The Crystal and Molecular Structures of 6-Deoxyversicolorin A and Versicolorin A, Metabolites from *Aspergillus versicolor*

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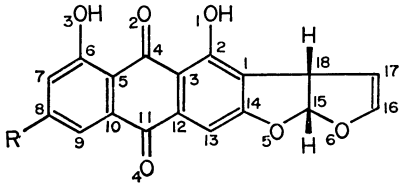
The structures of 6-deoxyversicolorin A, $C_{18}H_{10}O_6$, and versicolorin A, $C_{18}H_{10}O_7$, both isolated from *Aspergillus versicolor*, have been determined by the X-ray diffraction method. Both compounds crystallized in the space group $P2_12_12_1$, with four molecules per unit cell. The cell dimensions of 6-deoxyversicolorin A are $a=9.588$, $b=18.083$, $c=7.769$ Å, and those of versicolorin A are $a=9.524$, $b=18.629$, $c=7.629$ Å. The structure was refined to $R=0.055$ for 6-deoxyversicolorin A and to $R=0.043$ for versicolorin A. Both structures are in agreement with those assigned by chemical and spectroscopic methods. There are two intramolecular hydrogen bonds in each molecule. Although an intermolecular hydrogen bond is present in versicolorin A, both structures are isotypic. The dimensions of the anthraquinone skeleton and the dihydrofuro[2,3-*b*]furan moiety are compared with those in related compounds whose structures have been determined.

The dihydrofuro[2,3-*b*]furan moiety is the common structural unit in an important class of fungel metabolites which includes aflatoxins, B_1[1] and G_1,[2] and sterigmatocystin.[3,4] The structures of these metabolites have been extensively investigated by chemical, spectroscopic, and X-ray methods. The present compounds, 6-deoxyversicolorin A (I) and versicolorin A (II), were isolated from *Aspergillus versicolor* (Vuillemin) Tiraboschi, and the structures were proposed by Elsworthy *et al.*[5] and Hamasaki *et al.*[6] respectively by means of chemical and spectroscopic methods. Both the compounds have a dihydrofuro-[2,3-*b*]furan moiety with an anthraquinone skeleton, and were shown to be biogenetic precursors of sterigmatocystin and aflatoxins.[7] The present X-ray structure analysis was carried out to compare the structures of the title compounds with those of the related metabolites of this mold which have been studied in our laboratory.



I: R= H

II: R=7OH

Experimental

Crystallographic Measurements. 6-Deoxyversicolorin A and versicolorin A were crystallized from acetone solution in the forms of orange red prisms and orange red plates respectively. Although the crystals of versicolorin A appeared to be well-developed plates, the diffraction profiles were broad and not symmetrical about the peaks. The cell constants were obtained from the least-squares treatment of the angular settings of 13 reflections. The crystal data and details of experimental conditions for each compound are summarized in Table 1. The intensities of each compound were measured on a Rigaku-Denki computer-controlled four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. Attenuators were automatically inserted to keep the counting rate below 8000 cps. Backgrounds were counted for 10 s at the both sides of the scan range. The intensities were corrected for the Lorentz and polarization factors, but were not corrected for absorption.

TABLE 1. CRYSTAL DATA AND DETAILS OF EXPERIMENTAL CONDITIONS

	6-Deoxyversicolorin A	Versicolorin A
Molecular formula	$C_{18}H_{10}O_6$	$C_{18}H_{10}O_7$
Molecular weight	322.3	338.3
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a	9.588(4) Å	9.524(5) Å
b	18.083(6) Å	18.629(7) Å
c	7.769(4) Å	7.629(5) Å
Z	4	4
D_x	1.589 g/cm³	1.659 g/cm³
μ(for Cu $K\alpha$)	10.4 cm⁻¹	11.2 cm⁻¹
Crystal size	0.07×0.07×0.28 mm	0.08×0.20×0.30 mm
Scan technique	ω-2θ scan	ω scan
Scan range (ω)	1.0°+0.2° tan θ	1.6°+0.15° tan θ
Scan speed (ω)	2° min⁻¹	2° min⁻¹
Maximum 2θ	120°	127°
No. of reflections measured	1180	1296
No. of non-zero reflections	1046	1160

Structure Determination of 6-Deoxyversicolorin A. The structure was solved by application of the vector-search method;[8] the rigid group used in the calculations was an anthraquinone skeleton with two oxygen atoms. A three-dimensional Fourier synthesis based on the phases due to the rigid group revealed the positions of the remaining non-hydrogen atoms. The structure was refined by the block-diagonal least-squares calculations,[9] first with isotropic and subsequently with anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms were found in a difference electron density map, and included in the subsequent refinement with isotropic temperature factors. The final refinement was made using the following weighting scheme: $w=0.0$ for $F_o=0$, $w=1.0$ for $0<F_o\leqq 22$, and $w=[1.0+0.33(F_o-22)]^{-1}$ for $22<F_o$. However, the two strongest reflections, 022 and 032, were omitted from the calculations. The final R value was 0.055 for 1044 non-zero reflections. The final atomic parameters are listed in Tables

