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The Crystal Structure of Ascochlorin *p*-Bromobenzenesulfonate[1]

Yoshiharu NAWATA* and Yoichi IITAKA

Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo, Tokyo

**Research Laboratories, Chugai Pharmaceutical Co., Ltd., Takada, Toshima, Tokyo*

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The structure of ascochlorin, $C_{23}H_{29}O_4Cl$, has been determined by the three-dimensional X-ray crystal structure analysis of ascochlorin *p*-bromobenzenesulfonate. The crystal is orthorhombic, space group $P2_12_12_1$, with four molecules in a unit cell of dimensions, $a=13.86$, $b=30.04$, and $c=6.82$ Å. The structure was solved by the heavy atom method and refined by the method of block-matrix least-squares. The final R value was 0.102 for 1627 independent reflexions. Ascochlorin consists of (3-chloro) orcylic aldehyde and (2,3,4-trimethyl) cyclohexanone moieties which are connected with each other through a zigzag chain of *trans*-(3-methyl)penta(2,4) diene. The cyclohexanone ring takes a typical chair form, and the intramolecular hydrogen bond exists in the orcylic aldehyde residue. The absolute configuration was determined by the anomalous dispersion method.

Ascochlorin is a new antibiotics obtained from the filter cake of fermented broth of Ascochyte viciae Libert,[2] which exhibits significant inhibitory effect on the viral growth in cultured cells.[3] Since the molecular structure of ascochlorin had not been known, the present X-ray analysis was undertaken. The terpenoid metabolite (named LL-Z1272-γ) with the same chemical structure as ascochlorin has been isolated from an unclassified Fusarium species.[4] The crude products of ascochlorin containing both α and β forms are easily divided into each component by silica gel column chromatography. While the β form is syrup, the α form crystallizes as extremely fine

1) Presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

2) G. Tamura, S. Suzuki, A. Takatsuki, K. Ando, and K. Arima, *J. Antibiot.* (Tokyo), **21**, 539 (1968).

3) A. Takatsuki, G. Tamura, and K. Arima, *Appl. Microbiol.*, **17**, 825 (1969).

4) G. A. Ellestad, R. H. Evans, Jr., and M. P. Kunstmann, *Tetrahedron*, **25**, 1323 (1969).

TABLE 1. THE FINAL ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS

x, y, and z are the fractional coordinates. The temperature factors are expressed 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 given in parentheses are in the units of the least significant digits given for the correponding parameters. To represent the correct absolute configuration, the parameters should be referred to a right handed set of axes.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.1959 (2)	0.1273 (1)	1.0663 (5)	0.0074 (2)	0.0010 (0)	0.0360 (9)	0.0004 (1)	0.0044 (4)	0.0020 (2)
C(1)	0.1822 (16)	0.1792 (7)	0.9059 (37)	0.0043 (14)	0.0012 (3)	0.0201 (76)	-0.0009 (5)	0.0051 (30)	-0.0012 (12)
C(2)	0.1577 (15)	0.1764 (7)	0.7116 (40)	0.0032 (12)	0.0008 (2)	0.0280 (81)	-0.0002 (5)	0.0010 (27)	0.0002 (12)
C(3)	0.1523 (16)	0.2142 (8)	0.5959 (40)	0.0040 (14)	0.0014 (3)	0.0209 (79)	-0.0002 (5)	-0.0003 (28)	0.0010 (13)
C(4)	0.1798 (14)	0.2558 (7)	0.6812 (34)	0.0024 (12)	0.0009 (2)	0.0182 (64)	-0.0012 (5)	0.0008 (25)	0.0003 (11)
C(5)	0.2006 (13)	0.2581 (6)	0.8784 (30)	0.0017 (11)	0.0009 (2)	0.0135 (61)	-0.0006 (5)	-0.0011 (23)	-0.0003 (9)
C(6)	0.2062 (15)	0.2193 (6)	0.9911 (31)	0.0043 (12)	0.0006 (2)	0.0118 (65)	0.0000 (5)	-0.0016 (24)	0.0003 (9)
S	0.1764 (4)	0.3017 (2)	0.5316 (8)	0.0029 (3)	0.0008 (1)	0.0102 (14)	0.0001 (1)	0.0003 (6)	0.0001 (3)
O(1)	0.1431 (10)	0.2910 (5)	0.3418 (25)	0.0032 (9)	0.0015 (2)	0.0193 (47)	0.0010 (4)	-0.0044 (17)	-0.0003 (9)
O(2)	0.1373 (12)	0.3364 (5)	0.6415 (26)	0.0060 (11)	0.0012 (2)	0.0255 (55)	0.0009 (4)	0.0056 (21)	-0.0005 (9)
O(3)	0.2896 (9)	0.3131 (4)	0.5175 (18)	0.0032 (8)	0.0010 (2)	0.0041 (37)	-0.0006 (3)	-0.0009 (14)	-0.0005 (6)
C(7)	0.3377 (13)	0.3126 (6)	0.3365 (30)	0.0013 (10)	0.0009 (2)	0.0066 (51)	-0.0008 (4)	0.0021 (20)	-0.0010 (9)
C(8)	0.3382 (15)	0.3491 (6)	0.2256 (34)	0.0041 (13)	0.0003 (2)	0.0186 (66)	0.0002 (4)	0.0017 (24)	-0.0021 (10)
C(9)	0.3888 (13)	0.3461 (6)	0.0385 (31)	0.0025 (10)	0.0006 (2)	0.0082 (54)	-0.0000 (4)	-0.0010 (22)	0.0020 (9)
C(10)	0.4311 (15)	0.3069 (7)	-0.0196 (32)	0.0048 (13)	0.0008 (2)	0.0096 (63)	-0.0001 (5)	-0.0003 (24)	-0.0009 (10)
C(11)	0.4272 (13)	0.2690 (6)	0.0941 (33)	0.0013 (11)	0.0010 (2)	0.0149 (63)	0.0002 (4)	-0.0011 (22)	-0.0005 (11)
C(12)	0.3788 (16)	0.2731 (7)	0.2728 (35)	0.0044 (14)	0.0011 (3)	0.0133 (66)	-0.0008 (5)	-0.0018 (27)	-0.0014 (12)
O(4)	0.3961 (12)	0.3848 (4)	-0.0650 (27)	0.0080 (11)	0.0006 (2)	0.0258 (49)	-0.0003 (3)	0.0036 (24)	0.0020 (9)
O(5)	0.4868 (11)	0.3388 (5)	-0.3173 (23)	0.0055 (11)	0.0014 (2)	0.0118 (45)	-0.0004 (4)	-0.0007 (19)	-0.0011 (9)
C(13)	0.4770 (15)	0.3041 (8)	-0.2222 (37)	0.0030 (13)	0.0014 (3)	0.0173 (70)	-0.0006 (5)	-0.0044 (26)	-0.0017 (13)
C(14)	0.4643 (17)	0.2232 (7)	0.0284 (37)	0.0067 (16)	0.0010 (3)	0.0168 (73)	0.0004 (6)	0.0004 (31)	-0.0015 (13)
Cl	0.3796 (4)	0.2274 (2)	0.4373 (11)	0.0049 (4)	0.0009 (1)	0.0204 (17)	0.0004 (1)	-0.0017 (8)	0.0006 (3)
C(15)	0.2904 (15)	0.3941 (5)	0.2908 (35)	0.0034 (13)	0.0003 (2)	0.0282 (73)	-0.0004 (4)	0.0012 (27)	-0.0019 (10)
C(16)	0.3691 (18)	0.4230 (7)	0.3728 (35)	0.0065 (17)	0.0010 (3)	0.0138 (72)	-0.0006 (6)	-0.0029 (29)	-0.0007 (12)
C(17)	0.3625 (15)	0.4506 (6)	0.5251 (35)	0.0043 (13)	0.0007 (2)	0.0148 (69)	0.0003 (5)	0.0012 (25)	-0.0005 (11)
C(18)	0.4436 (16)	0.4808 (7)	0.5671 (36)	0.0050 (14)	0.0010 (3)	0.0087 (60)	-0.0002 (5)	0.0011 (28)	0.0008 (12)
C(19)	0.4499 (14)	0.5084 (6)	0.7202 (36)	0.0031 (12)	0.0003 (2)	0.0240 (73)	-0.0002 (4)	-0.0015 (26)	-0.0008 (10)
C(20)	0.2673 (16)	0.4568 (8)	0.6427 (38)	0.0043 (14)	0.0012 (3)	0.0185 (76)	-0.0005 (6)	0.0017 (27)	-0.0011 (13)
C(21)	0.5299 (15)	0.5392 (6)	0.7687 (34)	0.0040 (13)	0.0005 (2)	0.0174 (67)	-0.0004 (5)	-0.0006 (25)	0.0006 (11)
C(22)	0.4906 (15)	0.5903 (6)	0.7590 (38)	0.0031 (12)	0.0005 (2)	0.0257 (73)	0.0000 (5)	0.0032 (26)	-0.0002 (11)
C(23)	0.5662 (16)	0.6245 (7)	0.8251 (36)	0.0057 (15)	0.0006 (2)	0.0206 (69)	-0.0007 (6)	-0.0007 (29)	0.0004 (12)
C(24)	0.5992 (19)	0.6147 (6)	1.0359 (44)	0.0094 (20)	0.0005 (2)	0.0323 (89)	0.0004 (5)	-0.0075 (40)	0.0000 (13)
C(25)	0.6344 (15)	0.5668 (7)	1.0481 (42)	0.0039 (13)	0.0012 (3)	0.0224 (73)	0.0007 (5)	0.0001 (31)	-0.0005 (14)
C(26)	0.5621 (16)	0.5304 (6)	0.9858 (33)	0.0066 (15)	0.0003 (2)	0.0142 (71)	0.0002 (5)	-0.0058 (26)	0.0002 (9)
C(27)	0.4532 (19)	0.6027 (7)	0.5470 (43)	0.0085 (19)	0.0009 (3)	0.0214 (77)	-0.0008 (6)	-0.0023 (37)	0.0011 (14)
O(6)	0.7119 (12)	0.5565 (6)	1.1089 (30)	0.0052 (11)	0.0017 (2)	0.0437 (68)	0.0004 (4)	-0.0066 (25)	-0.0006 (11)
C(28)	0.5976 (16)	0.4825 (6)	1.0208 (39)	0.0064 (15)	0.0003 (2)	0.0279 (85)	0.0003 (5)	-0.0012 (32)	0.0011 (11)
C(29)	0.6165 (14)	0.5341 (6)	0.6297 (34)	0.0023 (12)	0.0008 (2)	0.0197 (71)	-0.0001 (5)	0.0034 (24)	-0.0003 (10)

