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X-ray Studies of C_{25} terpenoids. II. The Crystal Structure of Methyl Cephalonate Bromoacetate [a Heavy Atom Derivative of Cephalonic Acid (Ophiobolin D)]

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The crystal and molecular structure of methyl cephalonate bromoacetate, $C_{28}H_{39}O_5Br$, a heavy atom derivative of a fungus metabolite, cephalonic acid (ophiobolin D), $C_{25}H_{36}O_4$, has been determined by three-dimensional X-ray analysis. The unit cell of methyl cephalonate bromoacetate is orthorhombic, space group $P2_12_12_1$, with dimensions, $a=11{\cdot}36$, $b=29{\cdot}41$, $c=8{\cdot}13$ Å. Refinement was carried out for 1791 independent observed reflexions by the block-matrix least-squares method to an R value of 0·15. In this calculation, individual anisotropic thermal vibrations were allowed for. The main feature of the molecular structure is very similar to that found in ophiobolins A, B and C, indicating that cephalonic acid is a congener of ophiobolins and is the fourth example of a C_{25} terpenoid. The molecule consists of a five-, eight- and five-membered fused ring system. The side chain 2-methylhept-2-en-6-yl group is extended from C(14) of ring *C* in place of the side chain portion containing the C(14)–C(17) oxide bridge in ophiobolin A.

Introduction

Recent X-ray structure analysis of ophiobolin A (Nozoe, Morisaki, Tsuda, Iitaka, Takahashi, Tamura, Ishibashi & Shirasaka, 1965; Morisaki, Nozoe & Iitaka, 1968) and the subsequent chemical studies of the structures of ophiobolins B and C, the congeners of ophiobolin A (Nozoe, Hirai & Tsuda, 1966) have led to the conclusion that these compounds are new examples of C_{25} terpenoids. It has also been shown recently that a new compound, cephalonic acid, is found in the cultured broth of *Cephalosporium caerulence* which has hitherto been known as a helvolic acid producing micro-organism. Cephalonic acid is extracted from the cultured broth with ethyl acetate at *p*H 3 and fractionated against other metabolites (helvolic acid, ergosterol *etc.*) by means of silica gel chromatography. Chemical analysis indicated the formula, $C_{25}H_{36}O_4$, for this compound.

Cephalonic acid has now been chosen for X-ray structure analysis, since it has a rather unusual carbon number and is thought to be another example of the C_{25} terpenoids. As a result of the present work, it is well established that cephalonic acid is a congener of ophiobolins and is the fourth example of the C_{25} terpenoids. Just as the name 'ophiobolins' was proposed for the analogous substances of ophiobolin (Tsuda, Nozoe, Morisaki, Hirai, Itai, Okuda, Canonica, Fiecchi, Kienle & Scala, 1967), a new trivial name 'ophiobolin D' is given to cephalonic acid. A preliminary note of the present study has already been published (Itai, Nozoe, Tsuda, Okuda, Iitaka & Nakayama, 1967).

Experimental

A heavy atom derivative, methyl cephalonate bromoacetate, $C_{28}H_{39}O_5Br$, was prepared through bromoacetylation of methyl cephalonate with bromoacetyl bromide in benzene solution. The crystals of the bromoacetate grown from methanol solutions are colourless long prisms elongated along the *c* axis. The lattice constants were determined from precession photographs of (0*kl*) and (*h*0*l*) taken with Cu $K\alpha$ radiation. The density was measured by flotation in aqueous solutions of potassium iodide with various concentrations. The crystal data are summarized in the following:

Crystal data

Methyl cephalonate bromoacetate (methyl ester of ophiobolin D bromoacetate), $C_{28}H_{39}O_5Br$, m.p. 102°, M.W. 535·2.

Orthorhombic,
$a=11{\cdot}36\pm0{\cdot}02$, $b=29{\cdot}41\pm0{\cdot}04$, $c=8{\cdot}13\pm0{\cdot}01$ Å
$V=2716{\cdot}2$ Å^3,
$D_x=1{\cdot}303$ g.cm^{-3},
$D_m=1{\cdot}290$ g.cm^{-3},
$Z=4$,
$F(000)=1128$.
μ(Cu $K\alpha$) = 24·9 cm^{-1}.
Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.
Space group: $P2_12_12_1$.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photo-

graphs taken with Cu $K\alpha$ radiation. Layer lines of zero to four around a and zero to five around the c axis were recorded. The intensities were estimated visually with the aid of intensity scales prepared for each axis.

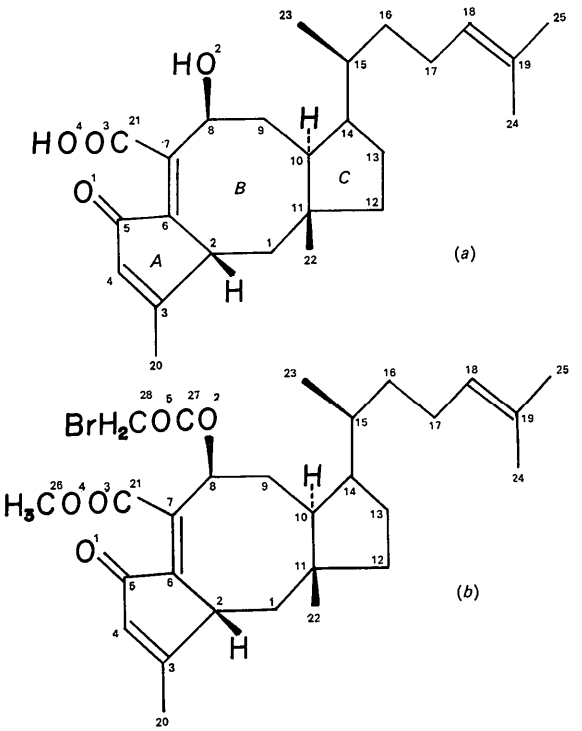

Fig. 1. Chemical structures of (*a*) cephalonic acid (ophiobolin D) and (*b*) methyl cephalonate bromoacetate.

Lorentz and polarization corrections were applied and a total of 1791 independent observed structure factors were derived. The interlayer correlation was carried out by comparing the equivalent structure factors recorded on various layers.

Determination and refinement of the structure

The coordinates of the bromine atom [$x=0{\cdot}218$, $y=0{\cdot}112$, $z=0{\cdot}250$, referred to the coordinate system given for $P2_12_12_1$ in *International Tables for X-ray Crystallography* (1952)] were determined by the three Harker sections of the sharpened Patterson function. The R value calculated for the structure containing only the bromine atom was 0·52. A three-dimensional Fourier synthesis was then calculated with the phase angles determined by the contributions of the bromine atoms. Since the bromine atoms are situated at rather special positions, there appeared as many spurious peaks as real ones in this electron density map, which are the mirror-image peaks related to the latter by the planes of symmetry at $z=\frac{1}{4}$ and $\frac{3}{4}$. A careful examination of the map revealed a five-membered ring lying approximately at $z=0{\cdot}4$. The second electron density map phased by eight atoms, while it still contained some residual false symmetry, revealed several additional well defined peaks. Several repeated cycles of structure factors and Fourier or difference-Fourier calculations yielded the whole structure except the carboxyl carbon atom C(17), for which the mirror-image peak persistently remained even at the seventh difference-Fourier synthesis, in the case when this atom had not been included in the phasing atoms. The R value at this stage was 0·30. There was naturally no

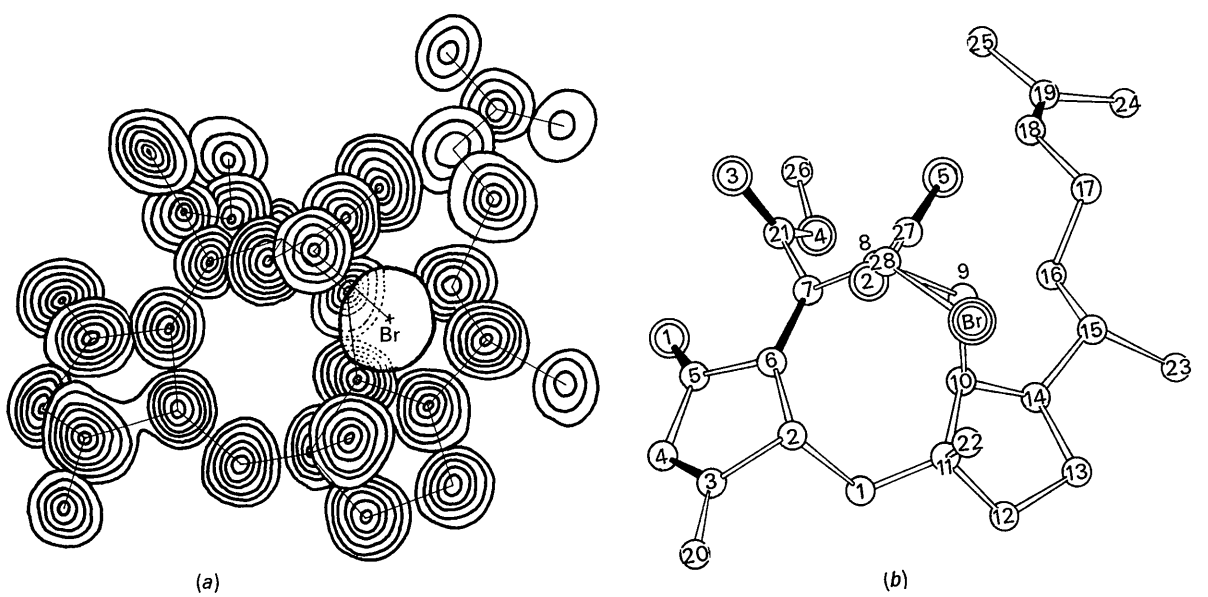

Fig. 2. (*a*) Composite electron density map projected along the a axis. Contours are drawn with 1, 2, 3 $\cdots$ e.Å^{-3} but those for the bromine atom are omitted. (*b*) Projection of the molecular structure of methyl cephalonate bromoacetate along the a axis Black rods represent double bonds.

Table 1. *Final atomic parameters and their standard deviations*

x, y and z are the fractional atomic coordinates. Temperature factors are expressed in the form of

