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The Crystal Structures of Aflatoxin B_1. I. The Structure of the Chloroform Solvate of Aflatoxin B_1 and the Absolute Configuration of Aflatoxin B_1

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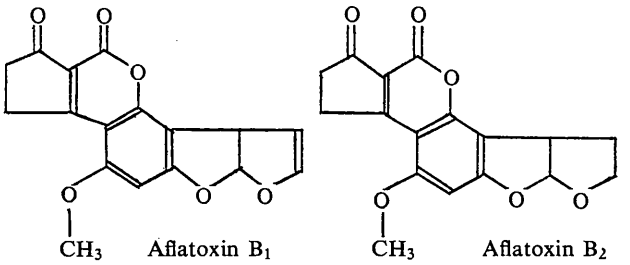
Aflatoxin $B_1 . CHCl_3$ forms orthorhombic crystals of space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a=6{\cdot}16$, $b=8{\cdot}04$ and $c=36{\cdot}25$ Å. The orientation of the aflatoxin B_1 molecule was found by means of a minimum function, calculated for two intramolecular vectors between light atoms; its position was determined by calculating the value of the residual while the molecule was moved systematically through the unit cell. The presence of the chloroform molecule appeared after a Fourier synthesis. The structure consists of alternating layers parallel to the plane (001) of chloroform and aflatoxin B_1 connected by CH...O hydrogen bonds. Within the aflatoxin B_1 layer, strings of coplanar molecules are present in the directions [110] and [$\bar{1}$10]). The molecules within a string have two short CH_3...O contacts of 3·04 and 3·15 Å, which points to a specific interaction. These contacts may be called hydrogen bonds.

The absolute configuration of the aflatoxin B_1 molecule is given.

Introduction

Aflatoxin B_1 is one of the carcinogenic metabolites of the mould *Aspergillus flavus* Link ex Fries (Hartley, Nesbitt & O'Kelly, 1963), which, in 1960, caused the death of 100,000 young turkeys as a result of liver damage. This compound is more toxic than aflatoxin B_2 – one of the other metabolites the crystal structure of which has been described by van Soest & Peerdeman (1970).

In the structural formula of aflatoxin B_1 which was elucidated by Asao, Büchi, Abdel-Kader, Chang, Wick & Wogan (1963), the tetrahydrofuran ring of aflatoxin B_2 is replaced by a dihydrofuran ring.



Aflatoxin B_1 Aflatoxin B_2

The crystal structure of aflatoxin B_1 has been determined to establish the influence of this small difference on the mode of packing of the molecules; owing to the presence of chloroform in the structure, we could also determine the absolute configuration of aflatoxin B_1.

Experimental

Aflatoxin B_1 (kindly supplied by Professor D. A. van Dorp of the Unilever Research Laboratory, Vlaardingen) was recrystallized from a saturated solution of the toxin in chloroform by a diffusion method. The solution was introduced in a tube with a diameter of about 3 mm. Ethanol, in which the toxin is much less readily soluble, was carefully added, after which aflatoxin B_1 crystallized at the interface of chloroform and ethanol in the form of pale yellow oblong platelets.

The unit-cell dimensions were determined from Weissenberg and rotation photographs and the space group $P2_12_12_1$ followed from the systematically absent reflexions. The density measured by the flotation method was 1·51 g.cm^{-3}, giving with $Z=4$ a weight of 404 for the asymmetric unit (W.A.U.).

This value is considerably greater than 312·3, the molecular weight of aflatoxin B_1, which indicates the presence of chloroform or ethanol in the crystal. In order to demonstrate this, an infrared spectrum of the crystals in KBr was made. Unfortunately, the spectrum only showed the absorption frequencies of aflatoxin B_1, since the chloroform or ethanol had probably evaporated during the preparation of the KBr disc.

As we were of the opinion that a structure determination would reveal the possible presence of chloroform or ethanol, no further attempts were made at that stage to elucidate this point.

Crystal data

Aflatoxin $B_1.CHCl_3$, $C_{17}H_{12}O_6.CHCl_3$, W.A.U. 431·7
Orthorhombic, $a=6{\cdot}16$, $b=8{\cdot}04$, $c=36{\cdot}25$ Å
$U=1796{\cdot}8$ Å^3, $D_m=1{\cdot}51$ g.cm^{-3}, $Z=4$, $D_x=1{\cdot}60$ g.cm^{-3}
$\mu=49{\cdot}2$ cm^{-1} for Cu $K\alpha$ radiation

The intensities were measured with a General Electric diffractometer (Furnas, 1957), using nickel-filtered Cu radiation, and a scintillation counter with pulse height discrimination. In order to keep the counting rate below a value of 1000 counts.sec^{-1}, several attenuating filters of increasing thickness were used.

