The Crystal and Molecular Structure of Obtusifolin, a New Flavanone, $C_{24}H_{22}O_7$

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The crystal and molecular structure of obtusifolin, $C_{24}H_{22}O_7$, a flavanone, has been determined by a direct phase-determination method, and has been refined by least squares to an R index of 7·9% for 1926 reflexions measured on a Siemens off-line diffractometer. The space group is $P2_12_12_1$ with four molecules in a unit cell of dimensions $a=20·96$, $b=12·47$ and $c=7·99$ Å. Obtusifolin is a dihydroxy-flavanone, which is linked with a tri-substituted 4-hydroxy-2-pyrone ring by a methylene bridge. Bond lengths and bond angles have been calculated. Best plane equations have also been calculated for various rings and for the pseudo-symmetry plane passing through the methylene carbon atom.

Introduction

Obtusifolin, $C_{24}H_{22}O_7$, a new flavanone was isolated by Hänsel, Ohlendorf & Pelter (1970) together with three other lipophilic substances from the leaves and stems of *Gnaphalium obtusifolium* (family: *Compositae*). An X-ray structure analysis was undertaken to determine the correct crystal and molecular structure of this natural compound. It crystallizes in colourless crystals from acetone (m.p. 202–204°C). It forms a tri-acetate and a dimethyl derivative at m.p. 168–171°C and a monomethyl derivative at m.p. 232–236°C. It is optically active; $[\alpha]_D = +91·2°$ ($c=0·523$).

Crystal data

The cell dimensions are:

a	20·96 Å
b	12·47
c	7·99
V	2088 Å³
M.W.	422·4

The space group is $P2_12_12_1$ and there are four molecules in a unit cell. The density of the crystals, measured by the flotation method in an aqueous potassium iodide solution, was $d_m=1·32$ g.cm⁻³ and the calculated density for four molecules per unit cell is $d_{cal}=1·34$ g.cm⁻³.

Intensity data

The three-dimensional X-ray diffraction intensity data were collected on a Siemens off-line four-circle single-crystal diffractometer, using Cu $K\alpha$ radiation (1·54178 Å). The photographic films showed a rapid fall off in intensity of the reflexions beyond $\theta=40°$. The first intensity data measurements below the $\theta=40°$ range gave a total of 778 reflexions and early attempts to solve the structure from these data proved futile. To collect more data, the thickest available crystal of size 0·4×0·4×0·7 mm was selected. All the re-flexions within $\theta \le 64°$ were measured (mode of measurement: $\theta/2\theta$ scan, 5-point measuring procedure). Of the 1926 reflexions measured 167 were classified as 'weak', with an observed intensity less than twice the standard deviation of the measurements. The intensities were corrected for the Lorentz–polarization (1/Lp) factors. No absorption correction was applied.

Structure analysis

The corrected intensity data were sorted on the data reduction program *DATRDN*, which sorts $|F_o|$ values on an arbitrary scale and $f(hkl)$ values at absolute zero temperature. The absolute scale factor k of the data $|F_o|$ and the overall temperature factor B were estimated from Wilson statistics (*DATFIX*). The values of the statistical averages for the normalized structure factors $|E|$ and $|E^2-1|$ for non-centrosymmetric reflexions were 0·849 and 0·843 respectively as compared with the theoretical values 0·886 and 0·736 for non-centrosymmetric space groups. The overall thermal parameter B was 5·3 Å², consistent with the rapid fall off of intensities at high angles. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). These intensities, set on an absolute scale, were used to solve the structure by a direct phase determination method, programmed by one of us (Zechmeister, 1969), which is based on a cyclic application of the statistical phase relationships given by Cochran (1955). This is also equivalent to the tangent formula (Karle & Hauptman, 1956).

The general formula for calculating the most probable value of the phase is

$$\langle\varphi_h\rangle=\text{phase of } \sum_{1}^{m} |U_h| |U_{h-h'}|\exp i (\varphi_h+\varphi_{h-h'}) \quad (1)$$

To limit the procedure the statistical error equation $(\overline{\Delta\varphi_h})$, associated with each term in (1) was used.

