

The Structure of Stemphone, a Yellow Fungal Metabolite*

BY CAROL SAUNDERSON HUBER

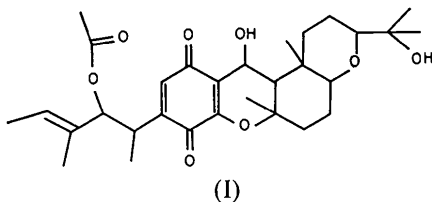
Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

(Received 5 August 1974; accepted 8 August 1974)

The structure of stemphone, $C_{30}H_{42}O_8$, a natural quinone from *Stemphylium sarcinaeforme* (Cav.) Wiltshire, has been determined by X-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=6.526(2)$, $b=19.071(7)$, $c=23.285(7)$ Å, $Z=4$. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to a final $R=0.061$ for the 1861 observed reflexions. All hydrogen atoms were located and refined isotropically. The quinone system is significantly non-planar and slightly boat-shaped. The other rings have half-chair and chair forms, with some distortions caused by the *cis* diaxial methyl substituents. The tertiary hydroxyl side chain is equatorial. The crystal structure is stabilized by intramolecular and intermolecular hydrogen bonds, the latter linking the molecules into chains along *b*.

Introduction

Stemphone is a yellow pigment produced by *Stemphylium sarcinaeforme* (Cav.) Wiltshire, a fungus which attacks red clover. The compound was isolated by Scott & Lawrence (1968), who characterized it as a benzoquinone and reported its toxicity in various bioassay systems. Edwards, Court and Devlin accumulated further evidence which permitted the identification of several portions of the molecule. However, the very limited amount of material available prevented complete solution of the structure by chemical and spectroscopic techniques, and an X-ray crystal-structure determination was therefore undertaken. This has shown the molecular structure to be (I).† Details of the chemical studies and a preliminary account of the X-ray result have been published elsewhere (Huber, Court, Devlin, Edwards & Scott, 1974).



Experimental

Yellow needle-shaped crystals of stemphone, $C_{30}H_{42}O_8$, were kindly provided by Dr W. A. Court. Preliminary photographic examination showed that the symmetry was orthorhombic, space group $P2_12_12_1$. Subsequently

* Issued as N.R.C.C. No. 14317.

† Note added in proof: - Dr P. M. Scott has kindly brought to my attention recently the fact that stemphone is the 31, 33-dehydro derivative of both cochlioquinone A, studied by Carruthers *et al.* (1971) and luteoleersin, studied by Barrow & Murphy (1972).

a specimen with approximate dimensions $0.30 \times 0.15 \times 0.15$ mm was mounted on a Picker four-circle diffractometer with the *a* axis of the crystal (its direction of elongation) parallel to the φ axis of the diffractometer. Measurements were made at room temperature with Ni-filtered Cu radiation, a scintillation counter and a pulse-height analyser. Cell dimensions, obtained from 2θ values of high-angle axial reflexions, were $a=$

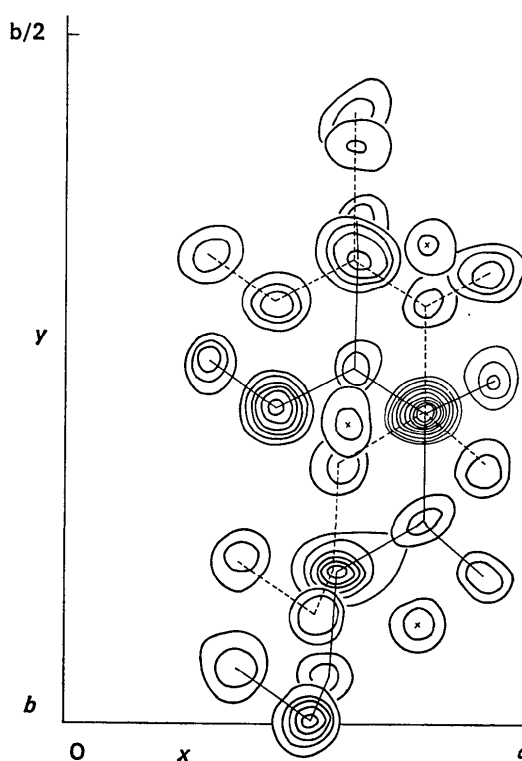


Fig. 1. A portion of the *E* map showing the two positions for the 13-atom molecular fragment. Final atomic coordinates correspond to the mean of the two positions. The three peaks marked with an X were completely spurious.