The intensities of 1230 of the 2400 theoretically possible independent reflexions were determined with a crystal measuring approximately $0{\cdot}6\times0{\cdot}4\times0{\cdot}02$ mm, using the stationary-crystal stationary-counter technique. The background for each reflexion was taken from a curve, determined by measuring the background at several values of θ, increasing from 5° to 65°. In the same range of θ values, also the integrated intensities were measured for a number of reflexions, in order to convert peak values into integrated values. Finally, the intensities were corrected for the Lorentz–polarization factor. Corrections of the intensities for absorption have only been made after chloroform appeared to be present in the structure.

Determination of the structure

A three-dimensional vector map, sharpened by the method of Jacobson, Wunderlich & Lipscomb (1961), was calculated. From this vector map, the orientation of the plane in which the aflatoxin B_1 molecule is situated could easily be deduced.

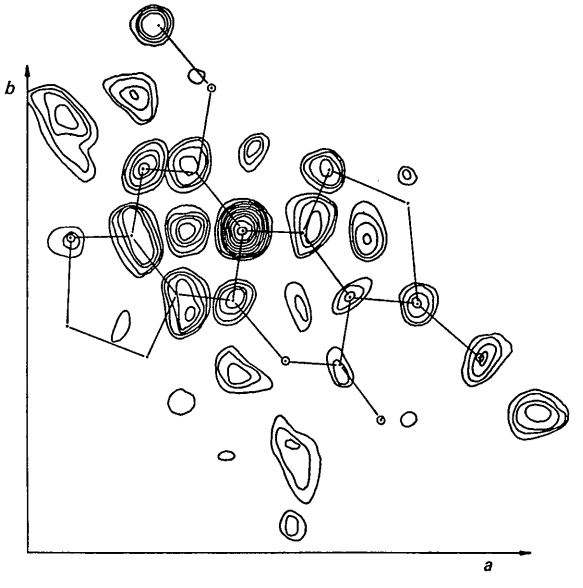


Fig. 1. Superimposed contour sections drawn parallel to the (001) plane of the minimum function calculated for the vectors V_1 (0·706, 0·979, 0·091) and V_2 (0·831, 0·115, 0·910) showing the orientation of the aflatoxin B_1 molecule.

However, the exact orientation of the molecule in this plane could not be determined from the 12 orientations which are all compatible with the vector map because of the shape of the molecule. Therefore, we decided to calculate the relative coordinates for all possible orientations of the molecule from the coordinates of the aflatoxin B_2 molecule (van Soest & Peerdeman, 1970) and to use the minimum residual method of Bhuiya & Stanley (1964) to determine the position of the molecule in the cell for each of these orientations. For this purpose, a minimum residual calculation program was written in Algol by the first author in cooperation with Drs H. Krabbendam of the Laboratory for Crystal Chemistry, Utrecht; later on, the program was translated into Fortran IV for use on an IBM 1800 computer. Using this program, it is possible to keep atoms of known position fixed, whereas a group of atoms of unknown position is being moved through the unit cell. This program can also be used to refine projections in case of a serious overlap.

We calculated the minimum residual functions $R(0YZ)$ and $R(X0Z)$ for every possible orientation of the molecule, using 43 strong low-order $0kl$ and 35 strong low-order $h0l$ reflexions. We tried to find a pronounced minimum in one projection and a corresponding one in the other projection. Unfortunately, these functions showed many minima ranging from 0·40 to 0·50 and, in the first instance, the correct combination of minima could not be found because of the many possibilities and owing to the fact that only part of the probably slightly-inaccurate structure was being displaced.

In the meantime, a program to calculate minimum functions was written for the Telefunken TR4 computer in Algol by the first author in cooperation with Drs H. Krabbendam.