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	F(OBS)	F(CAL)
0	4	0	8.71	5.28
0	6	0	16.94	25.70
0	8	0	53.30	37.99
0	10	0	29.48	33.98
0	12	0	184.72	194.00
0	14	0	23.38	27.12
0	16	0	41.08	44.03
0	18	0	25.08	16.92
0	20	0	83.40	59.02
0	26	0	35.22	35.82
0	28	0	53.67	54.71
0	32	0	21.23	20.87
0	34	0	19.00	17.11
0	36	0	15.94	8.35
1	3	0	37.48	39.08
1	4	0	105.95	101.14
1	5	0	100.67	117.80
1	6	0	80.62	82.83
1	7	0	89.34	82.34
1	8	0	84.17	73.54
1	9	0	78.98	70.78
1	10	0	46.16	45.82
1	11	0	150.44	141.38
1	12	0	19.08	13.56
1	14	0	32.07	32.90
1	15	0	33.65	33.09
1	16	0	29.77	22.79
1	17	0	71.75	67.28
1	18	0	41.08	39.31
1	20	0	14.00	12.30
1	21	0	70.45	74.44
1	22	0	17.70	5.94
1	23	0	101.87	93.32
1	25	0	27.90	34.47
1	27	0	23.27	19.04
1	28	0	19.93	11.99
1	29	0	19.74	10.90
1	30	0	19.37	7.44
1	31	0	28.97	30.13
1	32	0	18.17	20.45
1	33	0	17.24	15.19
1	36	0	19.37	29.19
2	0	0	89.64	94.13
2	1	0	36.00	31.47
2	2	0	107.43	100.05
2	3	0	82.50	80.34
2	4	0	76.47	74.80
2	5	0	132.37	137.76
2	6	0	10.38	13.07
2	8	0	15.11	15.75
2	9	0	34.95	31.02
2	10	0	33.65	31.69
2	11	0	47.27	45.41
2	12	0	77.49	81.51
2	13	0	10.66	4.27
2	14	0	12.88	6.87
2	15	0	11.68	4.96
2	16	0	112.90	106.08
2	17	0	74.06	75.89
2	18	0	15.20	20.53
2	19	0	15.85	15.93
2	20	0	16.41	10.35
2	21	0	22.71	20.07
2	22	0	16.59	9.77
2	23	0	10.04	30.95
2	24	0	24.29	24.51
2	25	0	102.80	96.27
2	26	0	23.17	20.06
2	27	0	23.27	23.37
2	29	0	19.65	20.09
2	31	0	10.72	10.54
2	32	0	17.98	9.79
2	34	0	15.94	12.25
2	36	0	13.26	6.43
3	1	0	31.42	42.10
3	2	0	148.22	143.25
3	3	0	96.49	91.28
3	4	0	62.20	63.49
3	5	0	51.17	44.84
3	6	0	145.99	149.00
3	7	0	52.84	54.84
3	8	0	21.78	27.67
3	10	0	68.59	66.13
3	11	0	14.37	7.78
3	12	0	31.33	32.44
3	13	0	32.63	23.95
3	14	0	43.47	45.11
3	15	0	66.65	62.09
3	16	0	12.51	14.85
3	17	0	12.98	14.80
3	18	0	41.25	45.07
3	20	0	22.43	25.33
3	22	0	59.09	57.28
3	23	0	19.00	17.52
3	24	0	55.52	61.59
3	25	0	19.74	9.42
3	27	0	26.14	27.18
3	28	0	23.08	25.56
3	30	0	19.09	6.45
3	32	0	17.61	11.37
3	34	0	28.74	38.66
3	36	0	12.70	14.89
4	0	0	130.24	134.31
4	1	0	278.77	246.42
4	2	0	81.66	86.14
4	3	0	80.64	71.29
4	4	0	47.46	51.87
4	5	0	18.76	46.19
4	6	0	8.99	15.05
4	7	0	55.52	49.04
4	8	0	13.72	4.55
4	9	0	86.58	83.41
4	11	0	100.57	99.70
4	12	0	12.98	10.17
4	13	0	71.19	70.73
4	14	0	34.20	22.56
4	15	0	38.38	39.94
4	16	0	18.45	25.84
4	17	0	55.71	59.14
4	18	0	32.16	37.13
4	19	0	20.39	15.21
4	20	0	26.51	30.30
4	21	0	58.40	53.60
4	22	0	21.32	21.39
4	23	0	69.61	64.90
4	24	0	20.09	26.49
4	25	0	28.36	21.00
4	26	0	32.91	34.55
4	27	0	23.17	24.46
4	29	0	50.33	49.14
5	1	0	15.02	6.71
5	2	0	107.06	112.23
5	3	0	26.05	30.73
5	4	0	87.02	89.44
5	5	0	9.73	8.44
5	6	0	84.07	85.33
5	7	0	14.46	13.01
5	8	0	31.78	25.65
5	9	0	45.41	41.15
5	10	0	70.87	69.46
5	11	0	36.61	32.74
5	12	0	11.96	8.24
5	13	0	17.43	12.35
5	14	0	45.05	45.14
5	15	0	18.63	24.23
5	16	0	29.38	29.77
5	17	0	46.25	44.03
5	18	0	66.00	56.32
5	19	0	24.01	17.85
5	22	0	72.58	71.10
5	23	0	19.66	13.17
5	24	0	28.36	25.01
5	25	0	30.87	25.75
5	26	0	19.93	13.83
5	27	0	19.74	8.12
5	30	0	21.32	20.71
5	34	0	16.50	18.99
6	0	0	102.98	136.97
6	1	0	75.87	79.25
6	2	0	99.92	131.86
6	3	0	22.82	23.70
6	4	0	43.10	40.49
6	6	0	40.14	33.58
6	7	0	120.94	129.37
6	8	0	60.62	66.20
6	9	0	65.35	65.68
6	10	0	12.05	20.64
6	11	0	12.42	7.80
6	12	0	14.74	8.76
6	13	0	53.30	45.68
6	14	0	15.57	19.96
6	15	0	13.90	6.44
6	16	0	26.05	24.82
6	17	0	34.67	33.23
6	18	0	24.19	29.21
6	19	0	33.18	29.92
6	20	0	21.41	22.74
6	21	0	45.23	36.53
6	24	0	40.23	30.55
6	25	0	19.84	9.03
6	28	0	24.93	12.57
6	30	0	17.61	7.42
7	1	0	16.22	5.10
7	2	0	57.10	55.65
7	3	0	26.41	12.93
7	4	0	34.48	35.06
7	5	0	87.04	87.83
7	6	0	12.05	7.62
7	7	0	60.81	59.39
7	8	0	36.71	39.98
7	9	0	14.74	15.41
7	10	0	55.15	57.63
7	11	0	53.21	55.81
7	17	0	27.90	30.23
7	18	0	25.12	24.57
7	19	0	18.35	12.71
7	20	0	19.00	16.51
7	21	0	43.10	43.04
7	22	0	23.17	19.68
7	23	0	80.55	67.13
7	28	0	18.35	7.32
7	30	0	19.47	19.25
7	32	0	16.96	20.00
7	33	0	13.16	15.25
8	0	0	53.30	51.67
8	1	0	37.08	39.04
8	2	0	17.80	15.40
8	3	0	14.65	10.83
8	4	0	37.73	33.94
8	5	0	12.98	11.05
8	6	0	35.50	33.00
8	8	0	49.22	51.07
8	9	0	44.77	50.24
8	10	0	37.82	40.50
8	11	0	20.11	21.50
8	12	0	57.93	50.57
8	13	0	17.06	17.89
8	14	0	23.36	22.97
8	15	0	19.84	20.25
8	16	0	96.96	91.03
8	17	0	71.60	24.76
8	18	0	81.55	51.63
8	22	0	23.27	13.12
8	24	0	22.80	16.74
8	27	0	18.17	7.12
9	2	0	19.47	23.11
9	3	0	31.89	25.93
9	4	0	19.65	15.39
9	5	0	48.57	45.75
9	6	0	15.48	13.95
9	7	0	64.05	61.23
9	11	0	23.36	21.15
9	12	0	21.69	26.84
9	13	0	21.97	15.41
9	14	0	27.25	23.24
9	15	0	31.09	30.89
9	16	0	27.90	25.25
9	18	0	23.17	15.10
9	22	0	25.77	11.28
9	24	0	31.24	17.15
9	28	0	21.23	7.45
10	0	0	47.64	43.35
10	1	0	89.34	70.58
10	2	0	21.60	15.38
10	4	0	48.85	47.00
10	5	0	28.83	31.06
10	6	0	20.67	22.02
10	7	0	18.45	20.81
10	8	0	55.52	53.44
10	9	0	18.82	5.64
10	10	0	22.25	14.32
10	11	0	19.19	15.43
10	12	0	25.40	18.44
10	13	0	22.80	20.69
10	14	0	19.65	16.02
10	15	0	19.84	19.76
10	16	0	30.67	30.15
10	20	0	22.90	15.05
10	28	0	14.55	18.46
11	1	0	26.23	27.70
11	2	0	24.66	21.11
11	5	0	20.86	19.32
11	6	0	28.18	26.37
11	9	0	27.44	23.80
11	10	0	22.99	23.56
11	11	0	54.23	52.70