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

Standard deviations are in parentheses. To represent the correct absolute configuration the coordinates should be referred to the right handed coordinate system.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·7208 (3)	0·3893 (1)	0·7669 (6)	0·0139 (3)	0·0019 (0)	0·0379 (9)	−0·0016 (1)	0·0073 (6)	0·0006 (2)
O(1)	0·1309 (14)	0·2184 (5)	0·8009 (18)	0·0079 (14)	0·0011 (2)	0·0104 (28)	−0·0008 (5)	−0·0006 (19)	0·0005 (6)
O(2)	0·4601 (11)	0·3329 (4)	0·8656 (17)	0·0035 (11)	0·0008 (2)	0·0104 (25)	0·0001 (4)	0·0013 (16)	0·0002 (6)
O(3)	0·2082 (17)	0·2654 (5)	1·1127 (19)	0·0113 (17)	0·0013 (2)	0·0112 (28)	−0·0008 (6)	−0·0026 (22)	0·0007 (7)
O(4)	0·0832 (14)	0·3091 (5)	0·9729 (20)	0·0078 (15)	0·0012 (2)	0·0135 (31)	−0·0001 (5)	0·0022 (19)	0·0006 (7)
O(5)	0·5106 (15)	0·3840 (6)	1·0516 (23)	0·0084 (17)	0·0015 (2)	0·0252 (39)	−0·0009 (6)	−0·0012 (22)	−0·0025 (9)
C(1)	0·3033 (20)	0·3145 (6)	0·4482 (28)	0·0055 (20)	0·0006 (2)	0·0160 (44)	0·0006 (6)	−0·0020 (26)	0·0002 (8)
C(2)	0·3486 (23)	0·2800 (7)	0·5836 (26)	0·0122 (26)	0·0008 (3)	0·0053 (33)	−0·0014 (7)	−0·0008 (27)	0·0004 (8)
C(3)	0·3512 (19)	0·2307 (7)	0·5019 (28)	0·0041 (18)	0·0010 (3)	0·0123 (39)	−0·0000 (6)	−0·0016 (25)	0·0004 (9)
C(4)	0·2575 (20)	0·2066 (7)	0·5738 (27)	0·0074 (24)	0·0012 (3)	0·0091 (36)	0·0008 (7)	−0·0018 (26)	−0·0004 (9)
C(5)	0·2093 (19)	0·2293 (7)	0·7137 (28)	0·0043 (18)	0·0013 (3)	0·0144 (44)	−0·0004 (6)	−0·0032 (28)	0·0010 (10)
C(6)	0·2785 (20)	0·2750 (6)	0·7251 (27)	0·0083 (20)	0·0008 (2)	0·0104 (37)	−0·0000 (6)	−0·0004 (29)	−0·0003 (9)
C(7)	0·2644 (17)	0·3000 (5)	0·8645 (23)	0·0048 (16)	0·0003 (2)	0·0078 (30)	0·0008 (5)	0·0003 (21)	0·0001 (7)
C(8)	0·3335 (17)	0·3437 (7)	0·8991 (25)	0·0042 (18)	0·0008 (2)	0·0098 (36)	−0·0007 (5)	−0·0007 (22)	−0·0007 (8)
C(9)	0·2907 (18)	0·3863 (6)	0·8078 (25)	0·0047 (16)	0·0006 (2)	0·0154 (41)	−0·0004 (6)	−0·0047 (24)	−0·0004 (8)
C(10)	0·2278 (20)	0·3781 (7)	0·6400 (26)	0·0063 (20)	0·0011 (3)	0·0101 (35)	0·0014 (6)	−0·0006 (26)	0·0000 (9)
C(11)	0·3147 (17)	0·3655 (6)	0·4936 (26)	0·0043 (18)	0·0008 (2)	0·0084 (35)	−0·0011 (5)	0·0017 (23)	0·0002 (8)
C(12)	0·2571 (18)	0·3928 (7)	0·3485 (26)	0·0076 (21)	0·0007 (2)	0·0117 (36)	−0·0002 (6)	−0·0012 (24)	−0·0000 (8)
C(13)	0·2168 (25)	0·4384 (7)	0·4263 (27)	0·0113 (26)	0·0012 (3)	0·0082 (37)	0·0003 (8)	0·0046 (32)	0·0002 (10)
C(14)	0·1543 (20)	0·4207 (6)	0·5832 (26)	0·0075 (21)	0·0005 (2)	0·0105 (37)	0·0005 (6)	−0·0024 (25)	0·0005 (8)
C(15)	0·1291 (22)	0·4576 (7)	0·7138 (29)	0·0094 (23)	0·0009 (3)	0·0107 (42)	0·0000 (7)	−0·0001 (30)	0·0008 (10)
C(16)	0·0376 (18)	0·4370 (7)	0·8339 (31)	0·0025 (17)	0·0010 (3)	0·0246 (55)	−0·0001 (6)	−0·0031 (26)	−0·0010 (10)
C(17)	0·0422 (29)	0·4632 (10)	1·0034 (38)	0·0153 (35)	0·0018 (4)	0·0199 (59)	−0·0007 (10)	0·0125 (43)	0·0002 (14)
C(18)	−0·0344 (27)	0·4364 (9)	1·1276 (33)	0·0137 (32)	0·0015 (4)	0·0141 (48)	−0·0001 (9)	−0·0034 (38)	0·0022 (12)
C(19)	−0·1333 (25)	0·4478 (8)	1·2002 (32)	0·0112 (28)	0·0015 (4)	0·0143 (49)	0·0008 (8)	0·0016 (35)	−0·0000 (11)
C(20)	0·4214 (22)	0·2179 (8)	0·3631 (32)	0·0087 (24)	0·0011 (3)	0·0151 (47)	0·0003 (7)	0·0037 (31)	−0·0012 (11)
C(21)	0·1898 (19)	0·2882 (7)	0·9960 (29)	0·0058 (20)	0·0008 (3)	0·0152 (43)	−0·0000 (6)	−0·0014 (27)	−0·0001 (9)
C(22)	0·4384 (24)	0·3785 (8)	0·5139 (33)	0·0095 (26)	0·0011 (3)	0·0176 (51)	−0·0003 (8)	−0·0005 (34)	0·0003 (11)
C(23)	0·0661 (27)	0·5022 (8)	0·6169 (42)	0·0128 (33)	0·0009 (3)	0·0288 (72)	0·0004 (9)	0·0039 (44)	0·0008 (14)
C(24)	−0·1962 (44)	0·4911 (14)	1·1706 (59)	0·0271 (70)	0·0028 (7)	0·0532 (133)	0·0040 (19)	0·0129 (86)	0·0035 (26)
C(25)	−0·1907 (32)	0·4160 (13)	1·3234 (45)	0·0142 (40)	0·0029 (6)	0·0306 (84)	0·0015 (14)	0·0058 (51)	0·0000 (20)
C(26)	−0·0049 (27)	0·2998 (11)	1·1071 (42)	0·0100 (31)	0·0024 (6)	0·0301 (77)	−0·0005 (11)	0·0114 (45)	−0·0011 (18)
C(27)	0·5389 (22)	0·3598 (8)	0·9554 (30)	0·0074 (23)	0·0012 (3)	0·0131 (46)	−0·0004 (7)	−0·0013 (29)	−0·0001 (10)
C(28)	0·6559 (22)	0·3455 (9)	0·9036 (35)	0·0047 (22)	0·0017 (4)	0·0213 (56)	0·0000 (8)	0·0004 (31)	0·0007 (13)

Mean standard deviations of bond lengths

$$\sigma(\text{Br–C})=0{\cdot}02\ \text{Å},\ \sigma(\text{O–C})=0{\cdot}03\ \text{Å},\ \sigma(\text{C–C})=0{\cdot}04\ \text{Å}.$$