TABLE 2. FINAL ATOMIC PARAMETERS AND e.s.d.'s ($\times 10^4$) 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}
(a)	6-Deoxyversicolorin A								
C(1)	8889 (5)	1043 (3)	9456 (7)	82 (6)	22 (1)	182 (11)	0 (5)	−20 (14)	−4 (7)
C(2)	8564 (5)	1687 (2)	8621 (7)	76 (5)	19 (1)	159 (9)	−12 (5)	1 (13)	−6 (7)
C(3)	7109 (5)	1879 (3)	8375 (6)	76 (5)	22 (1)	133 (9)	0 (5)	32 (13)	−16 (6)
C(4)	6749 (6)	2551 (3)	7477 (6)	100 (6)	20 (1)	141 (10)	6 (5)	23 (14)	−5 (6)
C(5)	5293 (5)	2719 (2)	7140 (7)	94 (6)	21 (1)	151 (10)	18 (5)	−52 (14)	−11 (7)
C(6)	4884 (6)	3356 (3)	6241 (7)	139 (8)	22 (2)	160 (10)	9 (6)	−30 (16)	−13 (7)
C(7)	3488 (6)	3517 (3)	5951 (8)	121 (8)	33 (2)	193 (12)	23 (6)	−31 (18)	−17 (8)
C(8)	2469 (6)	3052 (3)	6609 (8)	107 (7)	37 (2)	196 (12)	31 (6)	−41 (17)	−8 (9)
C(9)	2841 (6)	2416 (3)	7491 (8)	106 (7)	37 (2)	188 (12)	16 (7)	−16 (17)	−37 (9)
C(10)	4214 (5)	2261 (3)	7785 (7)	80 (6)	28 (2)	162 (10)	−2 (5)	−39 (14)	−27 (7)
C(11)	4605 (5)	1586 (3)	8801 (7)	78 (6)	27 (2)	167 (10)	−11 (5)	24 (14)	−11 (7)
C(12)	6089 (5)	1397 (3)	9051 (7)	92 (6)	21 (1)	151 (10)	−4 (5)	1 (14)	4 (7)
C(13)	6442 (6)	757 (3)	9922 (7)	97 (7)	27 (2)	159 (10)	−15 (6)	38 (15)	2 (7)
C(14)	7830 (6)	603 (2)	10101 (7)	120 (7)	19 (1)	148 (10)	−13 (5)	−20 (15)	12 (7)
C(15)	9829 (6)	7 (3)	10929 (8)	120 (7)	24 (1)	211 (12)	13 (6)	−83 (17)	−6 (8)
C(16)	10841 (7)	−422 (3)	8522 (9)	133 (8)	31 (2)	240 (14)	38 (7)	−55 (19)	−44 (9)
C(17)	10881 (6)	297 (3)	8261 (8)	108 (7)	34 (2)	208 (12)	25 (6)	−6 (17)	−20 (9)
C(18)	10276 (6)	677 (3)	9831 (7)	95 (6)	24 (1)	168 (10)	5 (5)	−20 (15)	−9 (7)
O(1)	9589 (4)	2129 (2)	8043 (5)	85 (4)	24 (1)	230 (8)	−8 (4)	38 (11)	10 (5)
O(2)	7690 (4)	2981 (2)	6931 (5)	106 (4)	24 (1)	202 (8)	−16 (4)	−1 (11)	37 (5)
O(3)	5838 (4)	3844 (2)	5623 (6)	136 (5)	28 (1)	243 (9)	6 (5)	−41 (13)	52 (6)
O(4)	3681 (4)	1203 (2)	9461 (6)	97 (5)	42 (2)	270 (10)	−18 (5)	40 (13)	37 (7)
O(5)	8319 (4)	−8 (2)	10936 (5)	116 (5)	25 (1)	236 (8)	−7 (4)	−24 (12)	34 (6)