11	15	0	19.93	17.82
11	16	0	19.84	11.41
11	18	0	22.71	23.68
11	19	0	22.43	17.97
11	20	0	21.97	22.52
11	22	0	17.80	24.28
12	0	0	46.07	40.29
12	1	0	23.08	19.69
12	3	0	23.08	17.48
12	6	0	26.14	23.90
12	7	0	19.93	5.14
12	8	0	28.46	31.10
12	9	0	19.93	4.73
12	10	0	23.27	22.08
12	14	0	19.56	10.38
12	15	0	25.49	23.16
12	16	0	19.19	5.49
12	17	0	41.16	40.95
12	18	0	24.29	25.30
12	20	0	25.03	24.75
12	22	0	18.91	17.47
13	3	0	23.17	25.79
13	4	0	19.84	11.82
13	6	0	58.86	53.53
13	14	0	21.69	20.58
13	15	0	21.32	20.82
13	16	0	20.86	19.15
13	22	0	16.43	17.66
14	6	0	29.38	12.18
14	15	0	19.19	19.72
14	17	0	17.98	14.82
16	0	0	18.08	17.72
16	10	0	19.37	4.53
0	3	1	59.60	63.05
0	4	1	32.81	19.36
0	5	1	153.78	157.39
0	6	1	30.22	33.24
0	7	1	167.50	164.23
0	8	1	41.06	40.61
0	9	1	124.58	125.92
0	10	1	14.92	13.27
0	11	1	50.43	42.43
0	12	1	59.05	52.92
0	13	1	19.47	10.25
0	14	1	56.00	46.78
0	15	1	16.50	17.33
0	16	1	17.15	14.24
0	17	1	42.64	37.67
0	18	1	30.40	34.71
0	19	1	31.52	36.43
0	21	1	43.01	38.58
0	24	1	18.72	13.44
0	25	1	45.42	40.42
0	26	1	32.54	32.06
0	28	1	22.99	20.47
0	30	1	22.25	23.51
0	31	1	21.60	20.49
0	33	1	19.65	24.43
0	34	1	13.07	12.93
0	37	1	13.18	28.45
1	0	1	53.58	42.03
1	1	1	82.50	79.17
1	2	1	175.01	165.17
1	3	1	115.59	120.56
1	4	1	86.85	90.09
1	5	1	29.01	32.98
1	6	1	47.74	45.29
1	7	1	85.19	65.77
1	8	1	58.58	45.70
1	9	1	80.07	63.67
1	10	1	57.01	43.53
1	11	1	64.70	55.10
1	12	1	91.40	82.42
1	13	1	73.04	69.06
1	14	1	111.97	104.82
1	15	1	39.40	36.97
1	16	1	55.62	57.65
1	17	1	32.81	27.98
1	18	1	40.41	38.28
1	19	1	35.41	33.16
1	20	1	28.36	32.36
1	21	1	16.96	22.35
1	22	1	34.85	33.86
1	23	1	33.93	27.30
1	24	1	36.06	37.80
1	25	1	21.97	25.40
1	26	1	45.98	46.52
1	29	1	19.47	19.72
1	30	1	19.09	15.66
1	31	1	21.60	17.67
1	32	1	17.70	16.99
1	35	1	16.87	14.03
1	36	1	15.11	15.22
1	37	1	13.07	15.13
2	0	1	138.11	126.52
2	1	1	43.01	35.02
2	2	1	102.15	113.20
2	3	1	72.86	75.63
2	4	1	104.10	106.02
2	5	1	99.37	87.93
2	6	1	69.80	65.33
2	7	1	92.23	95.13
2	8	1	89.36	82.06
2	9	1	124.86	130.36
2	10	1	72.12	75.33
2	11	1	40.23	37.25
2	12	1	47.83	36.05
2	13	1	15.57	23.33
2	14	1	26.51	27.45
2	16	1	40.53	45.50
2	17	1	29.65	27.86
2	18	1	30.96	31.33
2	19	1	51.26	52.33
2	20	1	83.01	88.85
2	21	1	53.30	55.08
2	22	1	52.00	45.58
2	23	1	39.86	31.08
2	24	1	19.28	17.27
2	25	1	45.70	41.57
2	26	1	39.66	35.56
2	28	1	19.65	16.87
2	31	1	18.35	21.09
2	32	1	20.49	12.21
3	0	1	205.04	195.35
3	1	1	108.82	115.59
3	2	1	161.75	159.74
3	3	1	166.76	172.39
3	4	1	83.98	81.31
3	5	1	85.00	71.42
3	6	1	62.20	53.98
3	7	1	35.13	32.82
3	8	1	89.91	82.84
3	9	1	101.96	92.44
3	10	1	75.64	79.21
3	11	1	71.00	71.11
3	12	1	79.44	84.28
3	13	1	13.16	7.62
3	14	1	56.17	55.63
3	15	1	54.50	61.06
3	16	1	44.31	35.48
3	17	1	30.59	27.94
3	18	1	40.41	37.74
3	19	1	14.18	8.96
3	20	1	32.07	31.87
3	21	1	36.89	33.97
3	22	1	17.80	14.21
3	23	1	26.05	22.52
3	24	1	26.08	23.21
3	25	1	22.52	18.97
3	26	1	23.08	15.82
3	27	1	28.27	25.11
3	28	1	22.80	14.72
3	29	1	22.43	22.30
3	30	1	21.88	22.22
3	31	1	33.28	30.18
3	32	1	17.15	16.02
3	37	1	14.37	19.04
4	0	1	87.87	91.95
4	1	1	104.93	105.84
4	2	1	72.86	60.99
4	3	1	89.36	81.70
4	4	1	102.61	101.37
4	5	1	55.80	52.70
4	6	1	57.75	55.52
4	7	1	85.19	75.77
4	8	1	49.31	46.12
4	9	1	60.53	55.31
4	10	1	44.49	40.63
4	11	1	22.34	11.09
4	12	1	54.50	47.85
4	13	1	53.11	54.47
4	14	1	17.52	20.29
4	15	1	29.57	29.82
4	16	1	73.04	74.97
4	17	1	15.85	10.90
4	18	1	23.00	23.19
4	19	1	31.42	26.81
4	20	1	56.27	59.16
4	21	1	24.47	28.31
4	22	1	44.77	47.98
4	23	1	18.91	20.82
4	24	1	22.90	22.58
4	25	1	19.74	9.93
4	32	1	23.92	29.24
5	0	1	43.01	39.13
5	1	1	32.35	34.07
5	2	1	54.32	53.46
5	3	1	11.31	9.74
5	4	1	29.11	33.65
5	5	1	45.70	47.01
5	6	1	14.65	15.75
5	7	1	34.20	31.00
5	8	1	14.09	11.27
5	9	1	12.88	7.34
5	10	1	26.60	17.81
5	11	1	40.51	34.01
5	12	1	47.00	51.48
5	13	1	68.32	72.16
5	14	1	64.70	64.12
5	15	1	78.23	90.54
5	16	1	19.56	16.81
5	17	1	16.41	16.41
5	18	1	14.65	10.88
5	19	1	23.27	27.26
5	20	1	34.76	30.46
5	21	1	21.04	13.73
5	22	1	34.67	30.19
5	23	1	45.70	45.14
5	24	1	22.99	29.34
5	25	1	28.27	22.82
5	26	1	22.99	25.92
5	27	1	39.39	39.41
5	28	1	27.25	29.17
6	0	1	102.43	97.28
6	1	1	49.59	49.49
6	2	1	25.21	26.67
6	3	1	61.46	61.16
6	4	1	97.08	96.28
6	5	1	38.10	38.71
6	6	1	65.81	63.07
6	7	1	49.50	50.15
6	8	1	52.84	52.94
6	9	1	84.07	86.61
6	10	1	26.70	26.09
6	11	1	47.09	47.91
6	12	1	46.48	46.78
6	13	1	26.70	27.62
6	14	1	27.44	28.67
6	15	1	22.99	22.94
6	16	1	31.61	28.27
6	17	1	16.68	15.46
6	18	1	24.75	20.56
6	19	1	40.23	37.53
6	20	1	21.88	10.53
6	21	1	42.36	46.02
6	24	1	46.16	38.28
6	25	1	19.65	12.20
6	26	1	32.16	31.47
6	32	1	21.60	29.23
7	0	1	27.07	24.09
7	1	1	49.87	50.65
7	2	1	87.23	90.47
7	3	1	56.54	57.87
7	4	1	69.98	79.00
7	5	1	43.20	43.35
7	6	1	41.43	40.43
7	7	1	25.03	26.16
7	8	1	47.64	48.55
7	9	1	15.02	15.96
7	10	1	48.39	49.34
7	11	1	44.22	46.13
7	12	1	15.94	12.85
7	13	1	30.50	20.77
7	14	1	48.39	49.83
7	15	1	30.50	27.09
7	16	1	20.21	23.79
7	17	1	18.17	11.90
7	18	1	41.43	36.67
7	19	1	22.43	21.19
7	20	1	27.90	32.29
7	21	1	19.65	12.36
7	22	1	19.74	13.75
7	23	1	23.08	26.15
7	24	1	19.65	19.41
7	25	1	19.37	12.71
7	26	1	19.00	18.39
7	27	1	18.54	14.06
7	30	1	23.17	28.66