6.526 (2), $b=19.071$ (7), $c=23.285$ (7) Å, $V=2898.0$ Å³, based on $\lambda(\text{Cu } K\alpha_1)=1.54051$, $\lambda(\text{Cu } K\alpha_2)=1.54433$ Å. $D_m=1.20$ g cm⁻³ (by flotation), $Z=4$, $D_x=1.21$ g cm⁻³.

The intensities of 2845 independent reflexions with $2\theta < 130^\circ$ were measured by the $\theta/2\theta$ scan technique, with scan ranges varying from 2.0 to 4.0° in 2θ . Backgrounds were counted for 20 s at the beginning and end of each scan. 984 reflexions were considered 'unobserved' on the basis that their net counts were less than 7 (deca)-counts or less than 10% of the total background count. Two standard reflexions were monitored at frequent intervals and used to scale the data. Lorentz and polarization but no absorption corrections were made [$\mu(\text{Cu } K\alpha)=7.2$ cm⁻¹].

Structure determination and refinement

Normalized structure amplitudes $|E_n|$ were obtained by isotropic normalization with the K -curve. Numerous applications of the symbolic addition procedure with various starting sets of reflexions led finally to one set

of phases with an $R_{\text{Karle}} (= \sum | |E_{\text{obs}}| - |E_{\text{calc}}| | / \sum |E_{\text{obs}}|)$ value of 0.252 for the 297 reflexions with $|E_{\text{obs}}| > 1.50$. The E map calculated from these phases was somewhat confused and initial attempts to develop a structure from the highest peaks failed. The map was then reinterpreted in terms of two identical molecular fragments of 13 atoms each, mutually displaced by about 1.5 Å parallel to \mathbf{b} , as shown in Fig. 1. Positioning the molecular fragment midway between the two possibilities suggested on the E map and using the tangent formula to extend the phasing from this partial structure (Karle, 1968) led to another E map which showed 34 of the 38 non-hydrogen atoms. The last four atoms were located on a difference map.

This occurrence of multiple molecular images in an E map obviously results from the same problem of translational regularities as experienced by Bürgi & Dunitz (1971) and Duffin (1968) in centric space groups. In this case the portion of the molecule which appeared in the E map was mostly planar, and the mutual displacement of the two fragments represented one of the dominant interatomic vectors.

Table 1. Final fractional coordinates, vibration tensor components (Å²) and their e.s.d.'s (all $\times 10^4$) for the carbon and oxygen atoms