Mean standard deviation of tetrahedral bond angles

$$\sigma(\text{C–C–C})=3°.$$

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
2	0	0	233.09	209.53
4	0	0	175.50	133.14
1	1	0	21.98	2.54
2	1	0	6.35	15.99
3	1	0	85.80	64.68
4	1	0	32.87	29.00
6	1	0	10.67	16.37
7	1	0	21.65	16.66
8	1	0	27.26	31.09
0	2	0	110.92	111.02
1	2	0	45.46	51.01
2	2	0	78.46	75.55
3	2	0	48.34	51.71
4	2	0	8.26	4.17
5	2	0	100.76	96.89
7	2	0	31.40	39.18
1	3	0	44.18	34.91
2	3	0	32.06	32.53
3	3	0	20.60	18.19
4	3	0	13.20	19.77
5	3	0	14.95	11.64
6	3	0	37.02	35.88
7	3	0	27.71	23.23
9	3	0	20.16	23.42
10	3	0	23.82	26.61
0	4	0	102.59	95.21
1	4	0	112.91	96.15
2	4	0	74.82	57.78
3	4	0	70.69	53.61
4	4	0	126.02	108.55
5	4	0	23.51	18.39
7	4	0	38.15	32.20
8	4	0	12.32	3.80
11	4	0	23.60	24.35
1	5	0	73.59	84.11
2	5	0	36.81	26.44
3	5	0	43.68	39.13
4	5	0	19.26	13.69
5	5	0	60.92	53.17
6	5	0	28.97	26.47
9	5	0	15.37	16.36
11	5	0	15.68	12.58
0	6	0	112.78	107.17
1	6	0	214.11	195.82
2	6	0	117.81	120.45
3	6	0	23.81	9.65
4	6	0	51.51	40.38
5	6	0	71.82	72.06
6	6	0	10.38	5.29
7	6	0	28.52	35.83
8	6	0	19.14	16.98
1	7	0	29.99	23.92
2	7	0	2.46	14.97
3	7	0	65.05	56.20
4	7	0	65.94	72.82
5	7	0	16.49	13.19
6	7	0	65.59	66.20
8	7	0	22.49	24.28
10	7	0	21.09	27.10
0	8	0	74.01	65.26
1	8	0	32.87	20.00
2	8	0	109.88	101.08
3	8	0	27.76	26.35
4	8	0	78.67	66.48
6	8	0	23.64	19.17
7	8	0	22.61	24.72
9	8	0	46.49	48.48
11	8	0	15.45	18.01
1	9	0	77.86	80.57
2	9	0	15.21	19.07
3	9	0	22.67	12.85
4	9	0	2.91	3.33
5	9	0	26.14	26.42
6	9	0	16.76	22.91
9	9	0	13.59	12.05
10	9	0	18.67	21.65
11	9	0	14.36	10.33
0	10	0	122.51	104.90
1	10	0	57.94	55.03
2	10	0	97.00	94.94
3	10	0	15.84	21.80
4	10	0	80.55	72.18
5	10	0	21.36	31.45
6	10	0	48.45	47.54
7	10	0	12.18	15.45
9	10	0	18.49	20.56
10	10	0	18.64	19.19
1	11	0	16.31	17.03
2	11	0	24.34	28.04
3	11	0	81.54	70.93
5	11	0	16.65	9.33
6	11	0	14.02	19.25
7	11	0	12.37	13.74
0	12	0	140.41	126.45
1	12	0	21.23	22.39
2	12	0	61.13	49.18
3	12	0	27.79	24.42
4	12	0	65.90	48.54
5	12	0	65.68	63.55
6	12	0	36.45	33.69
7	12	0	32.94	38.88
8	12	0	31.29	28.03
9	12	0	18.64	23.49
1	13	0	11.89	15.29
3	13	0	58.75	53.33
4	13	0	22.14	20.13
5	13	0	23.21	18.60
6	13	0	11.97	4.21
8	13	0	23.34	19.62
9	13	0	13.80	8.39
10	13	0	15.66	8.41
0	14	0	9.57	6.81
1	14	0	41.64	32.61
2	14	0	42.90	38.57
4	14	0	65.47	57.67
5	14	0	16.23	21.28
6	14	0	40.37	31.28
8	14	0	13.59	9.76
10	14	0	13.43	14.64
1	15	0	39.48	42.20
3	15	0	20.91	21.25
6	15	0	19.84	27.52
8	15	0	24.37	24.16
9	15	0	21.05	24.40
0	16	0	14.53	13.84
1	16	0	24.36	28.20
2	16	0	3.21	14.55
3	16	0	11.09	11.15
4	16	0	56.53	46.74
5	16	0	50.27	51.95
6	16	0	32.65	27.77
7	16	0	35.04	33.95
8	16	0	13.75	2.85
9	16	0	17.70	20.82
1	17	0	19.97	11.17
2	17	0	11.21	6.79
3	17	0	23.40	20.99
4	17	0	46.79	46.07
5	17	0	15.24	19.40
6	17	0	18.48	15.66
8	17	0	18.67	19.54
9	17	0	13.59	6.51
0	18	0	116.23	113.90
1	18	0	2.43	1.22
2	18	0	47.03	43.87
3	18	0	24.78	24.49
4	18	0	36.58	34.02
5	18	0	13.77	8.90
6	18	0	17.17	12.60
8	18	0	14.88	8.26
1	19	0	39.47	44.11
2	19	0	25.43	19.61
3	19	0	23.14	17.11
4	19	0	34.51	35.83
8	19	0	16.81	18.90
9	19	0	13.21	12.96
0	20	0	12.92	8.06
1	20	0	29.05	29.54
2	20	0	12.15	5.79
3	20	0	24.39	23.46
1	21	0	22.28	13.73
2	21	0	10.46	8.00
3	21	0	14.17	7.38
4	21	0	19.60	19.98
5	21	0	16.57	11.51
6	21	0	20.24	19.30
7	21	0	26.36	25.47
0	22	0	33.67	30.52
1	22	0	13.91	12.82
2	22	0	29.80	25.10
3	22	0	24.02	21.66
4	22	0	53.47	51.56
5	22	0	19.35	17.37
6	22	0	15.92	14.20
7	22	0	15.79	13.44
8	22	0	14.22	13.26
1	23	0	18.82	16.47
4	23	0	19.71	20.53
6	23	0	15.90	10.54
7	23	0	13.49	13.02
0	24	0	15.92	16.83
2	24	0	19.27	23.43
3	24	0	9.20	5.65
4	24	0	13.38	10.67
7	24	0	15.26	14.67
1	25	0	2.59	10.97
2	25	0	12.39	13.63
3	25	0	24.70	21.35
6	25	0	19.01	18.24
0	26	0	45.54	40.92
1	26	0	3.37	1.45
2	26	0	24.92	22.95
3	26	0	26.95	34.86
4	26	0	14.09	7.65
5	26	0	16.60	17.32
6	26	0	14.17	7.36
9	26	0	11.38	13.85
1	27	0	3.03	7.50
2	27	0	2.64	4.55
3	27	0	12.37	9.81
4	27	0	2.59	5.02
5	27	0	16.24	13.23
0	28	0	10.19	11.92
1	28	0	2.61	4.36
3	28	0	6.38	6.44
5	28	0	15.79	18.60
2	29	0	12.60	10.44
0	30	0	9.85	5.02
2	30	0	4.57	10.20
3	30	0	6.98	8.17
7	30	0	11.89	10.61
1	31	0	14.74	10.87
2	31	0	2.77	5.55
5	31	0	16.31	16.87
0	32	0	8.11	7.00
2	32	0	13.09	16.94
3	32	0	7.76	5.78
4	32	0	11.55	12.96
4	33	0	7.34	6.21
0	34	0	7.94	1.04
4	34	0	12.15	13.38
0	36	0	7.58	14.41
2	36	0	4.39	0.76
1	0	1	26.17	34.60
2	0	1	94.82	103.54
3	0	1	71.00	78.23
4	0	1	6.27	2.52
5	0	1	108.91	114.12
6	0	1	19.90	20.52
7	0	1	45.91	51.90
8	0	1	16.23	0.83
9	0	1	20.18	21.07
10	0	1	14.09	10.41
11	0	1	13.17	12.88
0	1	1	24.70	52.22
1	1	1	37.88	27.92
2	1	1	121.28	124.22
3	1	1	47.79	48.20
4	1	1	48.60	53.15
5	1	1	15.69	23.39
6	1	1	31.89	34.95
7	1	1	19.45	15.14
8	1	1	18.30	14.84
9	1	1	22.14	18.86
10	1	1	14.11	17.51
0	2	1	127.69	157.83
1	2	1	84.32	56.35
2	2	1	137.41	150.75
3	2	1	52.97	44.13
4	2	1	58.70	70.73
5	2	1	22.33	6.58
6	2	1	30.70	27.03
8	2	1	17.34	13.14
9	2	1	16.31	12.73
10	2	1	12.42	10.21
12	2	1	12.21	10.91
0	3	1	11.90	2.78
1	3	1	80.62	94.52
2	3	1	94.49	96.13
3	3	1	98.53	115.19
4	3	1	36.66	30.73
5	3	1	42.20	39.20
6	3	1	15.45	15.76
7	3	1	40.76	40.68
8	3	1	23.53	27.08
9	3	1	11.11	3.89
10	3	1	11.53	10.61
11	3	1	12.31	19.75
0	4	1	11.38	1.71
1	4	1	100.97	100.70
2	4	1	27.74	29.62
3	4	1	47.08	53.11
4	4	1	45.68	35.00
5	4	1	38.70	38.46
6	4	1	12.58	15.21
7	4	1	37.81	40.53
8	4	1	10.40	6.98
9	4	1	12.86	11.76
10	4	1	14.12	11.17
11	4	1	12.26	14.62
12	4	1	12.10	10.71
0	5	1	52.75	41.70
1	5	1	97.33	92.94
2	5	1	77.36	79.65
3	5	1	28.19	26.25
4	5	1	57.77	66.08
5	5	1	39.43	49.13
6	5	1	53.73	54.80
7	5	1	17.52	12.87
8	5	1	27.71	29.94
9	5	1	14.45	23.26
10	5	1	26.23	31.34
11	5	1	13.88	11.54
12	5	1	12.02	14.70
0	6	1	118.11	137.29
1	6	1	98.19	84.66
2	6	1	111.43	109.46
3	6	1	39.72	39.09
4	6	1	50.07	47.13
5	6	1	74.20	69.60
6	6	1	12.92	12.81
7	6	1	34.74	37.48
9	6	1	18.92	21.84
10	6	1	11.55	12.39
12	6	1	11.16	11.11
0	7	1	72.53	79.46
1	7	1	114.79	121.46
2	7	1	75.06	45.71
3	7	1	56.03	54.35
4	7	1	49.12	40.47
5	7	1	49.21	51.62
7	7	1	15.00	11.16
8	7	1	30.12	31.91
9	7	1	13.04	15.15
10	7	1	16.34	20.32
12	7	1	10.22	11.43
0	8	1	7.24	8.58
1	8	1	39.55	35.88
2	8	1	52.26	58.97
3	8	1	59.74	57.79
4	8	1	35.27	33.83
5	8	1	21.55	29.47
6	8	1	33.62	30.37
7	8	1	20.71	27.48
8	8	1	25.60	21.62
9	8	1	16.05	17.87
10	8	1	13.34	14.59
11	8	1	11.16	6.13
0	9	1	31.98	16.61
1	9	1	17.00	20.55
2	9	1	53.73	38.90
3	9	1	53.62	45.12
4	9	1	22.62	24.99
5	9	1	24.15	20.79
6	9	1	44.65	49.61
7	9	1	10.11	5.02
8	9	1	22.19	23.60
9	9	1	13.98	17.90
10	9	1	11.53	8.36
11	9	1	11.08	9.25
0	10	1	37.55	40.39
1	10	1	15.45	14.76
2	10	1	77.05	70.60
3	10	1	34.58	39.80
4	10	1	42.49	36.78
5	10	1	56.44	54.81
6	10	1	32.57	28.31
7	10	1	29.94	32.08
9	10	1	26.46	28.30
10	10	1	11.50	7.85
0	11	1	7.87	0.89
1	11	1	45.21	46.58
2	11	1	54.22	42.78
3	11	1	18.45	17.06
4	11	1	54.82	44.68
5	11	1	40.83	42.36
6	11	1	27.64	25.92
7	11	1	12.78	11.54
8	11	1	24.81	24.00
10	11	1	13.23	16.26
11	11	1	10.83	2.58
0	12	1	59.66	68.14
1	12	1	28.32	21.77
2	12	1	97.80	90.89
3	12	1	39.95	33.06
4	12	1	42.61	35.47
5	12	1	13.99	12.93
6	12	1	26.49	26.27
7	12	1	19.85	17.78
8	12	1	20.99	18.52
9	12	1	11.53	12.21
10	12	1	16.11	17.21
0	13	1	24.18	21.02
1	13	1	82.87	78.21
2	13	1	48.36	46.04
3	13	1	30.92	27.52
4	13	1	40.39	41.78
5	13	1	15.84	21.60
6	13	1	27.06	29.34
7	13	1	10.77	7.08
8	13	1	28.10	31.50
9	13	1	20.57	26.58
10	13	1	17.28	19.92
0	14	1	18.87	24.45
1	14	1	43.72	33.67
2	14	1	54.49	52.21
3	14	1	27.56	23.41
4	14	1	33.85	27.25
5	14	1	20.18	21.51
6	14	1	29.26	28.30
7	14	1	30.66	39.36
9	14	1	11.55	12.46
10	14	1	11.19	4.87
0	15	1	15.09	9.47
1	15	1	79.35	70.54
2	15	1	27.09	27.00
3	15	1	59.69	61.02
4	15	1	31.89	26.71
5	15	1	12.84	12.21
6	15	1	14.30	10.84
7	15	1	15.72	16.12
8	15	1	20.96	19.79
9	15	1	11.50	11.92
0	16	1	54.72	56.59
1	16	1	9.86	4.53
2	16	1	37.31	35.35
3	16	1	22.59	20.47
4	16	1	37.83	35.04
5	16	1	20.03	22.70
6	16	1	13.93	9.57
7	16	1	28.36	29.26
8	16	1	11.53	3.86
9	16	1	11.45	11.44
0	17	1	21.09	13.47
1	17	1	11.40	17.88
2	17	1	15.89	21.65
3	17	1	40.19	35.31
4	17	1	4.21	1.80
5	17	1	21.41	22.78
6	17	1	24.16	23.17
7	17	1	11.37	6.30
8	17	1	11.55	12.53
9	17	1	11.34	10.89
0	18	1	18.67	17.49
1	18	1	24.92	20.43
2	18	1	9.85	9.11
3	18	1	37.59	34.49
4	18	1	16.52	15.81
5	18	1	36.19	37.39
6	18	1	20.91	23.45
7	18	1	16.23	21.46
8	18	1	12.44	12.55
9	18	1	11.19	10.12
0	19	1	13.18	14.90
1	19	1	21.28	20.66
2	19	1	12.60	12.29
3	19	1	23.35	23.18
4	19	1	15.95	19.61
5	19	1	10.96	9.31
6	19	1	20.18	22.58
7	19	1	27.47	29.65
8	19	1	17.52	17.01
0	20	1	44.18	45.27
1	20	1	12.39	10.04
