by the unshared electron pair from Sb(2). The next nearest oxygen atom to K(1) is O(15) at 3·46 Å, and symmetrically related O(14) to K(2) at 3·44 Å. The coordination polyhedra about the potassium ions are similar to those found in other potassium salts where the potassium-oxygen distances are also in the range 2·62 to 3·20 Å (Palenik, 1967).

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X-ray Structure Determination of (+)-Dibromodehydrotetrahydrorugulosin, a Heavy Atom Derivative of (+)-Rugulosin

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The crystal structure of (+)-dibromodehydrotetrahydrorugulosin water and methanol solvate, $C_{30}H_{22}O_{10}Br_2.H_2O.2CH_3OH$, has been determined in order to elucidate the molecular structure and absolute configuration of rugulosin, $C_{30}H_{22}O_{10}$, a fungal pigment isolated from *Penicillium rugulosum* Thom. The crystals are monoclinic with space group $P2_1$ and the unit-cell dimensions are $a=9{\cdot}78$, $b=17{\cdot}04$, $c=9{\cdot}45$ Å and $\beta=98{\cdot}0°$. Two formula units are contained in the cell. The crystal structure was solved by the heavy-atom method and refined by the block-matrix least-squares method including anisotropic thermal parameters. The final R value for 1482 non-zero observed structure factors was 0·109. The absolute configuration was determined by the use of the anomalous dispersion of bromine atoms for Cu $K\alpha$ radiation.

The molecule consists of two tricyclic rings of partially hydrogenated anthraquinone cross-linked at the A and A' rings by means of four C–C covalent bonds. On the basis of the results obtained by the present structure determination, the structures and stereochemistry of (+)-rugulosin, (−)-luteoskyrin and (−)-rubroskyrin have been established, including their absolute configurations.

Introduction

(+)-Rugulosin, $C_{30}H_{22}O_{10}$, is a fungal pigment isolated from *Penicillium rugulosum* Thom and some other fungi (Shibata, Tanaka, Chihara & Mitsuhashi, 1952; Breen, Dacre, Raistrick & Smith, 1955; Shibata & Udagawa, 1963). The chemical structure of rugulosin has since been extensively investigated and it has been shown that it is a representative of a new group of colouring matters having a dimeric structure of partially hydrogenated anthraquinones (Shibata, Murakami, Kitagawa & Kishi, 1956; Shibata, Murakami & Takido, 1956; Briggs & LeQuesne, 1965; Shibata, Ogihara, Kobayashi, Seo & Kitagawa, 1968; Sankawa, Seo, Kobayashi, Ogihara & Shibata, 1968).

Among the related compounds obtained from *Penicillium islandicum* Sopp, (−)-luteoskyrin, $C_{30}H_{22}O_{12}$ and rubroskyrin, $C_{30}H_{22}O_{12}$, were shown to have very close structures to rugulosin. Luteoskyrin was particularly noted as a toxic principle causing liver damage and sometimes liver cancer in experimental animals. To date, several structures have been put forward for these substances mainly on the basis of chemical and spectroscopic data, but they are not conclusive. An X-ray structure analysis of a heavy-atom derivative of rugulosin was therefore undertaken. A preliminary report of the present study has already been published (Kobayashi, Iitaka, Sankawa, Ogihara & Shibata, 1968).

Experimental

Various attempts at bromination of the skeleton of rugulosin failed to produce a suitable derivative for X-ray analysis. It was finally found that only the hydro-

genation product of rugulosin, tetrahydrorugulosin (Fig. 3, II), can yield a heavy-atom derivative by bromination. This compound, (+)-tetrahydrorugulosin, $C_{30}H_{26}O_{10}$ [m.p. = 295° (decomposed), $[\alpha]_D = +172°$ (acetone)], was prepared by catalytic reduction of (+)-rugulosin and the bromination was carried out by treatment with dioxane dibromide in tetrahydrofuran solution in the presence of pyridine. The product thus obtained which should be named dibromodehydrotetrahydrorugulosin gave a molecular formula, $C_{30}H_{22}O_{10}Br_2$ and grew as well developed transparent yellow platy crystals elongated along the *c* axis when recrystallized from a mixed solution of methanol, acetone and water. At the final stage of the present structure determination, the crystal was found to contain two equivalent moles of methanol and one equivalent mole of water as solvents of crystallization. On leaving the crystals in air, they immediately deteriorated to give a sticky yellow powder presumably due to loss of the solvents of crystallization. The X-ray photographs were, therefore, taken with the crystals sealed in thin-walled glass capillaries together with the mother liquor.

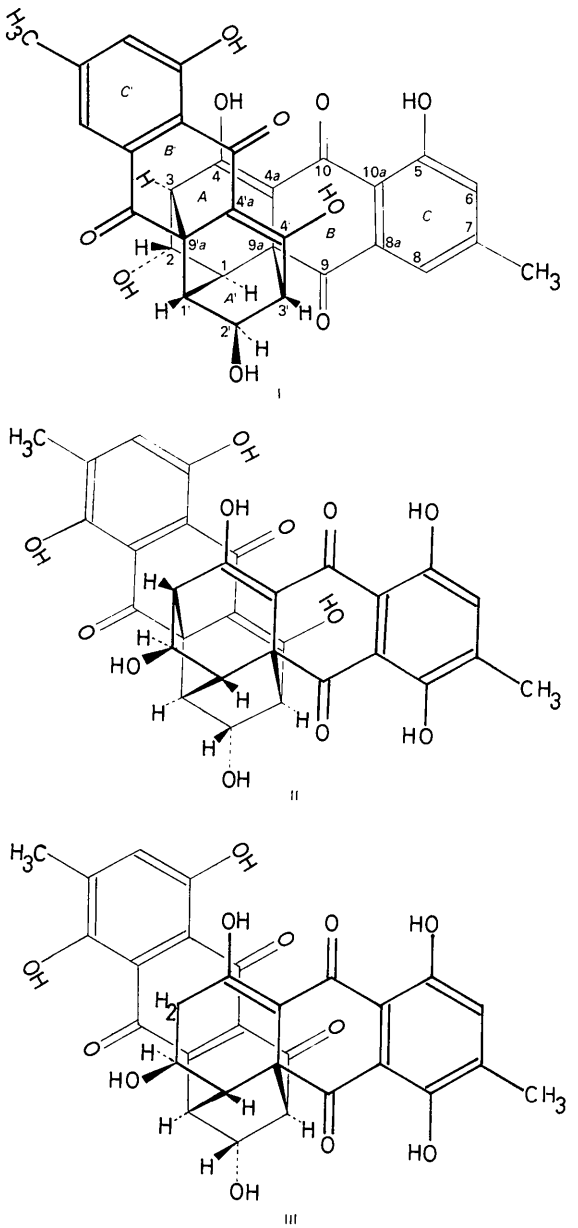

Fig. 1. The chemical structures and the absolute configurations of I, (+)-rugulosin; II, (−)-luteoskyrin; III, (−)-rubroskyrin.

The cell dimensions and space group were determined from the precession photographs of *hk*0 and *h*0*l* taken with Cu $K\alpha$ radiation, which showed the crystals to be monoclinic. The density was measured by the flotation method using two kinds of solution, one being a mixture of dibromomethane and chloroform and the other a mixture of dibromethane and methanol.

Crystal data

(+)-Dibromodehydrotetrahydrorugulosin water and methanol solvate, $C_{30}H_{22}O_{10}Br_2 . H_2O . 2CH_3OH$

M.W. = 784, $[\alpha]_D = +317°$ (in dioxane).

Monoclinic

$a = 9{\cdot}78 \pm 0{\cdot}02$, $b = 17{\cdot}04 \pm 0{\cdot}04$, $c = 9{\cdot}45 \pm 0{\cdot}02$ Å,

$\beta = 98{\cdot}0° \pm 0{\cdot}2°$

$U = 1558$ Å^3

$D_m = 1{\cdot}64_1$ g.cm^{-3} in dibromomethane–methanol solution,

$= 1{\cdot}68_4$ g.cm^{-3} in dibromomethane–chloroform solution.

$D_x = 1{\cdot}671$ g.cm^{-3} ($C_{30}H_{22}O_{10}Br_2 \cdot H_2O \cdot 2CH_3OH$),

$= 1{\cdot}602$ g.cm^{-3} ($C_{30}H_{22}O_{10}Br_2 \cdot H_2O \cdot CH_3OH$).

μ for Cu $K\alpha = 41{\cdot}7$ cm^{-1}

$F(000) = 796$.

Absent spectra: $0k0$ when k is odd.

Space group: $P2_1$, $Z = 2$.

Three-dimensional intensity data were collected from the equi-inclination Weissenberg photographs. The layers *hk*0–*hk*6 about the *c* axis and *h*0*l*–*h*3*l* about the *b* axis were taken with Cu $K\alpha$ radiation using the multiple-film technique. The intensities were estimated visually with the aid of calibrated intensity scales prepared for each axis. The specimens used for the intensity measurement were small enough to neglect the absorption correction. All the intensity data were then corrected for Lorentz and polarization factors and were put on a common scale by correlation of the structure factors on various layers. In this way, a total of 1482 independent non-zero observed structure factors were derived.

Determination of the structure

The positions of the two bromine atoms were determined from a three-dimensional Patterson function sharpened to correspond to atoms at rest. The *R* value calculated for the structure containing only the bromine atoms was 0·36. Successive use of Fourier and difference Fourier syntheses enabled us to locate all the

forty-two atoms belonging to the molecule and the three atoms of the solvation molecules. The oxygen atoms were identified on the electron density map with the help of chemical and structural considerations. The R value at this stage was 0·29.