O(6)	10302 (5)	−639 (2)	10072 (6)	170 (6)	24 (1)	274 (10)	30 (5)	−34 (15)	4 (6)
(b)	Versicolorin A								
C(1)	8946 (4)	1037 (2)	9391 (6)	72 (4)	21 (1)	137 (8)	1 (4)	−28 (11)	3 (5)
C(2)	8636 (4)	1683 (2)	8575 (5)	78 (5)	17 (1)	132 (8)	−6 (4)	12 (11)	−1 (5)
C(3)	7228 (4)	1877 (2)	8317 (5)	71 (4)	19 (1)	112 (7)	−1 (4)	−12 (11)	−2 (5)
C(4)	6872 (4)	2545 (2)	7473 (5)	74 (5)	18 (1)	139 (8)	6 (4)	−4 (11)	−9 (5)
C(5)	5416 (4)	2742 (2)	7187 (6)	75 (5)	19 (1)	132 (8)	−5 (4)	−10 (11)	−5 (5)
C(6)	5023 (5)	3373 (2)	6295 (6)	89 (5)	19 (1)	161 (8)	4 (4)	−1 (12)	3 (6)
C(7)	3646 (5)	3543 (2)	6001 (6)	97 (5)	17 (1)	179 (9)	3 (4)	−15 (13)	4 (6)
C(8)	2614 (5)	3088 (2)	6577 (6)	103 (6)	22 (1)	163 (9)	27 (4)	−52 (13)	−26 (6)
C(9)	2931 (5)	2449 (2)	7477 (6)	78 (5)	23 (1)	164 (9)	8 (4)	23 (12)	−4 (6)
C(10)	4319 (4)	2287 (2)	7763 (6)	75 (5)	20 (1)	128 (8)	7 (4)	−10 (11)	−12 (5)
C(11)	4651 (4)	1615 (2)	8729 (6)	73 (5)	21 (1)	140 (8)	−12 (4)	−1 (11)	1 (5)
C(12)	6161 (4)	1409 (2)	8950 (5)	75 (5)	20 (1)	117 (7)	−2 (4)	24 (10)	−9 (5)
C(13)	6458 (4)	774 (2)	9792 (6)	67 (4)	20 (1)	157 (8)	0 (4)	24 (11)	−9 (5)
C(14)	7880 (4)	603 (2)	9997 (5)	88 (5)	17 (1)	148 (8)	−5 (4)	−15 (12)	−23 (5)
C(15)	9865 (4)	12 (2)	10813 (6)	90 (5)	20 (1)	203 (9)	15 (5)	−58 (12)	3 (7)
C(16)	10913 (5)	−364 (2)	8344 (7)	100 (6)	29 (1)	200 (10)	16 (5)	−34 (14)	−29 (7)
C(17)	10981 (5)	332 (2)	8135 (7)	79 (5)	28 (1)	180 (9)	16 (4)	2 (12)	9 (7)
C(18)	10335 (4)	676 (2)	9768 (6)	66 (4)	19 (1)	165 (9)	8 (4)	−29 (11)	−3 (5)
O(1)	9725 (3)	2084 (1)	8049 (4)	70 (3)	24 (1)	208 (7)	−7 (3)	22 (9)	24 (4)
O(2)	7822 (3)	2962 (1)	6940 (4)	77 (3)	20 (1)	209 (6)	−7 (3)	0 (9)	30 (4)
O(3)	6006 (3)	3843 (2)	5723 (5)	109 (4)	22 (1)	223 (7)	−10 (3)	−29 (10)	48 (5)
O(4)	3734 (3)	1235 (2)	9343 (5)	73 (3)	38 (1)	254 (8)	−20 (3)	20 (10)	60 (6)
O(5)	8339 (3)	−2 (2)	10802 (4)	91 (3)	23 (1)	196 (6)	8 (3)	−5 (8)	56 (5)
O(6)	10335 (4)	−605 (1)	9896 (5)	128 (4)	19 (1)	241 (8)	18 (3)	2 (10)	−5 (4)
O(7)	1209 (3)	3218 (2)	6318 (5)	75 (4)	32 (1)	258 (8)	22 (3)	−54 (10)	15 (5)