Knowing the shape of the aflatoxin B_2 molecule, a number of possible single or double intramolecular vectors were derived from the vector map and a number of minimum functions for combinations of these vectors were calculated. Only the minimum function of the vectors V_1 (0·706, 0·979, 0·091) and V_2 (0·831, 0·115, 0·910) contained interpretable information: a distinct orientation of the molecule could be observed, as can be seen in the composite drawing of the relevant parts of the sections of the minimum function (Fig. 1). However, equivalent molecules and, consequently, the positions of the symmetry elements with respect to these molecules could not be found from this function. Now the minimum residual functions $R(0YZ)$ and $R(X0Z)$ belonging to the orientation in Fig. 1 were reinvestigated and, as a result, two corresponding minima could be found indicating the positions of the molecules, the intermolecular distances of which were reasonable. Although $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0·79 for 279 $0kl$ reflexions, the projection of the structure

along the *a* axis showed, in addition to aflatoxin B_1, also a chloroform molecule. The structure factors for the Fourier summation were weighted with the function tanh $[|F_o| . |F_c|/(12 f_{Cl})^2]$ (Woolfson, 1956).

Refinement of the structure

Because of the presence of chloroform in the structure and the unfavourable shape of the crystal, correction

Table 1. *Observed and calculated structure factors* ($\times$ 10) *and phase angles*

U's indicate reflexions omitted from the refinement.

for absorption became necessary. This was done with a program written by Duisenberg (1966), by which the absorption correction for a crystal of arbitrary shape can be calculated. The reflexions with a low l index were greatly affected by absorption because the c axis, being perpendicular to the largest crystal face, had been aligned parallel to the ω axis of the General Electric diffractometer. This is illustrated by the absorption correction curve for the structure factors $F(00l)$ shown in Fig. 2.

The refinement was carried out on an IBM 1800 computer, using a block-diagonal least-squares program written in Fortran by the first author. This program allows the refinement of a structure using anomalous atomic scattering factors. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). At first, only the real part corrected for dispersion was used for the chlorine atom.

In the course of the refinement procedures, 45 reflexions supposed to be unreliable were left out and with the remaining 1185 reflexions R decreased to 0·060, varying the positions of all 40 atoms, the anisotropic temperature factors of the 27 heavy atoms and the scaling factor. An overall temperature factor of 4·0 Å^2 was assigned to the hydrogen atoms the positions of which were found by means of a difference Fourier. Now structure factors were calculated after introducing the imaginary part $\Delta f''$ of the scattering factor of the chlorine atoms. R increased to 0·065 for $\Delta f'' = -0{\cdot}70$ and decreased to 0·058 for $\Delta f'' = +0{\cdot}70$, which means that the model need not be inverted. The structure was further refined with the positive value of $\Delta f''$ and with individual isotropic temperature factors of the hydrogen atoms. These values were calculated from the anisotropic temperature factors of the carbon atoms to which they are bound, using the formula:

$$B = \tfrac{4}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} (\mathbf{a}_i . \mathbf{a}_j)$$

derived by Hamilton (1959). The final R was 0·054; for the negative value of $\Delta f''$, the refinement stopped at $R = 0{\cdot}063$. The final shifts in the positional and thermal parameters for non-hydrogen atoms were all less than $\sigma/6$ and $\sigma/5$ respectively. Those for the hydrogen atoms were less than $\sigma/2$.

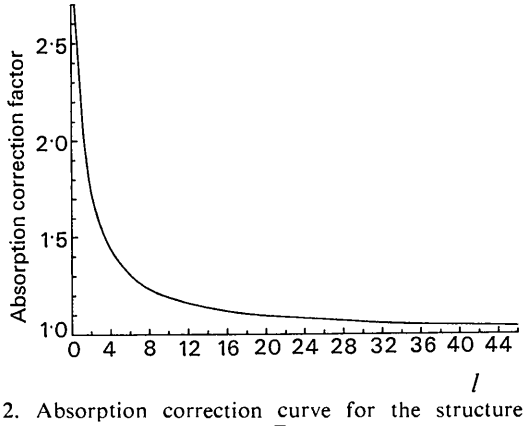


Fig. 2. Absorption correction curve for the structure factors F_{00l}.

A list of the final structure factors is given in Table 1 and the structural parameters are given in Tables 2 to 4. The arbitrary numbering of the atoms in the molecule is given in Fig. 3.