2	20	1	41.47	39.91
3	20	1	16.26	20.30
4	20	1	36.02	32.93
5	20	1	17.10	13.71
6	20	1	14.01	9.43
7	20	1	16.34	17.61
8	20	1	11.34	12.44
9	20	1	10.75	8.49
0	21	1	45.62	41.13
1	21	1	39.19	39.08
2	21	1	26.32	24.10
3	21	1	26.46	24.49
4	21	1	13.88	14.80
6	21	1	20.52	21.90
7	21	1	12.42	9.16
0	22	1	5.94	9.97
1	22	1	16.06	15.90
2	22	1	15.61	17.44
3	22	1	18.15	20.34
4	22	1	15.72	14.52
5	22	1	15.55	19.11
7	22	1	17.43	16.85
9	22	1	10.93	10.16
0	23	1	15.35	11.35
2	23	1	15.82	12.56
3	23	1	16.65	18.20
4	23	1	10.15	4.28
5	23	1	16.32	14.31
6	23	1	17.57	19.97
7	23	1	12.13	11.59
0	24	1	30.01	33.76
1	24	1	3.61	16.31
2	24	1	33.44	34.52
3	24	1	17.33	20.69
4	24	1	3.01	7.31
5	24	1	11.55	10.84
6	24	1	11.38	6.03
7	24	1	10.98	7.57
9	24	1	9.25	8.53
0	25	1	11.27	7.01
1	25	1	23.56	27.19
2	25	1	10.14	8.92
3	25	1	19.95	22.11
4	25	1	3.72	4.03
5	25	1	11.47	13.16
6	25	1	17.12	15.48
7	25	1	10.69	9.14
1	26	1	14.62	17.01
2	26	1	2.64	6.86
3	26	1	3.13	15.61
4	26	1	13.77	13.55
6	26	1	10.93	4.16
1	27	1	13.30	16.21
2	27	1	10.53	7.80
3	27	1	7.16	7.73
4	27	1	3.00	4.18
6	27	1	12.19	11.49
9	27	1	7.98	5.70
0	28	1	8.10	16.41
1	28	1	13.60	11.26
2	28	1	19.92	21.28
4	28	1	11.34	8.47
5	28	1	11.56	11.59
6	28	1	11.68	8.98
7	28	1	9.31	10.08
9	28	1	7.56	12.57
0	29	1	3.98	4.82
1	29	1	12.79	10.89
2	29	1	8.79	7.89
3	29	1	12.19	12.06
5	29	1	15.68	23.37
7	29	1	8.68	7.91
0	30	1	10.90	7.30
1	30	1	6.46	5.00
3	30	1	9.54	6.12
4	30	1	6.43	6.83
1	31	1	6.75	7.84
2	31	1	7.48	7.24
4	31	1	10.46	13.57
0	32	1	8.03	1.91
2	32	1	7.11	7.95
4	33	1	6.69	9.54
4	34	1	7.11	7.78
0	0	2	18.33	20.71
1	0	2	26.30	12.69
2	0	2	115.27	137.73
3	0	2	53.21	48.99
4	0	2	18.70	36.39
5	0	2	30.98	26.18
6	0	2	35.94	41.20
7	0	2	23.68	20.16
8	0	2	16.03	23.74
9	0	2	11.63	4.39
10	0	2	14.67	8.10
12	0	2	16.42	21.24
0	1	2	21.81	12.15
1	1	2	107.85	128.32
2	1	2	83.58	67.08
3	1	2	30.25	46.28
4	1	2	65.64	67.39
5	1	2	50.36	46.90
6	1	2	17.89	14.96
7	1	2	20.73	23.72
8	1	2	13.34	6.92
9	1	2	20.71	17.03
10	1	2	13.83	13.27
12	1	2	10.74	7.57
0	2	2	68.58	70.98
1	2	2	34.66	29.53
2	2	2	35.38	31.88
3	2	2	87.03	80.84
4	2	2	50.79	42.51
5	2	2	33.83	31.41
6	2	2	18.70	15.46
7	2	2	57.26	49.85
8	2	2	11.79	6.46
9	2	2	33.99	31.55
11	2	2	13.49	15.32
0	3	2	108.57	100.26
1	3	2	51.64	66.01
2	3	2	54.98	35.02
3	3	2	43.27	42.60
4	3	2	17.43	18.79
5	3	2	34.46	23.77
6	3	2	54.06	45.30
7	3	2	20.52	16.73
8	3	2	45.46	38.78
9	3	2	25.67	22.16
10	3	2	14.67	18.62
0	4	2	14.79	32.67
1	4	2	40.19	37.76
2	4	2	84.32	100.14
3	4	2	11.51	3.29
4	4	2	30.70	47.60
5	4	2	36.15	35.57
6	4	2	36.75	46.04
7	4	2	20.65	22.74
8	4	2	11.90	5.58
9	4	2	12.65	6.35
10	4	2	14.67	17.39
12	4	2	10.57	3.57
0	5	2	71.73	47.21
1	5	2	40.53	57.79
2	5	2	20.39	16.37
3	5	2	68.13	78.27
4	5	2	31.89	33.78
5	5	2	34.98	33.44
6	5	2	36.21	30.89
8	5	2	21.21	19.74
9	5	2	16.60	13.08
12	5	2	10.53	2.78
0	6	2	98.02	97.46
1	6	2	94.38	79.64
2	6	2	57.93	53.32
3	6	2	53.57	48.50
4	6	2	32.50	28.88
5	6	2	9.73	12.15
6	6	2	25.96	23.35
7	6	2	23.43	20.37
8	6	2	12.89	13.42
9	6	2	23.56	19.68
10	6	2	13.81	11.39
11	6	2	12.49	10.48
12	6	2	10.40	8.97
0	7	2	41.39	42.44
1	7	2	57.09	45.22
2	7	2	63.35	63.59
3	7	2	29.05	33.19
4	7	2	47.40	49.44
5	7	2	16.49	21.89
6	7	2	49.54	48.71
7	7	2	25.57	31.79
8	7	2	26.41	25.36
10	7	2	13.81	9.85
12	7	2	10.30	10.60
0	8	2	51.34	60.67
1	8	2	80.62	69.96
2	8	2	95.30	104.63
3	8	2	114.09	100.30
4	8	2	53.20	53.85
5	8	2	70.79	66.55
6	8	2	34.75	38.92
7	8	2	25.91	22.56
8	8	2	11.34	4.03
9	8	2	18.14	17.82
10	8	2	13.78	14.93
0	9	2	87.90	83.18
1	9	2	49.68	66.94
2	9	2	66.07	51.16
3	9	2	26.43	38.71
4	9	2	28.62	20.58
6	9	2	28.26	30.61
8	9	2	19.84	22.07
9	9	2	13.75	9.54
11	9	2	13.02	8.06
0	10	2	38.74	42.29
1	10	2	9.10	7.43
2	10	2	72.34	69.34
3	10	2	56.91	56.96
4	10	2	33.07	35.55
5	10	2	44.58	39.45
6	10	2	11.63	3.56
7	10	2	26.67	25.26
8	10	2	16.36	13.22
9	10	2	23.92	20.54
10	10	2	12.83	10.88
11	10	2	12.89	14.52
0	11	2	64.66	58.01
1	11	2	46.83	37.40
2	11	2	36.99	35.03
3	11	2	9.86	3.32
4	11	2	34.28	35.51
5	11	2	9.49	8.65
6	11	2	25.55	21.71
7	11	2	25.52	28.75
8	11	2	21.30	18.64
9	11	2	18.30	24.69
10	11	2	15.22	15.14
1	12	2	31.04	25.03
2	12	2	45.75	48.97
3	12	2	18.09	12.83
4	12	2	21.80	12.37
5	12	2	23.60	18.83
6	12	2	19.19	20.62
7	12	2	22.90	26.12
8	12	2	17.31	23.46
9	12	2	11.97	9.52
0	13	2	48.39	32.70
1	13	2	31.11	42.59
2	13	2	51.89	44.68
3	13	2	22.36	21.23
4	13	2	23.21	21.73
5	13	2	36.42	40.39
6	13	2	31.92	36.52
7	13	2	11.38	5.82
8	13	2	13.67	12.26
11	13	2	11.45	10.11
0	14	2	54.25	57.53
1	14	2	23.63	22.96
2	14	2	64.37	73.94
3	14	2	10.56	7.05
4	14	2	29.57	30.12
7	14	2	16.31	15.99
8	14	2	22.30	20.43
10	14	2	11.45	4.85
0	15	2	15.32	16.17
1	15	2	11.16	10.11
2	15	2	28.19	23.14
3	15	2	26.54	24.31
4	15	2	29.94	26.86
5	15	2	22.43	22.03
6	15	2	35.64	34.48
8	15	2	20.15	15.62
10	15	2	11.27	6.68
11	15	2	10.88	13.49
0	16	2	24.87	20.25
1	16	2	10.30	15.32
2	16	2	9.21	11.22
3	16	2	32.08	33.66
4	16	2	16.02	15.08
5	16	2	40.83	41.79
6	16	2	15.42	16.08
7	16	2	38.28	36.43
10	16	2	11.94	13.31
11	16	2	11.27	12.74
0	17	2	14.54	19.66
1	17	2	21.17	30.92
2	17	2	24.05	28.25
3	17	2	20.19	26.50
4	17	2	11.95	11.44
5	17	2	23.11	28.13
7	17	2	16.83	20.29
0	18	2	75.74	80.02
1	18	2	2.20	7.79
2	18	2	40.05	43.71
3	18	2	27.87	22.23
4	18	2	22.22	25.75
5	18	2	11.34	15.35
6	18	2	15.89	17.71
7	18	2	17.62	19.40
10	18	2	10.49	5.23
0	19	2	24.83	23.96
1	19	2	18.27	18.23
2	19	2	38.19	38.12
3	19	2	16.03	13.64
4	19	2	24.73	23.99
6	19	2	11.85	7.00
7	19	2	12.96	13.40
10	19	2	12.40	11.41
1	20	2	20.76	17.57
2	20	2	10.83	11.95
3	20	2	40.44	41.03
4	20	2	13.68	14.48
5	20	2	26.27	30.89
6	20	2	12.89	14.36
7	20	2	18.90	22.81
1	21	2	10.20	11.90
2	21	2	2.85	5.97
3	21	2	10.12	9.30
4	21	2	11.17	6.38
5	21	2	11.89	4.48
6	21	2	16.94	18.10
1	22	2	12.49	14.53
2	22	2	22.01	24.82
3	22	2	11.71	6.58
4	22	2	14.45	[illegible]
7	22	2	14.35	17.03
0	23	2	36.03	39.74
1	23	2	13.00	12.21
2	23	2	20.32	22.89
3	23	2	18.33	16.62
4	23	2	15.74	17.54
5	23	2	14.67	14.50
7	23	2	13.28	10.34
0	24	2	15.68	12.51
1	24	2	13.20	12.57
2	24	2	20.60	18.94
3	24	2	13.65	13.79
4	24	2	18.90	19.84
5	24	2	14.59	12.74
7	24	2	12.08	12.67
1	25	2	4.52	8.94
2	25	2	11.00	7.39
3	25	2	13.91	14.36
4	25	2	17.57	17.99
5	25	2	14.43	19.66
7	25	2	10.82	6.21
0	26	2	11.27	11.36
1	26	2	13.39	11.15
2	26	2	32.00	33.60
3	26	2	13.47	14.32
4	26	2	17.23	18.47
5	26	2	11.56	7.34
6	26	2	14.33	15.60
0	27	2	6.64	9.98
1	27	2	13.34	12.63
2	27	2	10.40	11.48
3	27	2	16.02	19.72
4	27	2	9.81	5.69
2	28	2	11.90	8.80
3	28	2	7.22	6.28
4	28	2	9.54	9.36
7	28	2	9.26	7.51
2	29	2	6.11	3.35
3	29	2	11.51	9.66
4	29	2	9.89	9.02
1	30	2	12.08	2.49
2	30	2	9.02	7.94
3	30	2	6.74	6.87
3	31	2	9.07	7.53
4	31	2	9.88	9.11
0	32	2	8.66	11.17
2	32	2	9.20	10.82
3	32	2	2.75	7.27
4	32	2	7.56	6.81
2	33	2	5.70	4.87
4	33	2	5.62	11.95
3	35	2	6.11	3.02
2	36	2	6.56	9.70
3	36	2	4.06	6.18
0	37	2	4.57	1.29
0	0	3	8.18	0.00
1	0	3	18.59	15.74
2	0	3	74.59	71.43
3	0	3	14.28	11.02
5	0	3	32.15	23.27
6	0	3	34.64	31.99
7	0	3	46.15	40.31
8	0	3	10.98	9.17
9	0	3	27.64	22.95
0	1	3	41.93	47.48
1	1	3	29.59	28.45
2	1	3	22.90	28.13
3	1	3	42.11	33.83
4	1	3	33.38	31.68
6	1	3	32.36	25.03
7	1	3	23.94	24.69
8	1	3	24.23	22.10
9	1	3	11.56	14.87
10	1	3	19.76	19.03
11	1	3	10.35	9.65
0	2	3	35.85	50.65
1	2	3	40.28	37.83
2	2	3	55.66	66.74
3	2	3	40.11	39.14
4	2	3	68.13	79.75
5	2	3	29.91	25.95
6	2	3	24.37	27.65
7	2	3	38.07	47.36
9	2	3	10.69	11.84
10	2	3	23.76	23.67
11	2	3	10.33	12.50
0	3	3	14.51	12.32
1	3	3	58.46	78.11
2	3	3	22.32	6.10
3	3	3	54.19	57.66
4	3	3	7.60	11.80
5	3	3	23.82	22.60
6	3	3	25.52	27.92
7	3	3	25.33	22.68
8	3	3	24.34	20.22
9	3	3	13.83	9.04
10	3	3	10.80	6.14
11	3	3	11.13	9.87
0	4	3	65.65	71.08
1	4	3	27.08	22.78
2	4	3	14.17	12.56
3	4	3	58.51	54.24
4	4	3	19.16	15.01
5	4	3	68.60	62.39
6	4	3	19.69	16.34
7	4	3	33.70	23.93
9	4	3	41.18	37.02
11	4	3	13.23	7.80
1	5	3	72.76	76.46
2	5	3	24.53	26.91
3	5	3	42.79	39.47
4	5	3	33.12	27.49
5	5	3	35.40	37.65
6	5	3	44.70	37.99
7	5	3	16.65	14.31
8	5	3	38.19	35.96
9	5	3	10.79	11.07
10	5	3	16.45	13.02
11	5	3	11.04	7.92
0	6	3	34.04	42.00
1	6	3	27.40	23.78
2	6	3	40.66	47.51
3	6	3	70.32	67.10
4	6	3	14.28	8.95
5	6	3	40.00	44.30
6	6	3	32.84	32.81
7	6	3	21.31	29.06
11	6	3	10.95	8.75
1	7	3	37.07	49.69
2	7	3	11.34	7.32
3	7	3	22.14	28.48
4	7	3	36.49	24.08
5	7	3	27.16	20.15
6	7	3	9.72	12.85
9	7	3	11.68	6.21
11	7	3	12.31	7.91
0	8	3	49.43	58.82
1	8	3	36.11	31.86
2	8	3	25.10	33.73
3	8	3	13.85	12.21
4	8	3	53.78	56.61
5	8	3	43.37	37.04
6	8	3	15.89	13.22
7	8	3	23.61	16.81
8	8	3	11.35	11.43
9	8	3	25.78	24.77
11	8	3	12.19	11.97
0	9	3	7.16	7.83
1	9	3	39.56	32.44
2	9	3	13.49	14.75