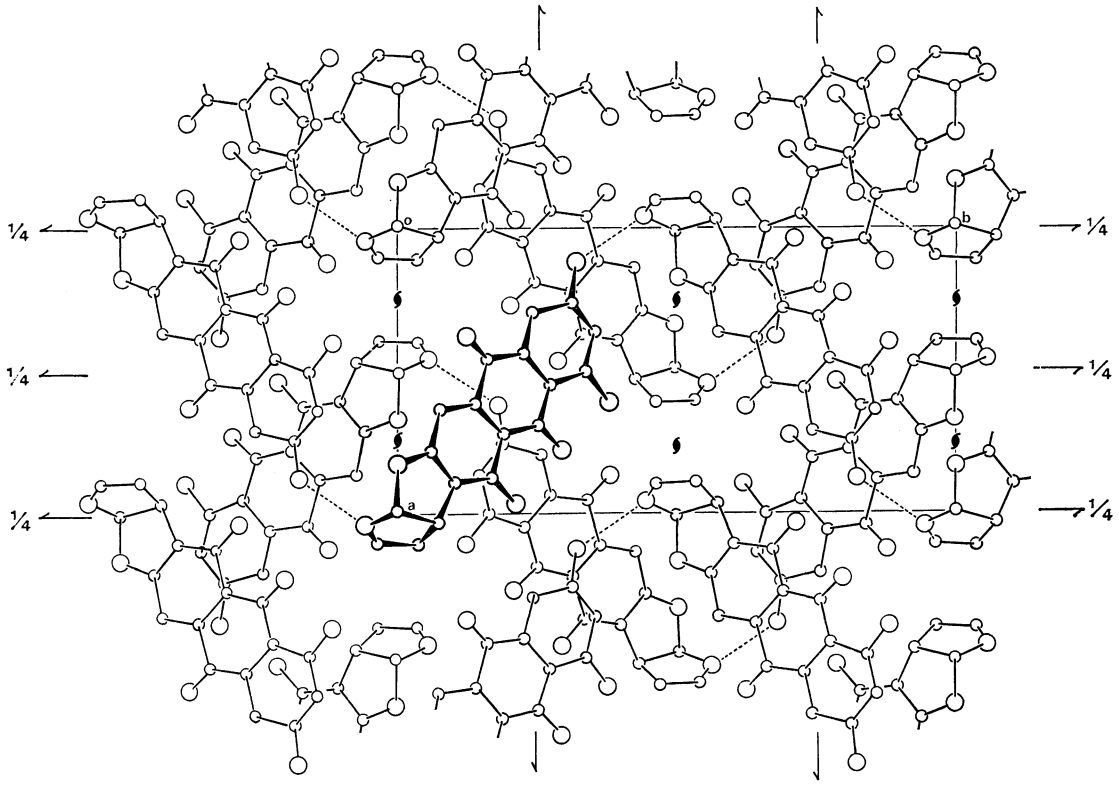


Fig. 1. The crystal structure of versicolorin A viewed along the c axis. Broken lines indicate intermolecular hydrogen bonds.

Table 3. Final positional parameters ($\times 10^3$) and isotropic temperature factors (Å^2) for hydrogen atoms

	x	y	z	B	d[a)]
(a) 6-Deoxyversicolorin A					
H(O1)	917(7)	265(3)	776(9)	4.6(17)	1.04
H(O3)	658(7)	371(3)	581(8)	4.5(16)	0.77
H(C7)	349(6)	400(3)	523(7)	2.6(13)	1.03
H(C8)	156(7)	318(3)	635(8)	4.6(16)	0.92
H(C9)	213(7)	207(3)	811(8)	4.6(17)	1.04
H(C13)	556(7)	48(3)	1066(8)	3.7(15)	1.13
H(C15)	1021(6)	−2(3)	1212(7)	2.1(11)	1.00
H(C16)	1134(6)	−81(3)	772(7)	2.9(14)	1.05
H(C17)	1122(7)	60(3)	734(8)	3.4(15)	0.96
H(C18)	1095(5)	99(3)	1054(7)	1.6(11)	1.02
(b) Versicolorin A					
H(O1)	959(6)	251(3)	757(8)	4.7(15)	0.89
H(O3)	686(7)	366(3)	600(8)	5.8(16)	0.91
H(C7)	333(6)	407(3)	544(7)	3.8(13)	1.12
H(O7)	108(6)	371(3)	581(8)	5.2(16)	1.01
H(C9)	216(6)	213(3)	785(7)	3.8(13)	0.98
H(C13)	580(7)	47(3)	1005(8)	4.3(14)	0.87
H(C15)	1014(5)	−4(3)	1218(7)	3.1(11)	1.08
H(C16)	1132(6)	−67(3)	741(8)	4.1(14)	0.99
H(C17)	1130(6)	66(3)	706(7)	3.9(13)	1.07
H(C18)	1098(5)	100(2)	1050(7)	2.5(11)	1.02

a) Length of covalent bond involving hydrogen atom in Å.

2(a) and 3(a).†††

Structure Determination of Versicolorin A. The structure was solved by the direct method with program MULTAN.[10] The refinement of versicolorin A was made in the same way as that of 6-deoxyversicolorin A. All hydrogen atoms were found in a difference electron density map after the anisotropic refinement for non-hydrogen atoms. The weighting scheme adopted in the final cycle of the refinement was: $w=0.0$ for $F_o=0$, $w=1.0$ for $0<F_o\leqq 17$, and $w=[1.0+0.11\times(F_o-17)]^{-1}$ for $17<F_o$. However, zero weight was given to the two strongest reflections, 022 and 032. The final R value was 0.043 for 1158 non-zero reflections. The final atomic parameters are listed in Tables 2(b) and 3(b).† The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[11]

Results and Discussion

The present crystallographic analysis has verified the structures of 6-deoxyversicolorin A and versicolorin A proposed by the chemical and spectroscopic methods.[5,6] The absolute configuration adopted is based on the assumption that the configuration of the dihydrofuro[2,3-*b*]furan moiety of the present molecules is the same as that of related molecules which has been established by X-ray method.[1,4,12] The crystal structure of versicolorin A is shown in

††† Lists of the observed and calculated structure factors are available from the authors on request and also kept as Document No. 7905 at the Chemical Society of Japan.

Table 4. Bond lengths and angles for non-hydrogen atoms

(a) Bond lengths (l/Å)