Table 2. *Final positional parameters and e.s.d.'s* (× 10^5) *for the non-hydrogen atoms*

	x/a	y/b	z/c
C(1)	80289 (126)	39533 (100)	34789 (20)
C(2)	77914 (131)	22805 (107)	32692 (21)
C(3)	58035 (139)	14075 (103)	34372 (20)
C(4)	61775 (119)	40366 (96)	37256 (19)
C(5)	49147 (120)	26349 (93)	37139 (18)
C(6)	56928 (129)	54303 (107)	39679 (22)
C(7)	30586 (119)	24614 (94)	39445 (18)
C(8)	16508 (119)	10659 (93)	39547 (19)
C(9)	26112 (116)	37850 (93)	41828 (19)
C(10)	− 1339 (130)	9954 (100)	41741 (21)
C(11)	8236 (128)	37827 (103)	44154 (19)
C(12)	−4807 (121)	23878 (109)	43984 (20)
C(13)	369 (137)	49130 (105)	47094 (21)
C(14)	−20175 (133)	40268 (111)	48303 (21)
C(15)	10134 (151)	−17271 (108)	37204 (25)
C(16)	13675 (141)	48844 (110)	50580 (20)
C(17)	2196 (170)	41293 (112)	53174 (23)
C(18)	81122 (152)	70100 (110)	27130 (25)
O(1)	94571 (92)	49297 (73)	34297 (15)
O(2)	66167 (104)	67168 (74)	39966 (17)
O(3)	38540 (81)	51988 (62)	41959 (14)
O(4)	−22317 (85)	25111 (79)	46332 (15)
O(5)	22459 (88)	−1800 (69)	37229 (16)
O(6)	−18138 (92)	36556 (81)	52101 (15)
Cl(1)	98459 (54)	87399 (41)	26735 (9)
Cl(2)	58279 (48)	75320 (42)	29594 (9)
Cl(3)	74896 (53)	62700 (40)	22749 (8)

Table 3. *Final parameters and e.s.d.'s* (× 10^3) and *the isotropic temperature factors* (Å) *for the hydrogen atoms*

	x/a	y/b	z/c	B
H(1)	757 (14)	243 (12)	299 (2)	3·46
H(2)	875 (13)	151 (11)	324 (2)	3·46
H(3)	483 (14)	124 (11)	321 (2)	3·51
H(4)	627 (14)	6 (12)	345 (2)	3·51
H(5)	187 (15)	779 (12)	351 (2)	4·30
H(6)	−9 (15)	−168 (12)	346 (2)	4·30
H(7)	85 (14)	786 (12)	393 (2)	4·30
H(8)	−78 (13)	7 (11)	420 (2)	3·15
H(9)	962 (15)	555 (12)	454 (2)	4·30
H(10)	641 (15)	461 (12)	475 (2)	4·51
H(11)	277 (16)	583 (11)	509 (2)	3·90
H(12)	9 (16)	411 (13)	553 (2)	5·54
H(13)	887 (15)	618 (12)	284 (2)	4·83

Absolute configuration of aflatoxin B_1

The refinement using the positive value of $\Delta f''$ is better than that when the negative value is used. Examination of the geometry of the diffractometer showed that the reflexions had been indexed with

respect to a right-handed set of reciprocal axes, so that the correct absolute configuration of the structure is given by the atomic coordinates *xyz* in a right-handed coordinate system. This configuration agrees with that found by Brechbühler, Büchi & Milne (1967) with degradative methods.

A perspective formula of the aflatoxin B_1 molecule is given in Fig. 3.

Discussion

The bond lengths and the bond angles of aflatoxin B_1, which are not corrected for thermal motion, are shown in Figs. 3 and 4 respectively. The standard deviations are also given.

Aflatoxin B_1 is largely a plane molecule. All heavy atoms but C(16), C(17) and O(6) lie within 0·12 Å from the plane given by the least-squares equation:

$$-0{\cdot}5643\ X+0{\cdot}4118\ Y-0{\cdot}7156\ Z+10{\cdot}489=0\ .$$

The outer dihydrofuran ring protrudes from this plane; the equation of the plane formed by the five atoms C(13), C(14), C(16), C(17) and O(6) is:

$$-0{\cdot}3842\ X+0{\cdot}8858\ Y+0{\cdot}2603\ Z-7{\cdot}926=0\ .$$

These atoms lie within 0·03 Å from this plane, which forms an angle of 113·3° with the first plane. The distance from the atoms to their respective planes are given in Table 5.

Table 5. *Distances from the heavy atoms to the least-squares planes of the aflatoxin* B_1 *molecule*

$-0{\cdot}5643X+0{\cdot}4118Y-0{\cdot}7156Z+10{\cdot}489=0$

C(1)	−0·019 Å
C(2)	+0·053
C(3)	+0·019
C(4)	+0·014
C(5)	+0·018
C(6)	+0·015
C(7)	+0·007
C(8)	+0·009
C(9)	−0·017
C(10)	+0·036
C(11)	+0·001
C(12)	+0·038
C(13)	−0·114
C(14)	−0·007
C(15)	−0·088
O(1)	−0·065
O(2)	+0·045
O(3)	−0·014
O(4)	+0·077
O(5)	−0·009

$-0{\cdot}3842X+0{\cdot}8858Y+0{\cdot}2603Z-7{\cdot}926=0$

C(13)	+0·009 Å
C(14)	−0·019
C(16)	+0·005
C(17)	−0·018
O(6)	+0·024

The structure of the aflatoxin B_1 molecule resembles of course very much that of aflatoxin B_2, a detailed survey of which has been presented by van Soest & Peerdeman (1970).

