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The Crystal and Molecular Structure of Monobromoduclauxin

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The crystal structure of monobromoduclauxin, $C_{29}H_{21}O_{11}Br$, has been determined in order to elucidate the molecular structure and absolute configuration of duclauxin, $C_{29}H_{22}O_{11}$, one of the metabolites of *Penicillium Duclauxi* Delacroix. Monobromoduclauxin was prepared by direct bromination of duclauxin with dioxan dibromide; it crystallized in a structure with space group $P2_12_12_1$ and the unit-cell dimensions, $a=15{\cdot}01$, $b=18{\cdot}83$, $c=9{\cdot}15$ Å; $Z=4$. The crystal structure was solved by the heavy atom method and refined by the method of least-squares. The final reliability index for 1811 observed reflexions was 0·136. The molecule consists of two nearly planar tricyclic rings, one containing an isocoumarin and the other containing a dihydroisocoumarin nucleus. A characteristic feature of duclauxin revealed by the present analysis is that these two tricyclic rings are joined together through a five-membered ring to form a hinge- or castanets-like structure.

Introduction

Duclauxin, $C_{29}H_{22}O_{11}$, is a metabolite isolated from mycelium of *Penicillium Duclauxi* Delacroix (Shibata, Ogihara, Tokutake & Tanaka, 1965). The structural study of this substance by chemical methods has been carried out for several years past, and partial structures indicating the existence of benzenoid groups, two hydroxyl groups (easily acetylated), an acetyl group and a methoxyl group *etc.*, have already been established. However, all attempts to find out the skeletal structure have been unsuccessful. In order to determine the chemical structure and the stereochemistry of duclauxin, we have carried out an X-ray study of monobromoduclauxin (II) and determined the molecular structure of duclauxin including its absolute configuration as (I) (Fig. 1). A preliminary short note on this work has already been published (Ogihara, Iitaka & Shibata, 1965).

Experimental

After a number of unsuccessful attempts to introduce heavy atoms into the structure of duclauxin, we finally found that a direct bromination can yield monobromoduclauxin. The bromination was carried out by treatment of duclauxin with dioxan dibromide in tetrahydrofuran solution in the presence of pyridine. Nuclear magnetic resonance spectra indicated that only one aromatic hydrogen atom is substituted by a bromine atom. Monobromoduclauxin was at first recrystallized from benzene to form crystals containing benzene as a solvent of crystallization. X-ray examination indicated that one of the crystallographic axes has a very long period, about 50 Å long, and often showed streak-like diffraction spots extended along the row lines in reciprocal space, indicating one-dimensional disorder in the crystal.

We therefore tried crystallization from acetone–ethanol solutions. The crystals obtained did not contain any solvation molecule and were colourless prisms elongated along the c axis. The density was measured by the flotation method in a mixture of benzene and carbon tetrachloride. The cell dimensions and space group were determined from rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation.

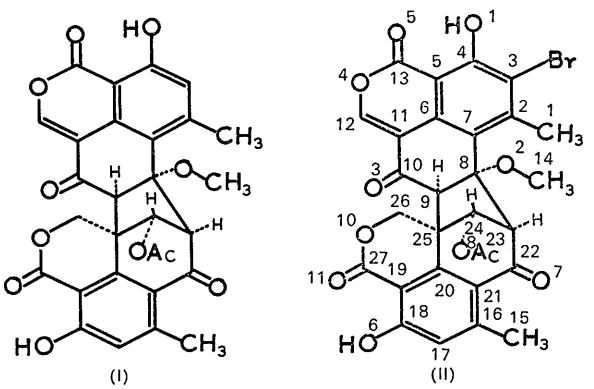

Fig. 1. Chemical formulae: (I) duclauxin. (II) monobromoduclauxin.

Crystal data

Monobromoduclauxin, $C_{29}H_{21}O_{11}Br$
M.W. 625·4, m.p. 260 °C (decomp.)
Orthorhombic
$a=15{\cdot}01\pm0{\cdot}02$, $b=18{\cdot}83\pm0{\cdot}025$, $c=9{\cdot}15\pm0{\cdot}015$ Å
$U=2586$ Å^3
$D_m=1{\cdot}57$ g.cm^{-3}, $D_x=1{\cdot}60$ g.cm^{-3}, $Z=4$
Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu=29$ cm^{-1}
$F(000)=1272$
Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd
Space group, $P2_12_12_1$.

The three-dimensional intensity data of $0kl$–$7kl$, $h0l$, $hk0$–$hk7$, were collected from equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation taken about the a, b and c axes using the multiple-film technique. The intensities of several thousands of reflexions were

estimated by visual comparison with a standard scale. The X-ray specimens used for the measurement were small enough to neglect the absorption correction. All the intensity data were corrected for Lorentz and polarization factors and they were put on a single scale. A total of 1811 independent structure factors were