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
O(1)	14219 (8)	3284 (2)	1315 (2)	674 (31)	521 (26)	1090 (38)	-367 (54)	-286 (65)	156 (53)
C(2)	12308 (11)	3226 (3)	1012 (3)	620 (45)	420 (37)	777 (47)	-434 (72)	16 (84)	1 (74)
C(3)	11456 (10)	3964 (3)	910 (3)	523 (39)	431 (35)	533 (38)	-144 (61)	132 (72)	-6 (68)
O(4)	11382 (6)	4310 (2)	1454 (2)	511 (25)	317 (20)	610 (25)	-135 (38)	-99 (48)	162 (40)
C(5)	10881 (9)	5033 (3)	1387 (2)	431 (35)	420 (33)	434 (33)	67 (58)	-6 (65)	-20 (62)
C(6)	8718 (9)	5150 (3)	1171 (2)	348 (33)	376 (33)	503 (33)	38 (56)	-122 (63)	18 (60)
C(7)	8604 (10)	4759 (3)	576 (3)	597 (43)	433 (37)	736 (44)	-61 (67)	-112 (83)	-34 (74)
C(8)	9415 (13)	4008 (3)	616 (3)	904 (54)	472 (39)	769 (49)	-322 (74)	-326 (98)	163 (86)
C(9)	11327 (10)	5414 (3)	1942 (2)	474 (39)	503 (37)	508 (36)	-171 (61)	-253 (69)	308 (69)
C(10)	11128 (10)	6205 (3)	1830 (2)	553 (41)	503 (37)	445 (36)	-373 (61)	-437 (71)	195 (70)
C(11)	9026 (9)	6391 (3)	1627 (2)	410 (36)	457 (35)	459 (36)	40 (58)	-194 (65)	13 (63)
C(12)	8414 (8)	5951 (3)	1081 (2)	339 (32)	427 (33)	349 (30)	128 (54)	-2 (58)	-117 (58)
C(13)	7107 (10)	4811 (3)	1565 (3)	456 (39)	534 (41)	761 (47)	337 (72)	-88 (77)	-150 (69)
C(14)	6372 (9)	6185 (3)	857 (2)	389 (35)	429 (35)	547 (38)	259 (58)	-274 (68)	-179 (63)
O(15)	6193 (7)	5960 (2)	273 (2)	763 (33)	580 (26)	673 (27)	-135 (45)	-727 (57)	55 (54)
C(16)	6203 (9)	6981 (3)	882 (2)	429 (36)	380 (33)	519 (36)	-74 (56)	2 (67)	148 (62)
C(17)	7651 (9)	7379 (3)	1133 (2)	352 (33)	378 (33)	533 (38)	67 (58)	-57 (63)	183 (59)
O(18)	9236 (6)	7121 (2)	1428 (2)	451 (24)	365 (20)	618 (25)	-74 (38)	-238 (47)	3 (40)
C(19)	7676 (9)	8160 (3)	1084 (3)	427 (37)	427 (35)	670 (44)	-119 (67)	-125 (73)	-90 (66)
O(20)	9156 (8)	8488 (2)	1219 (2)	602 (31)	472 (26)	1376 (44)	-112 (56)	-612 (69)	161 (50)
C(21)	5793 (9)	8493 (3)	844 (2)	444 (38)	462 (37)	503 (38)	13 (61)	-48 (70)	304 (66)
C(22)	4342 (10)	8093 (3)	634 (3)	476 (39)	663 (44)	637 (41)	-103 (74)	-314 (78)	344 (78)
C(23)	4503 (10)	7328 (3)	606 (3)	457 (38)	481 (39)	695 (44)	2 (70)	-303 (75)	4 (69)
O(24)	3161 (7)	6985 (2)	360 (2)	617 (30)	625 (29)	983 (36)	-45 (52)	-647 (59)	67 (52)
C(25)	5605 (10)	9285 (3)	872 (2)	611 (42)	512 (39)	448 (36)	214 (61)	-87 (75)	203 (73)
C(26)	7325 (12)	9663 (3)	548 (3)	899 (55)	531 (42)	689 (47)	189 (72)	199 (93)	264 (89)
C(27)	5426 (10)	9572 (3)	1480 (3)	439 (37)	496 (37)	621 (41)	198 (65)	-75 (72)	-48 (65)
O(28)	3770 (7)	9203 (2)	1760 (2)	647 (29)	549 (26)	505 (25)	171 (40)	35 (52)	-107 (49)
C(29)	4175 (12)	8726 (3)	2159 (3)	832 (54)	556 (41)	580 (41)	400 (67)	-125 (88)	-158 (85)
C(30)	2331 (15)	8341 (4)	2346 (3)	1281 (75)	665 (52)	703 (49)	205 (81)	164 (109)	-661 (110)
C(31)	4961 (10)	10346 (3)	1495 (2)	695 (46)	472 (37)	418 (36)	-25 (61)	100 (71)	69 (70)
C(32)	2830 (12)	10555 (4)	1288 (3)	799 (53)	599 (44)	983 (58)	9 (85)	-445 (99)	433 (87)
C(33)	6345 (11)	10794 (3)	1661 (3)	786 (51)	580 (42)	626 (41)	130 (70)	-89 (92)	-54 (83)
C(34)	6244 (15)	11581 (4)	1626 (3)	1148 (72)	558 (46)	1036 (60)	-108 (85)	59 (127)	7 (102)
C(35)	12848 (17)	2882 (4)	457 (4)	1465 (88)	766 (57)	1181 (71)	-724 (101)	-336 (139)	1158 (125)
C(36)	10910 (13)	2797 (3)	1366 (4)	748 (56)	422 (41)	1901 (91)	493 (106)	77 (140)	45 (86)
C(37)	7467 (11)	6405 (3)	2106 (3)	600 (46)	669 (44)	448 (36)	-61 (70)	131 (72)	242 (78)
O(38)	5836 (10)	8601 (4)	2316 (3)	948 (47)	1953 (72)	1670 (63)	2533 (115)	-403 (103)	12 (107)

Refinement of the structure was by block-diagonal least-squares calculations minimizing $\sum w||F_o| - |F_c||^2$. The weighting scheme was $w = 1/\{1 + [(|F_o| - 16.0)/16.0]^2\}$, where $3.8 < |F_o| < 283.9$. All the hydrogen atoms were located on difference maps and refined isotropically, while non-hydrogen atoms were refined anisotropically. As the refinement progressed, it became evident that the hydrogen atom bonded to O(1) could occupy either of two sites whose occupancy factors refined to 0.62 and 0.38. Scattering factors for C and O were taken from Hanson, Herman, Lea & Skillman (1964) and for H from Stewart, Davidson & Simpson (1965). The largest (shift/e.s.d.) in the final least-squares cycle was 0.48 and the average (shift/e.s.d.) was 0.09. The final R for all 1861 observed re-

flexions is 0.061₃.^{*} Final parameters are presented in Tables 1 and 2, and Fig. 2 gives a perspective view of the molecule. A difference map calculated from the final structure factors showed no density greater than $\pm 0.21 \text{ e } \text{Å}^{-3}$.