	6DVA	VA		6DVA	VA
C(1)-C(2)	1.370 (8)	1.387 (6)	C(1)-C(14)	1.384 (8)	1.377 (6)
C(1)-C(18)	1.514 (8)	1.512 (6)	C(2)-C(3)	1.450 (7)	1.402 (6)
C(2)-O(1)	1.344 (7)	1.340 (5)	C(3)-C(4)	1.442 (7)	1.442 (6)
C(3)-C(12)	1.412 (7)	1.422 (6)	C(4)-C(5)	1.453 (8)	1.452 (6)
C(4)-O(2)	1.265 (7)	1.259 (5)	C(5)-C(6)	1.404 (8)	1.408 (6)
C(5)-C(10)	1.417 (8)	1.416 (6)	C(6)-C(7)	1.389 (9)	1.368 (7)
C(6)-O(3)	1.358 (7)	1.354 (6)	C(7)-C(8)	1.387 (9)	1.370 (7)
C(8)-C(9)	1.386 (9)	1.408 (6)	C(8)-O(7)	—	1.374 (6)
C(9)-C(10)	1.366 (8)	1.373 (6)	C(10)-C(11)	1.501 (8)	1.487 (6)
C(11)-C(12)	1.477 (8)	1.498 (6)	C(11)-O(4)	1.236 (7)	1.217 (6)
C(12)-C(13)	1.383 (8)	1.376 (6)	C(13)-C(14)	1.367 (8)	1.400 (6)
C(14)-O(5)	1.363 (7)	1.356 (5)	C(15)-C(18)	1.543 (8)	1.538 (7)
C(15)-O(5)	1.447 (7)	1.454 (6)	C(15)-O(6)	1.418 (8)	1.417 (6)
C(16)-C(17)	1.316 (10)	1.309 (7)	C(16)-O(6)	1.368 (8)	1.381 (6)
C(17)-C(18)	1.516 (9)	1.530 (7)			

(b) Bond angles (φ/°)

	6DVA	VA		6DVA	VA
C(2)-C(1)-C(14)	119.6 (5)	120.2 (4)	C(2)-C(1)-C(18)	131.5 (5)	131.1 (4)
C(14)-C(1)-C(18)	108.9 (5)	108.7 (4)	C(1)-C(2)-C(3)	119.0 (5)	119.3 (4)
C(1)-C(2)-O(1)	119.9 (5)	116.9 (4)	C(3)-C(2)-O(1)	121.2 (5)	123.7 (4)
C(2)-C(3)-C(4)	119.7 (5)	120.6 (4)	C(2)-C(3)-C(12)	118.0 (5)	118.6 (4)
C(4)-C(3)-C(12)	122.3 (5)	120.8 (4)	C(3)-C(4)-C(5)	119.5 (5)	120.7 (4)
C(3)-C(4)-O(2)	120.7 (5)	120.5 (4)	C(5)-C(4)-O(2)	119.7 (5)	118.8 (4)
C(4)-C(5)-C(6)	122.0 (5)	122.5 (4)	C(4)-C(5)-C(10)	121.0 (5)	120.4 (4)
C(6)-C(5)-C(10)	116.9 (5)	117.0 (4)	C(5)-C(6)-C(7)	121.4 (5)	121.8 (4)
C(5)-C(6)-O(3)	121.5 (5)	120.8 (4)	C(7)-C(6)-O(3)	117.1 (5)	117.4 (4)
C(6)-C(7)-C(8)	119.5 (6)	119.5 (4)	C(7)-C(8)-C(9)	120.3 (6)	121.7 (4)
C(7)-C(8)-O(7)	—	122.9 (4)	C(9)-C(8)-O(7)	—	115.4 (4)
C(8)-C(9)-C(10)	120.1 (6)	118.0 (4)	C(5)-C(10)-C(9)	121.7 (5)	122.0 (4)
C(5)-C(10)-C(11)	118.6 (5)	120.1 (4)	C(9)-C(10)-C(11)	119.7 (5)	117.9 (4)
C(10)-C(11)-C(12)	119.9 (5)	118.4 (4)	C(10)-C(11)-O(4)	119.7 (5)	121.8 (4)
C(12)-C(11)-O(4)	120.4 (5)	119.8 (4)	C(3)-C(12)-C(11)	118.4 (5)	119.4 (4)
C(3)-C(12)-C(13)	122.0 (5)	122.6 (4)	C(11)-C(12)-C(13)	119.6 (5)	118.0 (4)
C(12)-C(13)-C(14)	117.3 (5)	116.5 (4)	C(1)-C(14)-C(13)	124.1 (5)	122.9 (4)
C(1)-C(14)-O(5)	112.6 (5)	113.7 (4)	C(13)-C(14)-O(5)	123.3 (5)	123.4 (4)
C(18)-C(15)-O(5)	107.1 (5)	107.6 (4)	C(18)-C(15)-O(6)	107.4 (5)	107.8 (4)
O(5)-C(15)-O(6)	107.9 (5)	107.3 (4)	C(17)-C(16)-O(6)	115.4 (6)	116.5 (5)
C(16)-C(17)-C(18)	108.3 (6)	107.2 (4)	C(1)-C(18)-C(15)	101.8 (5)	101.6 (4)
C(1)-C(18)-C(17)	112.3 (5)	112.5 (4)	C(15)-C(18)-C(17)	101.2 (5)	101.7 (4)
C(14)-O(5)-C(15)	109.2 (4)	108.1 (3)	C(15)-O(6)-C(16)	107.4 (5)	106.6 (4)

Fig. 1. The bond lengths and angles for non-hydrogen atoms are given in Table 4, the equations of the least-squares planes and perpendicular displacements of atoms from each plane in Table 5, and intermolecular distances in Table 6.