Refinement of the structural parameters was carried out by block-matrix least-squares calculations with the use of the program *HBLS* (Okaya & Ashida, 1967). Five cycles of calculation in which only the anisotropic thermal vibrations of the bromine atoms were allowed for, gave an R value of 0·15. Of the three solvation molecules, the presence of two methanol molecules was still suspected at this stage owing to the rather large temperature factors. To illustrate these molecules on the difference electron density map, three cycles of the block-matrix least-squares refinement were then carried out excluding the contributions of the two methanol molecules, and the refined atomic parameters were used to calculate the Fourier and difference Fourier syntheses. Fig. 2(*b*) shows the difference map which clearly

Table 1. *The final atomic parameters and their standard deviations*

The temperature factors are in the form
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
The e.s.d.'s are given in parentheses in units of the least significant digits. To represent the correct absolute configuration, the following coordinates should be referred to the left-handed coordinate system.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	1.2255 (3)	0.3310 (2)	0.9015 (4)	0.0163 (4)	0.0046 (1)	0.0145 (5)	-0.0004 (2)	-0.0049 (3)	0.0002 (2)
C(1)	0.5914 (23)	0.1110 (15)	0.3871 (24)	0.0073 (27)	0.0026 (9)	0.0168 (47)	0.0002 (13)	0.0022 (25)	0.0010 (15)
C(2)	0.4725 (23)	0.1676 (16)	0.3545 (26)	0.0081 (26)	0.0037 (10)	0.0108 (40)	-0.0008 (13)	-0.0013 (23)	0.0009 (16)
C(3)	0.5373 (24)	0.2262 (12)	0.2505 (23)	0.0131 (29)	0.0015 (7)	0.0031 (32)	-0.0001 (12)	0.0036 (21)	0.0001 (11)
C(4)	0.6193 (24)	0.2780 (16)	0.3463 (25)	0.0111 (29)	0.0045 (11)	0.0035 (35)	-0.0012 (14)	0.0037 (22)	0.0042 (15)
C(5)	1.0073 (26)	0.3021 (14)	0.7043 (33)	0.0094 (30)	0.0022 (8)	0.0205 (51)	0.0002 (12)	0.0006 (28)	-0.0021 (15)
C(6)	1.0857 (29)	0.2709 (15)	0.8156 (30)	0.0149 (34)	0.0031 (9)	0.0097 (40)	0.0007 (15)	-0.0006 (26)	-0.0003 (15)
C(7)	1.0467 (32)	0.1987 (19)	0.8557 (27)	0.0179 (40)	0.0055 (14)	0.0026 (37)	0.0026 (18)	-0.0019 (27)	-0.0011 (17)
C(8)	0.9364 (26)	0.1553 (17)	0.7845 (31)	0.0098 (30)	0.0038 (11)	0.0149 (47)	0.0024 (15)	0.0034 (27)	-0.0011 (17)
C(9)	0.7285 (28)	0.1464 (15)	0.5226 (30)	0.0134 (34)	0.0024 (9)	0.0153 (47)	-0.0035 (14)	-0.0033 (26)	0.0008 (14)
C(10)	0.8435 (23)	0.2927 (14)	0.4974 (29)	0.0087 (26)	0.0023 (8)	0.0151 (44)	0.0001 (12)	-0.0010 (25)	0.0014 (14)
C(11)	1.1391 (40)	0.1544 (25)	0.9765 (36)	0.0233 (56)	0.0064 (18)	0.0135 (57)	-0.0007 (25)	-0.0095 (42)	0.0039 (26)
C(4a)	0.7505 (22)	0.2384 (15)	0.3993 (26)	0.0073 (25)	0.0032 (9)	0.0101 (39)	-0.0000 (12)	-0.0014 (22)	-0.0006 (14)
C(8a)	0.8631 (24)	0.1872 (13)	0.5766 (25)	0.0109 (29)	0.0028 (8)	0.0041 (32)	0.0002 (12)	0.0006 (22)	0.0005 (11)
C(9a)	0.7257 (29)	0.1473 (14)	0.4626 (31)	0.0149 (37)	0.0020 (8)	0.0153 (49)	-0.0031 (14)	-0.0006 (30)	0.0000 (15)
C(10a)	0.9028 (27)	0.2585 (16)	0.6200 (29)	0.0130 (33)	0.0035 (10)	0.0093 (40)	0.0024 (15)	-0.0020 (26)	-0.0003 (15)
O(1)	0.4326 (17)	0.2082 (11)	0.4717 (23)	0.0086 (20)	0.0032 (7)	0.0226 (37)	0.0004 (10)	-0.0004 (20)	-0.0003 (12)
O(2)	0.5620 (16)	0.3487 (10)	0.3599 (19)	0.0107 (20)	0.0023 (6)	0.0144 (30)	0.0026 (9)	-0.0003 (17)	-0.0025 (10)
O(3)	0.8605 (20)	0.3599 (11)	0.4580 (21)	0.0154 (24)	0.0034 (7)	0.0130 (29)	-0.0015 (10)	-0.0050 (20)	0.0032 (11)
O(4)	1.0442 (18)	0.3750 (9)	0.6499 (19)	0.0134 (21)	0.0026 (5)	0.0102 (25)	-0.0016 (9)	-0.0011 (17)	-0.0009 (9)
O(5)	0.7374 (22)	0.0647 (11)	0.6519 (19)	0.0214 (31)	0.0030 (7)	0.0036 (27)	-0.0003 (12)	0.0013 (21)	0.0011 (11)
Br(1')	0.7789 (3)	0.4997 ([illegible])	-0.2169 (3)	0.0152 (4)	0.0032 (1)	0.0140 (5)	0.0005 (2)	-0.0015 (3)	0.0014 (2)
C(1')	0.6369 (24)	0.0907 (14)	0.2492 (30)	0.0087 (28)	0.0022 (9)	0.0162 (47)	-0.0012 (12)	-0.0014 (26)	0.0015 (15)
C(2')	0.7731 (26)	0.0450 (13)	0.2874 (39)	0.0123 (32)	0.0015 (8)	0.0172 (48)	-0.0008 (13)	-0.0043 (28)	-0.0001 (14)
C(3')	0.8476 (24)	0.1013 (13)	0.4017 (30)	0.0087 (28)	0.0016 (7)	0.0172 (47)	-0.0013 (12)	0.0009 (26)	-0.0025 (14)
C(4')	0.9132 (28)	0.1592 (13)	0.3068 (30)	0.0142 (34)	0.0017 (8)	0.0158 (46)	0.0007 (14)	-0.0043 (26)	0.0011 (14)
C(5')	0.6110 (22)	0.3766 (14)	-0.0277 (37)	0.0039 (23)	0.0022 (9)	0.0302 (59)	0.0024 (12)	-0.0003 (27)	0.0005 (17)
C(6')	0.7284 (33)	0.4067 (20)	-0.1291 (31)	0.0165 (41)	0.0052 (13)	0.0082 (45)	0.0025 (19)	0.0009 (30)	0.0023 (19)
C(7')	0.6162 (24)	0.3571 (14)	-0.1973 (39)	0.0095 (30)	0.0029 (9)	0.0139 (45)	0.0026 (13)	0.0031 (26)	-0.0029 (15)
C(8')	0.5870 (28)	0.2828 (17)	-0.1324 (29)	0.0140 (34)	0.0041 (11)	0.0093 (43)	0.0025 (15)	-0.0049 (29)	-0.0016 (16)
C(9')	0.6451 (23)	0.1774 (16)	0.0341 (26)	0.0082 (26)	0.0037 (9)	0.0072 (37)	0.0006 (13)	-0.0001 (22)	-0.0001 (14)
C(10')	0.8530 (27)	0.2827 (15)	0.1656 (29)	0.0132 (32)	0.0026 (9)	0.0121 (44)	-0.0019 (14)	-0.0041 (26)	-0.0005 (14)
C(11')	0.5346 (39)	0.3894 (24)	-0.3227 (34)	0.0234 (55)	0.0061 (15)	0.0126 (52)	-0.0004 (24)	-0.0050 (39)	0.0038 (23)
C(4'a)	0.7983 (27)	0.2135 (14)	0.2582 (25)	0.0158 (35)	0.0023 (6)	0.0051 (38)	-0.0004 (14)	-0.0014 (26)	-0.0011 (12)
C(8'a)	0.6731 (23)	0.2597 (14)	-0.0204 (25)	0.0096 (27)	0.0033 (9)	0.0065 (39)	-0.0006 (13)	0.0037 (22)	-0.0010 (13)
C(9'a)	0.6510 (23)	0.1747 (13)	0.1675 (30)	0.0073 (25)	0.0013 (7)	0.0200 (49)	-0.0012 (11)	0.0023 (25)	0.0023 (14)
C(10'a)	0.7755 (24)	0.3069 (16)	0.0367 (26)	0.0100 (26)	0.0037 (10)	0.0051 (37)	0.0009 (13)	-0.0036 (22)	0.0003 (15)
O(1')	0.5450 (16)	0.0339 (10)	0.1655 (20)	0.0123 (23)	0.0025 (6)	0.0137 (30)	-0.0007 (10)	-0.0030 (19)	-0.0009 (10)
O(2')	1.0386 (17)	0.1642 (11)	0.2925 (19)	0.0113 (21)	0.0034 (7)	0.0154 (31)	0.0001 (10)	-0.0037 (16)	0.0012 (12)
O(3')	0.9619 (18)	0.3154 (12)	0.2122 (20)	0.0135 (23)	0.0044 (6)	0.0137 (30)	0.0007 (11)	-0.0034 (19)	0.0031 (12)
O(4')	0.9177 (20)	0.4235 (11)	0.0289 (21)	0.0151 (25)	0.0039 (8)	0.0139 (34)	-0.0019 (12)	-0.0056 (20)	0.0015 (12)
O(5')	0.5124 (18)	0.1455 (10)	-0.0170 (20)	0.0115 (20)	0.0031 (6)	0.0131 (27)	-0.0013 (9)	-0.0052 (17)	-0.0002 (10)
O(6)	0.5241 (19)	0.0273 (11)	0.8154 (23)	0.0108 (21)	0.0040 (8)	0.0190 (35)	-0.0016 (10)	0.0000 (20)	0.0006 (12)
C(12)	0.2282 (32)	0.3853 (22)	0.3635 (50)	0.0065 (33)	0.0047 (15)	0.0351 (85)	0.0015 (19)	-0.0020 (41)	-0.0013 (30)
O(7)	0.2178 (27)	0.2990 (14)	0.3754 (43)	0.0184 (35)	0.0026 (8)	0.0552 (81)	0.0004 (13)	-0.0140 (44)	0.0001 (21)
C(13)	0.2009 (47)	0.0551 (31)	0.6255 (57)	0.0254 (64)	0.0085 (26)	0.0291 (94)	0.0041 (33)	-0.0036 (59)	-0.0100 (43)
O(8)	0.3087 (44)	0.0051 (21)	0.5572 (47)	0.0411 (65)	0.0046 (13)	0.0514 (82)	0.0027 (27)	-0.0265 (66)	-0.0030 (30)

Mean e.s.d.'s in bond lengths: σ(Br–C) = 0·03 Å, σ(C–O) = 0·03 Å, σ(C–C) = 0·04 Å.