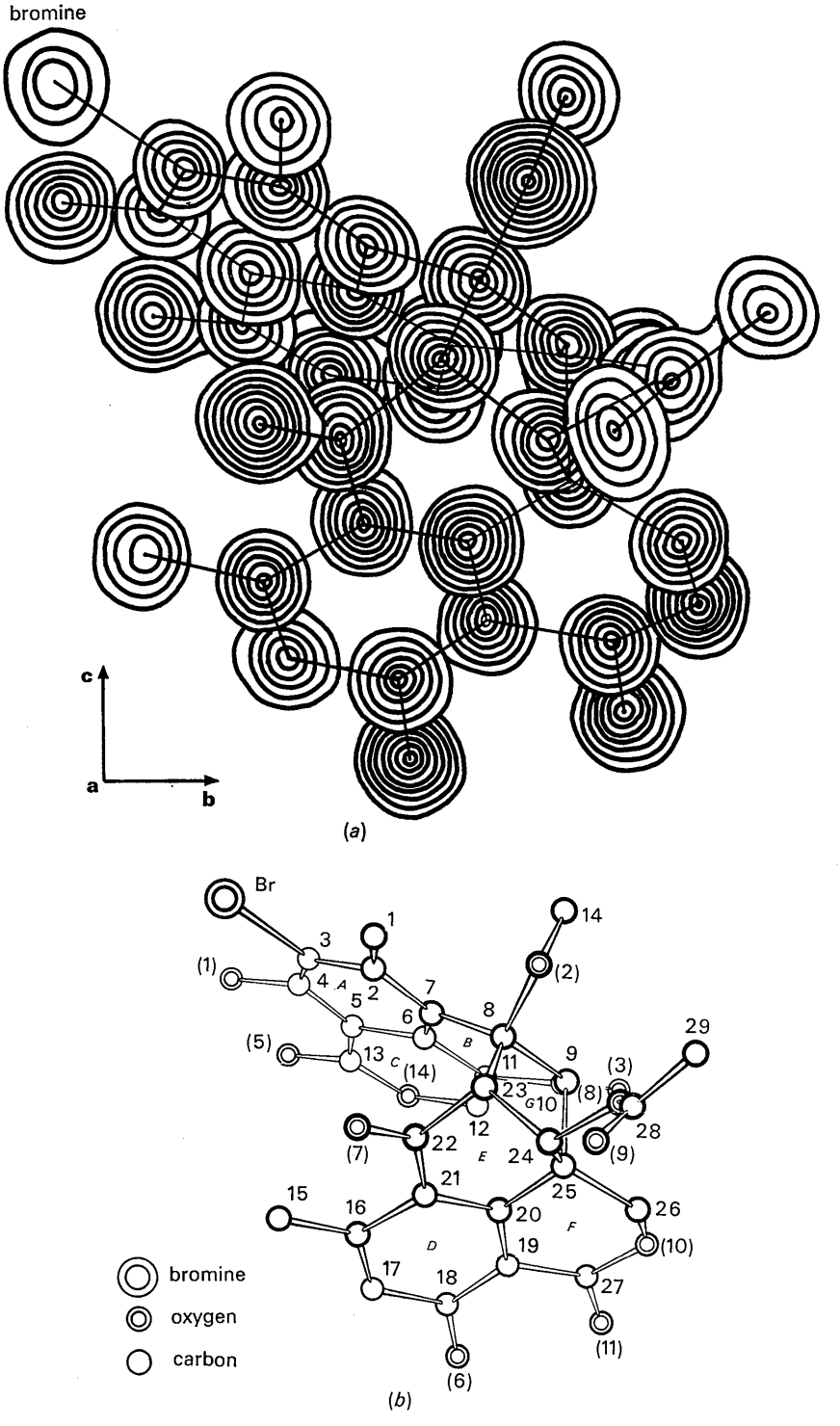

Fig. 2.(*a*) Composite drawing of the final electron density map viewed along the *a* axis. (*b*) The molecular structure viewed along the *a* axis (in correct absolute configuration).

finally evaluated. A Wilson plot was then made to estimate an approximate scale factor and an overall temperature factor ($B=6$ Å^2).

The following atomic scattering factors were used for the present structure determination: for bromine, those of Thomas & Umeda (1957); for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Determination of the structure

The positions of the bromine atom were determined by the sharpened Patterson Harker sections at $u=\frac{1}{2}$, $v=\frac{1}{2}$, and $w=\frac{1}{2}$ respectively. The coordinates of the bromine atom obtained were $x=0{\cdot}1849$, $y=0{\cdot}0678$, $z=0{\cdot}0578$ referred to the origin given in the *International Tables for X-ray Crystallography* (1952). The structure factors calculated for 1146 reflexions with the contributions of the bromine atom alone gave an R value 0·53. As the anisotropic temperature factor of the bromine atom was very large, the structure factors were calculated with two bromine atoms of half weight separated by about 0·4 Å along the **a** direction. The whole structure was determined at the ninth Fourier synthesis and the R value at this stage was 0·29. The oxygen atoms were identified on this Fourier map with

Table 1. *The final fractional atomic coordinates, thermal parameters* (Å^2) *and their standard deviations*

To represent the absolute configuration, the following coordinates should be referred to the left-handed coordinate system.

	x	$\sigma(ax)$	y	$\sigma(by)$	z	$\sigma(cz)$	B(Å^2)	$\sigma(B)$
Br	0·1797	0·004	0·0669	0·003	0·0588	0·003	(see below)*	
O(1)	0·3537	0·016	0·0729	0·017	0·9074	0·016	6·73	0·39
O(2)	0·1140	0·013	0·3586	0·012	0·9295	0·014	4·23	0·28
O(3)	0·3489	0·017	0·4305	0·018	0·6976	0·016	6·43	0·41
O(4)	0·4645	0·017	0·2372	0·017	0·6868	0·017	6·42	0·40
O(5)	0·4849	0·020	0·1301	0·019	0·7635	0·020	8·51	0·48
O(6)	0·3662	0·016	0·2813	0·015	0·1972	0·016	5·51	0·35
O(7)	0·0549	0·016	0·1889	0·016	0·6240	0·015	5·68	0·39
O(8)	0·0389	0·016	0·4314	0·015	0·6729	0·014	4·74	0·32
O(9)	0·4006	0·022	0·0890	0·020	0·3990	0·022	9·83	0·57
O(10)	0·2565	0·015	0·4579	0·012	0·4044	0·014	4·22	0·30
O(11)	0·3599	0·016	0·4143	0·015	0·2538	0·017	5·44	0·37
C(1)	0·0816	0·024	0·2061	0·022	0.9916	0·023	5·85	0·55
C(2)	0·1740	0·021	0·2043	0·017	0·9271	0·021	3·93	0·39
C(3)	0·2245	0·021	0·1442	0·019	0·9481	0·022	4·36	0·47
C(4)	0·3101	0·028	0·1355	0·023	0·8914	0·025	5·81	0·58
C(5)	0·3441	0·024	0·1884	0·021	0·8132	0·023	4·82	0·51
C(6)	0·3034	0·022	0·2521	0·020	0·7943	0·021	3·93	0·43
C(7)	0·2140	0·021	0·2576	0·020	0·8467	0·020	3·64	0·47
C(8)	0·1600	0·019	0·3260	0·017	0·7978	0·019	3·37	0·39
C(9)	0·2090	0·019	0·3828	0·017	0·7161	0·018	2·86	0·37
C(10)	0·3004	0·021	0·3792	0·018	0·7065	0·018	3·23	0·40
C(11)	0·3483	0·021	0·3097	0·019	0·7246	0·020	3·87	0·44
C(12)	0·4325	0·023	0·3014	0·020	0·6693	0·020	4·04	0·46
C(13)	0·4337	0·027	0·1858	0·027	0·7503	0·026	6·35	0·59
C(14)	0·1784	0·026	0·3834	0·022	0·0424	0·025	5·58	0·53
C(15)	0·1789	0·023	0·1168	0·020	0·4588	0·024	5·10	0·48
C(16)	0·2049	0·020	0·1910	0·018	0·4314	0·022	3·73	0·41
C(17)	0·2712	0·024	0·2058	0·022	0·3176	0·023	5·65	0·56
C(18)	0·2973	0·023	0·2750	0·021	0·2987	0·023	4·33	0·48
C(19)	0·2617	0·020	0·3306	0·016	0·3672	0·018	2·49	0·37
C(20)	0·2009	0·018	0·3194	0·015	0·4723	0·017	2·54	0·35
C(21)	0·1669	0·019	0·2516	0·018	0·5008	0·018	2·99	0·36
C(22)	0·0979	0·022	0·2410	0·019	0·6099	0·020	3·89	0·45
C(23)	0·0786	0·020	0·3051	0·017	0·7047	0·019	3·31	0·40
C(24)	0·0673	0·019	0·3685	0·017	0·6002	0·018	3·17	0·41
C(25)	0·1647	0·020	0·3796	0·017	0·5593	0·022	3·69	0·39
C(26)	0·1786	0·022	0·4483	0·018	0·4725	0·020	4·53	0·46
C(27)	0·2985	0·023	0·4041	0·020	0·3418	0·021	4·42	0·48
C(28)	0·4520	0·033	0·0563	0·032	0·3213	0·031	9·11	0·77
C(29)	0·4259	0·026	0·9955	0·025	0·2333	0·028	7·09	0·68