Hydrogen Bonds. There are two intramolecular hydrogen bonds in each molecule. The lengths of O(2)···H(O1) and O(2)···H(O3) are 1.67 and 1.87 Å respectively in 6-deoxyversicolorin A, and 1.97 and 1.75 Å respectively in versicolorin A. The angles of O(1)–H(O1)···O(2), O(3)–H(O3)···O(2), H(O1)···O(2)–C(4), and H(O3)···O(2)–C(4) are 137, 145, 105, and 101° respectively in 6-deoxyversicolorin A, and 126, 148, 107, and 102° respectively in versicolorin A. In the crystal of versicolorin A there is an intermolecular hydrogen bond, O(7)–H(O7)···O(6), which connects the molecules related by the screw axis along the b axis. The distance of H(O7)···O(6) is 1.93 Å, and the angles of O(7)–H(O7)···O(6), H(O7)···O(6)–C(15), and H(O7)···O(6)–C(16) are 143, 117, and 105° respectively. A short contact (2.865 Å) is observed in the crystal of versicolorin A between the atoms O(7) and O(1) of the molecule at $(-1+x, y, z)$; however, the final difference electron density map showed no peak in the region between these atoms. The molecular arrangements in both crystals are similar in spite of the existence of the intermolecular hydrogen bond in the crystal of versicolorin A.

Structure of Dihydrofuro[2,3-b]furan Moiety. The

Table 5. Equations of least-squares planes and deviations of atoms from each plane

X, *Y*, and *Z* are Cartesian coordinates in Å referred to the axes a, b, and c.

(a) Anthraquinone skeleton

6DVA: $0.004X-0.520Y-0.854Z+7.283=0$

VA: $0.001X-0.486Y-0.874Z+7.244=0$

	6DVA	VA		6DVA	VA
C(1)	0.066	0.050	C(12)	−0.011	0.006
C(2)	0.012	0.008	C(13)	0.015	0.020
C(3)	−0.011	0.005	C(14)	0.047	0.039
C(4)	−0.048	−0.039	O(2)	−0.087	−0.060
C(5)	0.011	−0.028	O(4)	−0.110	−0.100
C(6)	0.006	−0.006	C(15)[a]	0.067	0.032
C(7)	0.042	0.036	C(18)[a]	0.166	0.127
C(8)	0.039	0.063	O(1)[a]	−0.015	−0.004
C(9)	0.053	0.043	O(3)[a]	−0.038	−0.049
C(10)	0.009	0.000	O(5)[a]	0.069	0.051
C(11)	−0.029	−0.034	O(7)[a]	—	0.118

(b) C(1), C(14), C(15), C(18), and O(5) atoms

6DVA: $0.033X+0.528Y+0.848Z-7.488=0$

VA: $0.024X+0.498Y+0.867Z-7.353=0$

	6DVA	VA		6DVA	VA
C(1)	−0.024	−0.022	C(18)	0.033	0.031
C(14)	0.005	0.003	O(5)	0.022	0.021
C(15)	−0.035	−0.033			

(c) C(15), C(16), C(17), C(18), and O(6) atoms

6DVA: $0.899X+0.042Y+0.436Z-12.212=0$

VA: $0.890X+0.016Y+0.456Z-12.153=0$

	6DVA	VA		6DVA	VA
C(15)	0.036	0.032	C(18)	−0.028	−0.023
C(16)	0.013	0.013	O(6)	−0.032	−0.029
C(17)	0.012	0.008			

a) Not included in the least-squares calculation.

dihydrofuro[2,3-*b*]furan moiety has been widely found in fungal metabolites. The interatomic distances of this moiety for 10 molecules, whose structures were determined by means of X-ray crystallography, have been compared by a half-normal probability plot.[13] The slopes of the plots range from *ca.* 1.2 to 3.0 with intercept 0.0, and some of them are not straight. The plots for 6-deoxyversicolorin A-sterigmatocystin and for 6-deoxyversicolorin A-sterigmatin are shown in Fig. 2 as typical examples.†† Most of the extreme values are found between non-bonded atoms, especially between the atoms C(1), C(14), or O(5) and the atoms C(17), C(16), or O(6). This fact suggests that the environments affect the conformation of such a simple moiety.

The conformation of this moiety may be defined by the torsion angles about the C(18)–C(15) bond, and the values for these angles are listed in Table 7. The torsion angles of C(1)–C(18)–C(15)–O(5) and C(17)–C(18)–C(15)–O(6) are apt to be right-handed in helicity. However, it is difficult to generalize the conformation of this moiety, since there is no rule for the distribution of the torsion angles about the C(18)–C(15) bond except the right-handed helicity.

Structure of Anthraquinone Skeleton. The structure of the anthraquinone skeleton was also examined by the half-normal probability method. The slope of the plot (1.8) between the anthraquinone skeletons of the present compounds is not much greater than 1.0, which is in accordance with the result that the skew-senses of the skeletons of each of these compounds are similar to each other, as shown in Table 5. The slopes of the plots between the skeletons of the other molecules, averufin,[18] and versicolorin C,[19] are larger than that of the present compounds (1.8—2.5). The plot for versicolorins A and C is shown in Fig. 2 as an example. When interatomic distances greater than

†† The figures of 55 plots among these molecules are available from the authors on request.