In the acentric space groups with centrosymmetric projections such as $P2_12_12_1$, the origin is restricted to

Table 1. *Starting phase set for the cyclic procedure*

					Phase		
h	k	l	U		Initial	True (in cycles)	
1	11	3	0·31		0·25	0·216	⎫
6	10	1	0·31		0·00	0·004	⎬ Origin and enantiomorph
1	12	5	0·24		0·00	0·002	⎪
23	4	0	0·26		0·25	0·25	⎭
0	11	3	0·39		0·75	0·75	
12	8	0	0·29		0·00	0·00	

certain special positions. This condition for the restricted free choice of the origin in the unit cell and of the enantiomorphic structures allows the phases of four two-dimensional reflexions to be arbitrarily fixed in the space group concerned here. However, for the analysis of the present structure three of the four starting reflexions were three-dimensional. The initial phases of these three-dimensional reflexions were those obtained from the contributions of the strong two-dimensional reflexions in the triple product relations (see Table 2). The phases of these three-dimensional reflexions were continually refined during the cyclic procedure. In order to extend the initial phase set, two more two-dimensional reflexions were included [see also the multisolution method of Germain & Woolfson (1968)].

Table 2. *Triple-product relations for the starting three-dimensional reflexions*

h	k	l	h	k	l	h	k	l	Phase
			0	11	$\bar{5}\,i$	1	0	$8\,r$	
1	11	3	0	11	$\bar{3}\,i$	1	0	$6\,r$	$\pm i$
			0	12	$3\,r$	1	$\bar{1}$	$0\,i$	
			6	0	$\bar{4}\,r$	0	10	$5\,r$	
6	10	1	0	10	$\bar{5}\,r$	6	0	$6\,r$	$\pm r$
			0	11	$5\,i$	1	1	$0\,i$	
1	12	5	0	12	$\bar{3}\,r$	1	0	$8\,r$	$\pm r$
			0	12	$\bar{1}\,r$	1	0	$6\,r$	

i = imaginary; r = real.

Table 3. *Coordinates of the non-hydrogen atoms* $\times 10^5$

E.s.d.'s are given in parentheses.

	x/a	y/b	z/c
O(1)	33737 (21)	37918 (34)	20810 (70)
O(2)	21111 (24)	30528 (38)	22345 (80)
O(3)	8212 (24)	54212 (46)	29877 (84)
O(4)	14735 (23)	66833 (39)	19817 (82)
O(5)	26830 (24)	74131 (37)	21302 (87)
O(6)	47263 (23)	65958 (45)	42139 (84)
O(7)	50676 (25)	46499 (52)	42952 (89)
C(1)	36447 (43)	15051 (73)	855 (122)
C(2)	16065 (52)	94989 (77)	49075 (149)
C(3)	31551 (54)	−602 (75)	12199 (191)
C(4)	31667 (51)	3458 (89)	27065 (186)
C(5)	34106 (48)	14125 (78)	30606 (148)
C(6)	36543 (33)	19554 (67)	16655 (123)
C(7)	39287 (32)	30967 (53)	18753 (107)
C(8)	43829 (36)	32398 (65)	33744 (122)
C(9)	45618 (37)	43821 (65)	36676 (112)
C(10)	40782 (31)	51703 (61)	31750 (94)
C(11)	34950 (30)	48603 (52)	24147 (91)
C(12)	30226 (30)	55648 (50)	19796 (91)
C(13)	31196 (35)	66543 (60)	24508 (114)
C(14)	36940 (34)	70079 (57)	31671 (110)
C(15)	41676 (37)	62807 (62)	35149 (107)
C(16)	24479 (36)	52093 (52)	9680 (84)
C(17)	18618 (31)	48874 (53)	19325 (88)
C(18)	17135 (36)	38526 (59)	24105 (100)
C(19)	10893 (38)	35973 (66)	30948 (111)
C(20)	6581 (44)	43949 (78)	33488 (139)
C(21)	14000 (36)	57273 (68)	22657 (104)
C(22)	9424 (49)	24459 (79)	34951 (181)
C(23)	94 (49)	42419 (93)	40623 (218)
C(24)	3624 (51)	71 (147)	8342 (264)

Table 4. *Anisotropic temperature factor coefficients* $\times 10^5$

E.s.d.'s are given in parentheses.