* The temperature factor for the bromine atom is expressed as

$$T=-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\,,$$

where the β's have the following values:

β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$
0·01433	0·00027	0·00363	0·00008	0·02492	0·00050
β_{12}	$\sigma(\beta_{12})$	β_{13}	$\sigma(\beta_{13})$	β_{23}	$\sigma(\beta_{23})$
−0·00089	0·00014	0·00103	0·00037	0·00301	0·00021

Table 1 (*cont.*)

Mean standard deviations:

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Br	0·00025 (0·004 Å)	0·00015 (0·003 Å)	0·00037 (0·003 Å)
O	0·0011 (0·017 Å)	0·0008 (0·016 Å)	0·0018 (0·017 Å)
C	0·0015 (0·023 Å)	0·0011 (0·020 Å)	0·0024 (0·022 Å)
Br	$\sigma(r)=0·003$ Å		
C	$\sigma(r)=0·021$ Å		
O	$\sigma(r)=0·016$ Å		

Mean estimated standard deviations in bond lengths:

σ(C–C) = 0·030 Å σ(C–O) = 0·027 Å σ(Br–C) = 0·022 Å .

Mean estimated standard deviations in tetrahedral bond angles and aromatic carbon bond angles:

σ(C–C–C) = 1·7°, σ(C–C–C, aromatic carbon) = 2·0°.

the help of chemical and structural considerations. Subsequent structure factor calculation coupled with difference Fourier synthesis gave an R value of 0·23.

Refinement of the structure

Refinement of the structural parameters was carried out initially by diagonal least-squares method. Six cycles of calculations by Van den Hende's (1961) program using 1811 reflexions gave an R value of 0·16. The standard deviations of the positional parameters at this stage were: for carbon atoms, $\sigma(x)=0·0016$–0·0034, $\sigma(y)=0·0014$–0·0034, $\sigma(z)=0·0027$–0·0061; for oxygen $\sigma(x)=0·0014$–0·0033, $\sigma(y)=0·0012$–0·0034, $\sigma(z)=0·0024$–0·0060; hence the mean standard deviations for the bond lengths were: σ(C–C), 0·05 Å, σ(C–O), 0·05 Å. At this stage the absolute configuration of the molecule was determined by calculating the structure factors for the Friedel's pairs of reflexions with the dispersion correction. A final three-dimensional Fourier synthesis was then calculated. A composite projection of the electron density map is shown in Fig. 2.

At the end of the refinement, the full-matrix least-squares calculations were carried out with the program *ORFLS* of Busing, Martin & Levy (1962). Three cycles of calculations on the CDC-3600 computer with anisotropic thermal parameters for the bromine atom and isotropic parameters for light atoms gave the R value of 0·136 for 1811 reflexions.

The final atomic parameters and their standard deviations are given in Table 1 and the observed and calculated structure factors are listed in Table 2. The weighting functions were:

$$\sqrt{w}=F_o/20\,, \quad \text{when } F_o<20\,,$$
$$\sqrt{w}=20/F_o\,, \quad \text{when } 20\le F_o<80\,,$$
$$\sqrt{w}=20\times 80/F_o^2\,, \quad \text{when } 80\le F_o\,.$$

Absolute configuration

The X-ray study of the absolute configuration was performed by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The dispersion corrections of the bromine scattering factor for Cu $K\alpha$ radiation given by Dauben & Templeton (1955) ($\Delta f'=-0·9$ and $\Delta f''=1·5$) were used. The structure factors for the Friedel's pairs of reflexions were calculated assuming that the atomic parameters are referred to a right-handed set of axes. The equivalent positions of the atoms were located corresponding to space group $P2_12_12_1$, no. 19 in *International Tables for X-ray Crystallography* (1952). Of the thirty pairs of reflexions for which the intensity differences between hkl and $\bar{h}\bar{k}\bar{l}$ were expected to be detectable, twenty pairs showed significant differences in the lth layer Weissenberg photographs. Some of the results are shown in Table 3. A comparison between observed and calculated intensities indicated that the assumed configuration was actually the antipode of the true structure. The abso-

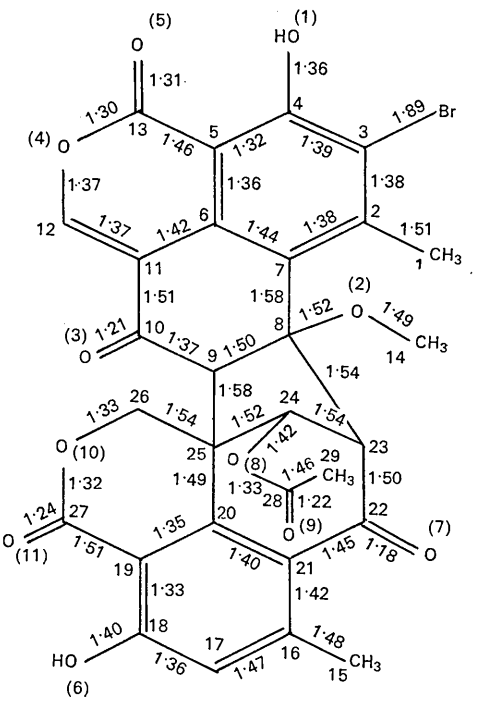

Fig. 3. Bond lengths (Å).