Results and discussion

Bond lengths and angles are given in Fig. 3 with the numbering scheme. E.s.d.'s of the bond lengths, calculated from the inverse of the normal equations matrix, are: C-C, 0.007-0.011; C-O, 0.006-0.010 Å; and the e.s.d.'s of the bond angles are 0.4-0.7°. The bond lengths have not been corrected for thermal libration although the thermal parameters were analysed for rigid-body motion.

The rigid-body approximation does not apply to the whole molecule, but does fit the 18-atom ring skeleton within experimental error. The r.m.s. $[U_{ij}(\text{obs}) - U_{ij}(\text{calc})]$ for this fragment is 0.0054 Å² whereas the standard deviations of the $[U_{ij}(\text{obs})]$ are about 0.0050

Table 2. Final fractional coordinates ($\times 10^3$), isotropic thermal parameters (Å²) and their e.s.d.'s for the hydrogen atoms

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
H(11)*	1437 (14)	370 (4)	139 (3)	3.7 (1.9)
H(12)	1376 (27)	337 (8)	178 (7)	6.9 (4.4)
H(31)	1250 (6)	420 (2)	68 (2)	1.5 (0.9)
H(51)	1187 (6)	520 (2)	109 (2)	0.8 (0.8)
H(71)	945 (8)	504 (2)	37 (2)	3.8 (1.2)
H(72)	709 (7)	475 (2)	45 (2)	2.9 (1.1)
H(81)	959 (9)	386 (3)	25 (2)	4.8 (1.4)
H(82)	845 (9)	375 (3)	82 (2)	5.3 (1.5)
H(91)	1260 (7)	528 (2)	203 (2)	2.3 (1.0)
H(92)	1048 (8)	529 (3)	226 (2)	4.0 (1.3)
H(101)	1219 (7)	633 (2)	151 (2)	1.4 (0.9)
H(102)	1138 (7)	644 (2)	219 (2)	1.6 (0.9)
H(121)	946 (7)	608 (2)	78 (2)	1.3 (0.9)
H(131)	593 (8)	488 (2)	143 (2)	3.8 (1.2)
H(132)	726 (10)	436 (3)	159 (2)	6.2 (1.6)
H(133)	716 (10)	499 (3)	196 (2)	6.0 (1.6)
H(141)	535 (9)	599 (3)	108 (2)	5.3 (1.4)
H(151)	498 (13)	618 (4)	21 (3)	10.0 (2.3)
H(221)	296 (9)	834 (3)	48 (2)	5.2 (1.5)
H(251)	447 (7)	939 (2)	66 (2)	2.7 (1.1)
H(261)	873 (10)	964 (3)	78 (3)	6.9 (1.7)
H(262)	700 (9)	1014 (3)	52 (2)	5.5 (1.5)
H(263)	734 (9)	947 (3)	10 (2)	5.1 (1.4)
H(271)	680 (7)	951 (2)	166 (2)	2.3 (1.0)
H(301)	112 (11)	864 (3)	235 (3)	7.7 (1.8)
H(302)	211 (13)	796 (4)	212 (3)	10.7 (2.4)
H(303)	241 (12)	812 (4)	263 (3)	9.1 (2.1)
H(321)	307 (10)	1064 (3)	91 (2)	6.1 (1.6)
H(322)	241 (13)	1096 (4)	141 (3)	9.5 (2.2)
H(323)	205 (13)	1014 (4)	137 (3)	10.0 (2.2)
H(331)	773 (8)	1056 (3)	173 (2)	4.4 (1.3)
H(341)	680 (14)	1170 (4)	121 (4)	13.5 (2.9)
H(342)	489 (10)	1174 (3)	164 (3)	7.2 (1.8)
H(343)	687 (16)	1176 (5)	196 (4)	15.0 (3.2)
H(351)	1380 (11)	251 (3)	50 (3)	7.3 (1.8)
H(352)	1184 (12)	284 (4)	27 (3)	9.4 (2.2)
H(353)	1373 (13)	314 (4)	18 (3)	10.7 (2.3)
H(361)	1130 (9)	232 (3)	142 (2)	5.1 (1.4)
H(362)	938 (13)	276 (4)	120 (3)	9.9 (2.2)
H(363)	1091 (11)	294 (3)	173 (3)	7.4 (1.8)
H(371)	772 (8)	677 (3)	234 (2)	3.5 (1.2)
H(372)	732 (8)	598 (3)	234 (2)	4.1 (1.3)
H(373)	596 (10)	639 (3)	199 (2)	5.7 (1.5)

* The number of the atom to which the hydrogen is bonded is obtained by dropping the least significant digit.