Table 4. *Final thermal parameters and e.s.d.'s* ($\times 10^5$) *for the non-hydrogen atoms*

The anisotropic temperature factor is defined as

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1940 (225)	1272 (145)	64 (6)	114 (170)	36 (32)	9 (26)
C(2)	2352 (248)	1401 (157)	78 (7)	−218 (190)	111 (34)	−140 (28)
C(3)	3106 (280)	1199 (145)	57 (6)	−200 (183)	74 (34)	−51 (26)
C(4)	1937 (220)	1258 (138)	49 (5)	−16 (163)	16 (29)	−42 (24)
C(5)	1921 (205)	888 (120)	55 (5)	57 (155)	−24 (29)	29 (23)
C(6)	2219 (242)	1348 (147)	78 (7)	−214 (171)	117 (35)	−16 (27)
C(7)	2241 (214)	769 (115)	53 (5)	51 (155)	−2 (29)	−6 (21)
C(8)	2014 (221)	916 (126)	65 (6)	50 (156)	−24 (32)	−48 (24)
C(9)	1869 (216)	937 (123)	65 (6)	−161 (154)	9 (31)	26 (24)
C(10)	2246 (233)	1257 (148)	74 (7)	−579 (174)	10 (36)	−2 (27)
C(11)	2224 (229)	1168 (137)	61 (6)	71 (176)	11 (30)	20 (25)
C(12)	1864 (232)	1490 (153)	68 (6)	−398 (183)	5 (30)	60 (28)
C(13)	2237 (236)	1400 (158)	77 (7)	336 (185)	65 (34)	48 (29)
C(14)	2301 (252)	1764 (173)	67 (7)	312 (194)	85 (34)	45 (29)
C(15)	3416 (311)	1403 (160)	96 (8)	−1145 (206)	46 (43)	−54 (30)
C(16)	3220 (287)	1466 (157)	58 (7)	−78 (199)	55 (36)	−34 (27)
C(17)	4470 (358)	1631 (181)	69 (7)	699 (235)	125 (45)	−37 (30)
C(18)	3245 (294)	1433 (165)	101 (8)	−65 (199)	−59 (45)	−0 (31)
O(1)	2599 (183)	1322 (106)	108 (6)	−488 (128)	160 (27)	−21 (21)
O(2)	3891 (221)	1397 (107)	124 (6)	−1172 (140)	332 (32)	−146 (22)
O(3)	2086 (146)	898 (85)	80 (5)	−49 (106)	96 (23)	−45 (17)
O(4)	2093 (163)	2009 (119)	94 (5)	−373 (140)	127 (24)	−66 (23)
O(5)	2372 (171)	1253 (99)	112 (6)	−524 (124)	103 (27)	−84 (20)
O(6)	2450 (172)	2127 (124)	88 (5)	−413 (145)	106 (25)	19 (22)
Cl(1)	5269 (111)	2629 (61)	156 (3)	−1416 (78)	87 (17)	−106 (12)
Cl(2)	4319 (100)	2588 (60)	176 (3)	336 (80)	244 (16)	−93 (13)
Cl(3)	5576 (116)	2753 (61)	122 (2)	−925 (81)	7 (16)	−136 (11)

The normal intramolecular distances and angles of the chloroform molecule are given in Table 6.

Table 6. *Bond lengths, bond angles and e.s.d.'s of the chloroform molecule*

C(18)–Cl(1)	1·760 (9) Å
C(18)–Cl(2)	1·719 (10)
C(18)–Cl(3)	1·739 (9)
C(18)–H(13)	0·93 (12)
Cl(1) –C(18)–Cl(2)	110·3 (5)°
Cl(1) –C(18)–Cl(3)	109·3 (5)
Cl(2) –C(18)–Cl(3)	112·2 (5)
H(13)–C(18)–Cl(1)	108 (7)
H(13)–C(18)–Cl(2)	110 (7)
H(13)–C(18)–Cl(3)	108 (7)

Fig. 5 shows that the structure consists of layers of aflatoxin B_1 molecules separated by layers of chloroform molecules. It appeared that the crystal could easily be cleaved, which is not unusual for a layer structure. The layers mentioned, the cleavage plane as well as the dominating face of the crystal have the same index (001). Within the aflatoxin B_1 layer, two molecules related to one another by the translation $\mathbf{a}+\mathbf{b}$, are almost coplanar. The distance between their best-fitting planes is 0·16 Å.