Mean e.s.d.'s in bond angles: σ(Br–C–C) = 2·2°, σ(C–C–C, trigonal) = 2·6°, σ(C–C–C, tetrahedral) = 2·0°, σ(C–C–O) = 2·0°, σ(C=C–O) = 2·4°.

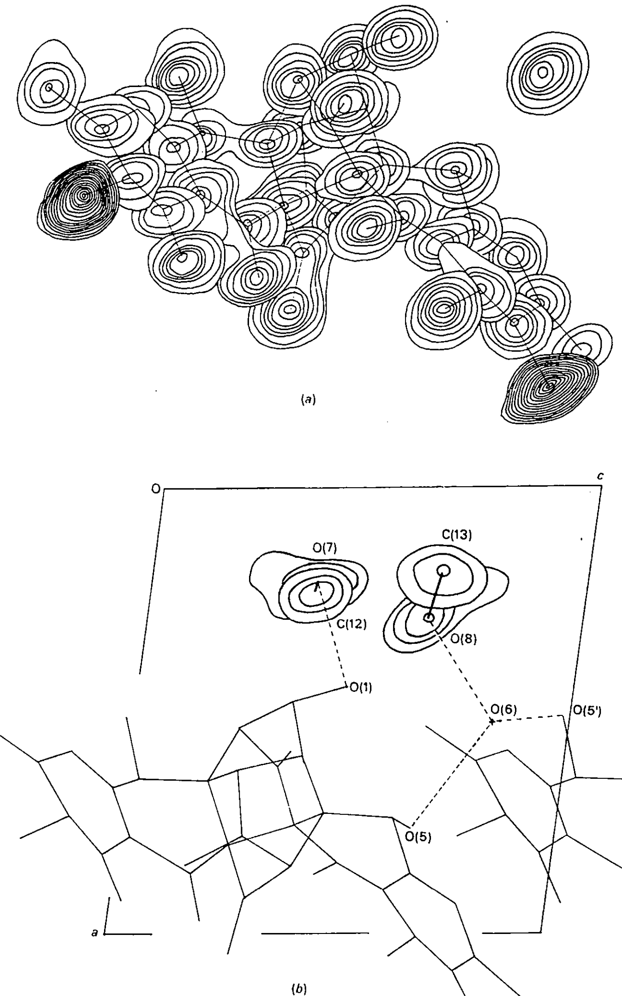

Fig. 2. (*a*) Composite drawing of the electron density map viewed along the *b* axis. Contours are drawn for light atoms at intervals of 1 e.Å^{-3} starting at 1 e.Å^{-3} and for bromine atoms at intervals of 2·5 e.Å^{-3} starting at 1 e.Å^{-3}. Those for methanol molecules are not shown. (*b*) Difference electron density map showing the contours of the two methanol molecules. This map was calculated by excluding the contributions to F_c of the methanol molecules. Contours are drawn at intervals of 0·5 e.Å^{-3} starting at 0·5 e.Å^{-3}. Broken lines indicate hydrogen bonds.

Table 2. *Observed and calculated structure factors*

Table 2 (*cont.*)

1	7	3	24.57	15.90
1	7	2	64.81	61.08
1	7	1	43.89	41.10
1	7	0	54.72	50.17
1	7	-1	46.55	45.59
1	7	-2	87.03	77.11
1	7	-3	25.07	17.87
1	7	-4	33.05	29.49
1	7	-5	37.45	33.63
1	7	-6	29.77	25.85
2	7	6	22.90	23.33
2	7	5	13.06	14.75
2	7	4	43.02	37.56
2	7	3	33.49	25.83
2	7	2	27.17	29.15
2	7	1	71.55	65.26
2	7	-1	43.70	42.99
2	7	-2	48.90	45.80
2	7	-3	35.96	35.75
2	7	-4	33.55	27.97
2	7	-5	28.66	21.92
2	7	-6	16.59	15.40
3	7	6	18.51	21.47
3	7	5	27.73	24.22
3	7	4	30.45	31.64
3	7	3	32.00	31.42
3	7	2	19.37	21.08
3	7	1	29.03	24.18
3	7	0	48.71	46.29
3	7	-1	47.48	47.56
3	7	-2	38.38	41.90
3	7	-3	13.18	13.10
3	7	-4	27.54	26.06
3	7	-5	21.54	19.94
4	7	6	12.69	12.77
4	7	5	11.88	12.41
4	7	4	26.55	25.60
4	7	3	21.42	19.86
4	7	2	50.26	47.68
4	7	1	28.41	24.29
4	7	0	48.47	36.89
4	7	-1	24.95	26.75
4	7	-2	30.45	33.64
4	7	-3	19.06	19.83
4	7	-5	34.11	28.74
4	7	-6	8.48	8.72
5	7	6	15.47	15.54
5	7	5	23.77	20.25
5	7	4	28.04	26.07
5	7	3	29.09	24.65
5	7	2	12.50	12.78
5	7	1	20.55	17.81
5	7	0	20.12	14.85
5	7	-1	34.73	36.04
5	7	-2	39.68	42.86
5	7	-4	21.17	19.47
5	7	-5	22.65	19.51
5	7	-6	17.64	17.27
6	7	5	14.86	14.06
6	7	4	15.35	16.33
6	7	3	7.61	5.58
6	7	2	30.83	27.99
6	7	1	14.48	16.26
6	7	0	17.27	15.53
6	7	-2	12.94	14.60
6	7	-3	19.44	23.76
6	7	-4	29.84	26.38
6	7	-5	22.78	24.07
7	7	6	9.22	10.53
7	7	5	11.39	12.84
7	7	4	10.58	10.29
7	7	3	18.82	20.39
7	7	2	17.76	17.90
7	7	1	21.48	17.85
7	7	-1	17.39	20.17
7	7	-2	13.62	14.16
7	7	-3	10.83	13.23
7	7	-4	7.68	9.69
8	7	5	10.96	11.38
8	7	4	9.59	10.07
8	7	3	12.57	10.42
8	7	2	15.41	14.60
8	7	1	17.46	16.29
8	7	0	11.64	8.83
8	7	-2	7.92	10.48
8	7	-3	13.25	13.90
9	7	4	7.86	6.26
9	7	2	11.95	11.44
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0	8	3	18.14	19.62
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0	8	0	49.21	42.51
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1	8	5	24.51	16.80
1	8	3	32.25	31.72
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1	8	0	37.14	27.63
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1	8	-2	73.78	72.81
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2	8	2	22.59	23.85
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3	8	6	22.65	23.52
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3	8	3	32.25	29.81
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4	8	-4	18.20	15.10
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6	8	6	11.64	12.94
6	8	5	24.70	23.12
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6	8	1	17.08	14.17
6	8	0	26.24	15.54
6	8	-1	37.70	40.20
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7	8	5	21.29	20.37
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8	8	3	6.99	5.32
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1	9	3	38.69	35.01
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5	9	1	29.96	25.16
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7	9	-3	24.33	24.25
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7	9	-6	11.95	12.35
8	9	1	11.88	12.99
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9	9	4	6.62	5.79
9	9	3	12.32	14.35
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5	14	2	13.12	16.61
5	14	1	12.13	12.68
5	14	-2	10.96	11.59
5	14	-5	9.53	9.26
6	14	5	13.18	12.04
6	14	1	18.07	15.25
6	14	0	18.94	18.91
6	14	-1	14.30	17.08
0	15	6	9.84	11.66
0	15	5	10.15	9.36
0	15	4	16.90	17.77
0	15	3	30.76	30.72
0	15	2	7.92	9.87
0	15	1	8.79	10.45
1	15	5	8.17	9.31
1	15	3	28.66	30.32
1	15	2	11.20	12.83
1	15	1	17.64	17.16
1	15	0	41.35	41.37
1	15	-1	17.64	14.72
1	15	-3	13.31	11.96
1	15	-5	8.29	8.28
1	15	-6	13.99	13.71
2	15	6	7.49	8.05
2	15	5	5.63	6.75
2	15	4	12.75	12.74
2	15	3	18.63	18.82
2	15	2	15.85	17.98
2	15	0	11.70	12.05
2	15	-3	30.64	30.52
2	15	-4	16.77	15.86
2	15	-5	5.82	8.18
2	15	-6	7.98	5.84
3	15	6	4.89	5.03
3	15	3	10.52	12.49
3	15	1	15.17	15.63
3	15	0	14.30	13.87
3	15	-2	11.14	12.34
3	15	-3	7.55	9.42
3	15	-4	7.37	7.13
3	15	-6	12.26	13.51
4	15	6	10.58	12.49
4	15	5	4.89	5.93
4	15	4	14.98	16.23
4	15	3	7.12	8.22
4	15	0	21.54	18.53
4	15	-2	10.96	11.61
4	15	-3	14.79	16.55
5	15	3	17.46	17.32
5	15	1	21.73	20.42
5	15	0	7.80	8.80
5	15	-4	6.75	8.57
5	15	-6	11.64	10.23
6	15	3	8.17	7.04
6	15	0	14.48	13.94
0	16	5	13.43	12.34
0	16	4	7.24	9.81
0	16	1	12.38	12.12
1	16	6	8.73	10.75
1	16	3	12.87	12.55
1	16	1	23.15	26.32
1	16	0	11.64	10.95
1	16	-1	23.21	22.98
1	16	-2	15.66	18.30
1	16	-4	12.57	13.39
1	16	-5	7.80	7.38
1	16	-6	7.37	9.11
2	16	5	12.63	13.84
2	16	4	9.84	10.28
2	16	1	12.26	14.62
2	16	0	18.32	20.01
2	16	-2	15.60	16.91
2	16	-4	14.36	16.10
2	16	-5	13.31	14.69
3	16	6	6.00	8.00
3	16	5	4.83	6.90
3	16	4	11.45	11.35
3	16	3	9.97	11.53
3	16	2	13.00	12.87
3	16	1	17.02	20.14
3	16	-1	12.13	11.51
4	16	5	7.43	9.64
4	16	4	8.60	11.78
4	16	3	11.45	14.03
4	16	1	14.17	15.11
4	16	0	15.60	16.21
4	16	-2	14.79	16.62
5	16	4	5.32	7.45
5	16	1	7.61	8.87
0	17	6	12.81	15.82
0	17	3	10.09	9.86
0	17	2	18.51	20.17
0	17	1	24.08	25.12
1	17	6	10.65	9.46
1	17	5	14.55	12.75
1	17	2	12.94	13.88
1	17	-2	16.84	18.57
1	17	-4	15.10	16.92
1	17	-5	8.67	10.60
2	17	6	3.96	6.64
2	17	5	4.58	4.65
2	17	3	9.66	8.91
2	17	2	16.34	18.75
2	17	0	7.66	8.67
2	17	-4	6.62	6.72
2	17	-5	15.60	15.50
3	17	5	15.60	15.86
3	17	3	6.50	9.04
3	17	0	13.25	15.01
3	17	-4	9.04	10.08
4	17	2	16.03	15.63
5	17	3	5.14	7.22
7	17	2	3.65	4.61
0	18	2	15.72	15.45
0	18	0	26.24	22.57
1	18	0	7.49	8.59
1	18	-3	14.55	14.47
2	18	0	10.40	12.47
3	18	0	7.06	8.08
4	18	0	11.33	10.05
5	18	0	10.89	9.31
0	19	3	8.11	11.94
1	19	0	9.66	11.78
0	20	0	8.42	10.07