Table 2. *Observed and calculated structure factors*

H	K	L	F(OBS)	F(CAL)
2	0	0	190.51	234.37
4	0	0	69.34	66.86
6	0	0	98.76	100.65
8	0	0	105.76	104.70
10	0	0	5.01	5.36
1	1	0	14.89	5.04
2	1	0	74.56	61.93
3	1	0	13.31	35.32
4	1	0	32.88	32.38
5	1	0	31.39	9.79
6	1	0	42.10	36.18
7	1	0	34.74	37.54
8	1	0	24.31	25.77
9	1	0	39.91	32.85
10	1	0	43.41	46.32
11	1	0	6.86	0.80
12	1	0	14.76	16.21
13	1	0	7.47	7.53
16	1	0	6.87	10.86
0	2	0	116.89	133.68
1	2	0	70.74	68.89
2	2	0	10.34	9.27
3	2	0	98.93	108.00
4	2	0	10.75	9.93
5	2	0	54.19	55.07
6	2	0	35.18	34.46
7	2	0	10.00	11.06
8	2	0	10.56	12.55
10	2	0	18.45	18.11
11	2	0	6.89	8.75
14	2	0	5.80	14.36
15	2	0	7.91	3.39
1	3	0	62.79	63.26
2	3	0	21.69	32.10
3	3	0	44.19	34.76
4	3	0	98.21	77.19
5	3	0	60.52	56.55
6	3	0	62.79	70.69
7	3	0	6.13	5.52
8	3	0	31.14	29.34
9	3	0	17.71	19.85
10	3	0	3.75	11.89
12	3	0	11.14	13.77
13	3	0	6.84	10.17
14	3	0	9.19	7.41
0	4	0	82.93	78.23
1	4	0	24.25	13.25
2	4	0	52.39	43.72
3	4	0	108.03	116.70
4	4	0	27.53	20.13
5	4	0	73.14	62.19
6	4	0	36.26	42.72
7	4	0	23.46	19.37
10	4	0	8.55	6.58
11	4	0	11.11	20.24
13	4	0	6.86	5.44
15	4	0	6.58	2.75
16	4	0	6.09	4.33
1	5	0	1.63	2.21
2	5	0	24.02	20.60
3	5	0	26.94	24.67
4	5	0	43.04	42.86
5	5	0	39.83	44.27
6	5	0	34.41	36.39
7	5	0	22.07	15.76
9	5	0	9.66	5.02
10	5	0	28.08	29.74
12	5	0	17.08	17.59
13	5	0	9.71	8.94
14	5	0	4.30	7.37
16	5	0	5.99	7.82
1	6	0	94.86	92.02
2	6	0	67.31	58.26
3	6	0	76.86	81.56
4	6	0	46.29	43.32
5	6	0	4.25	5.92
6	6	0	81.93	93.33
7	6	0	6.15	2.63
8	6	0	17.36	16.42
10	6	0	5.62	11.21
11	6	0	13.81	10.29
12	6	0	12.19	9.92
14	6	0	8.55	7.84
16	6	0	5.84	5.59
1	7	0	64.80	68.23
2	7	0	21.70	21.68
4	7	0	10.29	9.80
5	7	0	17.00	26.38
6	7	0	30.75	32.18
7	7	0	18.08	18.42
9	7	0	25.39	25.76
10	7	0	4.04	2.69
11	7	0	4.22	2.56
12	7	0	20.56	23.06
13	7	0	9.21	12.78
14	7	0	14.65	20.35
15	7	0	7.42	6.11
16	7	0	8.00	14.98
17	7	0	4.83	3.99
0	8	0	113.67	114.82
1	8	0	48.56	49.72
2	8	0	33.00	31.48
3	8	0	79.55	74.33
4	8	0	37.66	36.15
6	8	0	19.26	22.23
7	8	0	26.47	19.59
8	8	0	23.75	20.79
9	8	0	15.07	19.45
10	8	0	43.74	44.63
11	8	0	12.48	14.22
12	8	0	4.35	12.07
13	8	0	8.07	11.21
14	8	0	4.15	2.53
15	8	0	10.58	12.23
1	9	0	40.72	49.93
2	9	0	43.24	36.54
3	9	0	22.59	16.12
4	9	0	14.92	11.38
5	9	0	42.60	41.18
6	9	0	74.62	66.24
7	9	0	36.10	34.62
8	9	0	6.71	7.88
9	9	0	31.65	28.35
10	9	0	6.67	11.26
11	9	0	8.65	12.46
12	9	0	22.19	25.33
13	9	0	11.29	20.68
14	9	0	5.75	10.12
17	9	0	4.19	0.76
0	10	0	18.40	16.39
1	10	0	21.78	25.06
2	10	0	31.33	30.08
3	10	0	32.68	35.30
4	10	0	31.72	30.09
5	10	0	41.20	40.25
6	10	0	24.89	17.25
8	10	0	8.03	15.09
9	10	0	4.17	8.20
11	10	0	4.35	1.59
13	10	0	6.62	5.71
14	10	0	11.14	17.09
1	11	0	20.17	13.86
2	11	0	25.53	26.30
3	11	0	21.03	17.99
4	11	0	17.79	34.26
6	11	0	13.59	13.08
7	11	0	16.94	12.59
11	11	0	8.68	4.50
12	11	0	6.73	3.91
13	11	0	4.07	4.67
14	11	0	0.00	0.31
15	11	0	5.31	5.97
1	12	0	8.77	5.93
2	12	0	10.29	8.34
3	12	0	59.60	61.14
4	12	0	25.04	18.53
5	12	0	17.94	20.12
6	12	0	8.52	16.36
8	12	0	11.24	9.52
11	12	0	13.27	11.24
16	12	0	2.48	6.83
1	13	0	33.68	35.72
2	13	0	27.21	28.27
3	13	0	14.01	11.18
4	13	0	15.36	12.76
5	13	0	12.80	6.23
6	13	0	9.48	12.44
8	13	0	11.01	1.45
9	13	0	19.21	13.59
11	13	0	8.44	7.18
12	13	0	6.96	4.23
13	13	0	8.74	6.53
0	14	0	25.34	25.99
1	14	0	10.18	4.68
2	14	0	6.52	8.82
4	14	0	23.01	24.25
5	14	0	8.95	9.42
6	14	0	15.25	11.76
7	14	0	5.28	0.02
8	14	0	4.35	2.50
11	14	0	6.44	1.24
1	15	0	60.31	56.06
2	15	0	30.86	25.39
3	15	0	48.90	44.79
4	15	0	24.86	24.98
5	15	0	8.85	14.38
6	15	0	2.74	7.47
7	15	0	18.84	17.49
9	15	0	8.48	6.82
10	15	0	8.21	5.54
11	15	0	7.28	0.49
0	16	0	76.19	78.70
1	16	0	9.26	9.60
2	16	0	13.59	16.69
3	16	0	17.40	21.99
5	16	0	14.94	17.94
6	16	0	26.74	26.33
7	16	0	2.40	6.04
8	16	0	37.96	36.44
9	16	0	14.49	15.15
1	17	0	5.33	9.24
2	17	0	25.18	23.35
3	17	0	19.56	21.56
6	17	0	22.52	15.53
8	17	0	9.95	9.66
0	18	0	3.57	12.38
2	18	0	11.03	12.75
3	18	0	11.24	12.88
4	18	0	3.33	10.40
6	18	0	8.18	6.59
8	18	0	8.53	1.36
2	19	0	12.09	12.41
4	19	0	17.85	17.05
6	19	0	8.95	8.96
0	20	0	3.30	7.74
1	20	0	2.00	8.77
2	20	0	2.19	5.80
3	20	0	11.40	10.69
5	20	0	3.77	4.96
6	20	0	10.03	11.19
11	20	0	3.22	5.30
1	21	0	2.90	3.67
2	21	0	12.48	10.04
3	21	0	2.64	0.51
4	21	0	10.37	10.39