Table 2 (*cont.*)

3	9	3	13.49	10.52
4	9	3	39.43	38.36
5	9	3	10.49	10.86
6	9	3	26.66	20.45
7	9	3	15.34	16.46
8	9	3	16.73	17.73
0	10	3	42.74	50.84
1	10	3	62.45	56.11
2	10	3	30.83	34.93
3	10	3	40.62	42.86
4	10	3	27.06	31.93
5	10	3	36.73	37.05
7	10	3	28.15	30.47
8	10	3	15.06	15.05
9	10	3	16.57	23.96
0	11	3	30.61	24.69
1	11	3	60.83	67.21
2	11	3	43.66	42.73
3	11	3	54.88	60.47
4	11	3	3.76	8.64
5	11	3	32.86	36.54
6	11	3	18.54	20.75
7	11	3	17.81	21.82
11	11	3	10.98	10.32
0	12	3	55.74	67.52
1	12	3	17.75	18.55
2	12	3	34.01	33.29
3	12	3	16.58	14.12
4	12	3	26.43	23.60
5	12	3	38.79	41.01
6	12	3	23.47	23.98
7	12	3	22.51	17.49
9	12	3	12.45	8.57
1	13	3	27.92	21.60
2	13	3	25.70	21.56
3	13	3	24.66	21.99
4	13	3	19.09	14.51
5	13	3	18.09	15.30
6	13	3	19.26	12.40
7	13	3	23.19	27.62
8	13	3	18.22	14.43
10	13	3	17.15	16.32
11	13	3	11.16	13.62
0	14	3	44.24	45.14
1	14	3	24.78	19.99
2	14	3	18.22	16.51
3	14	3	27.81	27.93
4	14	3	23.35	24.36
5	14	3	40.53	40.28
6	14	3	20.44	16.62
7	14	3	16.83	14.88
9	14	3	17.41	15.09
11	14	3	10.87	4.22
0	15	3	5.94	10.28
1	15	3	12.62	20.61
2	15	3	35.24	31.55
3	15	3	31.63	33.48
4	15	3	14.33	16.64
5	15	3	26.54	32.98
6	15	3	15.29	18.48
7	15	3	12.37	12.03
8	15	3	15.32	12.85
11	15	3	10.51	10.30
0	16	3	56.91	58.82
1	16	3	33.13	32.79
2	16	3	41.34	52.09
3	16	3	25.73	23.38
4	16	3	17.21	17.40
7	16	3	14.64	18.82
8	16	3	15.90	18.75
9	16	3	12.02	16.89
1	17	3	15.43	13.66
2	17	3	16.06	13.95
3	17	3	25.31	24.27
4	17	3	19.34	16.02
5	17	3	12.66	11.43
6	17	3	16.31	9.26
7	17	3	16.57	18.37
10	17	3	12.60	12.81
11	17	3	9.12	5.05
0	18	3	18.70	20.71
1	18	3	17.91	15.99
5	18	3	22.72	19.89
7	18	3	25.04	24.11
8	18	3	10.61	10.70
9	18	3	18.28	18.40
11	18	3	11.43	10.28
0	19	3	27.76	27.77
2	19	3	34.11	32.30
3	19	3	16.94	10.19
4	19	3	20.91	22.77
6	19	3	15.30	15.36
8	19	3	10.45	5.20
0	20	3	19.40	20.62
1	20	3	19.08	20.35
2	20	3	17.93	16.70
3	20	3	30.67	33.80
4	20	3	32.03	31.41
5	20	3	11.61	7.38
6	20	3	16.57	19.44
0	21	3	20.08	19.72
1	21	3	29.99	29.88
2	21	3	2.70	6.34
3	21	3	22.41	22.69
4	21	3	16.42	20.22
5	21	3	17.13	16.35
6	21	3	18.17	17.81
11	21	3	10.23	8.68
0	22	3	22.93	25.66
2	22	3	16.26	13.23
3	22	3	12.49	11.72
5	22	3	10.83	9.28
9	22	3	11.21	11.55
1	23	3	31.66	37.92
2	23	3	5.10	9.05
3	23	3	14.77	16.64
4	23	3	20.32	22.37
5	23	3	13.18	16.72
6	23	3	16.68	21.35
8	23	3	12.03	13.30
0	24	3	16.13	18.50
1	24	3	2.79	3.50
2	24	3	3.63	6.53
4	24	3	11.34	11.61
6	24	3	12.62	15.24
1	25	3	13.70	9.27
2	25	3	12.15	13.21
3	25	3	12.42	9.88
7	25	3	9.34	5.92
0	26	3	14.51	14.52
1	26	3	10.30	12.11
2	26	3	17.91	17.38
3	26	3	2.95	5.93
4	26	3	12.15	11.28
5	26	3	12.44	13.45
7	26	3	10.87	8.76
9	26	3	6.82	7.23
1	27	3	8.73	5.25
3	27	3	6.27	5.56
3	28	3	10.25	8.45
4	28	3	9.77	13.26
5	28	3	11.48	13.28
7	28	3	9.49	10.67
0	29	3	12.96	15.08
1	29	3	10.32	8.17
2	29	3	2.96	6.08
3	29	3	12.58	13.17
4	29	3	8.91	8.86
0	30	3	13.67	13.14
1	30	3	10.51	7.68
2	30	3	11.71	8.98
4	30	3	5.73	4.28
5	30	3	10.67	10.26
7	30	3	7.95	6.47
3	31	3	2.07	5.22
3	32	3	8.63	11.90
3	33	3	5.55	7.34
3	33	3	5.55	7.34
0	0	4	15.29	16.62
1	0	4	12.66	1.62
2	0	4	37.41	33.89
3	0	4	31.34	41.33
4	0	4	11.50	11.74
5	0	4	20.18	19.52
8	0	4	15.68	12.94
9	0	4	19.55	16.12
10	0	4	18.77	20.42
0	1	4	11.69	9.76
1	1	4	40.24	43.04
2	1	4	29.31	25.77
3	1	4	39.53	41.60
4	1	4	27.81	36.21
5	1	4	22.28	19.90
6	1	4	21.44	22.13
7	1	4	21.51	19.15
8	1	4	13.43	8.01
9	1	4	15.03	15.57
0	2	4	8.21	7.91
1	2	4	21.60	19.24
2	2	4	16.37	11.35
3	2	4	29.93	19.16
4	2	4	24.08	17.22
5	2	4	50.09	45.24
7	2	4	37.38	33.38
8	2	4	9.94	6.54
9	2	4	22.06	22.44
0	3	4	5.91	1.13
1	3	4	33.30	32.59
2	3	4	10.45	6.57
3	3	4	33.57	30.20
4	3	4	31.30	29.84
5	3	4	28.99	24.04
6	3	4	29.83	22.58
7	3	4	9.36	4.73
8	3	4	16.76	15.68
9	3	4	28.89	33.40
10	3	4	15.27	14.33
0	4	4	28.16	34.57
1	4	4	37.59	36.78
2	4	4	30.66	28.95
3	4	4	18.17	18.32
4	4	4	32.47	40.00
5	4	4	20.23	15.85
6	4	4	19.43	18.85
7	4	4	12.16	13.64
8	4	4	21.20	22.84
9	4	4	10.22	11.47
10	4	4	12.87	14.80
0	5	4	72.57	81.38
1	5	4	46.75	47.10
2	5	4	25.98	33.13
3	5	4	39.11	44.52
4	5	4	11.26	18.67
5	5	4	21.78	22.30
6	5	4	15.19	15.66
7	5	4	14.49	15.87
9	5	4	11.79	8.23
10	5	4	10.74	9.91
0	6	4	30.48	30.26
1	6	4	26.40	24.05
2	6	4	17.34	12.63
3	6	4	41.81	37.62
4	6	4	9.77	8.00
5	6	4	25.39	27.08
6	6	4	18.82	22.34
7	6	4	25.00	20.93
9	6	4	10.22	5.07
0	7	4	9.75	4.10
1	7	4	8.47	5.00
2	7	4	27.69	20.48
3	7	4	16.52	11.91
4	7	4	32.97	31.99
5	7	4	41.77	42.13
6	7	4	22.02	23.38
7	7	4	13.64	10.84
8	7	4	21.02	22.12
10	7	4	9.83	6.61
0	8	4	47.98	48.49
1	8	4	48.18	43.95
2	8	4	18.01	12.55
3	8	4	6.56	13.68
4	8	4	29.04	31.08
5	8	4	25.46	24.02
6	8	4	20.40	18.81
7	8	4	19.89	18.13
8	8	4	10.95	7.24
9	8	4	16.10	18.44
10	8	4	9.77	7.52
0	9	4	51.40	52.26
1	9	4	51.13	55.13
2	9	4	35.56	36.80
3	9	4	42.04	39.77
4	9	4	17.65	25.78
5	9	4	9.25	9.36
6	9	4	13.64	9.80
7	9	4	18.40	20.89
8	9	4	12.45	13.21
10	9	4	9.67	5.45
0	10	4	27.76	24.54
1	10	4	23.06	20.21
2	10	4	24.00	24.42
3	10	4	21.47	17.28
5	10	4	26.59	26.38
6	10	4	20.68	18.35
7	10	4	37.99	36.61
8	10	4	21.21	23.13
9	10	4	16.52	12.33
10	10	4	9.55	10.37
0	11	4	31.03	29.71
1	11	4	26.19	22.92
2	11	4	29.02	28.00
3	11	4	11.90	9.31
4	11	4	37.15	33.68
5	11	4	27.68	24.03
6	11	4	16.06	11.76
7	11	4	15.29	11.12
8	11	4	22.06	23.19
9	11	4	10.06	3.50
10	11	4	10.19	10.20
0	12	4	56.81	58.73
1	12	4	16.65	11.39
2	12	4	3.60	1.52
3	12	4	24.08	20.34
4	12	4	5.96	8.13
5	12	4	14.98	13.48
8	12	4	15.61	15.06
1	13	4	11.56	12.59
2	13	4	3.11	8.86
3	13	4	51.90	54.19
4	13	4	18.01	22.95
5	13	4	17.10	21.30
6	13	4	16.06	18.05
7	13	4	17.07	21.26
0	14	4	46.56	44.84
1	14	4	26.25	31.01
2	14	4	3.76	6.83
3	14	4	14.38	12.78
4	14	4	8.89	11.80
5	14	4	12.34	9.61
6	14	4	13.47	12.90
8	14	4	12.44	13.34
9	14	4	12.58	17.18
0	15	4	28.19	24.78
1	15	4	41.81	39.36
2	15	4	26.95	24.06
3	15	4	13.41	11.90
4	15	4	18.90	20.21
6	15	4	15.37	15.16
7	15	4	17.18	16.61
8	15	4	13.02	7.43
9	15	4	11.72	9.85
1	16	4	11.82	15.42
3	16	4	21.88	20.18
4	16	4	12.91	10.53
5	16	4	22.14	24.45
6	16	4	13.72	11.02
7	16	4	25.00	31.40
9	16	4	15.79	18.68
0	17	4	17.41	20.90
1	17	4	39.17	37.55
2	17	4	25.77	23.56
3	17	4	22.28	17.76
4	17	4	19.30	24.16
5	17	4	14.74	17.92
6	17	4	17.17	19.28
1	18	4	13.36	12.72
2	18	4	39.79	36.01
3	18	4	21.52	26.61
4	18	4	16.45	10.75
5	18	4	18.02	22.44
7	18	4	12.36	11.83
8	18	4	10.45	12.95
1	19	4	15.79	16.86
4	19	4	18.48	20.11
5	19	4	19.55	19.44
6	19	4	10.98	10.93
1	20	4	9.83	8.46
2	20	4	11.50	12.23
3	20	4	11.16	14.01
4	20	4	17.75	19.91
5	20	4	11.79	12.21
7	20	4	11.98	7.63
9	20	4	10.62	11.78
0	21	4	13.41	19.39
2	21	4	21.80	17.12
3	21	4	12.65	10.50
4	21	4	25.67	24.22
5	21	4	10.98	11.07
6	21	4	16.31	18.33
7	21	4	11.71	10.78
8	21	4	10.23	9.79
9	21	4	8.44	14.18
0	22	4	13.33	16.01
1	22	4	11.22	7.28
2	22	4	9.34	7.95
3	22	4	11.35	9.98
4	22	4	2.80	7.45
5	22	4	14.27	15.86
0	23	4	12.58	13.97
1	23	4	26.95	28.61
2	23	4	9.83	9.30
3	23	4	23.22	25.40
4	23	4	14.15	14.96
5	23	4	9.93	9.49
6	23	4	11.04	10.03
0	24	4	14.75	14.30
1	24	4	14.33	12.48
2	24	4	3.21	4.07
3	24	4	14.49	10.96
8	24	4	7.60	9.05
9	24	4	8.37	7.62
0	25	4	5.38	12.76
1	25	4	14.53	15.39
3	25	4	12.53	11.12
5	25	4	9.43	10.02
6	25	4	9.59	5.71
8	25	4	7.04	10.66
0	26	4	5.30	6.42
1	26	4	10.46	11.45
2	26	4	3.09	7.67
4	26	4	9.54	5.95
5	26	4	9.80	9.50
6	26	4	9.77	13.37
1	27	4	10.33	8.72
2	27	4	9.83	10.66
3	27	4	10.40	11.11
0	28	4	12.66	10.50
1	28	4	5.75	4.83
2	28	4	9.47	10.04
4	28	4	8.34	8.49
7	28	4	8.11	7.02
2	29	4	8.47	10.13
3	29	4	7.29	4.73
4	29	4	7.85	7.88
5	29	4	7.56	10.75
0	30	4	4.91	9.29
1	30	4	6.70	4.14
3	30	4	8.05	6.42
4	30	4	8.60	12.75
6	30	4	7.14	9.19
2	31	4	2.67	7.67
3	31	4	8.00	6.82
0	32	4	8.21	5.09
0	33	4	6.48	6.25
2	33	4	7.97	12.49
2	33	4	7.97	12.49
0	0	5	6.33	0.00
1	0	5	6.92	9.19
2	0	5	33.72	32.68
3	0	5	17.78	17.48
5	0	5	7.76	3.97
6	0	5	23.13	21.36
7	0	5	22.77	21.26
8	0	5	8.83	8.82
9	0	5	13.44	8.28
11	0	5	9.59	10.32
0	1	5	7.34	0.99
1	1	5	23.40	23.70
2	1	5	12.68	10.98
3	1	5	24.45	19.49
4	1	5	24.05	16.62
5	1	5	14.70	12.89
6	1	5	19.71	20.16
7	1	5	12.03	8.73
8	1	5	11.97	10.52
9	1	5	13.44	16.61
11	1	5	8.02	7.02
0	2	5	17.23	18.68
1	2	5	11.42	15.94
2	2	5	27.58	24.81
3	2	5	3.58	9.94
5	2	5	11.82	15.97
6	2	5	23.21	24.87
7	2	5	19.37	17.95
0	3	5	20.76	25.05
1	3	5	46.96	48.58
2	3	5	41.41	42.84
3	3	5	25.28	19.28
4	3	5	31.53	33.52
5	3	5	23.68	20.97
6	3	5	31.00	31.25
7	3	5	9.21	9.15