indicates four peaks of 1·5–2·5 e.Å^{-3} in height at appropriate positions. The interatomic distances and the height of the peaks suggested that they should both be methanol molecules. Fig. 2(*a*) shows the electron density map calculated at the same time, excluding the contributions of the two methanol molecules.

Further refinement was carried out by the block-matrix least-squares method including all the forty-seven atoms with the individual anisotropic thermal vibrations. After five cycles of calculation, the R value was reduced to 0·109 for 1482 non-zero observed reflexions. The weighting functions used for this calculation were:

$$\left.\begin{array}{ll} w = 15/F_o, & \text{when } 15 < F_o, \\ w = 1{\cdot}0, & \text{when } 2 < F_o \leq 15, \\ w = 0, & \text{when } F_o \leq 2 \end{array}\right\}$$

The following atomic scattering factors were used for the present structure determination: for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for bromine, those of Thomas & Umeda (1957). The final atomic parameters are presented in Table 1 along with their standard deviations. The observed and calculated structure factors are compared in Table 2.

Absolute configuration

The absolute configuration of the structure was determined by the anomalous dispersion method. Dispersion corrections for the bromine scattering factor for Cu $K\alpha$ radiation of $\Delta f' = -0{\cdot}9$ and $\Delta f'' = 1{\cdot}5$ were used (Dauben & Templeton, 1955). The structure factors for Friedel pairs of reflexions were calculated assuming that the atomic parameters referred to a right-handed

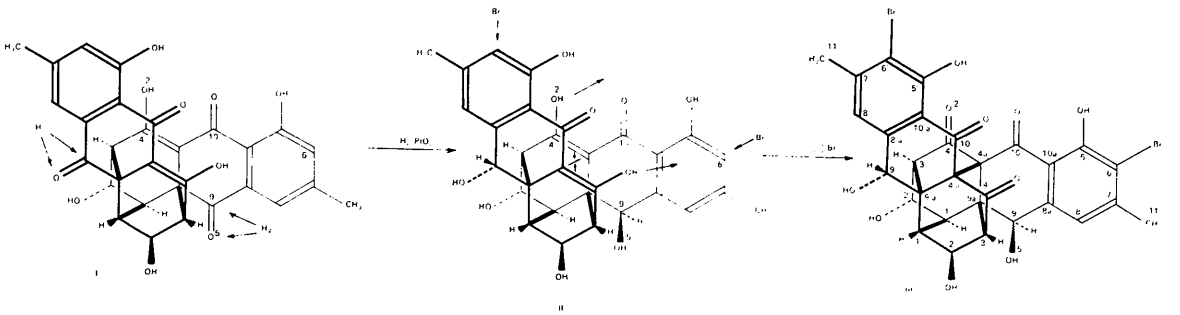


Fig. 3. Derivation of (+)-dibromodehydrotetrahydrorugulosin from (+)-rugulosin showing the structural changes suggested by spectroscopic data.

	(+)-Rugulosin Arrows indicate the positions of hydrogenation catalysed by PtO_2.		(+)-Tetrahydrorugulosin Arrows indicate the positions of bromination, dehydrogenation and bond formation.		(+)-Dibromodehydrotetrahydrorugulosin	
Infrared absorption bands at (measured on KBr disc)	1603 cm^{-1}	C(10)=O	1605 cm^{-1}	C(10)=O	1608 cm^{-1}	C(10)=O
	1688	C(9)=O	—	no C(9)=O	—	no C(9)=O
	—	no C(4)=O	—	no C(4)=O	1755	C(4)=O
Nuclear magnetic resonance absorption bands at (measured on fully deuterated dimethyl sulfoxide solution; 100 MHz)	—	no H at C(9)	δ=4·70 p.p.m.	H at C(9)	δ=4·93 p.p.m.	H at C(9)
	—	no H at O(5)	6·24	H at O(5)	6·48	H at O(5)
	δ=7·16 p.p.m.	H at C(6)	6·67	H at C(6)	—	no H at C(6)
	14·54	H at O(2)	14·90	H at O(2)	—	no H at O(2)

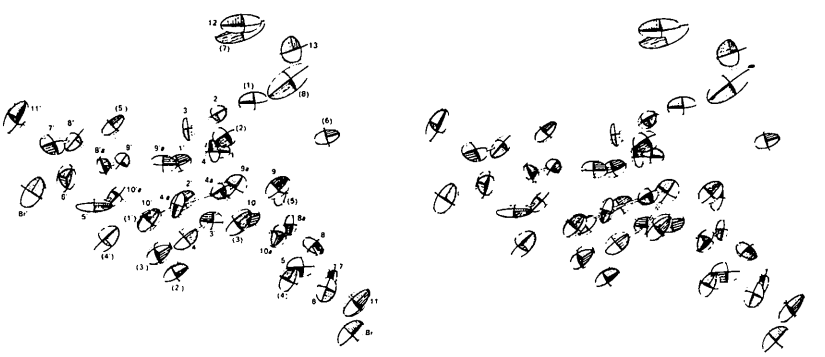


Fig. 4. Stereoscopic drawing of the molecule of (+)-dibromodehydrotetrahydrorugulosin and the solvent of crystallization. Each thermal ellipsoid encloses 50% of the probability of finding the centre of the atom in it.

set of axes. The equivalent positions of the atoms were located corresponding to space group $P2_1$ in *International Tables for X-ray Crystallography* (1952). Of the seventeen pairs of reflexions for which the intensity differences between hkl and $h\bar{k}l$ were expected to be detectable, sixteen pairs showed significant differences in the lth layer Weissenberg photographs. The results are shown in Table 3. A comparison between observed

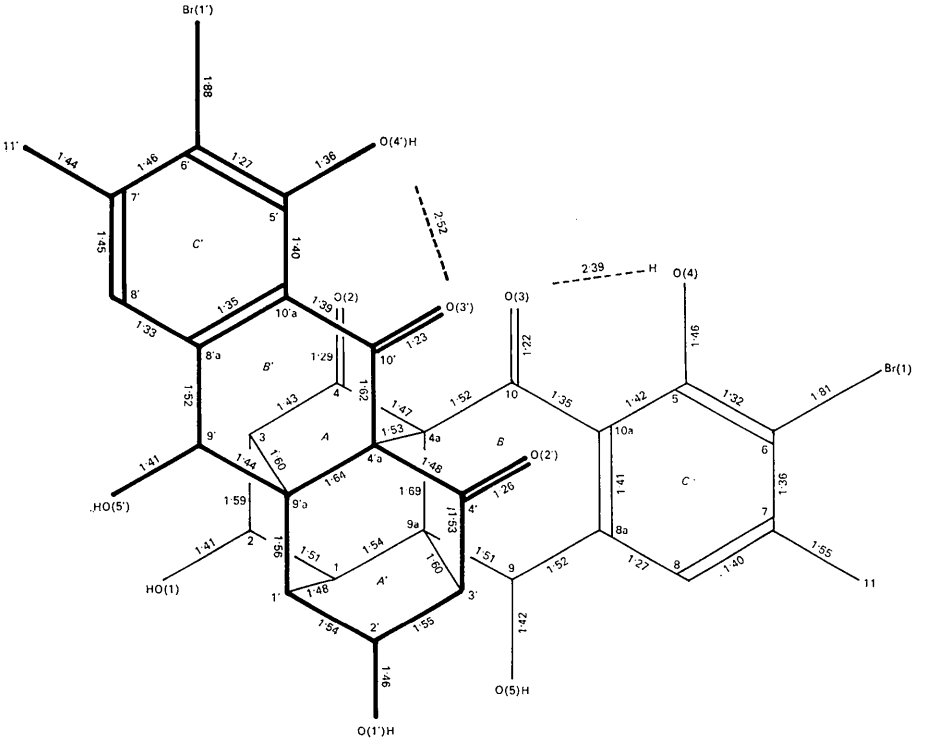


Fig. 5. Bond lengths in Å units.