5	21	0	4.67	8.70
0	22	0	10.87	11.67
2	22	0	10.22	7.14
3	22	0	1.64	2.19
6	22	0	9.13	9.16
8	22	0	3.96	6.90
1	23	0	14.83	14.67
2	23	0	4.33	4.52
3	23	0	2.99	5.43
4	23	0	5.59	4.13
1	24	0	3.56	4.40
3	24	0	3.45	6.14
1	0	1	55.01	42.85
2	0	1	52.95	46.60
3	0	1	8.77	4.98
4	0	1	39.36	46.54
5	0	1	65.88	78.27
6	0	1	12.36	10.17
7	0	1	59.99	61.00
8	0	1	30.14	30.94
9	0	1	30.82	32.06
10	0	1	12.53	12.86
11	0	1	26.69	30.03
0	1	1	42.23	43.94
1	1	1	95.34	87.21
2	1	1	75.36	72.10
3	1	1	131.39	114.08
4	1	1	79.82	74.60
5	1	1	49.70	49.81
6	1	1	39.09	41.14
7	1	1	60.18	59.08
8	1	1	23.83	23.72
9	1	1	26.23	25.90
10	1	1	14.94	12.95
11	1	1	22.57	18.59
15	1	1	6.91	10.59
0	2	1	47.48	46.75
1	2	1	133.23	160.55
2	2	1	58.04	65.83
3	2	1	112.75	115.19
4	2	1	58.86	63.89
5	2	1	16.82	16.39
6	2	1	13.25	12.49
7	2	1	51.58	54.97
8	2	1	35.44	37.15
9	2	1	21.33	17.16
10	2	1	16.26	16.13
11	2	1	14.63	19.10
0	3	1	56.30	66.58
1	3	1	57.09	61.13
2	3	1	93.25	86.26
3	3	1	55.46	49.89
4	3	1	28.43	25.25
5	3	1	28.53	26.77
6	3	1	49.62	52.34
7	3	1	6.75	11.07
8	3	1	17.71	16.46
9	3	1	21.25	20.89
10	3	1	14.57	9.30
11	3	1	4.65	11.24
13	3	1	12.30	17.26
0	4	1	67.96	78.66
1	4	1	70.70	113.20
2	4	1	45.76	46.92
3	4	1	36.05	33.39
4	4	1	21.32	17.63
5	4	1	53.27	47.21
6	4	1	47.16	41.87
7	4	1	43.76	46.95
8	4	1	22.52	26.12
9	4	1	12.48	12.47
10	4	1	4.44	8.05
11	4	1	9.43	7.95
12	4	1	4.78	17.79
14	4	1	11.19	11.11
0	5	1	10.29	16.80
1	5	1	65.30	72.65
2	5	1	51.68	53.54
3	5	1	23.97	9.20
5	5	1	18.74	16.75
6	5	1	48.57	46.44
7	5	1	15.38	14.62
8	5	1	41.25	40.67
9	5	1	14.10	13.93
10	5	1	11.09	4.31
11	5	1	10.69	11.99
13	5	1	8.73	8.06
14	5	1	9.93	13.57
0	6	1	4.19	7.22
1	6	1	83.06	83.50
2	6	1	40.19	43.59
3	6	1	12.07	11.09
4	6	1	40.86	46.79
5	6	1	55.05	48.70
6	6	1	50.51	47.91
7	6	1	14.62	17.75
8	6	1	10.00	7.04
9	6	1	19.51	18.56
10	6	1	13.86	17.61
11	6	1	4.85	12.85
12	6	1	11.16	11.06
13	6	1	13.33	19.41
14	6	1	11.03	17.38
16	6	1	8.48	11.58
0	7	1	2.43	1.47
1	7	1	60.29	61.67
2	7	1	39.46	36.77
3	7	1	98.37	102.28
4	7	1	53.69	54.76
5	7	1	60.60	53.94
6	7	1	37.43	32.32
7	7	1	1.69	8.38
8	7	1	12.67	10.07
9	7	1	11.85	13.58
10	7	1	13.33	7.17
11	7	1	34.71	37.50
12	7	1	13.28	11.93
13	7	1	13.28	14.64
14	7	1	10.92	6.69
0	8	1	10.58	3.50
1	8	1	21.38	13.08
2	8	1	62.37	58.82
3	8	1	79.05	81.05
4	8	1	60.97	63.73
5	8	1	40.52	37.24
6	8	1	29.75	28.05
7	8	1	13.04	17.73
8	8	1	8.73	17.47
10	8	1	26.39	34.16
12	8	1	14.25	8.80
13	8	1	11.14	11.04
14	8	1	9.58	13.04
0	9	1	20.50	17.79
1	9	1	43.28	41.52
2	9	1	12.35	16.30
3	9	1	57.72	59.00
4	9	1	29.09	25.51
5	9	1	50.67	53.19
6	9	1	37.77	37.92
7	9	1	19.13	17.27
8	9	1	14.31	8.23
9	9	1	18.92	17.89
10	9	1	20.24	21.19
11	9	1	30.07	38.32
12	9	1	17.42	26.83
13	9	1	13.91	16.40
14	9	1	8.10	10.46
16	9	1	5.28	7.62
0	10	1	39.75	40.00
1	10	1	59.76	60.48
2	10	1	19.95	17.52
3	10	1	18.68	15.50
4	10	1	20.58	19.67
5	10	1	44.77	40.37
6	10	1	34.21	31.91
7	10	1	24.68	22.39
8	10	1	0.10	8.16
10	10	1	18.63	18.52
11	10	1	14.25	9.19
14	10	1	7.84	7.25
0	11	1	60.66	57.46
1	11	1	18.31	13.65
2	11	1	51.42	46.28
3	11	1	2.95	2.98
4	11	1	16.41	16.72
5	11	1	12.12	15.71
6	11	1	23.78	21.22
7	11	1	18.05	7.49
8	11	1	21.54	18.01
9	11	1	19.79	22.58
10	11	1	11.24	8.28
11	11	1	13.30	12.57
12	11	1	4.91	6.32
0	12	1	12.85	9.17
1	12	1	50.78	47.43
2	12	1	12.01	6.67
3	12	1	20.19	20.08
4	12	1	15.02	11.57
5	12	1	12.75	13.93
7	12	1	30.75	33.63
8	12	1	13.04	10.86
9	12	1	10.01	8.06
10	12	1	12.33	7.65
11	12	1	4.96	6.41
12	12	1	8.32	3.55
0	13	1	56.11	55.45
1	13	1	14.75	15.35
2	13	1	34.71	33.38
3	13	1	30.56	15.02
4	13	1	19.01	17.80
5	13	1	24.17	23.52
6	13	1	17.39	15.81
7	13	1	11.38	5.69
8	13	1	14.17	15.09
9	13	1	8.73	9.76
10	13	1	13.22	12.88
0	14	1	37.53	37.66
1	14	1	29.91	25.92
2	14	1	42.83	42.23
3	14	1	18.90	15.04
4	14	1	33.05	33.81
5	14	1	13.81	10.82
6	14	1	13.67	10.36
7	14	1	3.46	8.89
8	14	1	10.06	6.48
9	14	1	12.27	8.57
10	14	1	11.99	12.14
12	14	1	7.63	9.47
13	14	1	6.92	6.57
0	15	1	62.87	38.36
1	15	1	33.52	33.47
2	15	1	13.85	11.91
3	15	1	25.12	25.89
4	15	1	10.40	8.32
5	15	1	20.66	21.83
7	15	1	17.52	14.04
8	15	1	4.99	5.04
9	15	1	4.89	8.71
10	15	1	4.72	6.06
12	15	1	8.21	8.45
0	16	1	15.01	15.83
1	16	1	13.46	12.81
2	16	1	4.70	5.66
3	16	1	35.95	37.87
4	16	1	12.70	11.28
5	16	1	21.24	19.03