The anisotropic thermal parameters are of the form $T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	229 (12)	559 (30)	2468 (117)	−10 (16)	−41 (32)	−50 (53)
O(2)	300 (14)	649 (34)	3469 (146)	−10 (18)	−130 (40)	306 (66)
O(3)	241 (14)	1041 (47)	3453 (149)	−62 (21)	103 (40)	−326 (78)
O(4)	262 (14)	703 (36)	3494 (143)	12 (19)	85 (40)	−45 (68)
O(5)	300 (15)	560 (32)	3815 (162)	−5 (19)	−29 (45)	74 (68)
O(6)	235 (13)	1072 (47)	3142 (139)	−209 (22)	−107 (38)	−187 (77)
O(7)	242 (15)	1317 (58)	3614 (161)	−18 (25)	−309 (43)	106 (93)
C(1)	368 (26)	821 (69)	2621 (195)	48 (35)	−83 (61)	−1 (102)
C(2)	512 (38)	728 (66)	3916 (277)	−68 (43)	174 (90)	202 (123)
C(3)	368 (31)	713 (69)	5185 (359)	−20 (37)	−223 (94)	52 (146)
C(4)	366 (29)	1019 (91)	4973 (365)	−58 (43)	142 (96)	1129 (161)
C(5)	426 (31)	980 (79)	3376 (261)	4 (41)	141 (82)	266 (132)
C(6)	202 (17)	637 (51)	3142 (202)	64 (24)	69 (52)	338 (93)
C(7)	228 (18)	594 (45)	2581 (169)	39 (24)	118 (49)	−54 (82)
C(8)	259 (20)	859 (62)	2755 (194)	98 (30)	5 (54)	280 (98)
C(9)	246 (20)	864 (62)	2446 (176)	46 (30)	5 (51)	38 (94)
C(10)	182 (16)	904 (58)	1796 (134)	−74 (25)	40 (40)	155 (82)

Table 4 (cont.)

|	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	213 (17)	639 (47)	1610 (123)	−20 (23)	58 (39)	3 (69)
C(12)	210 (16)	575 (43)	1624 (129)	−23 (23)	74 (41)	71 (69)
C(13)	265 (20)	718 (53)	2462 (181)	−17 (28)	135 (52)	166 (90)
C(14)	241 (19)	661 (51)	2429 (167)	−88 (26)	27 (49)	−16 (87)
C(15)	295 (21)	834 (60)	2035 (161)	−193 (30)	133 (49)	−8 (86)
C(16)	300 (19)	659 (50)	1531 (118)	8 (27)	−48 (42)	9 (68)
C(17)	244 (18)	727 (48)	1634 (124)	−22 (35)	−159 (41)	−45 (72)
C(18)	316 (21)	796 (56)	1942 (148)	−118 (30)	−178 (48)	215 (81)
C(19)	300 (22)	986 (66)	2508 (176)	−285 (33)	−189 (55)	323 (10)
C(20)	372 (27)	1078 (80)	3265 (231)	−185 (40)	31 (68)	−94 (125)
C(21)	262 (20)	1042 (71)	2035 (153)	−65 (31)	9 (48)	15 (94)
C(22)	454 (34)	1098 (80)	5919 (399)	−140 (46)	187 (103)	744 (170)
C(23)	302 (30)	1410 (105)	7810 (542)	−94 (45)	673 (113)	366 (217)
C(24)	246 (30)	3564 (254)	10389 (716)	−121 (70)	463 (123)	−2839 (411)

The resulting four phase sets were refined over 30 cycles till the phases of almost all the unitary structure factors used (300) were determined. A U-Fourier synthesis of the first two sets, selected on the basis of the 'best solution' criterion (in which the phases of the individual **h** terms having the highest correlation, i.e. minimal Q-value given by the equation

$$Q = 1 - \frac{\sum\limits^{h} |U_{\mathbf{h}}| \left\{ |\sum\limits^{h'} U_{\mathbf{h}'} U_{\mathbf{h}-\mathbf{h}'}| \exp i\, (\varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})/\sum\limits^{h'} |U_{\mathbf{h}'} U_{\mathbf{h}-\mathbf{h}'}| \right\}}{\sum\limits_{\mathbf{h}} |U_{\mathbf{h}}|},$$

are selected) did not lead to the correct solution of the structure. A subsequent U-Fourier synthesis of the third phase set given in Table 1 with Q-value 0·3576