8	0	1	69.52	67.43
8	1	1	69.52	65.82
8	2	1	51.54	45.30
8	3	1	27.99	22.82
8	4	1	26.14	23.64
8	7	1	50.92	61.29
8	8	1	17.70	19.35
8	9	1	44.03	48.23
8	10	1	20.02	23.37
8	11	1	15.63	19.24
8	12	1	32.07	35.18
8	13	1	41.34	36.47
8	14	1	24.78	21.48
8	15	1	18.26	6.61
8	16	1	35.04	27.73
8	17	1	19.28	13.41
8	18	1	19.47	7.35
8	19	1	62.75	55.28
8	20	1	23.08	21.87
8	21	1	51.63	50.19
8	27	1	17.70	15.77
9	0	1	17.98	20.10
9	1	1	16.04	7.67
9	2	1	41.06	44.33
9	3	1	34.30	35.35
9	4	1	36.43	32.10
9	5	1	30.68	36.99
9	6	1	30.96	31.80
9	7	1	16.68	23.63
9	8	1	18.91	25.67
9	9	1	35.13	32.23
9	10	1	33.37	30.90
9	11	1	27.01	25.99
9	13	1	48.57	45.37
9	14	1	39.77	39.05
9	15	1	24.01	28.38
9	16	1	22.06	24.60
9	17	1	22.15	24.72
9	18	1	32.63	33.24
9	25	1	21.04	25.56
10	0	1	48.11	43.62
10	1	1	36.15	35.78
10	2	1	55.71	65.63
10	3	1	40.23	36.87
10	4	1	52.46	45.59
10	5	1	21.04	10.77
10	6	1	25.42	22.44
10	7	1	21.69	14.97
10	8	1	37.91	34.89
10	9	1	44.22	42.72
10	10	1	25.12	22.36
10	11	1	22.43	22.34
10	12	1	22.62	10.81
10	13	1	27.90	23.84
10	14	1	28.09	25.25
10	18	1	19.65	17.89
10	23	1	18.08	22.69
10	25	1	24.01	21.12
11	1	1	35.22	32.89
11	2	1	25.12	20.09
11	3	1	27.34	23.79
11	4	1	27.44	27.88
11	6	1	22.62	22.41
11	7	1	25.49	25.68
11	8	1	19.47	10.78
11	9	1	22.90	18.70
11	10	1	19.65	15.86
11	13	1	39.95	41.25
11	14	1	23.08	18.71
11	15	1	19.65	19.42
11	18	1	22.34	15.86
11	19	1	21.97	22.29
11	20	1	18.45	14.72
11	21	1	17.98	16.88
11	22	1	22.90	27.15
11	25	1	17.61	15.54
12	2	1	28.18	23.64
12	3	1	19.74	11.91
12	4	1	25.95	15.01
12	5	1	19.74	24.77
13	6	1	27.99	33.02
12	8	1	28.27	31.09
12	11	1	22.99	23.89
12	20	1	22.43	25.12
13	1	1	22.99	23.86
13	3	1	22.99	27.98
13	4	1	22.90	15.06
14	0	1	31.24	35.98
14	3	1	26.97	31.40
14	8	1	24.01	30.31
14	20	1	16.41	14.11
16	0	1	17.43	21.78
17	4	1	13.07	4.40
17	6	1	10.57	13.83
0	0	2	205.41	192.83
0	1	2	33.65	24.62
0	2	2	47.27	47.78
0	3	2	81.48	73.59
0	5	2	103.17	103.35
0	6	2	22.80	19.32
0	7	2	33.09	35.01
0	8	2	29.66	27.51
0	9	2	92.69	97.43
0	10	2	55.06	49.59
0	11	2	13.35	16.28
0	12	2	119.11	122.18
0	13	2	66.09	65.82
0	15	2	92.60	87.99
0	16	2	46.72	50.25
0	19	2	45.05	47.99
0	20	2	43.75	49.39
0	21	2	31.79	29.87
0	22	2	16.31	12.56
0	23	2	38.65	44.13
0	24	2	16.50	16.36
0	25	2	17.06	11.57
0	26	2	20.30	16.54
0	27	2	17.98	19.86
0	28	2	35.87	42.15
0	34	2	13.44	7.04
0	36	2	17.52	9.58
1	0	2	28.83	29.45
1	1	2	82.50	76.27
1	2	2	9.27	9.81
1	3	2	36.06	29.48
1	4	2	96.12	103.55
1	5	2	58.40	54.56
1	6	2	83.70	76.02
1	7	2	44.68	39.06
1	8	2	82.40	78.69
1	9	2	93.34	85.61
1	10	2	37.26	32.95
1	11	2	101.59	97.04
1	12	2	55.34	55.35
1	13	2	45.05	51.43
1	14	2	30.77	26.44
1	15	2	26.14	25.15
1	16	2	35.57	31.02
1	17	2	41.06	38.98
1	18	2	30.96	33.34
1	19	2	28.18	22.02
1	21	2	44.59	43.36
1	22	2	18.63	12.48
1	23	2	31.24	31.51
1	24	2	53.50	46.12
1	25	2	20.95	16.36
1	26	2	36.43	37.82
1	28	2	23.27	25.32
1	32	2	15.39	15.79
1	33	2	16.87	12.08
1	35	2	15.85	14.52
2	0	2	76.57	85.14
2	1	2	19.65	27.85
2	2	2	40.41	34.37
2	3	2	54.50	50.26
2	4	2	46.90	40.95
2	5	2	66.46	69.85
2	6	2	52.74	50.91
2	7	2	67.26	70.24
2	8	2	29.85	25.44
2	9	2	68.50	60.20
2	10	2	97.70	95.49
2	11	2	58.30	54.62
2	12	2	86.21	85.41
2	13	2	40.80	35.83
2	14	2	25.58	22.57
2	16	2	48.76	51.44
2	17	2	37.82	39.09
2	18	2	16.50	21.94
2	19	2	34.11	31.18
2	20	2	17.15	14.59
2	21	2	18.35	15.93
2	22	2	21.51	25.45
2	23	2	24.56	23.56
2	24	2	46.53	46.41
2	25	2	20.95	21.05
2	27	2	20.86	15.53
2	28	2	23.17	28.25
2	29	2	20.11	15.21
2	36	2	11.86	7.89
3	0	2	49.50	40.38
3	1	2	114.38	120.03
3	2	2	27.62	25.70
3	3	2	57.56	52.11
3	4	2	24.29	17.40
3	5	2	95.10	83.60
3	6	2	61.55	67.98
3	7	2	45.05	43.78
3	8	2	28.97	31.49
3	9	2	41.06	35.41
3	10	2	50.33	43.49
3	11	2	20.49	22.94
3	12	2	53.86	59.62
3	13	2	55.99	52.28
3	14	2	36.15	31.81
3	15	2	16.78	17.96
3	16	2	24.47	24.84
3	17	2	17.89	15.59
3	18	2	33.00	29.90
3	19	2	39.21	34.19
3	20	2	26.14	30.65
3	21	2	30.68	32.44
3	22	2	51.91	43.10
3	23	2	23.27	19.60
3	24	2	20.95	13.52
3	27	2	17.80	15.30
3	29	2	24.38	26.77
3	30	2	23.54	12.85
3	34	2	14.74	15.62
3	35	2	16.13	15.63
3	36	2	12.51	22.98
3	37	2	11.12	4.94
4	0	2	80.18	74.95
4	1	2	89.26	89.34
4	2	2	70.91	71.38
4	3	2	18.72	15.77
4	4	2	33.74	32.91
4	5	2	27.53	31.79
4	6	2	60.90	62.44
4	7	2	35.41	33.66
4	9	2	29.65	24.68
4	10	2	63.50	61.57
4	11	2	85.83	87.27
4	12	2	28.83	25.97
4	13	2	48.94	45.20
4	14	2	55.80	61.22
4	15	2	22.43	21.71
4	16	2	25.31	15.09
4	17	2	28.18	25.18
4	18	2	28.92	29.39
4	19	2	17.70	22.67
4	20	2	17.80	17.50
4	22	2	29.11	33.34
4	24	2	20.95	23.43
4	26	2	29.48	22.34
4	27	2	25.21	26.03
4	29	2	19.56	15.51
4	32	2	16.78	11.51
4	35	2	12.33	6.27
5	0	2	59.88	54.91
5	2	2	28.27	23.04
5	3	2	51.26	45.67
5	4	2	40.04	35.03
5	5	2	39.95	44.52
5	6	2	33.37	35.10
5	7	2	16.07	24.44
5	8	2	29.85	31.84
5	9	2	34.20	33.65
5	10	2	53.48	55.99
5	11	2	43.20	46.48
5	12	2	41.71	40.49
5	13	2	51.91	56.55
5	14	2	14.37	9.23
5	15	2	23.36	21.70
5	16	2	3.36	25.07
5	17	2	19.68	53.78
5	18	2	47.74	45.53
5	19	2	16.22	15.48
5	20	2	43.01	37.33
5	22	2	51.03	51.18
5	24	2	21.04	27.97
5	25	2	29.57	31.18
5	29	2	19.00	20.88
5	35	2	11.03	11.93
6	0	2	38.10	34.35
6	1	2	69.71	73.30
6	2	2	37.08	40.33
6	3	2	45.88	42.60
6	4	2	26.05	25.14
6	5	2	29.20	32.97