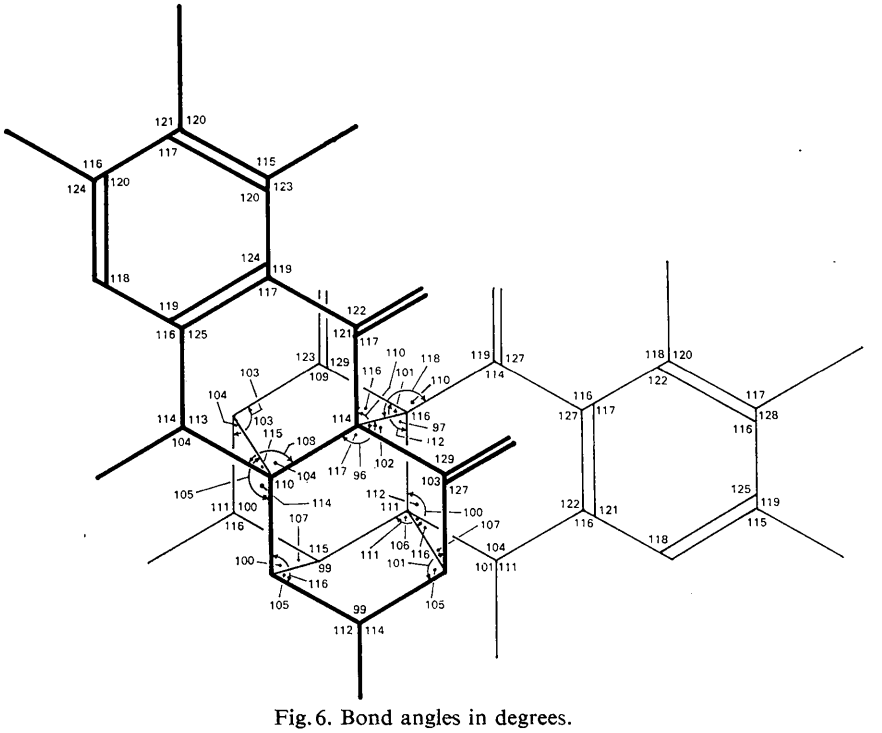


Fig. 6. Bond angles in degrees.

and calculated intensities indicated that the assumed configuration was actually the antipode of the true structure. The absolute configuration of (+)-dibromo dehydrotetrahydrorugulosin was, therefore, established as Fig. 3, III. All Figures presented in this paper are drawn with the correct absolute configuration.

Table 3. *Comparison of the observed and calculated intensity ratios used to establish the absolute configuration*

h	k	l	$\frac{F_c(hkl)^2}{F_c(\bar{h}\bar{k}\bar{l})^2}$	$\frac{I_o(hkl)}{I_o(\bar{h}\bar{k}\bar{l})}$
3	4	$\bar{1}$	1·64	< 1
8	4	$\bar{1}$	1·34	< 1

Table 3 (*cont.*)

9	1	$\bar{2}$	1·53	< 1
4	5	2	0·70	> 1
6	4	3	0·55	> 1
5	5	3	1·31	< 1
1	7	3	1·46	< 1
4	1	4	1·32	< 1
2	2	4	0·50	> 1
8	2	4	0·59	> 1
3	2	0	1·04	< 1
1	4	0	1·12	< 1
1	6	0	0·90	> 1
3	6	0	1·18	< 1
5	7	0	1·25	< 1
6	9	0	1·69	< 1

Table 4. *Bond lengths arranged in groups of similar bonds*

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

	C–Br		
C(6)–Br(1)	1·81 (0·03 Å)	C(6′)–Br(1′)	1·88 (0·03)
	Average value 1·845 Å		
	C–OH		
C(2)–O(1)H	1·41 (0·03)	C(2′)–O(1′)H	1·46 (0·04)
C(5)–O(4)H	1·46 (0·03)	C(5′)–O(4′)H	1·36 (0·03)
C(9)–O(5)H	1·42 (0·03)	C(9′)–O(5′)H	1·41 (0·03)
	Average value 1·420		
	C=O		
C(4)=O(2)	1·29 (0·03)	C(4′)=O(2′)	1·26 (0·03)
C(10)=O(3)	1·22 (0·03)	C(10′)=O(3′)	1·23 (0·03)
	Average value 1·250		
	Aromatic C–C		
C(5)—C(6)	1·32 (0·04)	C(5′)—C(6′)	1·27 (0·04)
C(6)—C(7)	1·36 (0·04)	C(6′)—C(7′)	1·46 (0·04)
C(7)—C(8)	1·40 (0·04)	C(7′)—C(8′)	1·45 (0·04)
C(8)—C(8*a*)	1·27 (0·04)	C(8′)—C(8′*a*)	1·33 (0·03)
C(8*a*)–C(10*a*)	1·41 (0·04)	C(8′*a*)–C(10′*a*)	1·35 (0·03)
C(5)—C(10*a*)	1·42 (0·04)	C(5′)—C(10′*a*)	1·40 (0·04)
	Average value 1·370		
	C(sp^2)–C(sp^2)		
C(10)–C(10*a*)	1·35 (0·04)	C(10′)–C(10′*a*)	1·39 (0·04)
	Average value 1·370		
	C(sp^2)–C(sp^3)		
C(3)—C(4)	1·43 (0·03)	C(3′)—C(4′)	1·53 (0·04)
C(4)—C(4*a*)	1·47 (0·03)	C(4′)—C(4′*a*)	1·48 (0·04)
C(4*a*)–C(10)	1·52 (0·03)	C(4′*a*)–C(10′)	1·62 (0·04)
C(7)—C(11)	1·55 (0·05)	C(7′)—C(11′)	1·44 (0·04)
C(8*a*)–C(9)	1·52 (0·04)	C(8′*a*)–C(9′)	1·52 (0·04)
	Average value 1·508		
	C(sp^3)–C(sp^3)		
C(1)—C(2)	1·51 (0·03)	C(1′)—C(2′)	1·54 (0·03)
C(1)—C(9*a*)	1·54 (0·04)	C(1′)—C(9′*a*)	1·56 (0·03)
C(2)—C(3)	1·59 (0·04)	C(2′)—C(3′)	1·55 (0·03)
C(4*a*)–C(9*a*)	1·69 (0·04)	C(4′*a*)–C(9′*a*)	1·64 (0·03)
C(9)—C(9*a*)	1·51 (0·04)	C(9′)—C(9′*a*)	1·44 (0·04)
	C(1)—C(1′) 1·48 (0·04)		
	C(3)—C(9′*a*) 1·60 (0·03)		
	C(3′)--C(9*a*) 1·60 (0·04)		
	C(4*a*)–C(4′*a*) 1·53 (0·04)		
	Average value 1·556		
	Intramolecular hydrogen bonds		
O(4)–H···O(3)	2·39 (0·03)	O(4′)–H···O(3′)	2·52 (0·03)
	C–OH bonds in solvation molecules		
	C(12)–O(7)H 1·50 (0·05)		
	C(13)–O(8)H 1·35 (0·06)		

Discussion of the structure

The molecular structure

The molecular structure of (+)-dibromodehydrotetrahydrorugulosin determined by the present analysis is shown in Fig. 3, III. Fig. 4 is a stereoscopic representation of the structure. Before the present study was completed, two plausible structures had been proposed for rugulosin mainly on the basis of nuclear magnetic resonance (n.m.r.) spectra. A comparison of the n.m.r. spectra of tetrahydrorugulosin and dibromodehydrotetrahydrorugulosin (Fig. 3) indicated the exclusion of an aromatic proton signal ($\delta = 6{\cdot}67$ p.p.m.) on replacement with a bromine atom, and the effect of this replacement on the neighbouring protons and the disappearance of the proton signal of the two enolic OH groups (at the 4 and 4′ positions in tetrahydrorugulosin). The infrared absorption spectra of these compounds showed the absorption band at 1755 cm^{-1} in dibromodehydrotetrahydrorugulosin, which could be assigned to a ketone group attached to the five-membered ring.

The above mentioned facts indicate that the bromination of tetrahydrorugulosin is not a simple reaction but is accompanied by dehydrogenation of the OH groups at the 4 and 4′ positions and by cross-linking between the two carbon atoms at the 4(*a*) and 4′(*a*) positions. The structural change brought about by the bromination reaction is presumed to be as shown in Fig. 3. The structure of rugulosin deduced in this way is in agreement with that proposed on the basis of a detailed analysis of the n.m.r. spectra using the spin decoupling technique (Sankawa, Seo, Kobayashi, Ogihara & Shibata, 1968). This structure of rugulosin

Table 5. *Deviations of the atoms from the least-squares planes*

The planes are of the form $AX+BY+CZ=D$, where X, Y, Z and D are in Å units relative to the axes a^*, b and c.

