)	65(4)	588(33)	-81(7)	194(19)	-180(19)
O(A1)	2940(3)	4896(3)	-4215(8)	86(3)	76(3)	784(27)	-126(5)	248(15)	-180(15)
O(A2)	1301(3)	6816(3)	-3269(9)	97(3)	66(3)	777(26)	-118(5)	225(15)	-174(14)
O(A3)	-328(4)	8663(3)	-2139(10)	143(4)	65(3)	1066(34)	-129(7)	355(21)	-245(17)
O(A4)	44(2)	4966(2)	188(8)	59(3)	60(3)	663(23)	-77(4)	179(13)	-178(13)
O(A5)	3124(3)	1453(3)	-1020(8)	66(3)	53(3)	759(26)	-69(4)	186(14)	-183(13)
O(A6)	5177(3)	239(3)	649(10)	65(3)	71(3)	952(32)	-41(5)	126(16)	-71(16)
C(B1)	5121(4)	6264(4)	4901(10)	70(4)	51(4)	425(28)	-74(6)	145(17)	-103(17)
C(B2)	6296(4)	5596(4)	5287(10)	67(4)	65(4)	409(28)	-93(7)	115(17)	-111(17)
C(B3)	6806(3)	4561(4)	4301(10)	50(3)	51(3)	441(28)	-64(6)	113(16)	-105(16)
C(B4)	8022(4)	3847(4)	4572(11)	56(4)	65(4)	498(30)	-80(6)	123(17)	-104(17)
C(B5)	8443(4)	2831(4)	3467(10)	51(3)	49(3)	441(28)	-57(6)	83(15)	-51(16)
C(B6)	9627(4)	2049(4)	3625(11)	57(4)	79(4)	496(32)	-77(7)	108(18)	-78(19)
C(B7)	10003(4)	1081(4)	2633(13)	63(4)	67(4)	750(39)	-65(7)	201(20)	-153(21)
C(B8)	9208(4)	861(4)	1401(13)	77(5)	62(4)	825(41)	-74(8)	237(23)	-176(22)
C(B9)	8029(4)	1602(4)	1188(13)	76(4)	61(4)	768(38)	-81(7)	212(21)	-210(21)
C(B10)	7674(4)	2570(4)	2270(11)	54(3)	54(4)	525(31)	-56(6)	143(17)	-115(17)
C(B11)	6074(4)	4265(3)	3021(10)	60(3)	48(3)	485(28)	-74(6)	145(16)	-132(16)
C(B12)	4882(4)	4916(4)	2611(11)	58(3)	53(4)	578(32)	-70(6)	126(17)	-126(18)
C(B13)	4452(4)	5917(4)	3582(10)	58(4)	54(4)	512(31)	-73(6)	165(17)	-116(17)
C(B14)	3133(4)	7633(4)	4438(13)	82(4)	58(4)	780(40)	-75(7)	275(22)	-195(21)
C(B15)	2943(5)	9215(4)	961(14)	106(5)	55(4)	891(44)	-80(8)	306(26)	-182(23)
C(B16)	4051(5)	8544(4)	3030(13)	98(5)	65(4)	822(41)	-100(8)	323(23)	-228(22)
C(B17)	4331(4)	7413(4)	5531(11)	91(5)	60(4)	529(32)	-96(7)	216(20)	-177(18)
O(B1)	6965(3)	5917(3)	6594(9)	85(3)	90(3)	823(27)	-132(6)	207(15)	-294(16)
O(B2)	8702(3)	4103(3)	5732(9)	65(3)	85(3)	773(25)	-106(5)	137(13)	-224(15)
O(B3)	10427(2)	2248(3)	4826(9)	58(3)	101(3)	903(29)	-99(5)	195(14)	-256(16)
O(B4)	6510(2)	3278(2)	2011(8)	48(2)	55(3)	753(25)	-64(4)	151(12)	-207(13)
O(B5)	3295(3)	6672(3)	3301(8)	57(3)	58(3)	816(26)	-65(4)	210(13)	-188(14)
O(B6)	2330(3)	8746(3)	1602(10)	68(3)	50(3)	1103(34)	-45(5)	152(16)	-102(15)

TABLE 2. FINAL POSITIONAL PARAMETERS ($\times10^3$) AND ISOTROPIC TEMPERATURE FACTORS (Å^2) FOR HYDROGEN ATOMS

	x	y	z	B		x	y	z	B
H(A1)	262(6)	562(6)	-387(17)	5.5(1.6)	H(B1)	784(6)	537(6)	679(17)	6.2(1.8)
H(A2)	22(7)	823(7)	-302(19)	7.8(2.1)	H(B2)	1012(5)	279(5)	567(15)	4.3(1.4)
H(A3)	-217(5)	927(5)	-4(14)	3.9(1.3)	H(B3)	1089(5)	49(5)	306(13)	3.4(1.2)
H(A4)	-277(5)	817(5)	163(14)	4.2(1.4)	H(B4)	947(6)	9(6)	70(16)	5.2(1.6)
H(A5)	-170(4)	607(5)	191(13)	3.1(1.2)	H(B5)	740(5)	148(5)	-7(14)	3.7(1.3)
H(A6)	132(4)	271(4)	127(13)	3.0(1.2)	H(B6)	437(5)	469(5)	148(14)	3.4(1.2)
H(A7)	405(4)	74(4)	-391(12)	2.6(1.1)	H(B7)	271(4)	775(4)	601(12)	2.3(1.1)
H(A8)	645(5)	18(5)	350(15)	4.3(1.4)	H(B8)	240(5)	1002(5)	-110(14)	3.6(1.3)
H(A9)	550(6)	234(6)	-31(17)	5.7(1.6)	H(B9)	462(5)	856(5)	244(15)	4.9(1.5)
H(A10)	401(5)	249(5)	-570(13)	3.1(1.2)	H(B10)	466(5)	725(5)	816(14)	3.8(1.3)