TABLE 2. (Continued)

needles from methanol solution. Thus, the *p*-bromobenzenesulfonyl derivative of the α form was subjected to the crystal structure analysis. A preliminary report has already been published.[5]

Experimental

The *p*-bromobenzenesulfonyl derivative of ascochlorin was prepared by the esterification of the phenolic hydroxyl group with *p*-bromobenzenesulfonyl chloride in pyridine (heating for 30 min on boiling water bath). The reaction mixture was poured into cold water, and the product was extracted with ether. The crystals obtained from acetone solution were needles developed along the *c*-axis. Two single crystals of 0.20×0.12 and 0.15×0.05 mm in cross section, measured along the diagonal lines, were used for the intensity data collection around the *c*- and *a*-axes, respectively. Precession photographs of (0*kl*) and (*hk*0) were used for the measurements of cell parameters, and the higher layer line spectra of Weissenberg photographs were also used for the determination of the space group.

Crystal data. Ascochlorin-*p*-bromobenzenesulfonate, $C_{29}H_{33}O_6SClBr$, mol wt, 624.4.

Orthorhombic,

$a=13.86\pm0.03$, $b=30.04\pm0.03$, $c=6.82\pm0.01$ Å;

$U=2839.5$ Å^3, $Z=4$, $Dx=1.460$ g.cm^{-3}.

μ(Cu $K\alpha$)$=41.2$ cm^{-1}, F(000)$=1160$.

Absent spectra, $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

Space group, D_2^4—$P2_12_12_1$.

Intensity data were collected with Cu$K\alpha$ radiation on the multiple film packs of Weissenberg photographs with the use of equi-inclination method. Layers from 0th to 5th around the *c*-axis and from 0th to 6th around the *a*-axis were recorded. Intensities were measured visually by comparison with the standard intensity scale. These data were then corrected for Lorentz, polarization and spot elongation factors but not for absorption. The derived structure factors on different layers were correlated and scaled in a common base by comparing the common reflexions. The total number of independent reflexions was 1627.

Determination of the Crystal Structure

The crystal structure was elucidated by the heavy atom method. The positional parameters of bromine atom were determined from the three Harker sections of $P(0.5, v, w)$, $P(u, 0.5, w)$, and $P(u, v, 0.5)$, sharpened to correspond to the atoms at rest. The structure factor calculated for the bromine atom alone gave the R value of 0.44. The coordinates of the atoms in

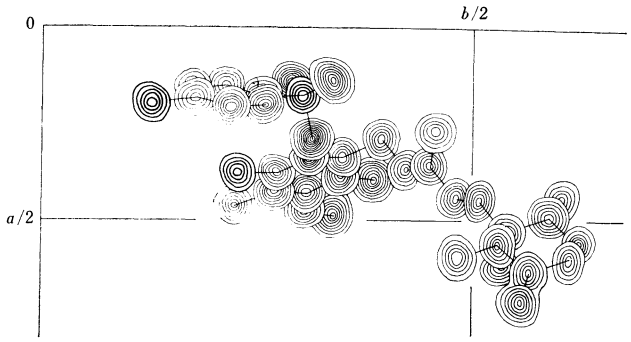

Fig. 1(a). Composite drawing of the final electron density map viewed along the *c*-axis. Contours for carbon and oxygen atoms are drawn at intervals of 1 e.Å^{-3} starting at 1 e.Å^{-3}, and for sulfur and chlorine atoms are at intervals of 3 e.Å^{-3} starting at 3 e.Å^{-3}. Those for bromine atom are drawn by arbitrary scale.