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30611 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

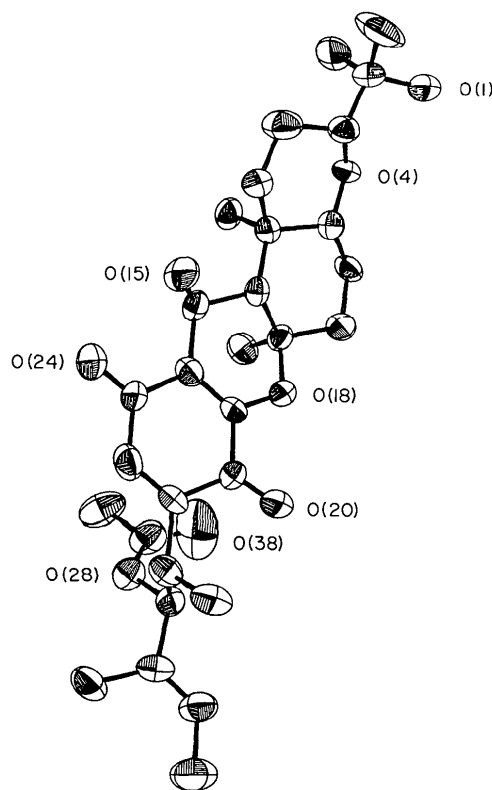


Fig. 2. Perspective view of the molecule. The thermal ellipsoids enclose 50% probability.

\AA^2 . The librational motion of the ring skeleton is very anisotropic, with one r.m.s. amplitude of 5.6° about an axis nearly parallel to C(2)–C(3). The other two principal libration axes represent oscillations of 1.8° and 1.5° . The translational motion of the fragment is essentially isotropic with r.m.s. amplitudes of 0.204, 0.200 and 0.180 \AA . Bond length corrections for libration would be in the range 0.001 to 0.007 \AA , but have not been applied because each is smaller than the corresponding bond length e.s.d. Riding-motion corrections (Busing & Levy, 1964) were calculated for the 13 terminal bonds, and these corrected bond lengths are also indicated in parentheses in Fig. 3.

Most of the bond lengths and angles have normal values; the $C(sp^3)$ – $C(sp^3)$ and $C(sp^3)$ –O bonds have mean values 1.531 and 1.447 \AA respectively. The long C(6)–C(12) and C(12)–C(11) bonds and the enlarged bond angles C(13)–C(12)–C(6) and C(12)–C(11)–C(37) are obviously due to repulsion between the *cis* diaxial methyl groups, C(13) and O(37). Bending these methyl groups away from each other [C(6)···C(11)=2.60, C(13)···C(37)=3.30 \AA] forces them into closer prox-

imity to C(7) and O(18), causing lengthening of C(6)–C(7) and C(11)–O(18) while angle reductions are distributed among C(7)–C(6)–C(13), C(7)–C(6)–C(5), O(18)–C(11)–C(37), O(18)–C(11)–C(10) and O(18)–C(11)–C(12).

The apparent shortening of C(16)–C(23) and C(23)–C(22) relative to C(17)–C(19) and C(19)–C(21) may be associated with the non-substitution of C(22). In the structure of 2-methyl-4,5-dimethoxy-*p*-quinone (Silverman, Stam-Thole & Stam, 1971) the pair of $C(sp^2)$ – $C(sp^2)$ single bonds at the end of the quinone ring near the unsubstituted C(3) are also shorter than the pair of single bonds at the other end of the ring, and by about the same amount. In the crystal structure of bikaverin (de Boer, Bright, Dallinga & Hewitt, 1971), the same pattern may be present, considering the averages of the two pairs of bonds, but the standard deviations (0.02 \AA) make the effect of doubtful statistical significance.

The C–H distances in the present structure are normal, ranging from 0.79 to 1.11 \AA , with average 0.95 \AA .