(b)
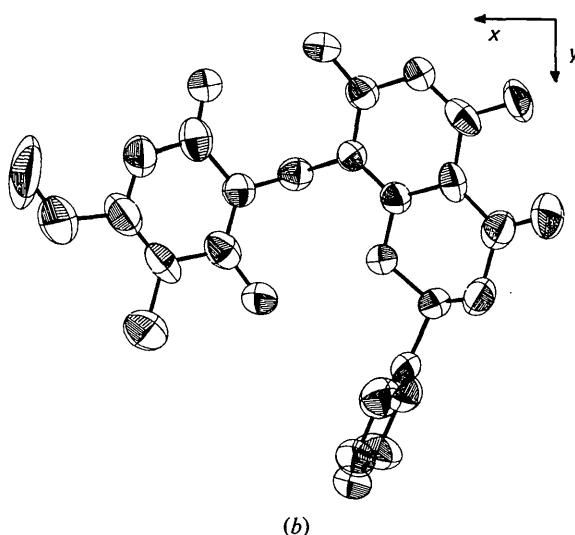
Fig. 1. (cont.) (b) Perspective view of the molecule along the c axis with 50% probability thermal ellipsoids.

Table 5. Coordinates of hydrogen atoms ($\times 10^3$) and temperature factor coefficients

$$T = \exp\,(-B \sin^2 \theta/\lambda^2)$$

	x/a	y/b	z/c	B
H(1)	125	768	427	5·0 Å²
H(2)	157	992	381	5·0
H(3)	304	915	112	5·0
H(4)	302	35	407	5·0
H(5)	333	200	410	5·0
H(7)	402	327	67	5·0
H(8)	411	290	447	5·0
H(9)	473	262	355	5·0
H(14)	377	777	344	5·0
H(16)	255	457	0	5·0
H(17)	233	585	31	5·0
H(20)	82	210	438	5·0
H(21)	114	203	306	5·0
H(22)	46	227	266	5·0
H(54)*	237	709	156	5·0

* H(54) belongs to the atom O(5).

(a)
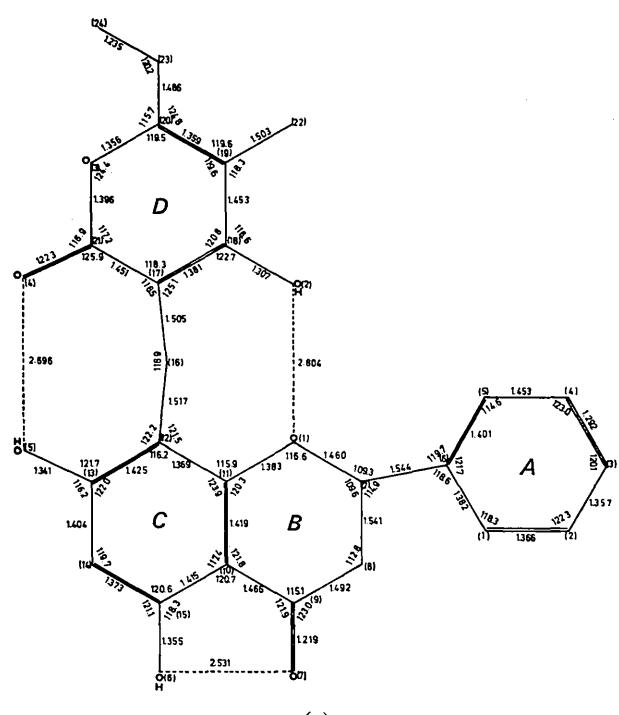
Fig. 1. (a) Numbering of atoms, bond distances and angles (excluding H-atoms).

immediately revealed 29 out of 31 non-hydrogen atoms of the molecule, with an R index of 33%. A Fourier synthesis using the phases of all reflexions, calculated

from the coordinates of 29 atoms, yielded the two remaining atoms. After 3 cycles of isotropic refinement the R index fell to 17·3%. After five cycles of aniso- tropic refinement the R index was 10·3%. From the difference Fourier synthesis computed at this stage 15 hydrogen atoms could be located. With the inclusion of

Table 6. *Observed and calculated structure factors*

Table 6 (cont.)

these hydrogen atoms, two more cycles of anisotropic refinement of the non-hydrogen atoms were performed. No extinction correction was applied. The refinement was terminated when the shifts in the positional and thermal parameters for non-hydrogen atoms were all less than the standard deviation, $\sigma/3$ and $\sigma/2$ respectively. The final R index is 7·9%. The structural parameters with standard deviations in parentheses are given in Tables 3 to 4 for non-hydrogen atoms and in Table 5 for hydrogen atoms.