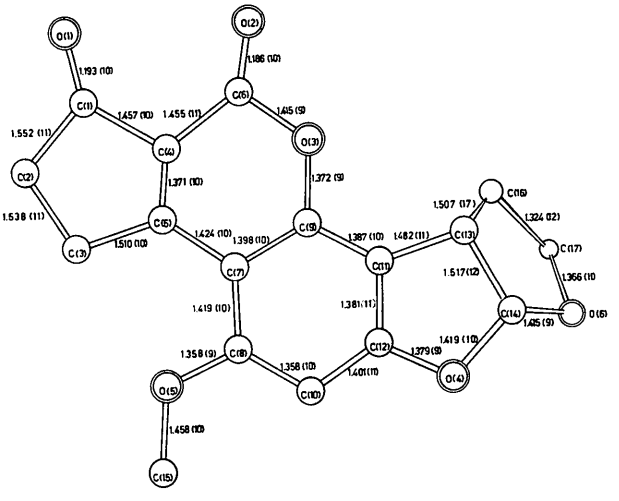


Fig. 3. Arbitrary numbering of the atoms, the bond lengths (e.s.d.'s) and a perspective view of the aflatoxin B_1 molecule, showing the correct absolute configuration.

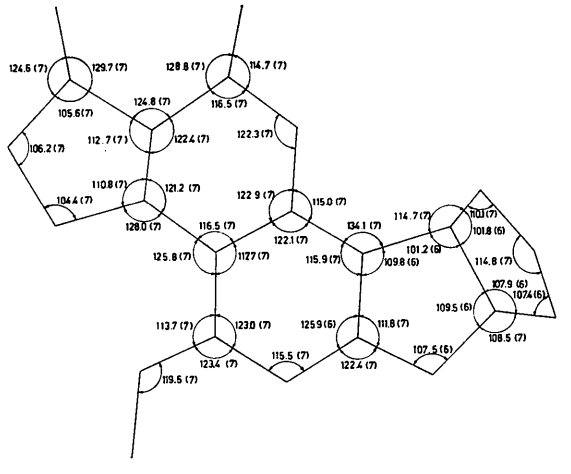


Fig. 4. The bond angles, together with their standard deviations, of the aflatoxin B_1 molecule.

The methyl group of the first molecule is very close to the two carbonyl oxygen atoms O(1) and O(2) of the second molecule, as is shown by the short distances C(15)...O(1) and C(15)...O(2) of 3·04 Å and 3·15 Å respectively. It seems as if the aflatoxin B_1 molecules are interconnected to form a planar string of molecules by an interaction between the methyl group and the carbonyl oxygen atoms. Sutor (1963) has reported a number of crystal structures which contain short CH_3...O contacts; they mainly occur in the crystal structures of heterocyclic molecules of biological importance, having in many cases, a conjugated double bond system. According to this author, the interactions would be due to hydrogen bonding. None of the methyl groups in the compounds reported by Sutor forms more than one short contact; however, the methyl group of aflatoxin B_1 has two short contacts as mentioned above.

Within the aflatoxin B_1 layer, strings of almost coplanar molecules exist in two directions: [110] and [$\bar{1}$10]. Molecules arranged in parallel strings and related by the translation **a**, have an interplanar distance of 3·48 Å as was calculated from the equation for the least-squares plane. The double bond C(16)–C(17) of the protruding dihydrofuran ring of one molecule is parallel to the plane of the molecule related to it by $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$. It touches the latter molecule in the neighbourhood of the benzene nucleus, the distance between the double bond and the benzene nucleus being 3·62 Å.

The molecules are packed rather closely as can be seen from the intermolecular contacts shown in Fig. 5. The distances C(17)...O(2), C(17)...O(4), being 3·35 and 3·29 Å, are shorter than the sum of the van der Waals radii.