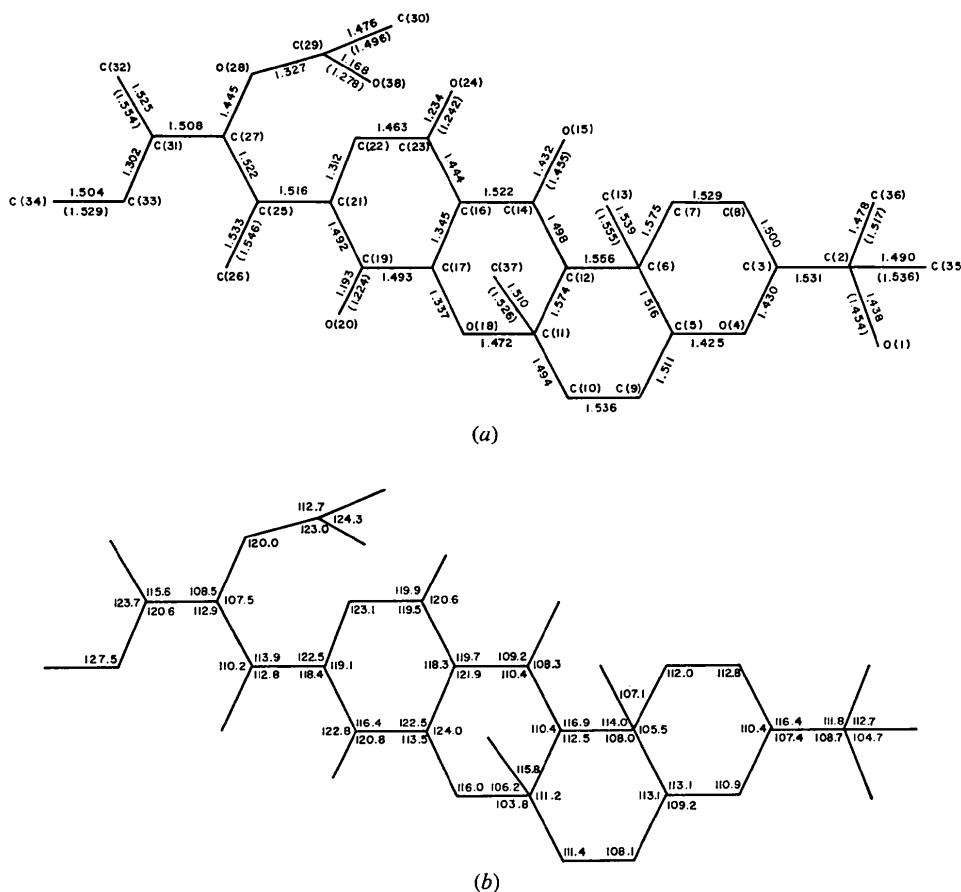


Fig. 3. (a) Bond lengths (\AA) and numbering scheme. Riding-motion corrections have been applied to the bond length values in parentheses. The value in parentheses for C(23)–O(24) should be 1.255 not 1.242. (b) Bond angles ($^\circ$). Angles not shown in the diagram are: O(1)–C(2)–C(36) 107.6° ; C(3)–C(2)–C(35) 110.9° ; C(5)–C(6)–C(13) 112.0° ; C(7)–C(6)–C(12) 110.0° ; C(10)–C(11)–C(37) 112.9° ; C(12)–C(11)–O(18) 105.9° .

Conformation

The quinone ring is slightly but significantly boat-shaped. C(19) and C(23) are displaced 0.113 and 0.060 Å respectively from the mean plane through C(16), C(17), C(21), C(22), carrying O(20) and O(24) 0.315 and 0.127 Å respectively out of this plane. The larger displacement of O(20) may be caused by repulsion between O(20) and O(18), which is displaced to the other side of the plane by 0.132 Å. Even so, their intramolecular non-bonded distance is only 2.65₃ Å. The displacement of O(24) is toward O(15), to which it is hydrogen-bonded (see below).

The dihydropyran ring is closer to a half-chair conformation than to a sofa form, judging by the torsional angles which are given in Fig. 4. The cyclohexane and tetrahydropyran rings are chair-shaped, and the ring junctions at C(5)–C(6) and C(11)–C(12) are *trans*. The ring system is convex towards the C(13) and C(37) methyl groups; the dihedral angle between the mean planes through the cyclohexane and tetrahydropyran rings is 13.4°.