Fig. 1(a) gives the numbering of atoms, distances and bond angles (excluding H atoms) of the molecule. Fig. 1(b) shows a perspective view of the molecule along the c axis with 50% probability thermal ellipsoids. The configuration of the molecule is shown in Fig. 2. The observed and calculated structure factors are listed in Table 6.

Discussion

Bond lengths and bond angles involving non-hydrogen atoms are listed in Tables 7 and 8 respectively with

Table 7. Bond lengths

E.s.d.'s $\times 10^3$ are given in parentheses.

Carbon–carbon bonds

C(1)—C(2)	1·366 (13) Å
C(1)—C(6)	1·382 (14)
C(2)—C(3)	1·357 (18)
C(3)—C(4)	1·292 (21)
C(4)—C(5)	1·453 (15)
C(5)—C(6)	1·401 (14)
C(6)—C(7)	1·544 (10)
C(7)—C(8)	1·541 (12)
C(8)—C(9)	1·492 (11)
C(9)—C(10)	1·466 (11)
C(10)-C(11)	1·419 (9)
C(10)-C(15)	1·424 (11)
C(11)-C(12)	1·369 (9)
C(12)-C(13)	1·425 (10)
C(12)-C(16)	1·517 (10)
C(13)-C(14)	1·404 (11)
C(14)-C(15)	1·373 (11)
C(16)-C(17)	1·505 (7)
C(17)-C(18)	1·381 (10)
C(17)-C(21)	1·451 (10)
C(18)-C(19)	1·453 (11)
C(19)-C(20)	1·359 (13)
C(19)-C(22)	1·503 (13)
C(20)-C(23)	1·486 (15)
C(23)-C(24)	1·235 (19)

C–O bonds

C(7)—O(1)	1·460 (8)
C(11)-O(1)	1·383 (8)
C(15)-O(6)	1·355 (9)
C(13)-O(5)	1·341 (9)
C(18)-O(2)	1·307 (9)
C(20)-O(3)	1·356 (11)
C(21)-O(3)	1·396 (9)

C=O bonds

C(9)—O(7)	1·219 (10) Å
C(21)-O(4)	1·223 (10)

C–H bonds

C(1)—H(1)	1·225
C(2)—H(2)	1·023
C(3)—H(3)	1·019
C(4)—H(4)	1·129
C(5)—H(5)	1·114
C(7)—H(7)	1·006
C(8)—H(8)	1·136
C(8)—H(9)	1·065
C(14)-H(14)	0·984
C(16)-H(16)	1·132
C(16)-H(17)	0·983
C(22)-H(20)	0·867
C(22)-H(21)	0·753
C(22)-H(22)	1·225

O–H bonds

O(5)—H(54)	0·901

O···H–O bonds

O(1)···H–O(2)	2·804 (5)
O(4)···H–O(5)	2·696 (5)
O(7)···H–O(6)	2·531 (8)

their associated standard deviations. Obtusifolin is a dihydroxyflavanone which is linked with a trisubstituted 4-hydroxy-2-pyrone ring by a methylene bridge.

Table 8. Bond angles

E.s.d.'s × 10 are given in parentheses.