Table 6. Short intermolecular contacts between non-hydrogen atoms

		6DVA	VA			6DVA	VA
O(7)	C(16)^{I}	—	3.336	O(7)	O(6)^{I}	—	2.798[a]
O(2)	C(16)^{II}	3.231	3.351	O(2)	O(6)^{II}	3.515	3.490
O(3)	C(16)^{II}	3.513	3.362	C(6)	O(1)^{III}	3.454	3.434
C(7)	O(1)^{III}	3.480	3.460	C(8)	C(4)^{III}	3.426	3.381
C(8)	O(2)^{III}	3.331	3.326	C(9)	O(2)^{III}	3.512	3.456
O(3)	C(17)^{III}	3.394	3.320	O(7)	C(4)^{III}	—	3.283
O(7)	C(5)^{III}	—	3.304	C(6)	C(18)^{IV}	3.536	3.499
C(9)	C(2)^{IV}	3.498	3.484	C(10)	C(2)^{IV}	3.435	3.451
C(10)	O(1)^{IV}	3.443	3.425	C(11)	O(1)^{IV}	3.378	3.453
O(4)	O(2)^{IV}	3.308	3.322	C(8)	O(1)^{V}	3.413	3.511
C(9)	O(1)^{V}	3.189	3.158	O(4)	C(17)^{V}	3.280	3.249
O(4)	C(18)^{V}	3.412	3.416	O(7)	O(1)^{V}	—	2.865
O(7)	O(2)^{V}	—	3.296	O(4)	C(16)^{VI}	3.487	3.474
O(5)	C(13)^{VI}	3.388	3.372	O(6)	C(11)^{VI}	3.367	3.477

Roman numeral superscripts refer to the following transformations of the coordinates:

(I) $1-x,\ 1/2+y,\ 3/2-z$ (II) $2-x,\ 1/2+y,\ 3/2-z$ (III) $-1/2+x,\ 1/2-y,\ 1-z$

(IV) $-1/2+x,\ 1/2-y,\ 2-z$ (V) $-1+x,\ y,\ z$ (VI) $3/2-x,\ -y,\ 1/2+z$

a) Hydrogen bond.

TABLE 7. TORSION ANGLES ABOUT THE C(18)-C(15) BOND

	A	B	C	D
6DVA	5.9	5.7	121.6	−110.0
VA	5.6	4.9	121.1	−110.6
ST(A)	2.1	1.8	118.6	−114.7
ST(B)	0.5	−1.5	117.0	−118.0
STERIG	4.6	3.6	121.2	−112.9
OMST	4.8	1.6	121.0	−114.6
DMST	13.6	11.2	127.8	−103.0
MTST	1.3	0.9	119.4	−117.1
AF(C)	3.2	2.8	121.1	−115.1
AF(O)	2.0	−0.1	117.7	−115.7
AF(M)	3.0	0.7	117.9	−114.1

A: C(1)-C(18)-C(15)-O(5), B: C(17)-C(18)-C(15)-O(6), C: C(1)-C(18)-C(15)-O(6), D: C(17)-C(18)-C(15)-O(5).
Abbreviation: 6DVA, 6-deoxyversicolorin A; VA, versicolorin A; ST(A) and ST(B), two crystallographically independent molecules (A and B) of sterigmatin;[15] STERIG, sterigmatocystin;[4] OMST, *O*-methylsterigmatocystin;[4] DMST, demethylsterigmatocystin;[17] MTST, 5-methoxysterigmatocystin;[16] AF(C), aflatoxin B_1 (chloroform-solvated);[1] AF(O), aflatoxin B_1 (orthorhombic form);[1] AF(M), aflatoxin B_1 (monoclinic form).[1] The sign convention of the torsion angle is such that the sign is positive if a clockwise rotation is requested of the atom (1) to eclipse atom (4) whilst looking down the (2)-(3) bond. The configurations of the moiety in these molecules are assumed to be similar to each other.

3.0 Å were excluded from the drawing, most of the extreme values were eliminated and the slopes decreased slightly to 1.6—2.2. This fact shows that the structure of the skeleton is affected by the environment, as in the case of the dihydrofuro[2,3-*b*]furan moiety. However, the difference of substituents attached to the atoms C(1), C(8), and C(14) of this skeleton does not seem to affect the short interatomic distances.