C(29), C(30), O(28) and O(38) of the acetate group are coplanar within 0.02 Å ($\chi^2=16.9$) and C(27) is displaced only 0.14 Å from this plane. The adjacent double-bond system C(27), C(31), C(32), C(33), C(34) is significantly non-planar with $\chi^2=204.3$ and individual deviations up to 0.06₄ Å. This system makes a dihedral angle of 9.5° with the mean plane through the quinone ring [C(16), C(17), C(19), C(21), C(22), C(23)]. The approximate plane through C(21), C(25), C(27), C(31) (with $\chi^2=203.8$) makes a dihedral angle of 63.5° with the quinone ring plane. The orientation of both side chains with respect to the ring system may be seen in Fig. 5. The slight twisting about C(2)–C(3) from a fully staggered conformation brings O(1) closer to O(4), improving the hydrogen-bonding geometry (see below).

Hydrogen bonds and molecular packing

Both hydroxyl groups are apparently involved in intramolecular hydrogen bonding. Pertinent distances and angles are presented in Table 3. The hydrogen bond O(15)–H(151)···O(24) exists in solution (Huber *et al.*, 1974) as well as in the crystalline state. The two possible alternative locations for the hydrogen atom attached to O(1) are both involved in probable hydrogen bonds. The major site, H(11), with 62% occupancy, permits formation of an intramolecular

hydrogen bond to O(4), while the minor site, H(12), is within hydrogen-bonding distance of O(38) of a neighbouring molecule. These intermolecular hydrogen bonds connect the stemphone molecules into chains parallel to *b*, as shown in Fig. 6. Other intermolecular contacts correspond to normal van der Waals distances.

The author thanks Dr O. E. Edwards for suggesting the problem and for valuable discussions, and Dr

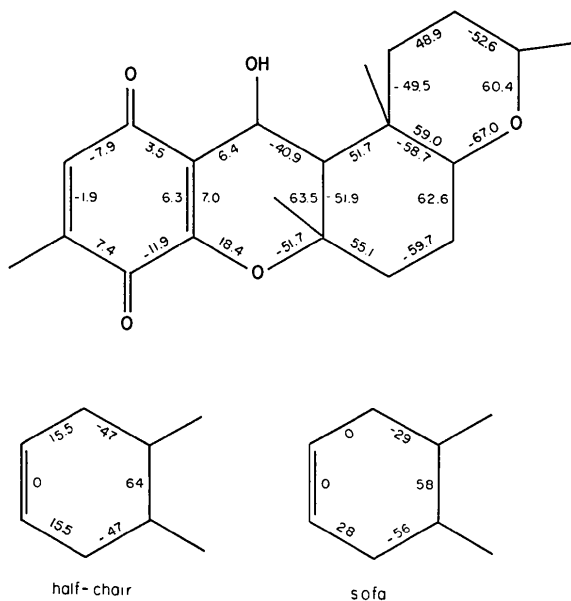


Fig. 4. Observed ring torsional angles, and, below, calculated torsional angles (Bucourt & Hainaut, 1965) for two forms of cyclohexane ring. The e.s.d.'s for the observed torsional angles are 0.6–0.9°.

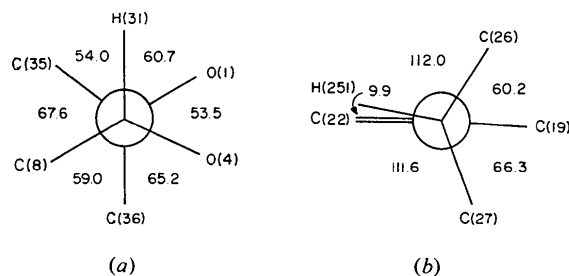


Fig. 5. Newman projections (a) along the C(2)–C(3) bond, (b) along the C(21)–C(25) bond.

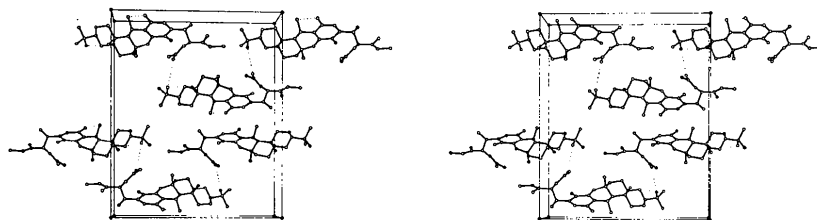


Fig. 6. Stereoscopic view of the crystal structure with *z*↑, *y*←, and *x* pointing away from the observer. Hydrogen bonds are indicated by broken lines.