	θ
C(6)—C(1)—C(2)	118·3 (9)°
C(1)—C(2)—C(3)	122·3 (11)
C(2)—C(3)—C(4)	120·1 (10)
C(3)—C(4)—C(5)	123·0 (12)
C(4)—C(5)—C(6)	114·6 (10)
C(5)—C(6)—C(1)	121·7 (8)
C(1)—C(6)—C(7)	118·6 (8)
C(5)—C(6)—C(7)	119·7 (7)
C(6)—C(7)—C(8)	114·9 (7)
C(6)—C(7)—O(1)	105·3 (6)
C(8)—C(7)—O(1)	109·6 (6)
C(7)—C(8)—C(9)	112·8 (7)
C(8)—C(9)—C(10)	115·1 (7)
C(8)—C(9)—O(7)	123·0 (7)
C(10)-C(9)—O(7)	121·9 (7)
C(9)—C(10)-C(11)	121·9 (7)
C(11)-C(10)-C(15)	117·4 (6)
C(9)—C(10)-C(15)	120·7 (6)
C(10)-C(11)-C(12)	123·9 (6)
C(10)-C(11)-O(1)	120·3 (6)
O(1)—C(11)-C(12)	115·9 (6)
C(7)—O(1)—C(11)	116·6 (5)
C(11)-C(12)-C(13)	116·2 (6)
C(11)-C(12)-C(16)	121·5 (6)
C(13)-C(12)-C(16)	122·2 (6)
C(12)-C(13)-C(14)	122·0 (7)
C(12)-C(13)-O(5)	121·7 (7)
C(14)-C(13)-O(5)	116·2 (6)
C(13)-C(14)-C(15)	119·7 (7)
C(14)-C(15)-C(10)	120·6 (7)
C(14)-C(15)-O(6)	121·1 (7)
C(10)-C(15)-O(6)	118·3 (7)
C(12)-C(16)-C(17)	116·9 (5)
C(16)-C(17)-C(18)	125·1 (6)
C(16)-C(17)-C(21)	116·5 (6)
C(21)-C(17)-C(18)	118·3 (6)
C(17)-C(18)-C(19)	120·8 (7)
C(17)-C(18)-O(2)	122·7 (7)
C(19)-C(18)-O(2)	116·6 (6)
C(18)-C(19)-C(20)	119·6 (8)
C(18)-C(19)-C(22)	118·3 (7)
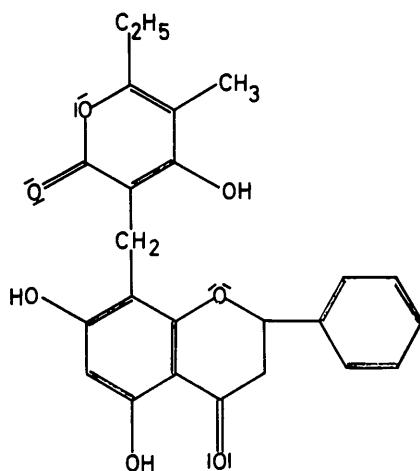
Table 8 (cont.)

	θ
C(22)-C(19)-C(20)	122·1 (8)
C(19)-C(20)-O(3)	119·5 (8)
C(19)-C(20)-C(23)	124·8 (9)
C(23)-C(20)-O(3)	115·7 (8)
C(20)-C(23)-C(24)	120·2 (12)
C(20)-O(3)—C(21)	124·4 (6)
C(17)-C(21)-O(3)	117·2 (7)
C(17)-C(21)-O(4)	125·9 (7)
O(3)—C(21)-O(4)	116·9 (7)

Bond angles involving H-atoms

C(13)-O(5)—H(54)	106°
C(2)—C(1)—H(1)	140
C(6)—C(1)—H(1)	98
C(1)—C(2)—H(2)	121
C(3)—C(2)—H(2)	115
C(2)—C(3)—H(3)	121
C(4)—C(3)—H(3)	117
C(3)—C(4)—H(4)	152
C(5)—C(4)—H(4)	84
C(4)—C(5)—H(5)	133
C(6)—C(5)—H(5)	109
C(6)—C(7)—H(7)	99
C(8)—C(7)—H(7)	126
O(1)—C(7)—H(7)	97
C(7)—C(8)—H(8)	104
C(9)—C(8)—H(8)	111
C(7)—C(8)—H(9)	115
C(9)—C(8)—H(9)	120
H(8)—C(8)—H(9)	88
C(13)-C(14)-H(14)	121
C(15)-C(14)-H(14)	118
C(12)-C(16)-H(16)	115
C(17)-C(16)-H(16)	108
C(12)-C(16)-H(17)	104
C(17)-C(16)-H(17)	106
H(16)-C(16)-H(17)	104
C(19)-C(22)-H(20)	135
C(19)-C(22)-H(21)	116
C(19)-C(22)-H(22)	102
H(20)-C(22)-H(21)	101
H(20)-C(22)-H(22)	96
H(21)-C(22)-H(22)	94

Fig. 2. Configuration of the molecule.

In the phenyl ring A the bond lengths C(3)–C(4) and C(4)–C(5) and the corresponding bond angles C(3)–C(4)–C(5) and C(4)–C(5)–C(6) vary significantly from the standard values, 1·395 Å and 120°. This extremely high deviation is surprising. Whereas all other bond length deviations are just within the allowed significance range of approximately 3σ, this bond length C(3)–C(4) is far too short. One of the reasons for the accuracy of this determination not being very high is certainly the value of the temperature factor $B \simeq 5·5$ Å², which weakens the high order reflexions. Even this does not explain the difference. Ring B has half-chair configuration. The bond length C(7)–O(1) corresponds to the C–O bond length in pyranoses and pyranosides, as found, for example, in the structure analysis of α-glucose by McDonald & Beevers (1952). The bond length C(11)–O(1) agrees with the C–O bond length found in the structure analysis of 2,6-dimethyl-γ-pyrone by Hope (1965).