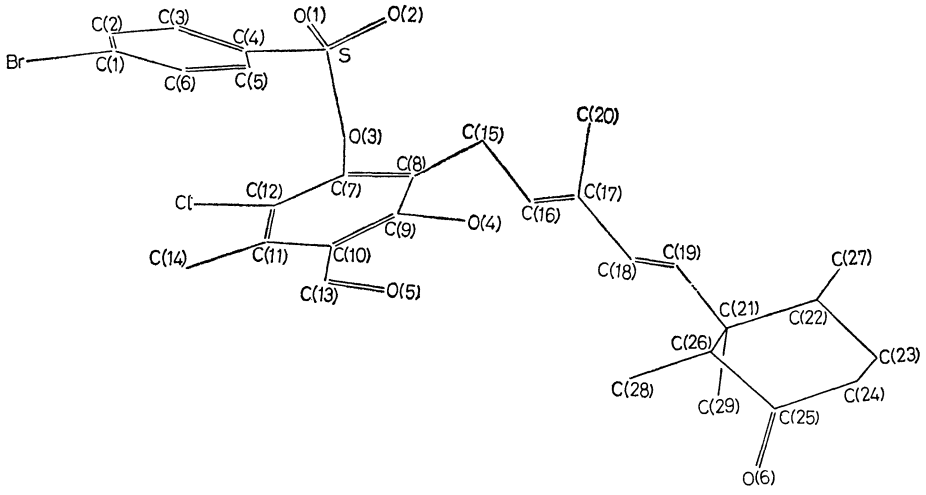

Fig. 1(b). The molecular structure viewed along the *c*-axis.

5) Y. Nawata, K. Ando, G. Tamura, K. Arima, and Y. Iitaka, *J. Antibiot.* (Tokyo), **22**, 511 (1969).

the *p*-bromobenzenesulfonyl group and the chlorine atom were determined on the Fourier map and used for the next structure factor Fourier calculations. The *R* value for the structure factors of these twelve atoms was 0.34. The subsequent Fourier and difference Fourier syntheses revealed all the positions of the atoms at the stage where the *R* value reached 0.24. The four oxygen atoms of the ascochlorin molecule were distinguished easily from the carbon atoms on the difference Fourier map. The molecular structure of ascochlorin elucidated in this way consisted of (3-chloro)orcylic aldehyde and (2,3,4-trimethyl)cyclohexanone moieties linked together through the zigzag chain of *trans*-(3-methyl)penta(2,4)diene. Further refinement of the parameters was carried out by the least-squares method of block matrix approximation with the use of the program HBLS.[6] Anisotropic thermal motions were considered only for bromine atom. The *R* value dropped to 0.123 after four cycles of refinement, and the positions of single and double bonds in the molecule were confirmed. The characters of the four oxygen atoms of ascochlorin molecule were made clear at this stage; one was of keto group in the cyclohexanone moiety, and the others were of two hydroxyl and one aldehyde groups in the orcylic aldehyde moiety. Finally, the least-squares refinement was carried out with the anisotropic temperature factors for all atoms. The *R* value was converged to 0.102 after three cycles of calculations. In these calculations all reflexions were treated with equal weight. Atomic scattering factors used were those given in *International Tables for X-ray Crystallography*.[7] Final values of atomic parameters and anisotropic temperature factors are given in Table 1. Figure 1(a) shows the final three-dimensional Fourier map.

Absolute Configuration

The absolute configuration of ascochlorin-*p*-bromobenzenesulfonate molecule was determined by Bijovet's method with the use of anomalous dispersion of Cu$K\alpha$ radiation by bromine, sulfur, and chlorine atoms. Dispersion corrections of the scattering factors used were those given by Dauben and Templeton.[8] The values of $\Delta f'$ and $\Delta f''$ are as follows:

Br	$\Delta f' = -1.0$	$\Delta f'' = 1.4$
S	0.3	0.7
Cl	0.3	0.6

The structure factors for both hkl and $h\bar{k}l$ were calculated with final atomic parameters. If one takes the left-handed coordinate system, the observed and calculated values of the ratios of the intensities $I(hkl)/I(h\bar{k}l)$ are not coincident for all pairs, as shown in Table 3, and the assumed configuration proves to be reversed. In this report, the molecules are shown by the correct absolute configuration.

Table 3. The determination of the absolute configuration

h	k	l	$\lvert F_c(hkl)\rvert^2/\lvert F_c(h\bar{k}l)\rvert^2$	$I_0(hkl)/I_0(h\bar{k}l)$
5	1	1	1.42	<1
1	6	1	1.22	<1
5	9	1	7.01	<1
6	5	2	1.27	<1
2	6	2	1.22	<1
5	6	2	1.27	<1
5	3	1	0.60	>1
4	8	1	0.79	>1
5	8	1	0.63	>1
1	10	1	0.76	>1
5	10	1	0.83	>1
4	11	1	0.69	>1
3	13	1	0.26	>1
3	4	2	0.59	>1
1	7	2	0.79	>1
1	16	2	0.75	>1

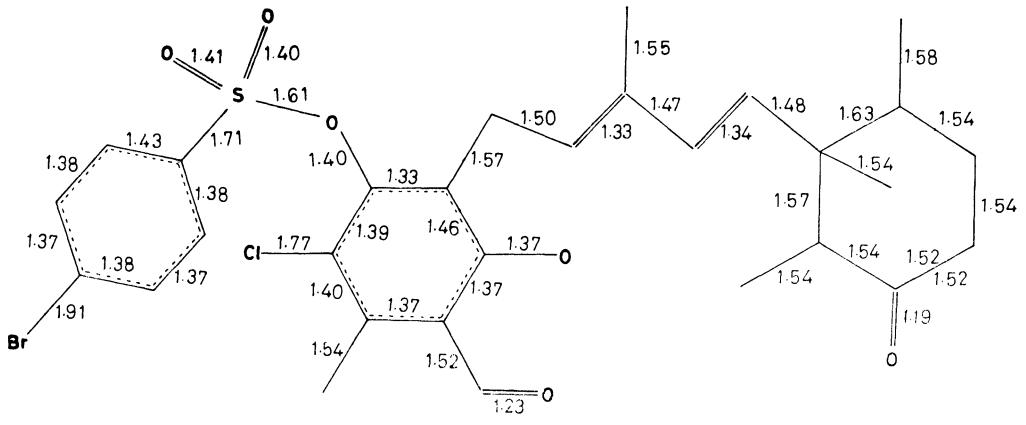

Fig. 2. Bond lengths (Å).

6) Y. Okaya and T. Ashida, *HBLS IV, The Universal Crystallographic Computing System (I)*, p. 65, Japanese Crystallographic Association.

7) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).

8) C. H. Dauben and D. H. Templeton, *Acta Cryst.* **8**, 841 (1955).

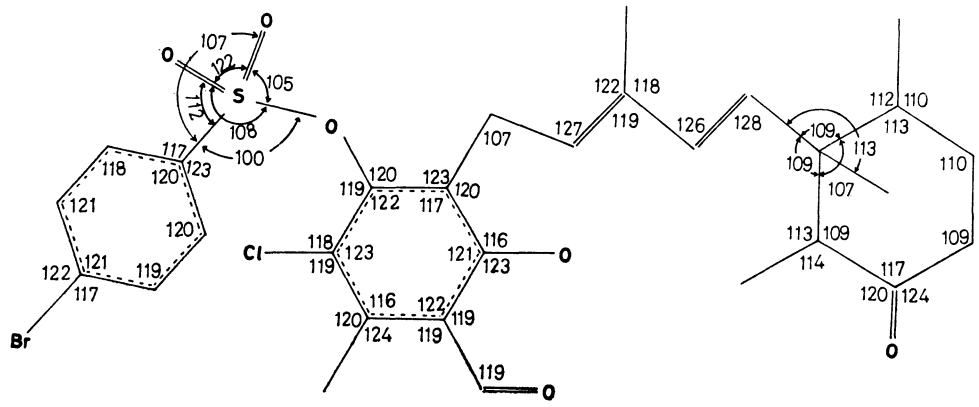

Fig. 3. Bond angles (°).