Plane forming atoms and distances from the plane		Distances from the plane		Coefficients of the equation of the plane	
A ring					
C(1)	−0·048 Å	C(3)	−0·902 Å	*A*	−0·087 Å
C(2)	0·054	C(9*a*)	0·456	*B*	0·152
C(4)	−0·055	O(2)	0·429	*C*	0·985
C(4*a*)	0·049	O(1)	1·337	*D*	11·949
B ring					
C(4*a*)	−0·052	C(9)	−0·650	*A*	0·785
C(8*a*)	−0·064	C(10)	−0·091	*B*	−0·387
C(9*a*)	0·053	O(3)	−0·214	*C*	−0·484
C(10*a*)	0·063	O(5)	−0·172	*D*	−1·725
C ring					
C(5)	−0·001	C(7)	0·031	*A*	−0·589
C(6)	0·001	C(10*a*)	−0·164	*B*	0·402
C(8)	−0·001	O(4)	−0·088	*C*	0·701
C(8*a*)	0·001	Br(1)	0·049	*D*	6·657
		C(11)	−0·085		
		C(9)	0·246		
		C(10)	−0·347		
Ketone group at *A* ring					
O(2)	−0·009			*A*	−0·420
C(4)	0·023			*B*	−0·344
C(3)	−0·007			*C*	0·840
C(4*a*)	−0·007			*D*	5·808
Ketone group at *B* ring					
O(3)	0·004	C(9*a*)	−0·086	*A*	0·778
C(10)	−0·011	C(8*a*)	−0·282	*B*	−0·290
C(4*a*)	0·003	C(5)	0·210	*C*	−0·558
C(10*a*)	0·004	C(6)	0·427	*D*	−2·332
Five-membered rings joining *A* and *A*′ rings					
C(1)	0·014	C(1′)	−0·709	*A*	0·017
C(9*a*)	−0·021			*B*	−0·702
C(2′)	−0·014			*C*	0·712
C(3′)	0·021			*D*	7·509
C(2)	0·016	C(1)	0·681	*A*	0·698
C(3)	−0·024			*B*	0·245
C(1′)	−0·016			*C*	0·674
C(9′*a*)	0·024			*D*	12·058

Plane forming atoms and distances from the plane		Distances from the plane		Coefficients of the equation of the plane	
A′ ring					
C(1′)	0·030 Å	C(3′)	0·963 Å	*A*	−0·112Å
C(2′)	−0·033	C(9′*a*)	−0·410	*B*	0·117
C(4′)	0·035	O(2′)	−0·395	*C*	0·987
C(4′*a*)	−0·031	O(1′)	−1·382	*D*	10·246
B′ ring					
C(4′*a*)	0·069	C(9′)	0·575	*A*	0·568
C(8′*a*)	0·091	C(10′)	0·075	*B*	−0·658
C(9′*a*)	−0·075	O(3′)	0·151	*C*	−0·495
C(10′*a*)	−0·086	O(5′)	0·322	*D*	−3·417
C′ ring					
C(6′)	−0·003	C(5′)	0·152	*A*	0·622
C(7′)	0·002	C(8′)	−0·068	*B*	−0·421
C(8′*a*)	−0·003	O(4′)	0·201	*C*	−0·661
C(10′*a*)	0·003	Br(1′)	0·228	*D*	−3·309
		C(11′)	−0·011		
		C(9′)	0·047		
		C(10′)	−0·074		
Ketone group at *A*′ ring					
O(2′)	0·021			*A*	0·215
C(4′)	−0·049			*B*	0·583
C(3′)	0·013			*C*	0·784
C(4′*a*)	0·014			*D*	12·228
Ketone group at *B*′ ring					
O(3′)	0·008	C(9′*a*)	0·004	*A*	−0·491
C(10′)	−0·021	C(8′*a*)	−0·277	*B*	0·663
C(4′*a*)	0·006	C(5′)	0·253	*C*	0·565
C(10′*a*)	0·007	C(6′)	0·509	*D*	4·710
Five-membered rings joining *A* and *A*′ rings					
C(3)	−0·025	C(4*a*)	0·744	*A*	0·031
C(4)	0·018			*B*	−0·658
C(4′*a*)	−0·015			*C*	0·753
C(9′*a*)	0·023			*D*	5·996
C(4*a*)	0·023	C(4′*a*)	−0·768	*A*	0·661
C(9*a*)	−0·034			*B*	0·226
C(3′)	0·037			*C*	0·716
C(4′)	−0·026			*D*	14·430

consists of two tricyclic rings of partially hydrogenated anthraquinone joined together through three bonds connecting the rings *A* and *A'*. Owing to the peculiar cage-type multi-bonded structure around the *A* and *A'* rings, the two enolic groups, $\overset{HO}{\diagdown}C(4)=C(4a)<$ and $\underset{OH}{\diagdown}C(4')=C(4'a)<$, in tetrahydrorugulosin are so close on top of one another that it would not be surprising to find a dimerization reaction between the different molecular halves induced by the bromination of tetrahydrorugulosin resulting in dehydrogenation of the two enolic OH groups and formation of a fourth bond between C(4*a*) and C(4'*a*).

Several groups of compounds having the dimeric structure of anthraquinones have been shown to exist in natural products. The structures of this sort of compounds is, however, mostly of the bianthraquinone type and the multi-bonded structure of the present type has not been found yet. The present determination of the structure of dibromodehydrotetrahydrorugulosin has established not only the unique structure of rugulosin but also the structures of luteoskyrin and rubroskyrin which were shown to have close structural correlations with rugulosin on the basis of chemical and spectroscopic data (Shibata & Kitagawa, 1960; Sankawa *et al.*, 1968). Studies on biogenesis of this sort of structure showing how such cage structures are derived may be of great interest.

The absolute configuration of (+)-rugulosin has also been established on the basis of the absolute configuration of (+)-dibromodehydrotetrahydrorugulosin determined by the present analysis, which also leads to the absolute configurations of naturally occurring (−)-rugulosin, (−)-luteoskyrin and (−)-rubroskyrin (Kobayashi, Iitaka, Sankawa, Ogihara & Shibata, 1968). The structures of (+)-rugulosin and the latter two compounds are shown in Fig. 1.

Bond lengths and angles of dibromodehydrotetrahydrorugulosin calculated from the coordinates given in Table 1 are shown in Figs. 5 and 6. The mean standard deviations in the bond lengths and angles calculated for each type of bond are listed in Table 1. Table 4 is a list of bond lengths arranged in groups of similar type. Since the present molecule consists of two essentially identical structural units of tricyclic rings which are related by a pseudo-twofold rotation axis passing through each midpoint of the bonds C(4*a*)–C(4'*a*) and C(1)–C(1') (the two units are equivalent when the molecule is dissolved in solution), the bond lengths found in the corresponding part of the molecule are tabulated in pairs. As seen in Table 4 the corresponding values agree in general, although some of the bond lengths differ significantly from one another. In view of the rather large standard deviations it may not be practicable to ascribe the differences to interactions between neighbouring molecules. However, the mean bond length averaged over each type of bond is in

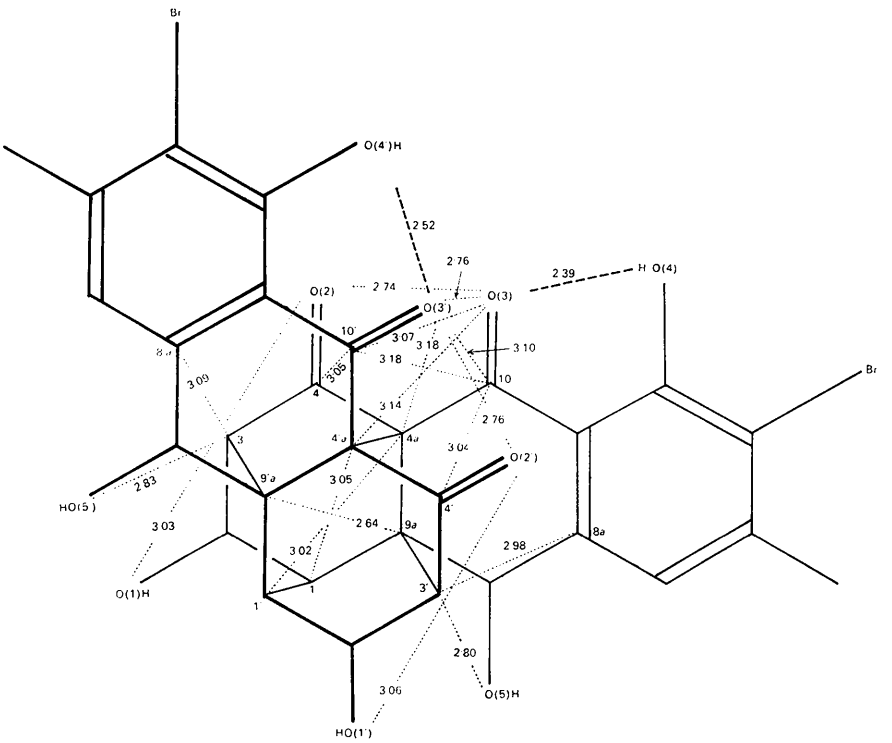


Fig. 7. Closest approaches of atoms shorter than 3·3 Å found between the two halves of the molecule. The distances between the atoms at the second-next positions are not shown.

agreement with the normally accepted length, although the averaged value, 1·370 Å for the C–C partial double bonds involved in the aromatic rings C and C′, is slightly smaller than the average value of 1·395 Å found in aromatic compounds.