Ring C is planar; the mean value of the C–C bonds in this aromatic ring is 1·40 Å. The individual bond

lengths, however, vary considerably from the standard values for a benzene ring. The carbonyl groups in rings B and D have bond lengths of 1·22 Å; the bond lengths of the phenolic hydroxy groups in ring C are as expected. Ring D, an α-pyrone ring, is planar and the bond lengths C(20)–O(3) and C(21)–O(3) agree with the values found in 2,6-dimethyl-γ-pyrone (Hope, 1965). The ethyl group C(23), C(24) is statistically disordered. The molecule has intramolecular hydrogen bonds between the atoms O(1)–O(2), O(4)–O(5) and O(6)–O(7) [see Fig. 1(a)]. The angles C(12)–C(13)–O(5), C(17)–C(21)–O(4) and C(17)–C(18)–O(2) are widened, and the angle C(12)–C(16)–C(17) at C(16) is greater than the normal tetrahedral angle. This means that there is a tendency (probably due to van der Waals repulsion of the oxygen atoms) to enlarge the distance between the two ring systems in spite of the hydrogen bonds O(1)–O(2) and O(4)–O(5).

Planarity of the rings and dihedral angles

Best-plane equations have been calculated for rings A, B, C and D and for the pseudo-symmetry plane S passing through C(16), by the method of Schomaker, Waser, Marsh & Bergman (1959). The least-squares plane equations are:

$$1\cdot894 \ x-0\cdot4941 \ y+0\cdot1298 \ z-0\cdot6167=0 \ (A)$$
$$0\cdot9186 \ x+0\cdot0800 \ y-0\cdot7166 \ z-0\cdot1889=0 \ (B)$$
$$0\cdot8424 \ x+0\cdot1819 \ y-0\cdot7225 \ z-0\cdot2096=0 \ (C)$$
$$0\cdot7862 \ x+0\cdot1733 \ y+0\cdot7325 \ z-0\cdot3752=0 \ (D)$$
$$2\cdot001 \ \ x+0\cdot3692 \ y+0\cdot0159 \ z-0\cdot6828=0 \ (S)$$

Plane A defined by atoms C(1) through C(6) is planar with standard deviation 0·007 Å and atom C(7) deviates from this plane by 0·015 Å. The standard deviation of the atoms defining the plane B [C(8) through C(11) and O(1)] is 0·022 Å. Ring B is planar except for the atom C(7) whose deviation from this plane (−0·623 Å) gives the half-chair configuration to this ring; the deviation of O(7) from this best plane is −0·060 Å. The dihedral angle between planes A and B is 77·0°. The planarity of ring C is defined by atoms C(10) through C(15) ($\sigma=0\cdot022$ Å). The atoms O(5), O(6) and C(16) deviate from this plane by 0·026, −0·040 and −0·215 Å respectively. Planes B and C are coplanar (dihedral angle = 5·1°). The standard deviation of the atoms defining plane D [C(17) through C(21) and O(3)] is 0·022 Å. The deviations of other atoms from this plane, namely C(16), O(2), C(22), C(23), C(24) and O(4) are 0·216, −0·073, 0·027, 0·034, 0·117 and −0·016 Å respectively. The fractional coordinates of the centroids of the best planes C and D are

	C	D
$x/a=$	0·3596	0·1257
$y/b=$	0·5923	0·4647
$z/c=$	0·2783	0·2673

The z coordinate is almost identical for the two planes, i.e. both are at the same height, and are tilted with

respect to each other (131·1°), the atom C(16) being the pivot, and C(16) deviates equally from these planes (−0·215 and 0·216 Å). Part of the molecule possesses an internal pseudo-symmetry plane (S), defined by coordinates of six points, namely the coordinates of atom C(16) and the mean of the coordinates of the pairs of atoms O(4)–O(5); C(13)–C(21); C(12)–C(17); C(11)–C(18) and O(1)–O(2) ($\sigma=0\cdot030$ Å). Most of the atoms in rings B and C lie symmetrically with respect to those in ring D with respect to this best plane S. The deviations of the atoms in these rings and also in ring A, from this plane are listed in Table 9. The dihedral angles between this plane (S) and planes C and D are 65·8 and 65·3° almost equal. The dihedral angles between this plane (S) and the other two planes (A and B) are 41·5 and 65·2° respectively.