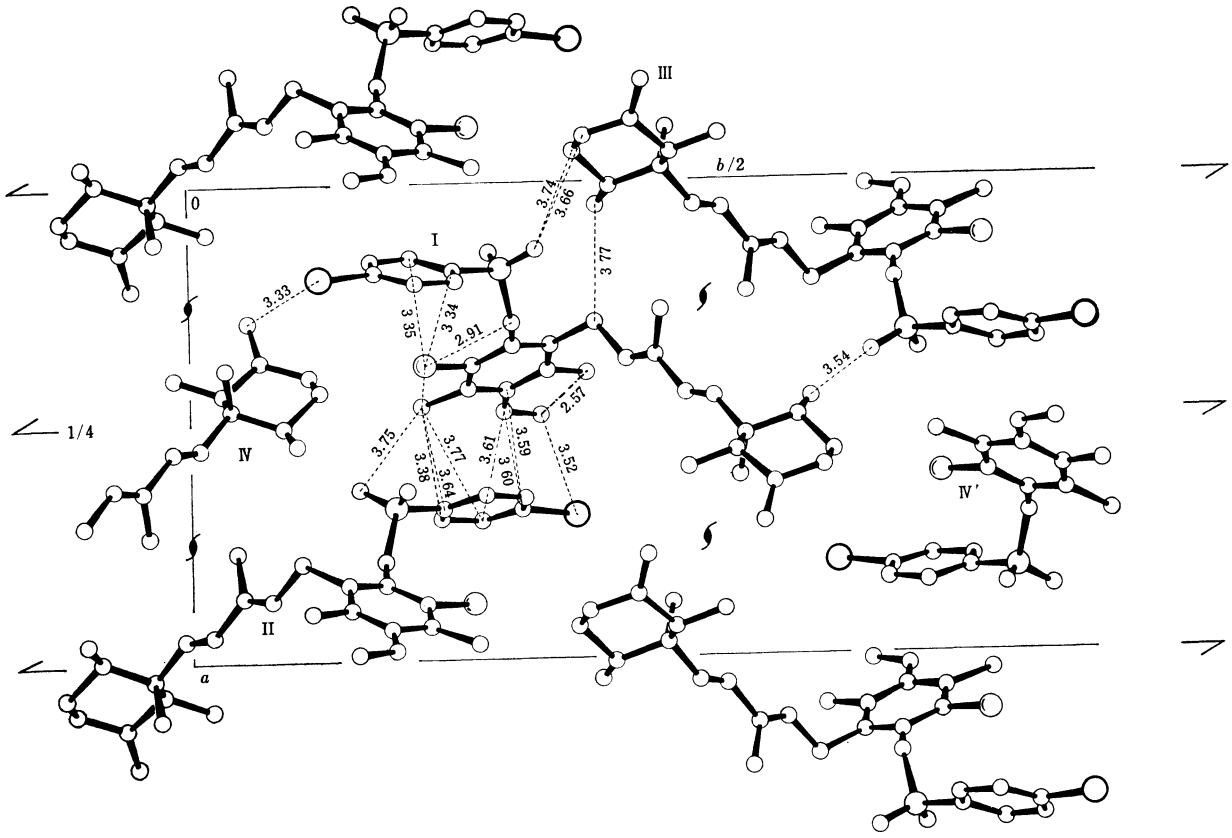

Fig. 4. Arrangement of the molecules in the unit cell viewed down [001].

Discussion of the Structure

The molecular structure of ascochlorin-*p*-bromobenzenesulfonate is illustrated in Fig. 1(b), in which the numbers and symbols of the atoms are also given. Ascochlorin is built up of chloroorcylic aldehyde residue, trimethylcyclohexanone ring and the zigzag chain of *trans*-methylpentadiene. As shown in Table 5, all atoms of chloroorcylic aldehyde residue lie approximately on a plane. Of these, the six carbon atoms of the benzene ring lie on an almost complete plane, the average deviation from the least-squares plane being only 0.009 Å. Chlorine atom and its adjacent methyl group(C(14)), which are separated only by 3.03 Å, deviate by −0.124 and +0.134 Å from the benzene ring in order to balance the repulsive forces between the *ortho*-substituents. The short distance(2.57 Å) between the two oxygen atoms of hydroxyl(O(4)) and aldehyde group (O(5)), indicates the existence of an intramolecular hydrogen bond between them, in consistence with the spectral data of proton magnetic resonance.[5] The four oxygen atoms of the sulfonyl group are arranged in a distorted tetrahedral configuration around the central sulfur atom, and O(1) lies nearly on the plane passing through the benzene ring(perpendicular distance to the plane is +0.027 Å), O(2) lies above the plane(+0.795 Å) and O(3) below the plane(−1.540 Å). As the conformation of O(1)—S—O(3)—C(7) bonds at the ester linkage

Table 4. Bond length and angles with their standard deviations (e.s.d.)

Br——C (1)	1.914 Å	(0.023)	C (1)—C (2)	1.370 Å	(0.037)	C (2)—C (3)	1.384 Å	(0.034)
C (3)—C (4)	1.431	(0.031)	C (5)—C (6)	1.400	(0.027)	C (6)—C (1)	1.379	(0.029)
S——C (4)	1.714	(0.022)	S——O (1)	1.411	(0.017)	S——O (2)	1.396	(0.017)
S——O (3)	1.609	(0.013)	S (3)—C (7)	1.402	(0.023)	C (7)—C (8)	1.331	(0.027)
C (8)—C (9)	1.459	(0.030)	C (9)—C (10)	1.374	(0.027)	C (10)-C (11)	1.378	(0.029)
C (11)-C (12)	1.398	(0.032)	C (12)-C (7)	1.386	(0.029)	O (4)—C (9)	1.366	(0.023)
C (10)-C (13)	1.524	(0.033)	O (5)—C (13)	1.234	(0.028)	C (11)-C (14)	1.535	(0.029)
Cl——C (12)	1.773	(0.023)	C (8)—C (15)	1.570	(0.025)	C (15)-C (16)	1.501	(0.031)
C (16)-C (17)	1.332	(0.032)	C (17)-C (20)	1.555	(0.032)	C (17)-C (18)	1.474	(0.029)
C (18)-C (19)	1.335	(0.031)	C (19)-C (21)	1.482	(0.027)	C (21)-C (22)	1.629	(0.026)
C (22)-C (27)	1.581	(0.038)	C (22)-C (23)	1.537	(0.029)	C (23)-C (24)	1.537	(0.038)
C (24)-C (25)	1.523	(0.029)	O (6)—C (25)	1.193	(0.028)	C (25)-C (26)	1.542	(0.029)
C (26)-C (28)	1.539	(0.025)	C (26)-C (21)	1.569	(0.032)			

Br——C (1)—C (2)	121.9°	(1.8)	Br——C (1)—C (6)	116.5°	(1.6)
C (1)—C (2)—C (3)	121.0	(2.2)	C (2)—C (3)—C (4)	118.1	(2.1)
C (3)—C (4)—C (5)	119.8	(1.9)	C (3)—C (4)—S	117.0	(1.6)
C (4)—C (5)—C (6)	120.4	(1.8)	C (5)—C (6)—C (1)	119.0	(1.9)
C (6)—C (1)—C (2)	121.4	(2.1)	O (1)—S——O (2)	122.4	(1.0)
O (1)—S——O (3)	108·2	(0.8)	O (1)—S——C (4)	111.8	(1.0)
O (2)—S——O (3)	104.5	(0.9)	O (2)—S——C (4)	107.0	(1.0)
O (3)—S——C (4)	100.4	(0.9)	S——C (4)—C (5)	123.1	(1.6)
O (3)—C (7)—C (8)	119.6	(1.7)	O (3)—C (7)—C (12)	118.6	(1.7)
C (7)—C (8)—C (9)	116.7	(1.8)	C (7)—C (8)—C (15)	123.1	(1.8)
C (8)—C (9)—C (10)	120.7	(1.8)	C (8)—C (9)—O (4)	115.8	(1.7)
C (9)—C (8)—C (15)	120.3	(1.7)	O (4)—C (9)—C (10)	123.4	(1.8)
C (9)—C (10)-C (11)	122.0	(1.9)	C (9)—C (10)-C (13)	119.1	(1.8)
C (10)-C (11)-C (12)	115.8	(1.9)	C (10)-C (11)-C (14)	124.3	(1.9)
C (10)-C (13)-O (5)	118.5	(2.0)	C (13)-C (10)-C (11)	118.8	(1.9)
C (11)-C (12)-C (7)	123.2	(2.0)	C (11)-C (12)-Cl	118.7	(1.7)
C (14)-C (11)-C (12)	119.7	(1.9)	C (12)-C (7)—C (8)	121.6	(1.9)
Cl——C (12)-C (7)	117.9	(1.6)	C (8)—C (15)-C (16)	107.3	(1.7)
C (15)-C (16)-C (17)	126.9	(2.1)	C (16)-C (17)-C (18)	118.9	(2.0)
C (16)-C (17)-C (20)	122.3	(2.0)	C (17)-C (18)-C (19)	125.7	(2.0)
C (20)-C (17)-C (18)	118.2	(1.8)	C (18)-C (19)-C (21)	127.6	(2.0)
C (19)-C (21)-C (22)	109.2	(1.7)	C (19)-C (21)-C (29)	112.6	(1.7)
C (19)-C (21)-C (26)	108.6	(1.7)	C (21)-C (22)-C (23)	113.0	(1.7)
C (21)-C (22)-C (27)	111.7	(1.8)	C (22)-C (23)-C (24)	110.4	(1.9)
C (27)-C (22)-C (23)	109.5	(1.8)	C (23)-C (24)-C (25)	109.1	(2.0)
C (24)-C (25)-C (26)	116.6	(2.0)	C (24)-C (25)-O (6)	123.5	(2.2)
C (25)-C (26)-C (21)	109.0	(1.7)	C (25)-C (26)-C (28)	114.3	(1.8)
O (6)—C (25)-C (26)	119.8	(2.1)	C (26)-C (21)-C (22)	107.0	(1.6)
C (28)-C (26)-C (21)	113.2	(1.7)			