As was pointed out by Hall & Maslen (1965), there is a tendency to lengthen the C–C single bond of fully substituted carbon atoms. Thus the longest C–C bonds, C(4*a*)–C(9*a*) of 1·69 Å and C(4′*a*)–C(9′*a*) of 1·64 Å, are all associated with this sort of carbon atom. The short bond lengths of C(10)–C(10*a*), 1·35 Å, and C(10′)–C(10′*a*), 1·39 Å, indicate the extension of the resonance structure of the aromatic rings to the carbonyl groups, C(10)=O(3) and C(10′)=O(3′), which seems to stabilize the strong intramolecular hydrogen bond between O(3) and O(4) and that between O(3′) and O(4′).

The planarity and conformation of each ring can be seen in Table 5. The *A* and *A*′ rings take a chair conformation but they are distorted in such a way that the C(3) and C(3′) atoms are displaced towards the confronted rings by about twice as much as would be expected in the usual chair conformation. These distortions may be a result of the formation of the bonds C(3)–C(9′*a*) and C(3′)–C(9*a*) which connect the *A* and *A*′ rings. The hydroxyl groups O(1)H and O(1′)H are oriented in the axial direction.

Rings *B* and *B*′ tend to adopt a boat-like conformation. The atoms C(9) and C(9′) are considerably displaced but C(10) and C(10′), which form carbonyl groups, are only slightly (about 0·08 Å) displaced from the least-squares planes. The displacements of C(10) and C(10′) are nearly of the same order of magnitude as those of the atoms involved in the least-squares planes and it might be assumed that they are coplanar with the respective least-squares planes. The displacements of O(3) and O(3′) are, however, rather large and

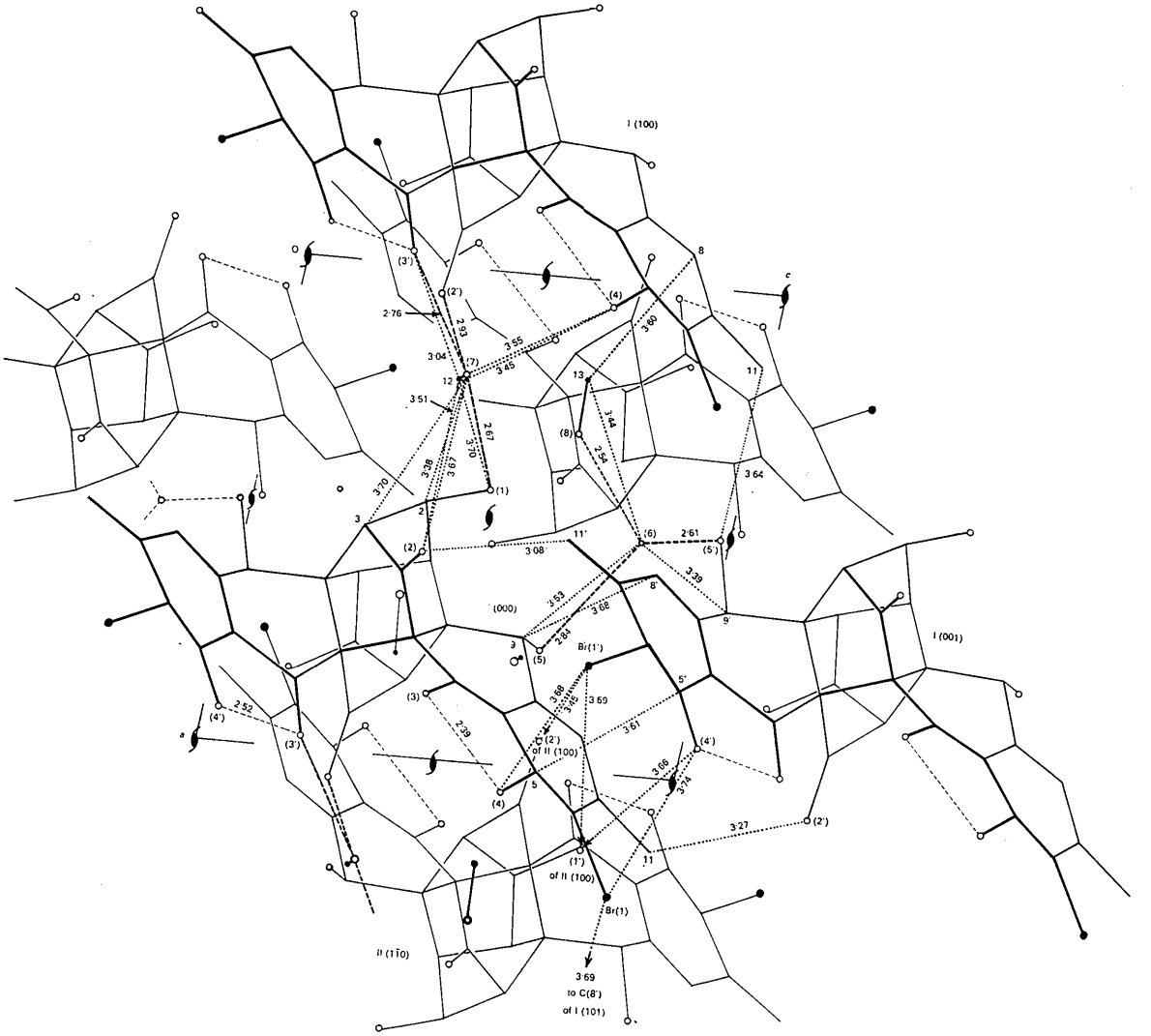


Fig. 8. The crystal structure projected along the *b* axis. The *b* axis is taken upwards towards the observer. Hydrogen bonds are shown by broken lines and the intermolecular contacts shorter than 3·7 Å are shown by dotted lines. The numbers in parentheses are those for oxygen atoms.

are in the same direction as those of C(9) and C(9′) respectively, suggesting a boat-like conformation. The hydroxyl groups O(5)H and O(5′)H are oriented in the equatorial direction.

The aromatic rings *C* and *C′* are expected to be planar. However, if the least-squares planes are calculated including all the members of the rings, the deviation of these rings from the planar conformation is obvious; the deviations of the atoms from the least-squares planes amount to as much as about 0·1 Å. The distortions of the rings may be demonstrated by choosing the planar groups as shown in Table 5. It is seen that both rings tend to adopt a chair-like conformation. In ring C, the atoms C(7) and C(10*a*) are displaced by 0·031 and −0·164 Å respectively above and below the plane, whereas in ring *C′*, C(5′) and C(8′) are displaced by 0·152 and −0·068 Å respectively.

The conformations of the four five-membered rings which join the two halves of the molecule at the *A* and *A′* rings are all well described by a usual puckered form. In every five-membered ring, the four atoms which form the planar part are coplanar within about ±0·02 Å and the fifth atom is displaced by about 0·7 Å.

Because of the peculiar structure of the present molecule, some of the atoms are forced to have rather short approach distances. Approaches shorter than 3·3 Å found between the two halves of the molecule are shown in Fig. 7. In this Figure, the distances between the atoms at the second-next positions are not indicated. It is seen that most of the shortest distances are found for the contacts involving carbonyl or hydroxyl oxygen atoms.

The structure of the present molecule may be regarded as being composed of a cage unit and two hydrogen-