6	16	1	14.54	12.68
7	16	1	13.57	15.60
0	17	1	17.89	14.46
1	17	1	23.17	23.65
2	17	1	24.26	21.96
3	17	1	14.83	14.47
4	17	1	11.59	6.38
5	17	1	13.11	14.34
6	17	1	15.96	14.17
9	17	1	4.44	3.79
0	18	1	16.68	18.20
1	18	1	16.26	15.35
2	18	1	18.02	17.89
5	18	1	14.96	15.50
6	18	1	15.83	13.73
7	18	1	10.72	11.68
0	19	1	14.22	12.77
1	19	1	5.25	6.56
2	19	1	13.25	9.76
6	19	1	9.71	9.01
0	20	1	12.65	10.36
1	20	1	12.49	11.13
4	20	1	6.31	7.62
0	21	1	2.06	10.39
1	21	1	9.13	9.04
2	21	1	9.39	9.12
3	21	1	8.65	7.95
3	22	1	6.63	6.17
4	22	1	4.02	7.06
6	22	1	6.54	7.73
3	23	1	1.48	5.97
5	23	1	4.70	5.32
0	24	1	7.23	11.14
2	24	1	6.10	7.80
0	0	2	45.19	41.81
1	0	2	82.96	75.73
2	0	2	136.17	122.44
3	0	2	111.59	135.78
4	0	2	31.56	30.46
5	0	2	0.87	3.32
6	0	2	22.94	26.48
7	0	2	58.97	60.70
8	0	2	30.86	34.30
10	0	2	25.21	22.01
11	0	2	19.14	15.15
12	0	2	21.01	22.63
14	0	2	20.79	28.28
18	0	2	5.68	7.94
0	1	2	37.27	29.07
1	1	2	77.84	122.86
2	1	2	202.92	212.65
3	1	2	34.28	27.56
4	1	2	106.82	101.51
5	1	2	64.98	65.48
6	1	2	42.46	41.07
7	1	2	50.76	47.21
8	1	2	23.54	20.32
9	1	2	14.75	15.19
10	1	2	13.52	11.45
11	1	2	10.18	6.38
12	1	2	10.66	7.76
13	1	2	5.46	10.11
14	1	2	5.46	9.96
0	2	2	103.96	97.49
1	2	2	69.10	68.79
2	2	2	105.63	108.96
3	2	2	107.95	110.58
5	2	2	69.07	64.59
5	2	2	69.07	64.59
6	2	2	47.40	48.94
7	2	2	54.50	50.58
8	2	2	22.67	20.33
9	2	2	19.03	21.90
10	2	2	6.79	7.34
11	2	2	12.53	13.88
12	2	2	7.55	6.41
13	2	2	5.46	7.78
14	2	2	5.44	6.00
0	3	2	89.74	77.41
1	3	2	105.84	110.09
2	3	2	77.73	77.02
3	3	2	54.79	56.29
4	3	2	67.23	70.19
5	3	2	65.35	60.33
6	3	2	19.66	16.48
7	3	2	15.10	10.46
8	3	2	29.74	31.34
9	3	2	19.80	23.73
10	3	2	18.21	19.27
11	3	2	8.92	10.11
12	3	2	14.22	12.51
13	3	2	5.46	4.40
14	3	2	5.43	7.04
0	4	2	52.70	50.45
1	4	2	27.27	19.06
2	4	2	40.48	41.55
3	4	2	60.89	57.89
4	4	2	68.02	71.09
5	4	2	42.31	39.47
6	4	2	14.70	11.97
7	4	2	28.61	27.83
8	4	2	8.58	9.44
9	4	2	13.86	11.26
10	4	2	16.36	14.90
11	4	2	13.77	10.67
12	4	2	14.28	9.23
13	4	2	19.77	19.53
0	5	2	35.42	28.77
1	5	2	52.79	56.65
2	5	2	65.43	69.54
3	5	2	58.73	59.73
4	5	2	70.24	71.67
5	5	2	9.71	6.83
6	5	2	18.48	17.97
7	5	2	17.53	16.63
8	5	2	25.73	25.93
9	5	2	6.68	6.71
10	5	2	16.62	22.23
11	5	2	13.91	12.19
13	5	2	17.34	13.34
14	5	2	5.36	4.59
0	6	2	22.77	19.08
1	6	2	56.19	65.41
2	6	2	69.04	59.54
3	6	2	31.39	31.87
4	6	2	45.13	42.40
5	6	2	19.77	22.68
6	6	2	19.59	20.72
7	6	2	26.31	29.48
8	6	2	30.14	27.33
9	6	2	19.34	19.78
10	6	2	17.69	21.93
11	6	2	5.33	11.61
12	6	2	31.85	38.48
13	6	2	13.40	15.12
0	7	2	13.68	13.28
1	7	2	94.70	98.04
2	7	2	49.85	51.77
3	7	2	70.70	72.96
4	7	2	38.38	37.84
5	7	2	46.80	49.84
6	7	2	26.21	26.26
7	7	2	24.42	22.94
8	7	2	35.76	42.14
9	7	2	7.02	5.02
10	7	2	18.77	20.22
11	7	2	18.68	20.46
0	8	2	21.96	27.83
1	8	2	10.16	13.00
2	8	2	42.02	44.68
3	8	2	25.95	23.42
4	8	2	44.84	47.29
5	8	2	2.30	3.54
6	8	2	21.03	22.10
7	8	2	28.17	30.80
8	8	2	27.87	22.81
9	8	2	14.39	11.65
10	8	2	37.83	41.23
11	8	2	10.87	14.00
12	8	2	18.98	24.44
13	8	2	10.77	8.13
0	9	2	56.00	58.12
1	9	2	32.10	32.07
2	9	2	60.23	60.45
3	9	2	14.72	14.09
4	9	2	31.67	30.87
5	9	2	12.30	17.81
6	9	2	7.05	7.36
7	9	2	21.41	20.08
8	9	2	4.99	6.96
9	9	2	15.65	14.75
11	9	2	17.31	18.09
12	9	2	17.24	17.19
13	9	2	10.61	11.23
0	10	2	60.44	59.58
1	10	2	20.17	17.96
2	10	2	57.35	58.42
3	10	2	30.53	33.10
4	10	2	39.96	42.34
5	10	2	21.99	20.82
6	10	2	8.19	9.00
7	10	2	11.59	15.90
8	10	2	21.28	23.79
9	10	2	19.22	20.79
10	10	2	21.78	23.38
11	10	2	13.44	11.10
1	11	2	22.91	21.38
2	11	2	13.19	16.51
3	11	2	35.58	35.11
4	11	2	25.07	24.73
5	11	2	16.73	16.74
6	11	2	13.14	9.80
7	11	2	8.95	1.26
8	11	2	19.11	15.38
9	11	2	21.67	20.46
10	11	2	13.44	7.47
11	11	2	10.88	12.27
13	11	2	8.68	10.33
1	12	2	10.63	9.51
1	12	2	10.63	9.51
2	12	2	34.23	31.38
3	12	2	10.87	8.23
4	12	2	48.75	44.66
5	12	2	28.27	27.69
7	12	2	5.89	4.70
8	12	2	9.37	7.86
12	12	2	10.29	10.86
13	12	2	6.78	11.05
0	13	2	39.14	39.97
1	13	2	27.84	25.44
2	13	2	37.74	35.48
4	13	2	17.55	18.09
5	13	2	28.80	27.46
6	13	2	15.97	16.41
7	13	2	14.83	10.05
8	13	2	18.16	19.50
9	13	2	14.49	13.96
10	13	2	14.28	14.92
0	14	2	20.09	19.22
1	14	2	30.64	31.36
2	14	2	12.99	12.80
3	14	2	20.03	20.41
4	14	2	4.86	7.35
5	14	2	4.25	7.11
6	14	2	15.13	12.28
7	14	2	16.84	15.75
8	14	2	13.41	7.19