9	3	5	10.15	11.14
11	3	5	8.49	10.43
0	4	5	29.81	27.50
1	4	5	11.97	8.60
2	4	5	23.77	21.06
3	4	5	25.36	21.80
4	4	5	16.71	15.95
5	4	5	28.57	25.40
6	4	5	17.41	15.96
7	4	5	22.15	21.72
9	4	5	13.41	11.94
11	4	5	7.87	6.44
0	5	5	19.09	19.21
1	5	5	30.41	28.07
2	5	5	18.19	15.78
3	5	5	16.29	12.15
4	5	5	29.55	32.07
5	5	5	18.56	13.12
6	5	5	18.45	19.00
7	5	5	24.63	30.43
8	5	5	11.43	10.37
9	5	5	9.44	9.05
10	5	5	8.21	8.47
0	6	5	28.21	25.12
1	6	5	13.77	14.82
2	6	5	31.63	31.25
3	6	5	12.42	7.31
4	6	5	26.25	21.51
5	6	5	18.85	16.15
6	6	5	18.64	20.38
7	6	5	22.07	24.35
8	6	5	8.86	5.04
9	6	5	9.43	7.03
11	6	5	7.71	6.79
1	7	5	22.80	24.47
2	7	5	9.77	11.40
3	7	5	18.70	16.51
6	7	5	8.29	8.99
7	7	5	20.11	21.90
8	7	5	11.98	17.32
9	7	5	11.74	11.27
10	7	5	8.05	8.51
0	8	5	27.71	21.82
1	8	5	21.04	20.85
2	8	5	24.96	19.72
3	8	5	21.17	19.30
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5	8	5	27.17	27.54
6	8	5	13.67	14.79
7	8	5	21.44	27.86
8	8	5	8.84	9.40
11	8	5	7.94	6.51
0	9	5	41.12	39.77
1	9	5	19.77	19.40
2	9	5	25.54	22.06
3	9	5	27.94	27.16
4	9	5	23.89	21.41
5	9	5	13.44	8.48
6	9	5	14.28	13.20
7	9	5	12.42	13.51
8	9	5	13.52	16.05
11	9	5	7.76	10.42
0	10	5	30.90	23.61
1	10	5	15.30	20.75
2	10	5	27.35	20.24
3	10	5	14.82	10.78
4	10	5	21.65	14.03
5	10	5	13.30	11.07
6	10	5	8.55	6.57
7	10	5	15.71	11.75
8	10	5	11.97	12.00
0	11	5	38.58	43.39
1	11	5	22.45	15.81
2	11	5	25.64	26.18
3	11	5	39.14	36.33
4	11	5	12.70	10.86
5	11	5	20.00	23.61
6	11	5	13.23	12.26
7	11	5	17.34	20.39
9	11	5	9.04	10.01
0	12	5	14.85	11.57
1	12	5	10.57	10.68
2	12	5	17.34	14.60
3	12	5	13.99	14.89
4	12	5	4.79	2.43
5	12	5	12.84	11.61
6	12	5	15.55	12.90
7	12	5	10.85	13.36
8	12	5	8.73	8.56
9	12	5	8.91	10.20
11	12	5	7.45	8.38
0	13	5	15.90	12.64
1	13	5	4.73	4.80
2	13	5	15.22	12.50
3	13	5	12.76	10.14
4	13	5	22.72	21.21
5	13	5	13.49	15.20
6	13	5	15.66	13.13
8	13	5	17.67	16.81
9	13	5	8.76	8.43
10	13	5	8.81	10.47
11	13	5	5.78	2.60
0	14	5	12.44	10.23
1	14	5	17.62	16.79
2	14	5	22.75	29.23
3	14	5	17.38	15.92
4	14	5	17.30	16.98
5	14	5	13.70	13.70
7	14	5	11.40	10.16
9	14	5	9.72	10.03
11	14	5	5.46	7.71
1	15	5	32.96	30.19
2	15	5	15.29	15.53
3	15	5	36.18	33.22
4	15	5	13.88	15.51
5	15	5	9.46	7.93
6	15	5	11.98	11.47
7	15	5	10.75	9.38
0	16	5	15.27	11.89
1	16	5	9.72	[illegible]
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3	16	5	2.95	4.37
4	16	5	20.32	15.92
6	16	5	13.54	13.59
11	16	5	4.50	6.70
0	17	5	12.31	9.79
1	17	5	9.91	10.68
2	17	5	8.71	6.10
3	17	5	17.78	17.50
4	17	5	13.51	12.24
5	17	5	8.84	6.65
0	18	5	4.49	4.67
1	18	5	15.95	12.24
3	18	5	26.32	27.00
4	18	5	8.92	8.93
5	18	5	10.23	8.63
6	18	5	9.46	11.13
7	18	5	17.21	16.59
9	18	5	8.50	11.80
1	19	5	9.57	5.65
2	19	5	10.64	14.86
3	19	5	2.59	2.74
4	19	5	9.36	5.57
5	19	5	10.80	8.60
6	19	5	9.33	5.79
8	19	5	10.25	9.18
9	19	5	8.10	10.32
1	20	5	3.22	0.98
2	20	5	23.09	23.12
3	20	5	8.73	8.50
5	20	5	9.44	8.14
9	20	5	7.17	12.17
0	21	5	13.96	13.59
1	21	5	19.37	15.45
2	21	5	17.78	18.40
3	21	5	5.31	5.03
4	21	5	12.73	13.93
5	21	5	8.62	7.00
6	21	5	8.29	7.77
0	22	5	11.06	10.03
3	22	5	17.26	17.86
5	22	5	10.33	8.38
7	22	5	10.04	8.47
1	23	5	8.10	6.05
2	23	5	16.26	16.63
3	23	5	9.88	9.11
4	23	5	11.85	12.54
5	23	5	12.08	14.91
7	23	5	10.75	14.84
8	23	5	6.98	9.50
1	24	5	3.06	6.65
5	24	5	7.92	7.93
7	24	5	6.59	5.15
8	24	5	5.47	6.42
1	25	5	8.53	8.63
3	25	5	4.96	4.56
4	25	5	7.61	7.03
8	25	5	4.73	1.01
0	26	5	12.55	12.65
1	26	5	2.49	6.66
2	26	5	9.02	9.05
4	26	5	12.89	14.57
0	27	5	17.59	17.75
1	27	5	2.77	4.43
2	27	5	8.37	8.17
3	27	5	5.57	12.25
4	27	5	7.51	6.08
7	27	5	6.35	11.25
0	28	5	11.04	11.95
1	28	5	8.37	8.42
2	28	5	7.68	6.45
3	28	5	7.55	3.19
4	28	5	6.07	2.96
0	29	5	16.24	21.01
2	29	5	6.59	9.45
3	29	5	2.12	4.20
0	30	5	7.11	6.74
2	30	5	5.78	7.34
3	30	5	1.91	0.78
0	31	5	7.29	11.44
2	31	5	5.68	5.00
3	31	5	5.67	7.02
0	0	6	9.34	6.54
1	0	6	10.64	8.40
2	0	6	28.05	26.67
3	0	6	9.94	9.39
4	0	6	16.52	6.41
0	1	6	13.85	9.06
1	1	6	30.19	30.63
2	1	6	15.72	13.98
3	1	6	11.14	8.15
4	1	6	19.47	22.62
1	2	6	10.12	8.75
2	2	6	7.66	6.29
3	2	6	12.71	13.82
4	2	6	13.49	14.47
0	3	6	7.29	7.29
1	3	6	29.78	27.05
2	3	6	29.47	28.02
3	3	6	27.64	24.33
4	3	6	26.22	25.97
0	4	6	11.17	4.20
1	4	6	9.64	8.05
2	4	6	9.17	6.49
3	4	6	19.77	23.64
4	4	6	11.09	14.28
0	5	6	7.35	8.87
1	5	6	25.41	22.37
2	5	6	20.31	22.12
3	5	6	19.21	10.32
4	5	6	11.81	11.49
0	6	6	13.52	7.75
1	6	6	11.95	12.75
2	6	6	14.43	11.31
3	6	6	8.02	6.67
4	6	6	10.46	11.09
1	7	6	28.26	23.47
2	7	6	22.32	20.30
4	7	6	16.39	13.61
2	8	6	6.14	10.74
3	8	6	12.03	11.60
4	8	6	16.96	17.07
0	9	6	22.80	23.23
1	9	6	29.15	25.05
2	9	6	17.57	17.47
3	9	6	32.55	31.15
0	10	6	7.66	2.48
1	10	6	8.73	10.57
3	10	6	29.70	28.63
4	10	6	16.65	15.13
0	11	6	9.98	4.05
1	11	6	7.17	7.23
4	11	6	17.65	19.44
0	12	6	10.06	11.34
2	12	6	7.32	1.93
4	12	6	18.62	16.65
1	13	6	45.88	41.26
2	13	6	14.74	11.04
3	13	6	21.47	14.73
4	13	6	8.11	5.80
0	14	6	7.87	3.29
2	14	6	9.78	4.45
3	14	6	11.24	12.42
4	14	6	9.94	10.01
0	15	6	11.19	12.88
1	15	6	8.23	9.56
2	15	6	23.43	21.99
3	15	6	21.20	20.86
4	15	6	15.14	11.97
1	16	6	19.50	18.15
3	16	6	15.84	12.32
4	16	6	11.37	8.97
0	17	6	13.72	13.58
1	17	6	6.35	5.30
2	17	6	23.37	23.96
4	17	6	7.95	10.85
0	18	6	10.17	3.56
2	18	6	15.55	12.26
3	18	6	8.21	9.28
0	19	6	13.52	15.13
1	19	6	19.17	19.25
3	19	6	12.55	12.23
3	20	6	12.83	15.54
0	21	6	9.78	8.35
1	21	6	8.57	7.20
2	21	6	7.81	10.56
3	21	6	9.17	7.27
0	22	6	11.29	8.02
1	22	6	5.91	7.99
2	22	6	8.99	10.78
0	23	6	8.26	9.63
1	23	6	9.36	11.42
2	23	6	5.70	1.34
2	24	6	7.04	7.65
1	25	6	5.26	5.16
2	25	6	5.18	4.82
1	27	6	4.62	4.55
2	27	6	5.85	4.12
1	29	6	6.22	11.07
1	30	6	3.22	8.89
0	0	7	10.12	0.00
1	0	7	15.92	17.43
2	0	7	8.23	13.31
3	0	7	17.15	13.66
0	1	7	7.85	7.18
1	1	7	14.12	14.99
2	1	7	7.38	6.01
3	1	7	7.48	6.35
4	1	7	8.11	10.65
0	2	7	19.79	16.22
1	2	7	13.17	17.39
2	2	7	23.63	21.23
3	2	7	17.94	18.13
0	3	7	22.70	20.88
1	3	7	10.35	6.17
2	3	7	26.11	29.73
3	3	7	12.42	9.20
4	3	7	17.23	23.99
1	4	7	7.32	3.92
3	4	7	6.48	7.90
0	5	7	25.78	28.55
1	5	7	15.13	13.90
2	5	7	23.13	22.02
3	5	7	6.48	5.15
4	5	7	16.24	16.97
1	6	7	29.64	32.72
2	6	7	10.46	8.93
3	6	7	7.48	8.03
4	6	7	9.07	9.50
0	7	7	36.89	38.38
1	7	7	21.12	14.60
2	7	7	9.80	9.11
3	7	7	15.90	12.88
4	7	7	15.69	18.44
1	8	7	15.63	17.42
3	8	7	13.49	11.58
0	9	7	18.90	22.52
2	9	7	16.58	15.83
3	9	7	11.21	12.10
4	9	7	6.95	6.02
1	10	7	6.38	3.19
3	10	7	6.43	8.98
4	10	7	12.66	13.57
0	11	7	17.72	15.05
1	11	7	14.23	9.29
3	11	7	7.42	8.68
4	11	7	14.88	11.85
0	12	7	7.87	3.10
1	12	7	7.32	8.17
2	12	7	7.34	5.20
4	12	7	16.73	17.10
1	13	7	11.51	9.62
2	13	7	16.73	18.10
4	13	7	15.58	16.92
0	14	7	9.02	9.41
1	14	7	7.22	5.11
2	14	7	8.87	8.68
4	14	7	10.88	8.37
0	15	7	11.81	11.78
2	15	7	12.89	15.75
4	15	7	12.53	13.85
0	16	7	10.77	6.63
2	16	7	6.09	7.87
1	17	7	8.50	5.58
2	17	7	5.98	6.27
3	17	7	11.37	10.55
1	18	7	6.80	8.61
1	19	7	7.38	7.01
3	19	7	9.15	7.73
1	20	7	5.54	1.57
1	21	7	5.34	4.02
3	21	7	5.94	4.81
3	22	7	6.92	9.91
3	22	7	6.92	9.91
0	0	8	19.13	14.24
1	0	8	16.57	23.46
2	0	8	7.22	0.57
3	0	8	10.23	9.62
4	0	8	10.88	8.39
1	1	8	6.25	2.26
2	1	8	8.08	7.68
3	1	8	8.08	4.67
4	1	8	13.83	12.33
1	2	8	10.22	12.65
2	2	8	6.25	7.63
3	2	8	7.21	9.91
4	2	8	8.55	8.27
1	3	8	8.06	13.35
2	3	8	6.23	3.71
4	3	8	6.62	3.76
1	4	8	9.51	8.57
2	4	8	8.39	5.08
3	4	8	16.42	16.01
4	4	8	6.57	3.41
0	5	8	16.11	15.50
1	5	8	15.21	13.15
2	5	8	7.16	3.09
3	5	8	11.30	8.30
4	5	8	6.56	4.02
1	6	8	12.37	12.71
3	6	8	15.48	11.02
4	6	8	6.49	3.81
0	7	8	15.95	17.40
3	7	8	12.70	12.07
4	7	8	9.85	8.48
0	8	8	16.45	11.15
1	8	8	7.03	10.75
3	8	8	12.60	12.74
4	8	8	7.35	8.09
2	9	8	8.52	8.30
3	9	8	6.92	11.23
4	9	8	7.27	5.18
1	10	8	10.93	15.48
2	10	8	5.94	3.06
3	10	8	8.34	8.24
4	10	8	7.14	6.93
1	11	8	7.63	7.98
2	11	8	6.77	6.91
3	11	8	12.55	12.42
4	11	8	7.01	5.87
2	12	8	7.45	7.83
4	12	8	5.96	4.28
1	13	8	6.59	3.97
3	13	8	9.65	8.65
1	14	8	5.59	1.46
3	14	8	8.87	9.49
4	14	8	5.65	6.57
1	15	8	5.43	8.46
4	15	8	5.46	4.20
1	16	8	5.28	5.26
3	16	8	5.09	9.08
1	17	8	10.17	9.96
3	17	8	8.91	7.56
4	17	8	4.99	6.09
4	19	8	5.67	9.94
3	0	9	4.32	7.84
1	1	9	8.32	7.62
2	1	9	6.22	6.91
1	2	9	5.43	2.46
1	3	9	6.98	2.00
2	3	9	6.17	8.26
1	4	9	7.60	6.23
1	5	9	5.31	5.69
3	5	9	11.11	8.82
1	6	9	7.45	5.25
3	6	9	8.78	8.02
1	7	9	7.34	6.27
1	9	9	5.78	4.10
3	9	9	4.79	4.75
3	10	9	10.07	8.05
3	11	9	5.20	2.84
1	12	9	5.33	4.12
1	13	9	4.42	2.43
3	13	9	8.65	9.31
3	15	9	6.69	6.01