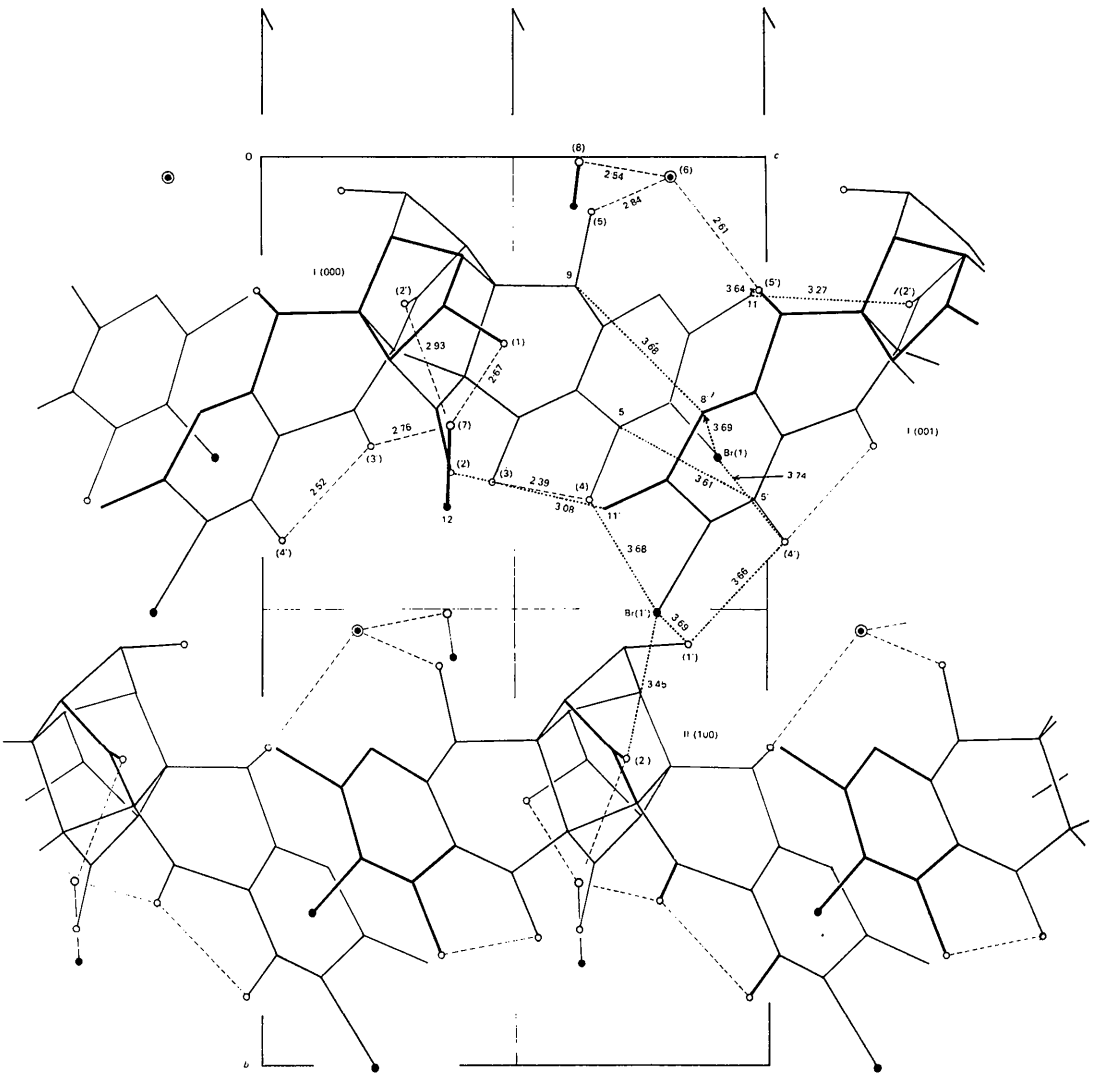


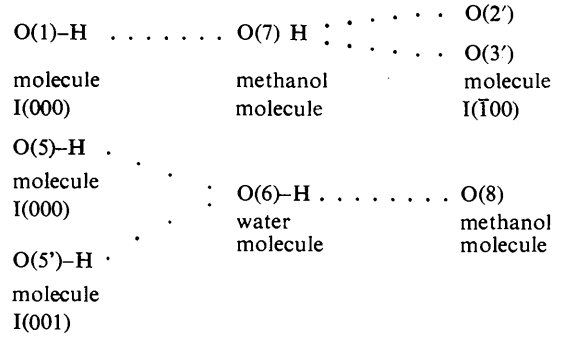
Fig. 9. The crystal structure projected along the *a* axis. The *a* axis is taken downwards from the observer. Hydrogen bonds are shown by broken lines. The intermolecular contacts shorter than 3·7 Å are shown by dotted lines but those involving the solvation molecules are not shown. The numbers in parentheses are those for oxygen atoms.

ated naphthoquinone groups. The cage unit consisting of the two six-membered (*A* and *A'*) rings and the four five-membered rings is winged by the two hydrogenated naphthoquinone groups at C(4*a*)–C(9*a*) and C(4'*a*)–C(9'*a*) bonds, respectively. As is often observed in cage structures, several very close approaches of carbon atoms are found within the cage unit, the shortest being 2·64 Å found between C(9*a*) and C(9'*a*).

The crystal structure

The projections of the crystal structure along the *b* and *a* axes are shown in Figs. 8 and 9. In these Figures, suggested hydrogen bonds are shown by broken lines and the shortest intermolecular distances less than or equal to 3·7 Å (in case the bromine atoms are involved the limit is extended to 3·8 Å) are shown by dotted lines. These distances are classified in groups and are listed in Tables 6 and 7. The molecules are designated by the molecular number specifying the equivalent positions in the unit cell and also by the subscript in parentheses denoting the translations along the three edges of the cell. The equivalent positions are; I at x,y,z and II at $1-x, \frac{1}{2}+y, 1-z$ where x,y and z are the coordinates given in Table 1.

As is clearly seen in the Figures, the molecules are packed along the *c* axis forming a train of molecules. Several close contacts are observed for the neighbouring molecules in the *c* direction among the confronted aromatic rings *C* and *C'* and the bromine atoms. The trains of molecules are bound together in the *a* direction through the solvation molecules, mainly by means of hydrogen bonds. Although the hydrogen atoms were not located by the present structure determination, the following systems of intermolecular hydrogen bonds may be assumed.



The former system connects the molecules in the **a** direction while the latter binds them in the **c** direction. There is no electronegative atom near O(1)H at distances suggesting hydrogen bonds, only one hydroxyl oxygen atom O(4') being situated at a distance of 3·66 Å. The packing of the molecules in the **b** direction is rather loose. As shown in Fig. 9, the molecules are held together in this direction only by means of van der Waals forces and the closest approaches of the molecules are, Br(1')···O(2') of 3·45 Å, Br(1')···O(1') of 3·69 Å and O(4')···O(1') of 3·66 Å.

Table 6. *Closest approaches of atoms less than or equal to* 3·7 Å *between the molecules*

From atom at I(000)	To atom at		Distance
Between the molecules*			
Br(1)	O(4')	I(001)	3·74 Å
Br(1)	C(8')	I(101)	3·69
Br(1')	O(4)	I(00$\bar{1}$)	3·68
Br(1')	O(1')	II(10$\bar{1}$)	3·69
Br(1')	O(2')	II(10$\bar{1}$)	3·45
C(5)	C(5')	I(001)	3·61
C(9)	C(8')	I(001)	3·68
C(11)	O(2')	I(001)	3·27
O(2)	C(11')	I(001)	3·08
C(11)	O(5')	I(101)	3·64
O(4')	O(1')	II(10$\bar{1}$)	3·66
Between the molecule and the solvation molecules			
C(2)	O(7)	I(000)	3·38
C(3)	O(7)	I(000)	3·70
C(9)	O(6)	I(000)	3·53
O(1)	C(12)	I(000)	3·70
O(2)	C(12)	I(000)	3·51
O(2)	O(7)	I(000)	3·67
O(4)	C(12)	I(100)	3·45
O(4)	O(7)	I(100)	3·55
O(3')	C(12)	I(100)	3·04
C(8)	C(13)	I(100)	3·60
C(9')	O(6)	I(00$\bar{1}$)	3·39
Between the solvation molecules			
C(13)	O(6)	I(000)	3·44

* Distances up to 3·8 Å are listed in case the bromine atoms are involved.

In Fig. 4 the ellipsoids of thermal vibration are shown by stereoscopic drawings which were calculated by using plotter program *ORTEP* (Johnson, 1965). The area covered by the ellipsoid is such that the probability of finding the centre of the atom in it is 50%.

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Table 7. *Distances and angles of the suggested hydrogen bonds*

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

From atom at I(000)	to atom at		Distance	Angle	
		Intramolecular hydrogen bonds			
O(4)	O(3)	I(000)	2·39 (0·03) Å	C(5)---O(4) ···O(3)	87 (2)°
O(4′)	O(3′)	I(000)	2·52 (0·03)	C(5′)—O(4′)···O(3′)	83 (2)
		Intermolecular hydrogen bonds			
O(1)	O(7)	I(000)	2·67 (0·03)	C(2)---O(1) ···O(7)	108 (2)
O(5)	O(6)	I(000)	2·84 (0·03)	C(9)---O(5) ···O(6)	107 (2)
O(5′)	O(6)	I(00$\bar{1}$)	2·61 (0·03)	C(9′)—O(5′)···O(6)	113 (2)
O(7)	O(2′)	I($\bar{1}$00)	2·93* (0·03)	C(12)--O(7) ···O(2′)	145 (2)
O(7)	O(3′)	I($\bar{1}$00)	2·76* (0·03)	C(12)--O(7) ···O(3′)	83 (2)
O(8)	O(6)	I(000)	2·54 (0·04)		

* The hydrogen atom of O(7) is presumed to be shared in these two bonds.

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Die Kristallstruktur von Stephanit, $[SbS_3|S|Ag_5^{III}]$*

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The crystal structure of stephanite has been determined with the use of three-dimensional intensity data obtained by counter measurements. Four chemical units of Ag_5SbS_4 are contained in the orthorhombic unit cell of symmetry $Cmc2_1$ (C_{2v}^{12}) with $a=7{\cdot}837\pm0{\cdot}003$, $b=12{\cdot}467\pm0{\cdot}006$, $c=8{\cdot}538\pm0{\cdot}002$ Å; $d_m=6{\cdot}26$ g.cm^{-3}, $d_x=6{\cdot}28$ g.cm^{-3}. The structure was solved from a three-dimensional Patterson and a three-dimensional minimum function. The refinement yielded an R value of 9·4% for all 443 reflexions. The Sb atoms have a trigonal-pyramidal coordination by S atoms. Sb–S distances of 2·47 (2×) and 2·48 Å are in good agreement with the Sb–S covalent bond length. The SbS_3 pyramids are isolated. Ag(1) has a planar threefold coordination with Ag–S 2·51 and 2·55 Å (2×). Ag(2) and Ag(3) have three nearest neighbours between 2·49 and 2·72 Å with which they form a group which is a very flat pyramid. A fourth S atom around Ag(2) and Ag(3) is at an intermediate distance of 3·00 and 2·92 Å. In addition each Ag(2) has 1 Ag(3) at 2·95, 1 Ag(2) at 2·96 and 1 Ag(3) at 2·97 Å. Ag(3) too has in addition 1 Ag(3) at 2·91, 1 Ag(2) at 2·95 and 1 Ag(2) at 2·97 Å. These Ag–Ag distances correspond to metal–metal bonds. The metal atoms form a layer parallel to the (023) plane. The S atoms hold the metal atoms in and between the layers together.

Einleitung

Bisher sind nur die Strukturen von Enargit (Pauling & Weinbaum, 1934*a*), Luzonit (Marumo & Nowacki, 1967) und Sulvanit (Troyer, 1966) mit $\varphi=4$

$$\left(\varphi=\frac{\text{Zahl der S}}{\text{Zahl der As}+\text{Sb}+\text{Bi}}\right)$$

bekannt. Die Struktur von Stephanit wurde bestimmt, um zu erfahren, zu welchem Strukturtyp dieses Mineral gemäss der Klassifikation von Nowacki (1969) gehört. Stephanit ist schon sehr lange bekannt. Agricola (1556) hat es schon als *Argentum rude nigrum* erwähnt. Peacock (1940) hatte gefunden, dass das Mineral Goldschmidtin mit Stephanit identisch ist.

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