We have seen that the carbonyl oxygen atoms of the aflatoxin B_1 molecule show a tendency to interact with a CH_3 group. On the other hand, it is generally known that chloroform associates with ketones through the C–H group; according to Pimentel & McClellan (1960), the evidence for such an association through hydrogen bonding is conclusive, so it might be expected that chloroform is hydrogen bonded to aflatoxin B_1 in this structure. The atom C(18) of the chloroform molecule is indeed very near to the atom O(1) of the aflatoxin B_1 molecule: their distance is 3·19 Å. Also the H(13)...O(1) distance of 2·40 Å and the angles H(13)–C(18)...O(1), C(18)–H(13)...O(1) and H(13)...O(1)...C(18), being 26, 144 and 10° respectively are, according to Sutor (1963), appropriate for a CH...O hydrogen bond.

In the literature, we could find only one other structure containing chloroform, namely the chloroform solvate of dioxodi-8-quinolinolato-8-quinolinoluranium(VI) (Hall, Rae & Waters, 1967). In this structure, the chloroform molecules are also situated near a carbonyl oxygen atom. The chloroform C–quinolinol O distance is 2·98 Å; the angles Cl–C...O vary from 99·5 to 123·4°. It seems that also in this case, the chloroform molecule is hydrogen-bonded to a carbonyl oxygen atom. An interesting point is that in the quinolinol structure, the chlorine atoms of the chloroform molecule are disordered in contrast with its carbon atom, the disorder of which is possibly prevented by the hydrogen bond to the oxygen atom of the quinolinol molecule.

Thermal motion

The atomic vibration ellipsoids have been analysed in terms of the rigid-body tensors of translation (**T**), libration (**L**) and screw motion (**S**) (Schomaker & Trueblood, 1968). All 23 heavy atoms were considered; the results of the analysis are given in Table 7.

The r.m.s. deviation between the thermal parameters obtained by the least-squares refinement and those calculated from the rigid-body tensors is 0·0065 Å^2. The translation tensor is slightly anisotropic; however, an explanation for the directions of its principal axes could not be found. Just as for the aflatoxin B_2 molecule, the libration tensor is anisotropic. One of its principal axes is appreciably longer than the other two.

The aflatoxin B_2 molecule has its greatest libration around an axis, the moment of inertia of which is smallest. It is interesting to see whether this is also the case with the aflatoxin B_1 molecule in a different crystal structure. Therefore, the inertia tensor **I** (the principal axes and their directions with respect to the crystallographic axes) of the aflatoxin B_1 molecule was calculated, using the unique origin obtained by symmetrizing S. This tensor is anisotropic as well, one of its principal axes being shorter than the other two. The angle between the largest principal axis of **L** and the smallest principal axis of **I** is again small: 11°. This means that the libration of the molecule is influenced by its moment of inertia. The libration tensor related to the axial system defined by the principal axes of the inertial tensor is given in Table 7.

Table 7. *Rigid-body thermal parameters*

$$\mathbf{T} = \begin{pmatrix} 342 & -15 & -17 \\ & 304 & -7 \\ & & 377 \end{pmatrix} \times 10^{-4}\ \text{Å}^2$$

$$\sigma(\mathbf{T}) = \begin{pmatrix} 19 & 18 & 18 \\ & 20 & 18 \\ & & 20 \end{pmatrix} \times 10^{-4}\ \text{Å}^2$$

$$\mathbf{L} = \begin{pmatrix} 72 & -15 & -52 \\ & 48 & 14 \\ & & 102 \end{pmatrix} \times 10^{-1}\ (^\circ)^2$$

$$\sigma(\mathbf{L}) = \begin{pmatrix} 10 & 7 & 8 \\ & 7 & 8 \\ & & 11 \end{pmatrix} \times 10^{-1}\ (^\circ)^2$$

Unique origin (Å)*	2·332	2·168	14·587
Centre of gravity (Å)	1·743	2·602	15·065

Principal axes of **I**†

Eigenvalue	Direction cosines (×10^4)		
1210 Å^2	−7036	631	7078
2792	−3660	−8859	−2849
3721	6091	−4594	6464

Principal axes of **T**‡

Eigenvalue	Direction cosines (×10^4)		
0·0384 Å^2	−3786	−90	9255
0·0342	−8463	4080	−3422
0·0296	−3745	−9129	−1621

Principal axes of **L**

Eigenvalue	Direction cosines (×10^4)		
14·6 (°)^2	−5951	1985	7787
4·5	−942	9449	−3134
3·2	−7981	−2593	−5437

Libration tensor **L** related to the principal axes of **I**

$$\mathbf{L} = \begin{pmatrix} 43 & -5 & 1 \\ & 12 & 1 \\ & & 11 \end{pmatrix} \times 10^{-4}\ \text{rad}^2$$

r.m.s. difference between 'observed' and calculated U_{ij}: 65×10^{-4} Å^2.