choice but to take one of the peaks, since the other atoms of the carboxyl group had clearly been shown on the electron density map. The false peak disappeared from the electron density map as soon as the contribution of the correct atom was taken into account.

Refinement of the structure was first carried out by the isotropic full-matrix least-squares calculations to an R value of 0·17 and then by three cycles of block-matrix calculations (program by Okaya & Ashida, 1967). The R value reduced to 0·15. In the latter calculations, anisotropic thermal vibrations for all atoms were allowed for. The weighting system adopted was:

$$\sqrt{w}=40/F_o \quad \text{when} \quad F_o>40$$
$$\sqrt{w}=1 \quad \text{when} \quad F_o\leq 40\,.$$

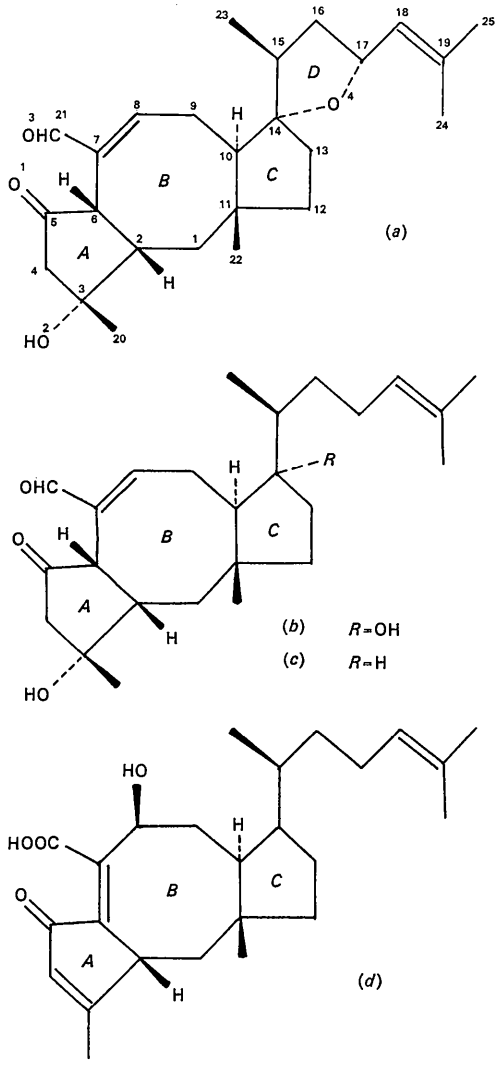

Fig. 3. Chemical structures of (*a*) ophiobolin A (*b*) ophiobolin B (zizanin B) (*c*) ophiobolin C (zizanin A) and (*d*) ophiobolin D (cephalonic acid).

The final atomic parameters and their standard deviations are given in Table 1. A list of the observed and calculated structure factors is given in Table 2. A composite electron density map obtained from the final Fourier synthesis is shown in Fig. 2 in which the perspective drawing of the molecule is also shown.

Absolute configuration

The absolute configuration of methyl cephalonate bromoacetate has been determined by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The values of the real and imaginary dispersion correction terms of the scattering factor of the bromine atom were taken as $\Delta f'=-0{\cdot}9$ and $\Delta f''=1{\cdot}5$ (*International Tables for X-ray Crystallography*, 1962). Intensities of more than fifty Friedel's pairs of reflexions were calculated with the assumption that the atomic coordinates given in Table 1 are referred to a right-handed set of axes. Some of the results used for the establishment of the absolute configuration are shown in Table 3. All Figures shown in this paper are drawn with the correct absolute configuration.

Table 3. *Comparison of the calculated and observed intensity ratios of the Friedel's pairs of reflexions used for the establishment of the absolute configuration*

h	k	l	$\frac{\lvert F_c(hkl)\rvert^2}{\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert^2}$	$\frac{I_o(hkl)}{I_o(\bar{h}\bar{k}\bar{l})}$
6	3	1	1·43	>1
10	3	1	0·78	<1
5	4	1	0·79	<1
3	5	1	1·23	>1
6	6	1	1·62	>1
7	9	1	0·50	<1
3	11	1	1·29	>1
6	1	2	0·69	<1
8	1	2	2·16	>1
8	2	2	0·79	<1
2	3	2	1·21	>1
4	3	2	1·30	>1
3	4	2	0·36	<1
5	6	2	1·61	>1
7	6	2	1·37	>1
3	9	2	0·75	<1
6	10	2	1·73	>1
3	11	2	1·44	>1
1	1	3	1·30	>1
3	1	3	1·24	>1
4	3	3	0·54	<1
2	4	3	1·53	>1
4	6	3	0·42	<1
5	7	3	0·71	<1
2	9	3	1·43	>1
8	9	3	0·75	<1
8	3	4	1·28	>1
2	4	4	1·36	>1
5	4	4	0·79	<1

Discussion of the structure

Molecular structure

The molecular structure of methyl cephalonate bromoacetate determined by the present analysis is

shown in Fig. 2(*b*). The plane formula is given in Fig. 1(*b*). The structure of cephalonic acid (ophiobolin D) is, therefore, deduced as Fig. 1(*a*). Fig. 3 shows the chemical structure of ophiobolins A, B, C and D. The observed ultraviolet absorption spectra (maximum at 259 mμ with $\varepsilon = 11{,}700$) and the main feature of the

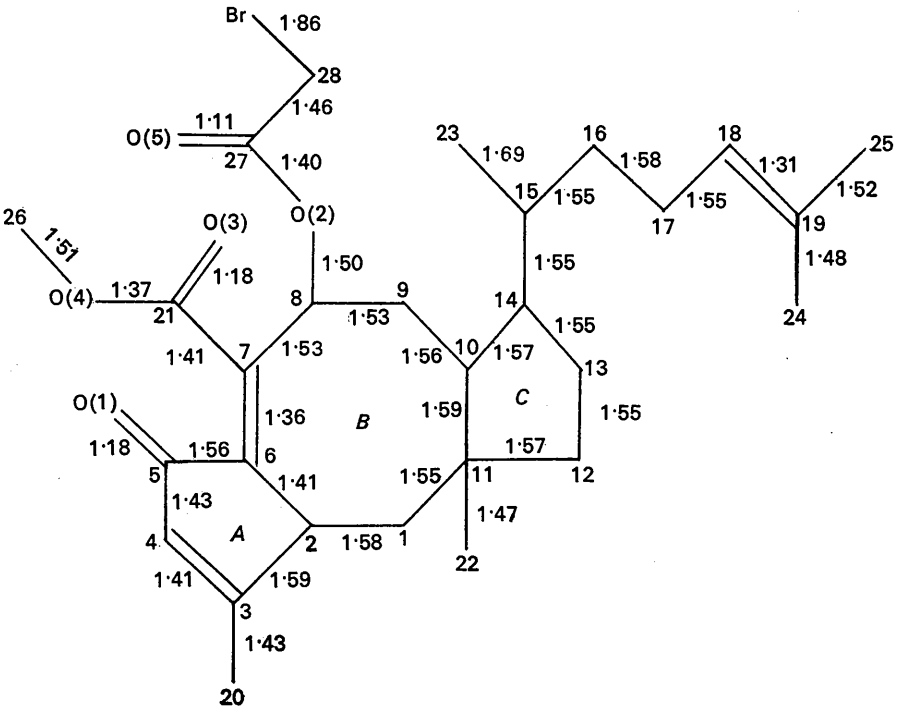

Fig. 4. Bond lengths found in methyl cephalonate bromoacetate (in Å).

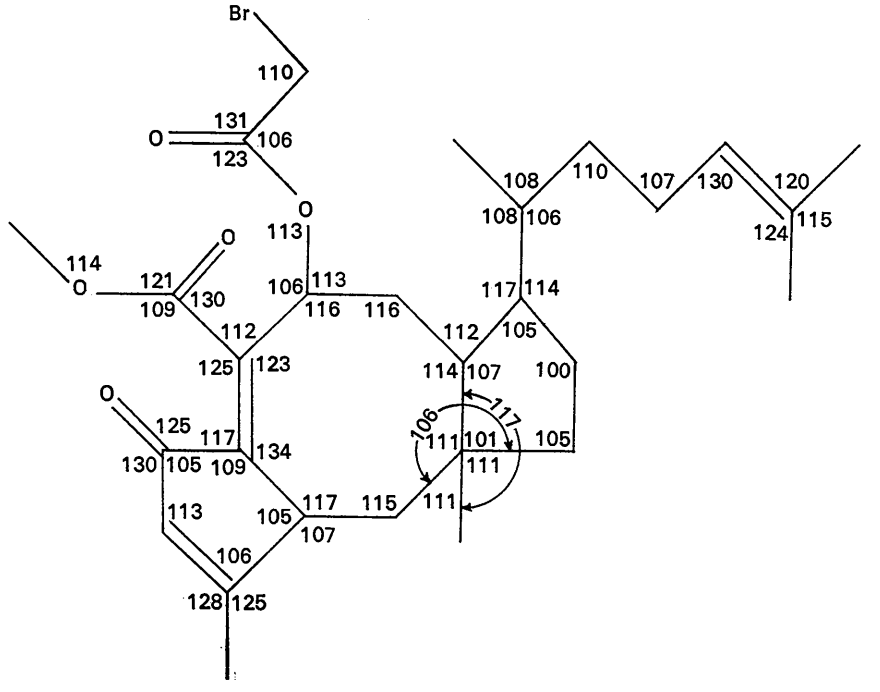

Fig. 5. Bond angles in degrees.

infrared absorption bands (at 3000, 1680 and 1610 cm^{-1}) as well as the nuclear magnetic resonance spectra are all very well accounted for with the present structure.

As shown in Fig. 2(*b*), the main feature of the structure is very similar to that found in ophiobolin A (Morisaki, Nozoe & Iitaka, 1968) and its congeners; ophiobolin B (zizanin B; Nozoe, Hirai & Tsuda, 1966) and ophiobolin C (zizanin A; Nozoe, Hirai & Tsuda, 1966). Every one of these consists of a fused five-, eight- and five-membered ring system, characteristic of the C_{25} terpenoids. In these compounds, the junction between *B* and *C* rings is found to be *trans* and the absolute configurations at C(2), C(10), C(11), C(14) and C(15) are the same. Furthermore, the side chains attached to the C(14) carbon atom have closely related structures. It is believed that the ether bridge, C(14)–O(4)–C(17), in ophiobolin A is completed during biosynthesis of ophiobolin A from ophiobolin B and that the latter is formed through a hydroxylation reaction of ophiobolin C at C(14).