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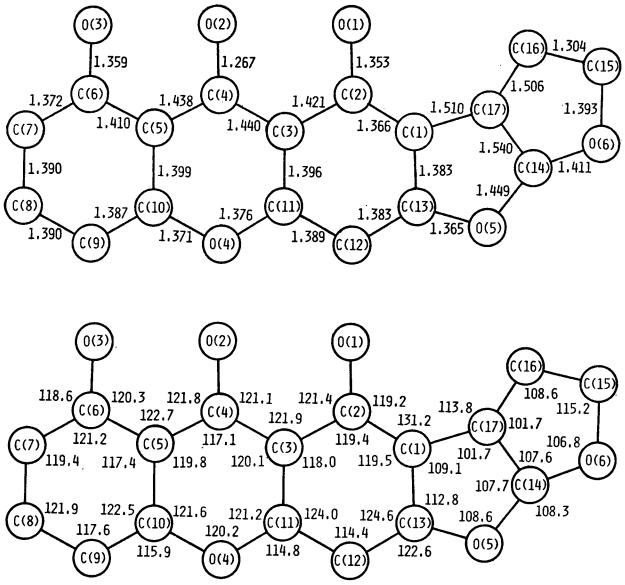

Fig. 1. Mean values of bond lengths and angles.
The e.s.d.'s of bond lengths and angles are about 0.007 Å and 0.5 °, respectively.

TABLE 3. MEAN BOND LENGTHS (Å) AND ANGLES (°) INVOLVING HYDROGEN ATOMS

Broken lines indicate hydrogen bonds.

(a) Mean bond lengths

O(1)–H(1)	0.98	O(3)–H(2)	0.87
C(7)–H(3)	0.98	C(8)–H(4)	1.03
C(9)–H(5)	1.05	C(12)–H(6)	1.05
C(14)–H(7)	1.00	C(15)–H(8)	1.01
C(16)–H(9)	0.94	C(17)–H(10)	1.03
O(2)···H(1)	1.79	O(2)···H(2)	1.83

(b) Mean bond angles

C(2)–O(1)–H(1)	112	C(6)–O(3)–H(2)	107
C(6)–C(7)–H(3)	124	C(8)–C(7)–H(3)	116
C(7)–C(8)–H(4)	121	C(9)–C(8)–H(4)	117
C(8)–C(9)–H(5)	123	C(10)–C(9)–H(5)	120
C(11)–C(12)–H(6)	120	C(13)–C(12)–H(6)	124
C(17)–C(14)–H(7)	120	O(5)–C(14)–H(7)	107
O(6)–C(14)–H(7)	105	C(16)–C(15)–H(8)	135
O(6)–C(15)–H(8)	110	C(15)–C(16)–H(9)	123
C(17)–C(16)–H(9)	125	C(1)–C(17)–H(10)	111
C(14)–C(17)–H(10)	110	C(16)–C(17)–H(10)	117
O(1)–H(1)···O(2)	139	C(4)–O(2)···H(1)	104
O(3)–H(2)···O(2)	148	C(4)–O(2)···H(2)	98
H(1)···O(2)···H(2)	158		

structure. The mean value of the C(4)–O(2) bond lengths is 1.267 Å, which is longer than the accepted value of the C–O double bond length. Such an elongation has also been found in averufin.[2] The bond lengths of C(3)–C(4) and C(4)–C(5) are 1.440 and 1.438 Å respectively; they are considerably longer than the mean

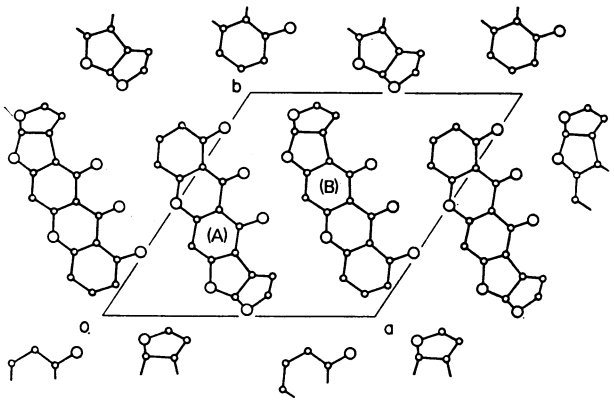

Fig. 2. The crystal structure of sterigmatin projected along the c*-axis.
The large circles indicate oxygen atoms and the small ones carbon atoms. The hydrogen atoms are omitted in the figure.

C–C bond length (1.390 Å) in the benzenoid rings. There are two intramolecular hydrogen bonds, O(1)–H(1)·····O(2) and O(3)–H(2)·····O(2). In each molecule the xanthone skeleton and terminal five-membered ring are planar within ±0.06 Å and ±0.02 Å respectively. The dihedral angles between the planes are 67.3 ° in the A molecule and 65.0 ° in the B molecule.

The crystal structure projected along the c* axis is shown in Fig. 2. Although the closest intermolecular contact (2.86 Å) of non-hydrogen atoms is found between O(A1) and O(B5), the difference electron density map calculated using the final atomic parameters showed no peak in the region between these two oxygen atoms. Therefore, there is no intermolecular hydrogen bond between the O(A1) and O(B5) atoms. The other intermolecular distances require no special comment.

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