is *cis* form, the chlorine atom of the chloroorcylic aldehyde residue comes at a position close to the benzene ring of the *p*-bromobenzenesulfonyl residue. The perpendicular line from the chlorine atom to the latter benzene ring drops inside the ring(distance 3.22 Å). This conformation is thus stabilized by the interaction between the benzene ring and the chlorine atom which has a larger electron affinity than the other atoms. These two benzene planes of the same molecule make an angle of 133°25′. In the case of siccanin-*p*-bromobenzenesulfonate,[9] the conformation of O–S–O–C bonds(at the ester linkage) is *trans* form and the ether oxygen atom in *D*-ring of siccanin comes above the benzene ring of *p*-bromobenzenesulfonyl residue.

The zigzag chain of the methylpentadiene residue takes all *trans* conformations, and the internal rotation angle[10] around the C(17)—C(18) bond is 175.9°. The bond lengths of C(17)—C(18) and C(19)—C(21), 1.47 and 1.48 Å, respectively, suggest that the π electrons in the methylpentadiene residue is delocalized.

The cyclohexanone ring adopts a typical chair form. As shown in Table 5, the two carbon atoms,

9) K. Hirai, S. Okuda, S. Nozoe, and Y. Iitaka, *Acta Cryst.*, **B25**, 2630 (1969).

10) The internal rotation angle around the B—C bond of A—B—C—D is defined as the angle between projection of A—B and that of C—D, when the projection is taken along the B—C bond. The positive value is taken in the same sense as that of the turning direction of a right handed screw advancing along the B—C bond.

TABLE 5. THE LEAST-SQUARE PLANES AND THE PERPENDICULAR DISTANCES OF THE ATOMS FROM THE PLANES

p-Bromobenzensulfonyl benzene:	$0.9602X-0.1337Y-0.2453Z+1.86488=0$		
C (1)	0.008 Å	C (4)	−0.029
C (2)	−0.023	C (5)	0.013
C (3)	0.033	C (6)	−0.003
Br	0.121	S	0.055
Chlorocyclic aldehyde benzene:	$0.8559X+0.2710Y+0.4406Z+4.53956=0$		
C (7)	0.017	C (10)	0.008
C (8)	−0.013	C (11)	−0.005
C (9)	0.000	C (12)	−0.008
Cl	0.124	C (14)	−0.134
C (13)	−0.077	O (5)	0.035
O (4)	0.092	O (3)	−0.005
salicyl aldehyde:	$0.8629X+0.2487Y+0.4399Z+4.37469=0$		
C (7)	0.009	C (10)	0.015
C (8)	−0.046	C (11)	0.026
C (9)	−0.024	C (12)	0.014
C (13)	−0.064	O (5)	0.027
O (4)	0.043		

where X, Y, Z are taken along the crystallographic a, b, and c axes, respectively, and measured in Å units.

C(25) and C(22), deviate by +0.64 and −0.70 Å, respectively, from the plane(A) formed by the four carbon atoms of C(21), C(23), C(24), and C(26). The two planes formed by C(21), C(22), and C(23), and by C(24), C(25), C(26), and O(6), intersect with the plane (A) at angles of 126.6° and 128.5°, respectively. Of the three methyl groups attached to the cyclohexanone ring, two are in equatorial (C(27), C(28)) and the other in axial position (C(29)). The same conclusion was deduced for the terpenoid metabolite (LL-Z1272-γ) from the NMR spectral data.[4]

The structures of the crystal projected along the c and a axes are shown in Figs. 4 and 5, respectively. As is clear from Fig. 5, the orcylic aldehyde and *p*-bromobenzenesulfonyl residues are stacked to construct the columns of aromatic rings along the a-axis and form the layers parallel to the (010) plane. The stacking of the two phenyl groups is such that the Br-ϕ and Cl-ϕ groups are arranged in anti-parallel fashion with respect to the halogen position. The cyclohexanone and the methylpentadiene residues are extended from the aromatic layers and fill up the spaces between them. The shortest intermolecular distances less than 3.8 Å are shown in Fig. 4, in which the molecules are designated by the molecular number I to IV as follows:

I at (x, y, z)
II at $(0.5+x, 0.5-y, 1-z)$
III at $(0.5-x, 1-y, -0.5+z)$
IV at $(1-x, -0.5+y, 2.5-z)$

The distance between the oxygen atom O(6) of keto group (IV) and the bromine atom (I) (3.33 Å) suggests the existence of rather strong van der Waals interaction between them (the sum of the van der Waals radii=3.35 Å).

Thanks are due to C. Itoh Electronic Computing Service for use of a CDC 3600 computer.

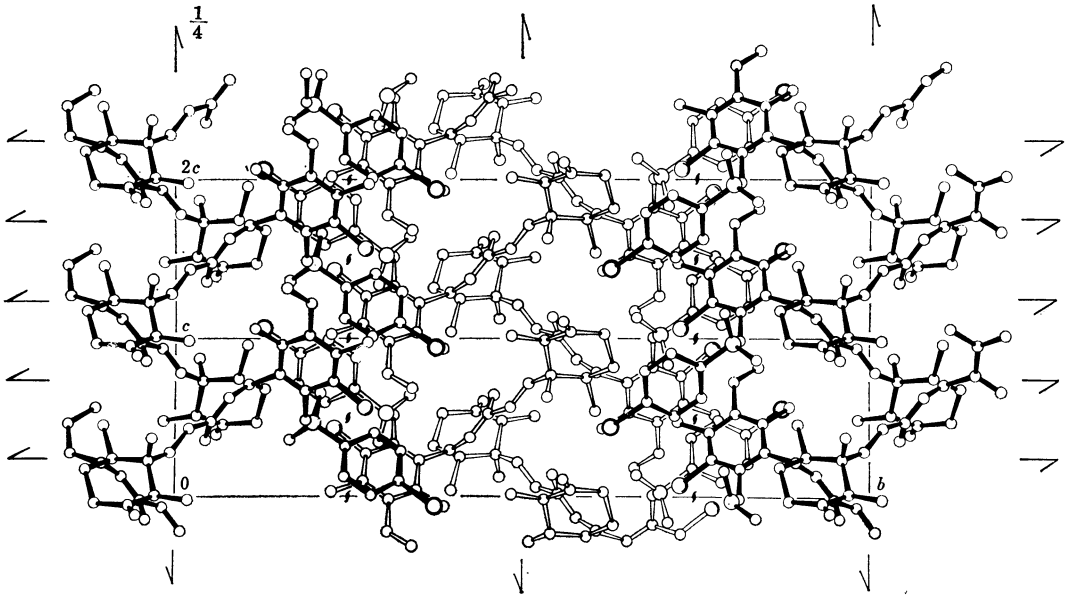

Fig. 5. Arrangement of the molecules in the unit cell viewed down [100].