Table 3. *Details of the hydrogen bonds*

O(1) ... O(4)	2.71 ₄ Å	O(15) ... O(24)	2.78 ₈ Å
H(11) ... O(4)	2.27	H(151) ... O(24)	1.97
O(1) ... O(38)*	3.24 ₄	O(1)—H(11) ... O(4)	114°
H(12) ... O(38)*	2.17	O(1)—H(12) ... O(38)*	157
		O(15)—H(151) ... O(24)	148

* O(38) at equivalent position $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

F. R. Ahmed for critically reading the manuscript. Computer programs used for this analysis were *MGTLS* (Schomaker & Trueblood, 1968), *ORTEP* (Johnson, 1970) and the NRC series of crystallographic programs (Ahmed, Hall, Pippy & Huber, 1973).

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC Crystallographic Programs for the IBM/360 System, accession numbers 133–147 in *J. Appl. Cryst.* **6**, 309–346.
- BARROW, K. D. & MURPHY, W. S. (1972). *J. Chem. Soc. Perkin I*, pp. 2837–2839.
- BOER, J. J. DE, BRIGHT, D., DALLINGA, G. & HEWITT, T. G. (1971). *J. Chem. Soc. (C)*, pp. 2788–2791.
- BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
- BÜRGI, H. B. & DUNITZ, J. D. (1971). *Acta Cryst.* **A27**, 117–119.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- CARRUTHERS, J. R., CERRINE, S., FEDELI, W., CASINOV, C. G., GALEFFI, C., TORRACCA VACCARO, A. M. & SCALA, A. (1971). *Chem. Commun.* pp. 174–166.
- DUFFIN, B. (1968). *Acta Cryst.* **B24**, 1256–1261.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- HUBER, C., COURT, W. A., DEVLIN, J. P., EDWARDS, O. E. & SCOTT, P. M. (1974). *Tetrahedron Lett.* pp. 2545–2548.
- JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794 (2nd rev.), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KARLE, J. (1968). *Acta Cryst.* **B24**, 182–186.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCOTT, P. M. & LAWRENCE, J. W. (1968). *Canad. J. Microbiol.* **14**, 1015–1016.
- SILVERMAN, J., STAM-THOLE, I. & STAM, C. H. (1971). *Acta Cryst.* **B27**, 1846–1851.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1975). **B31**, 113

The Crystal Structure of V_8Ga_{41}

BY K. GIRGIS, W. PETTER AND G. PUPP*

Institut für Kristallographie und Petrographie, ETH Zürich, Sonneggstrasse 5, CH-8006 Zürich, Switzerland

(Received 4 July 1974; accepted 5 August 1974)

The structure of V_8Ga_{41} has been determined by trial-and-error methods. In the space group $R\bar{3}$ a rhombohedral unit cell with $a=9.456$ Å, $\alpha=94.958^\circ$, contains one $Ga(VGa_5)_8$ formula unit. One Ga is in the centre of a cuboctahedron of Ga atoms, whose triangular faces are each shared by a face of a $[VGa_{10}]$ polyhedron. This $[VGa_{10}]$ polyhedron is formed by ten triangular and three almost-square faces and can be described as consisting of half an icosahedron and half a cube. The structure has been refined anisotropically with 2457 unique reflexions to $R=0.044$.

Introduction

This work is part of a programme of study of Ga-rich compounds to gain understanding of the crystal chemistry of the Ga metal (Girgis, 1970). The V–Ga system (Girgis, 1969) is of interest because V_3Ga is a superconductor with a relatively high critical temperature. The Ga-richest phase in this system is V_8Ga_{41} (formerly called ‘ $VGa_{\sim 5}$ ’) (Girgis, Laves & Reinmann, 1966).

Preparation of the crystals

Earlier experiments to obtain single crystals of ‘ VGa_5 ’ by cooling from the melt resulted in twinned crystals (Girgis, Laves & Reinmann, 1966). Untwinned single crystals were prepared by one of us (K.G.) by the following procedure. A cylindrical vanadium sheet was dipped in gallium in a quartz tube, which was then evacuated and sealed. This ampoule was heated to $450^\circ C$. After four months the gallium had fully reacted with the vanadium sheet, which had been converted to ‘ VGa_5 ’. Crystals from the lower part of this sheet were used in this investigation. The chemical analysis of these crystals showed a ratio $V:Ga=1:5.17 \pm 0.05$.

* Present address: Institut für Mineralogie, Kristallographie und Strukturchemie, TH Wien, Getreidemarkt 9, A-1060 Wien, Austria.