0	15	2	31.38	29.70
1	15	2	25.92	24.30
2	15	2	17.36	11.38
3	15	2	6.28	5.95
4	15	2	19.22	20.12
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6	15	2	21.57	19.23
7	15	2	15.05	14.85
8	15	2	12.07	8.81
9	15	2	10.53	4.51
10	15	2	13.38	14.93
12	15	2	6.15	8.16
0	16	2	18.51	15.27
1	16	2	20.41	21.60
2	16	2	23.97	25.53
3	16	2	11.29	7.91
4	16	2	16.21	14.63
5	16	2	14.99	14.60
6	16	2	17.53	18.78
7	16	2	3.61	10.03
8	16	2	10.50	7.42
9	16	2	5.06	5.21
10	16	2	9.53	3.57
11	16	2	6.23	7.11
0	17	2	16.26	16.54
1	17	2	19.08	18.04
2	17	2	16.23	19.87
3	17	2	17.16	14.33
4	17	2	18.14	17.64
9	17	2	12.54	13.82
11	17	2	3.96	7.48
0	18	2	3.74	4.62
1	18	2	10.63	9.35
2	18	2	15.97	14.32
3	18	2	11.54	6.69
4	18	2	18.34	20.08
5	18	2	10.08	9.64
6	18	2	11.58	5.84
11	18	2	4.86	9.89
0	19	2	3.59	4.80
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2	19	2	2.85	3.30
3	19	2	9.27	8.80
4	19	2	8.32	8.06
5	19	2	11.04	9.74
1	20	2	14.36	12.99
3	20	2	12.20	12.73
4	20	2	3.48	3.87
5	20	2	6.18	7.73
7	20	2	8.03	7.37
1	21	2	9.77	9.47
2	21	2	8.90	6.73
4	21	2	10.37	8.20
0	22	2	5.91	5.36
1	22	2	12.70	11.75
2	22	2	2.98	2.93
4	22	2	7.86	8.67
6	22	2	2.80	9.15
7	22	2	4.17	5.47
1	23	2	10.51	9.21
2	23	2	2.38	2.01
3	23	2	6.57	4.14
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2	0	3	10.45	9.00
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5	0	3	66.82	67.21
6	0	3	27.26	27.90
7	0	3	11.14	7.70
8	0	3	2.01	3.87
9	0	3	13.80	22.00
10	0	3	9.40	7.82
11	0	3	11.90	9.69
12	0	3	2.46	3.26
13	0	3	10.98	10.69
14	0	3	2.48	4.38
15	0	3	10.18	11.83
0	1	3	80.71	83.26
1	1	3	49.44	41.97
2	1	3	90.72	83.72
3	1	3	105.66	98.55
4	1	3	79.94	76.06
5	1	3	38.98	39.53
6	1	3	64.29	60.19
7	1	3	37.24	35.28
8	1	3	15.75	12.33
9	1	3	17.63	16.22
10	1	3	13.80	16.10
11	1	3	11.51	8.36
13	1	3	7.66	7.82
15	1	3	7.18	5.22
0	2	3	38.35	42.76
1	2	3	82.14	81.09
2	2	3	56.12	48.65
3	2	3	49.73	44.59
4	2	3	65.43	59.35
5	2	3	24.58	19.59
6	2	3	57.46	50.68
7	2	3	4.89	4.31
9	2	3	23.39	25.35
10	2	3	12.01	13.70
11	2	3	10.34	9.24
0	3	3	84.49	90.31
1	3	3	85.36	88.22
2	3	3	80.21	73.88
3	3	3	38.46	39.24
4	3	3	22.17	17.81
5	3	3	14.73	13.34
6	3	3	53.74	44.45
7	3	3	30.41	27.17
8	3	3	14.96	14.13
9	3	3	25.87	25.86
10	3	3	7.00	8.60
11	3	3	12.75	9.83
12	3	3	15.18	15.53
13	3	3	10.85	13.44
0	4	3	69.66	70.71
1	4	3	27.61	24.98
2	4	3	31.73	31.30
3	4	3	38.51	36.82
4	4	3	21.43	24.12
5	4	3	36.74	34.94
6	4	3	41.97	40.57
7	4	3	5.80	5.96
8	4	3	38.19	32.28
9	4	3	18.87	20.49
10	4	3	8.68	10.43
11	4	3	12.86	14.28
12	4	3	10.79	11.43
13	4	3	7.65	9.39
0	5	3	44.73	43.87
1	5	3	63.97	62.38
2	5	3	75.62	69.53
3	5	3	17.07	19.73
4	5	3	24.42	28.00
5	5	3	4.15	8.59
6	5	3	30.45	28.45
7	5	3	20.91	23.92
8	5	3	16.92	22.18
9	5	3	15.97	18.54
10	5	3	20.33	28.49
14	5	3	7.37	5.40
15	5	3	6.09	9.67
0	6	3	31.97	28.24
1	6	3	73.19	70.52
2	6	3	48.98	45.94
3	6	3	60.17	55.29
4	6	3	23.10	18.56
5	6	3	24.78	25.39
6	6	3	15.09	18.32
7	6	3	34.08	31.58
8	6	3	22.77	22.57
9	6	3	17.76	23.86
10	6	3	20.00	24.44
11	6	3	17.73	18.66
12	6	3	16.20	21.83
15	6	3	6.73	4.92
0	7	3	24.28	22.19
1	7	3	51.41	47.63
2	7	3	13.04	9.87
3	7	3	58.23	54.71
4	7	3	59.28	66.32
5	7	3	10.69	8.38
6	7	3	33.65	27.87
7	7	3	19.08	15.24
8	7	3	4.78	14.18
9	7	3	5.04	17.41
10	7	3	16.58	17.95
11	7	3	20.14	22.42
15	7	3	4.62	5.95
0	8	3	37.13	38.38
1	8	3	44.21	42.99
2	8	3	46.96	39.95
3	8	3	55.13	49.56
4	8	3	4.93	8.24
5	8	3	34.21	32.36
6	8	3	13.72	13.21
7	8	3	22.19	24.18
8	8	3	13.96	21.77
9	8	3	16.26	17.29
10	8	3	14.87	18.76
11	8	3	14.31	10.78
12	8	3	10.88	4.50
13	8	3	9.08	7.75
0	9	3	51.99	48.23
1	9	3	40.81	46.74
2	9	3	29.01	32.50
3	9	3	58.20	52.30
4	9	3	34.95	34.17
5	9	3	23.28	25.78
6	9	3	9.23	2.25
7	9	3	16.73	15.27
8	9	3	16.05	20.20
9	9	3	19.87	22.88
10	9	3	13.17	10.80
12	9	3	7.55	6.50
13	9	3	10.26	5.46
0	10	3	16.21	16.39
1	10	3	13.48	12.32
2	10	3	40.36	41.36
3	10	3	23.31	18.15
4	10	3	13.51	19.04
5	10	3	22.60	15.47
6	10	3	9.48	12.15
7	10	3	19.18	19.16
8	10	3	21.49	19.20
9	10	3	32.94	34.60
10	10	3	14.31	15.28
0	11	3	2.79	2.59
1	11	3	28.37	27.91
2	11	3	21.96	21.88
3	11	3	15.41	10.76
4	11	3	13.57	11.41
5	11	3	19.48	18.83
6	11	3	16.26	15.52
7	11	3	21.06	27.33
8	11	3	14.07	15.60
9	11	3	12.07	5.99
10	11	3	12.11	13.24
11	11	3	14.10	12.53
0	12	3	37.51	40.58
1	12	3	33.25	35.15