Although the interatomic distances are dependent on the cell constants, the underestimation (about 1/1.6) of e.s.d.'s can scarcely be ascribed to their error. The underestimation may be due to other sources, such as the effect of thermal motion and/or the inherent tendency of underestimation in a block-diagonal least-squares technique. The same underestimation has been reported by several authors.[14]

Average Dimensions of Dihydrofuro[2,3-b]furan Moiety and Anthraquinone Skeleton. The average dimensions of the dihydrofuro[2,3-*b*]furan moiety and the anthraquinone skeleton were calculated by using the e.s.d.'s of each length as a weight (Fig. 3). Although the e.s.d. is underestimated, this may be reasonable weighting, because the underestimation of e.s.d. for each bond length is not so different. The dimensions of the anthraquinone skeleton seem to be affected by two hydroxyl groups, O(1)H and O(3)H; the lengths of the C(3)–C(4) and C(4)–C(5) bonds are shorter than those of the C(10)–C(11) and C(11)–C(12) bonds, while the lengths of the C(4)–O(2), C(2)–C(3), and C(5)–C(6) bonds are longer than those of the C(11)–O(4), C(12)–C(13), and C(9)–C(10) bonds. Such an

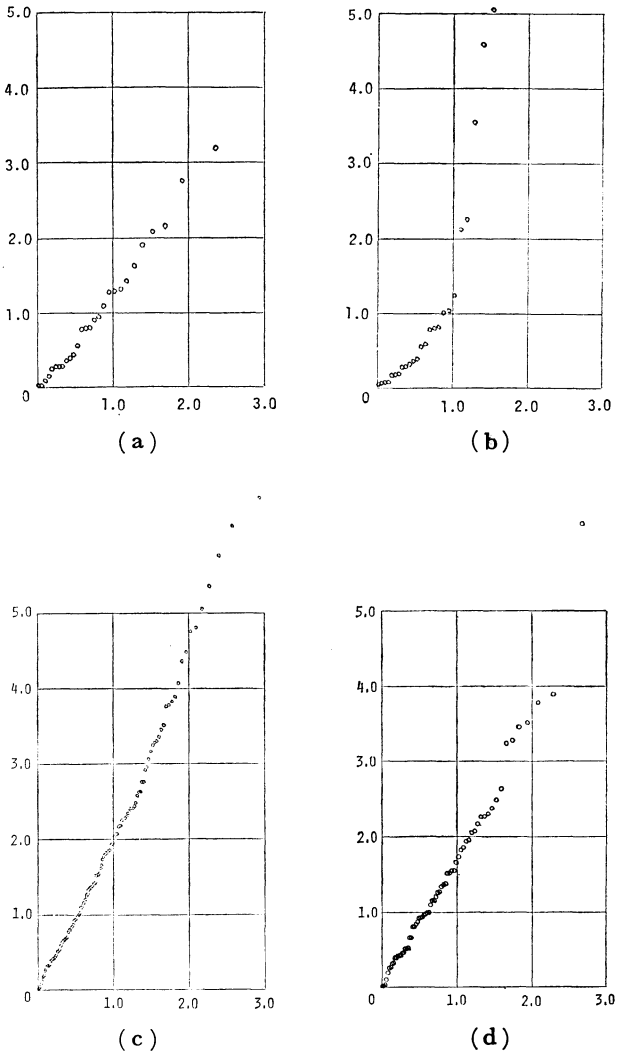


Fig. 2. Half-normal probability plot : the vertical axis is observed δp_i; the horizontal axis is the expected δp_i. $\delta p_i = |d(1)-d(2)|/\{\sigma^2(1)+\sigma^2(2)\}^{1/2}$, where d and σ are the interatomic distance and its e.s.d. respectively. (a) 6-Deoxyversicolorin A-sterigmatocystin as an example that the conformation of the dihydrofuro[2,3-*b*]furan moiety is similar to each other, (b) 6-deoxyversicolorin A-sterigmatin (B molecule) as an example that the conformation is different. (Table 7) (c) Half-normal probability plot for the anthraquinone skeletons of versicolorin A-versicolorin C including all data, and (d) that excluding the data of interatomic distances greater than 3.0 Å.

unequivalence of bond lengths in the anthraquinone skeleton is also found in 1,5-dianilinoanthraquinone and 1,8-dianilinoanthraquinone.[20] As expected from the chemical structure, however, the symmetry of the dimensions of the skeleton about the vector O(2)–

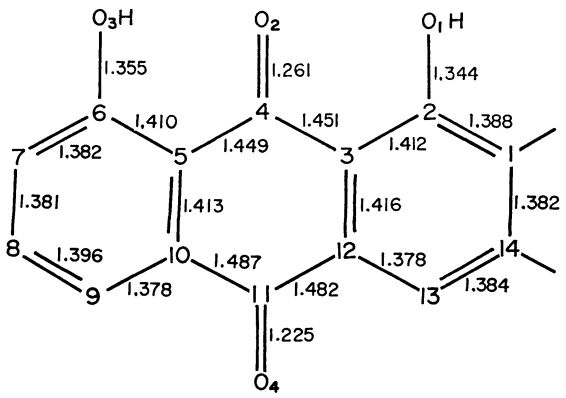


Fig. 3. Averaged dimensions of (a) anthraquinone skeleton and (b) dihydrofuro[2,3-*b*]furan moiety. Taking account of the underestimation of e.s.d. of bond length of individual molecule, the e.s.d. of the mean length may be about 0.004 Å for both anthraquinone skeleton and dihydrofuro[2,3-*b*]furan moiety.

O(4) is excellent.

The computations were performed, using programs written by the authors, on a TOSBAC-3400 computer at the Tottori University Computing Center, and on a NEAC2200-N700 computer at the Computation Center of Osaka University.

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