Table 9. *Deviations of the atoms in the obtusifolin molecule from the symmetry plane S*

	Deviation
O(5)	−1·31 Å
O(4)	1·38
C(13)	−1·91
C(21)	1·88
C(12)	−1·31
C(17)	1·27
C(11)	−2·00
C(18)	1·94
O(1)	−1·36
O(2)	1·44
C(9)	−3·98
C(22)	3·98
C(10)	−3·29
C(19)	3·27
C(15)	−3·89
C(20)	3·84
C(14)	−3·20
O(3)	3·14
O(6)	−5·13
C(23)	5·18
C(1)	−1·02
C(2)	−0·15
C(3)	0·52
C(4)	0·32
C(5)	−0·57
C(6)	−1·23
C(7)	−2·21
C(8)	−3·19
C(24)	5·64
O(7)	−5·10

Molecular structure

Obtusifolin is a dihydroxyflavanone, which is linked with a tri-substituted 4-hydroxy-2-pyrone ring by a methylene bridge. The molecular environment is: planar phenyl ring A inclined to the complanar planes B and C (77·0 and 80·9° to planes B and C), these planes being in turn tilted against planar ring D with methylene carbon atom C(16) as the centre (tilt of

plane B to plane $D = 130 \cdot 4°$) and a pseudo-symmetry plane through C(16). The oxygen atoms in the molecule are bound by intramolecular hydrogen bonds. Intermolecular van der Waals forces hold the molecules together in the structure.

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The Crystal and Molecular Structure of Hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl Molybdenum HB(pz)₃Mo(CO)₂NNC₆H₅

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Hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl molybdenum, $HB(C_3N_2H_3)_3Mo(CO)_2N_2C_6H_5$, crystallizes in the space group $P\bar{1}$. The unit-cell constants are: $a = 9 \cdot 495 \pm 0 \cdot 010$, $b = 11 \cdot 878 \pm 0 \cdot 014$, $c = 9 \cdot 190 \pm 0 \cdot 009$ Å; $\alpha = 102° 56' \pm 5'$, $\beta = 85° 56' \pm 3'$, $\gamma = 100° 44' \pm 4'$, $Z = 2$; $D_x = 1 \cdot 59$, $D_{meas} = 1 \cdot 59 \pm 0 \cdot 01$. Data for 2571 reflections were collected at room temperature on a Picker automated diffractometer. The crystal structure was solved by the Patterson method and refined by block-matrix least-squares calculations on 2375 observed reflections to a reliability index of 0·038. Molybdenum and boron lie on the pseudo threefold axis of the molecule and are bonded to adjacent nitrogen atoms on each of the three pyrazole rings. The average B–N bond distance is 1·55 Å. The average Mo–N(pyrazolyl)bond distance is 2·22 Å whereas the Mo–N(diazo) bond distance is 1·83 Å. The geometry about the Mo atom is that of a slightly distorted octahedron. The boron atom exhibits slightly distorted tetrahedral geometry.

Introduction

In the last few years a number of transition metal pyrazolyl borate complexes have been prepared (Trofimenko, 1967, 1968, 1969). In order to gain more insight into the stereochemistry of such compounds we have undertaken the structural determination of the pyrazolyl borate complex hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl molybdenum.

A similar compound: hydrotris(1-pyrazolyl)boratodicarbonylnitrosylmolybdenum, $HB(pz)_3Mo(CO)_2NO$, has been recently studied (Holt, 1970). However, in the nitrosyl complex a statistical disorder involving the carbonyl and nitrosyl groups has been found. In addition the presence of a disordered solvent molecule has prevented the successful refinement of the structure. The present complex does not show a disordering of the carbonyl and benzenediazo groups because of the very different steric encumbrance of these ligands.

Experimental

Red-orange crystals of the complex were provided by S. Trofimenko. The one chosen was a plate of dimensions $0 \cdot 45 \times 0 \cdot 24 \times 0 \cdot 04$ mm. Weissenberg photographs showed that the crystal was triclinic. Centrosymmetry was assumed and confirmed by the subsequent refinement.

The crystal was mounted on a Picker automated diffractometer with the a axis parallel to the spindle axis. The unit-cell constants were determined from a least-squares fit of the angular positions of twelve independent reflections. Data were taken to a 2θ value

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