The bond lengths and angles found in the present molecule are shown in Figs. 4 and 5. The mean standard deviations of these values are calculated from those of the positional parameters and they are listed in Table 1 for groups of similar bond type. The mean values of bond lengths for the twenty-four C–C, three C=C, two ester C–O, two ether C–O and three C=O bonds are 1·55 Å, 1·36 Å, 1·39 Å, 1·51 Å and 1·16 Å, respectively. Some unusual values are found at the junctions of two rings, but as the standard deviations in bond lengths are rather large, it does not seem reasonable to put much reliance on these values. The mean values of the bond lengths and endocyclic bond angles found in *A*, *B* and *C* rings are 1·48 Å, 1·52 Å, 1·57 Å and 108°, 118°, 104°, respectively, which may be compared with the values, 1·56 Å, 1·54 Å, 1·59 Å and 104°, 115°, 104°, found in ophiobolin A methoxybromide (Morisaki, Nozoe & Iitaka, 1968). The smaller bond length and the larger angle in ring *A* for the present structure, may result from the presence of a double bond at C(3)=C(4).

The internal rotation angles are calculated for the molecule and are shown in Fig. 6. The definition and the way of describing the internal rotation angles are given in Fig. 5 of the preceding paper (Morisaki, Nozoe & Iitaka, 1968). The planarity and conformation of each ring will be seen in Table 4. The deviations of atoms from each best plane of atomic groups are also shown in the Table. As is usually seen in five-membered rings, the *A* and *C* rings (as well as the tetrahydrofuran ring *D* in ophiobolin A) take a puckered form. However, most of them are more or less distorted because of the presence of double bonds or the fusion

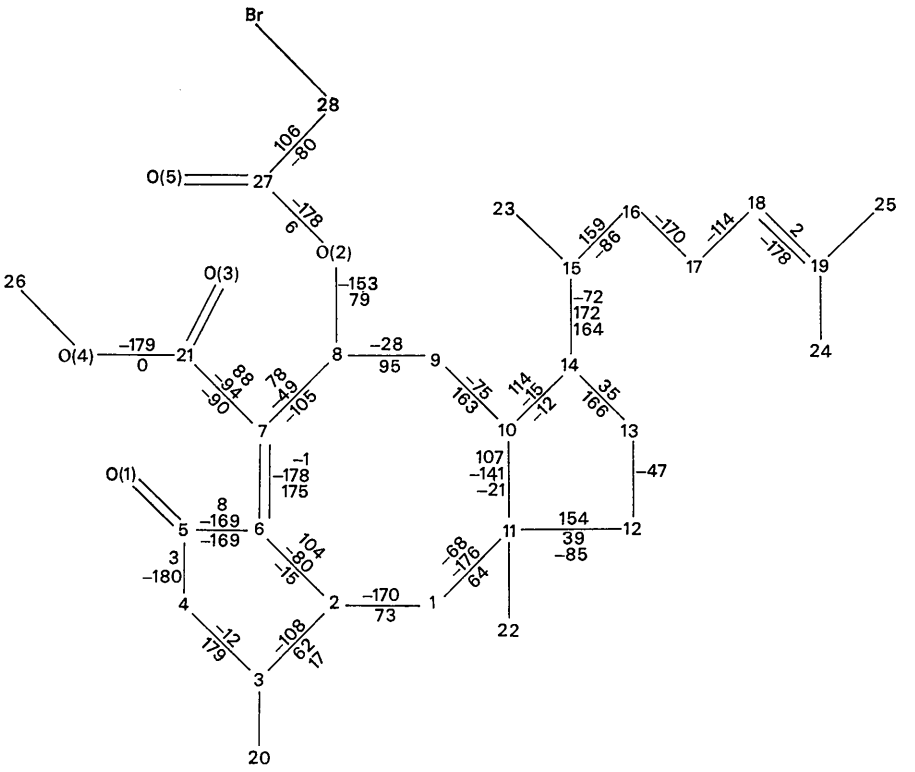

Fig. 6. Internal rotation angles. For definition and the way of describing the internal rotation angles see Fig. 5 of the paper by Morisaki, Nozoe & Iitaka (1968).

of the rings. As seen in Table 4, both of the eight-membered *B* rings in ophiobolin A and D take a distorted chair conformation. In ophiobolin A methoxybromide, the four atoms C(1), C(2), C(9) and C(10) lie roughly on a plane, but an alternative choice of the best plane through the atoms C(1), C(8), C(9) and C(11) may also be possible. In the present structure, the four atoms C(2), C(6), C(10) and C(11) lie almost perfectly on a plane and the three atoms on one side, C(7), C(8) and C(9), are displaced upwards and the atom on the other side, C(1), is displaced downwards. The two substituents, a methoxycarbonyl group and a bromoacetyl group, are attached to the ring *B* at the 7 and 8 positions, respectively. The former group is oriented equatorially and the latter axially, the plane of each group [formed by C(7), C(21), O(3) and O(4) or by O(2), C(27), C(28) and O(5)] being roughly perpendicular to the plane of the *B* ring. It is rather unusual for such a bulky substituent as the bromoacetyl group to be attached in an axial position to the ring. This may be the consequence of the equatorial arrangement of the neighbouring methoxycarbonyl group which is fixed in its position through a double bond. It should also be noted that the side chain (2-methylhept-2-en-6-yl) does not take a planar zigzag chain conformation. The internal rotation angles around C(15)–C(16) and C(17)–C(18) deviate significantly from those expected for the *trans* conformation. As a result, one of the hydrogen atoms at C(17) is almost eclipsed by C(19). This side chain is extended in a direction such that C(16) is nearly in the *trans* position to C(13).

Table 4. *Perpendicular distances of atoms from the best plane formed by each of the five- and eight-membered rings in methyl cephalonate bromoacetate and ophiobolin A methoxybromide*

Methyl cephalonate bromoacetate		Ophiobolin A methoxybromide	
A ring			
best plane formed by		*A* ring	
C(3)	0·011 Å	C(2)	−0·038 Å
C(4)	−0·018	C(4)	0·044
C(5)	0·016	C(5)	−0·065
C(6)	−0·009	C(6)	0·059
Perpendicular distances			
C(2)	−0·249 Å	C(3)	0·565
O(1)	0·005	O(2)	−0·253
C(20)	0·017		
C(7)	0·249		
B ring		*B* ring	
C(2)	0·005	C(1)	0·064
C(6)	−0·004	C(2)	−0·047
C(10)	0·004	C(9)	0·045
C(11)	−0·005	C(10)	−0·061
C(1)	−0·732	C(11)	−0·837
C(7)	0·717	C(6)	0·483
C(8)	1·845	C(7)	1·583
C(9)	1·397	C(8)	1·377
C ring		*B* ring (alternative choice of the best plane)	
C(10)	0·072	C(1)	−0·070
C(11)	−0·045	C(8)	0·073
C(13)	0·046	C(9)	−0·094
C(14)	−0·073	C(11)	0·091
C(12)	−0·664		

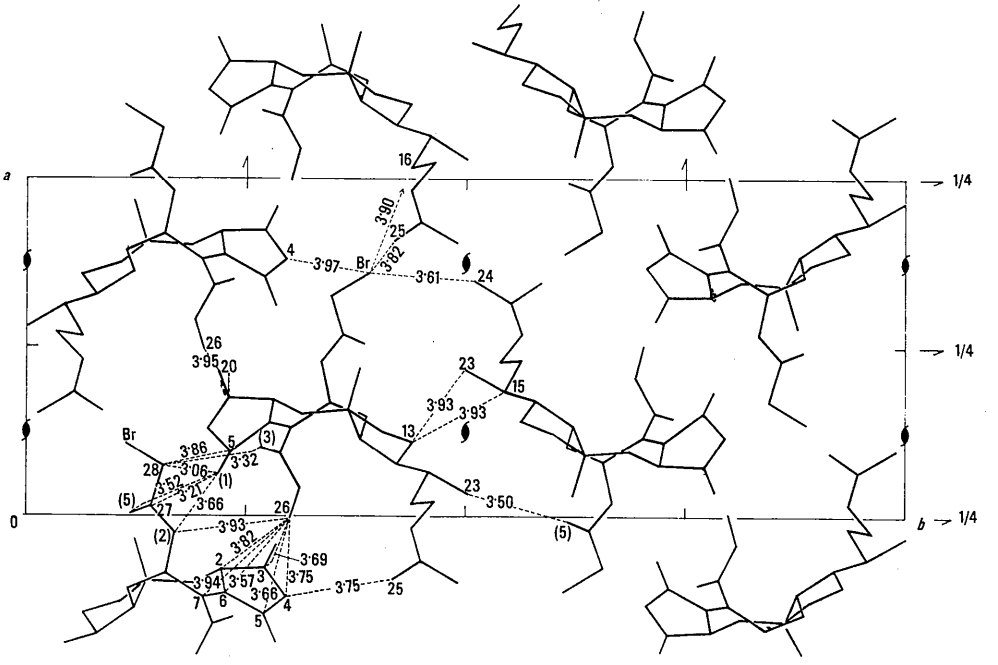

Fig. 7. Projection of the crystal structure along the *c* axis. The positive direction of the *c* axis is downwards. Intermolecular short contacts less than 4 Å are shown by broken lines. The numbers in parentheses indicate those for oxygen atoms.

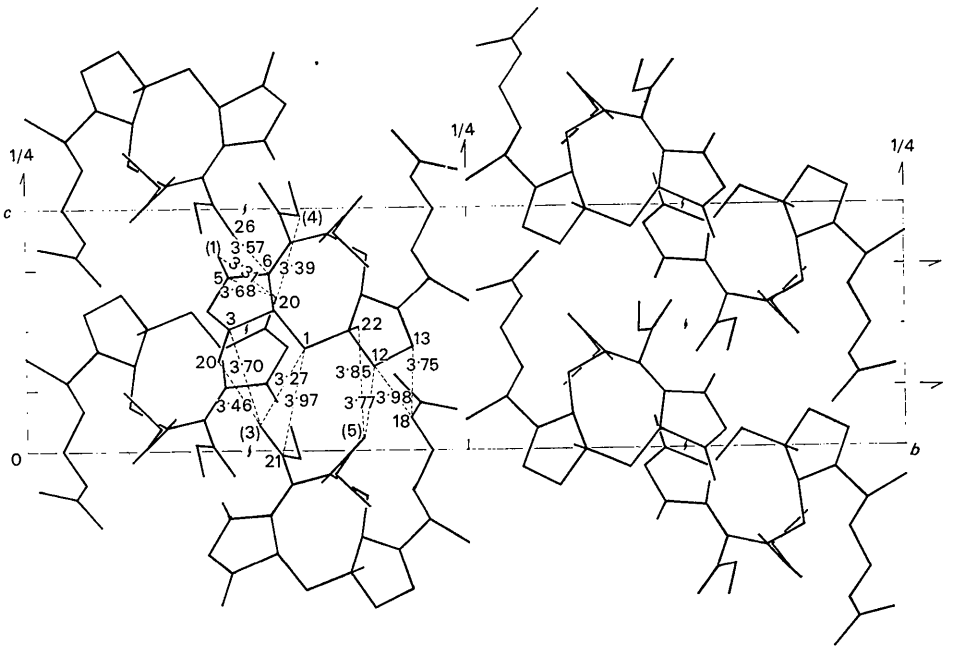

Fig. 8. Projection of the crystal structure along the *a* axis. The positive direction of the *a* axis is upwards. Intermolecular short contacts less than 4 Å are shown by broken lines. The numbers in parentheses indicate those for oxygen atoms.

Table 4 (*cont.*)

Bromoacetyl group	
O(2)	0·007
C(27)	−0·025
O(5)	0·011
C(28)	0·007
C(8)	−0·060
Br	−1·675
Methoxycarbonyl group	
C(7)	0·002
C(21)	−0·007
O(3)	0·003
O(4)	0·002
C(26)	0·012
3-Methyl-2-butenyl group	
C(17)	0·012
C(18)	−0·017
C(19)	−0·004
C(24)	−0·001
C(25)	0·010
C(16)	−1·374
C(10)	0·794
C(2)	−1·362
C(6)	−1·691
C(7)	−0·570
C ring	
C(10)	−0·026
C(12)	0·027
C(13)	−0·040
C(14)	0·040
C(11)	−0·698
D ring	
C(14)	−0·040
C(16)	0·036
C(17)	−0·063
O(4)	0·066
C(15)	0·531

The crystal structure

Two projections of the crystal structure viewed along the *c* and *a* axis are shown in Figs. 7 and 8, respectively. Intermolecular short contracts less than 4 Å are shown in the Figures. The molecules are packed together mainly through van der Waals forces and there are no abnormal distances between the molecules. The shortest distance is 3·06 Å found between O(1) and C(28), the former being the carbonyl oxygen atom and the latter is the methylene carbon atom lying between the bromine atom and the carbonyl group.

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