* This origin symmetrizes **S**.

† Calculated for the unique origin, using atomic weights instead of mass weights.

‡ Calculated after **S** had been symmetrized.

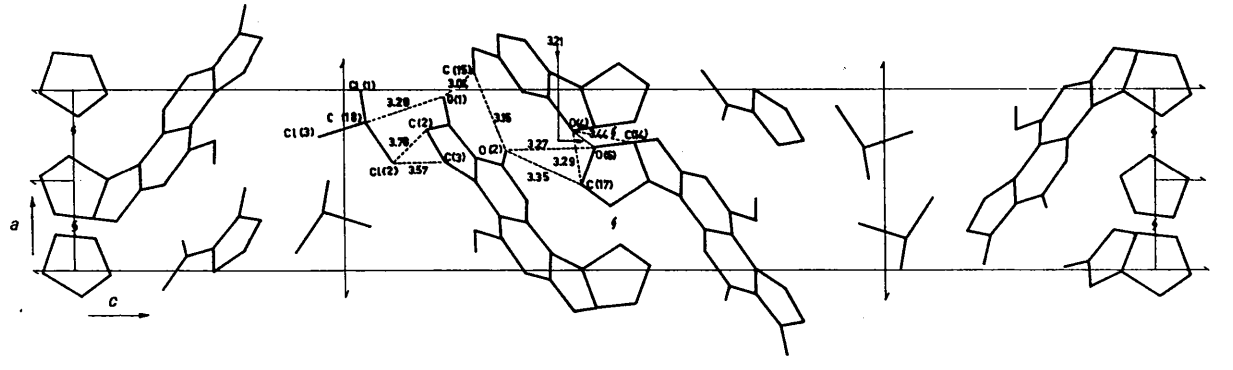


Fig. 5. Projection of the structure of aflatoxin B_1.$CHCl_3$ on the (010) plane.

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The Crystal Structures of Aflatoxin B_1. II. The Structure of an Orthorhombic and a Monoclinic Modification

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If aflatoxin B_1 is recrystallized from a chloroform–ethanol mixture, both an orthorhombic and a monoclinic modification are formed. The orthorhombic crystals have the unit-cell constants $a=7{\cdot}84$, $b=6{\cdot}36$ and $c=28{\cdot}35$ Å and the space group is $P2_12_12_1$, while the constants for the monoclinic crystals are $a=7{\cdot}93$, $b=6{\cdot}21$, $c=14{\cdot}04$ Å and $\alpha=95{\cdot}8°$. Their space group is $P2_1$. The crystal structures of the two modifications have been solved with the aid of the structure of aflatoxin $B_1.CHCl_3$ already known. The orientations of the aflatoxin B_1 molecule were assumed to be the same in all three structures and the positions of the molecules were determined by calculating the value of the residual while they were moved systematically through the unit cell. Both structures consist (just as the structure of aflatoxin $B_1.CHCl_3$) of strings of coplanar molecules in the directions [110] and [$\bar{1}$10]. The molecules within a string have again two short $CH_3\cdots O$ contacts: 2·97 and 3·18 Å for the orthorhombic form and 3·00 and 3·10 Å for the monoclinic form. These short contacts point to an interaction between the molecules and may be called hydrogen bonds.

Introduction

If aflatoxin B_1 is recrystallized by diffusion of ethanol (in which it is only slightly soluble) into a saturated solution of the toxin in chloroform, crystals containing chloroform (modification I) are formed (van Soest & Peerdeman, 1970*a*). However, if a solution of the toxin in a mixture of chloroform and ethanol is slowly evaporated, two new modifications (II and III) are formed. Their crystal structures were determined in order to compare them with the crystal structures already found for aflatoxin B_2 (van Soest & Peerdeman, 1970*b*) and for aflatoxin $B_1.CHCl_3$.

Experimental

For both modifications, the unit-cell dimensions were determined from Weissenberg and rotation photographs; their space groups followed from the systematically absent reflexions. The intensities were measured automatically with a PAILRED diffractometer, using nickel-filtered copper radiation. The monochromator was not applied in view of the small scattering power of the crystals. The intensities were corrected for Lorentz and polarization factors.

Most of the crystals obtained from the chloroform–ethanol solution are thin pale-yellow platelets. They