Table 2 (*cont.*)

lute configuration of duclauxin itself is then established as (I) (Fig. 1). All figures presented in this paper are drawn with the correct absolute configuration.

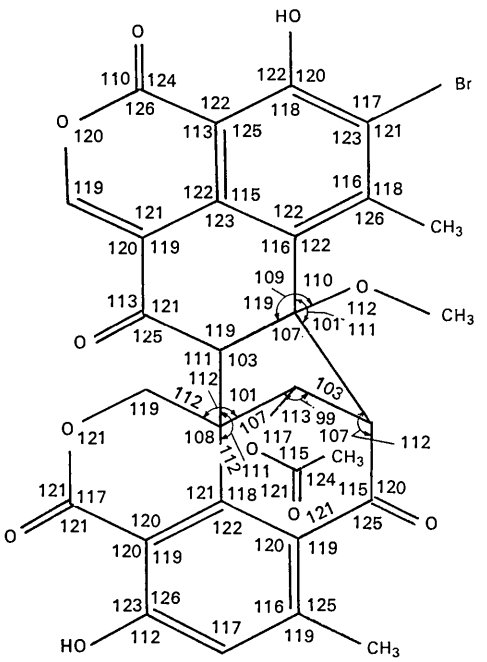

Fig. 4. Bond angles (°).

Table 3. *Comparison of the observed and calculated intensity differences used for the establishment of absolute configuration*

h	k	l	$\frac{F_c^2(hkl)}{F_c^2(\bar{h}\bar{k}\bar{l})}$	$\frac{I_o(hkl)}{I_o(\bar{h}\bar{k}\bar{l})}$
3	1	1	0·873	>1
5	1	1	1·107	<1
10	1	1	1·136	<1
5	2	1	0·882	>1
2	3	1	1·130	<1
7	3	1	1·185	<1
3	1	2	0·850	>1
8	1	2	0·767	>1
8	2	2	1·186	<1
4	2	2	0·867	>1
11	2	2	1·179	<1
6	3	2	0·717	>1
9	3	2	1·118	<1
12	3	2	0·897	>1
4	1	1	0·961	>1

Discussion of the structure

The molecular structure

The present analysis revealed that monobromoduclauxin possesses a unique structure previously unknown. The molecule consists of two nearly planar tricyclic ring-systems of oxygen heterocycles, one containing an isocoumarin and the other containing a dihydroisocoumarin nucleus. A surprising feature re-

Table 4. *The bond distances arranged in groups of similar type*

C–C single bonds		Aromatic C–C bonds	
C(1)—C(2)	1·51 Å	*A* ring	
C(7)—C(8)	1·58	C(2)–C(3)	1·38 Å
C(8)—C(9)	1·50	C(3)–C(4)	1·39
C(8)—C(23)	1·54	C(4)–C(5)	1·32
C(9)—C(25)	1·58	C(5)–C(6)	1·36
C(15)–C(16)	1·48	C(6)–C(7)	1·44
C(23)–C(24)	1·54	C(7)–C(2)	1·38
C(24)–C(25)	1·52		
C(25)–C(26)	1·54	Mean value	1·38 Å
C(28)–C(29)	1·46		
		D ring	
Mean value	1·53 Å	C(16)–C(17)	1·47 Å
		C(17)–C(18)	1·36
		C(18)–C(19)	1·33
		C(19)–C(20)	1·35
		C(20)–C(21)	1·40
		C(21)–C(16)	1·42
		Mean value	1·39 Å

C–O bonds	
C(22)–O(7) (ketone)	1·18 Å
C(10)–O(3) (ketone)	1·21
C(28)–O(9) (ketone)	1·22
C(27)–O(11) (lactone)	1·24
C(13)–O(4) (lactone)	1·30
C(13)–O(5) (lactone)	1·31
C(27)–O(10) (lactone)	1·32
C(26)–O(10) (lactone)	1·33
C(4)—O(1) (phenol)	1·36
C(12)–O(4) (lactone)	1·37
C(28)–O(8) (acetyle)	1·40
C(18)–O(6) (phenol)	1·40
C(24)–O(8) (ether)	1·42
C(14)–O(2) (ether)	1·49
C(8)—O(2) (ether)	1·52

vealed in the present analysis is that these two tricyclic systems are joined together through a five-membered ring to form a hinge- or castanets-like structure.

The bond lengths and angles in the molecule, calculated from the coordinates given in Table 1, are shown in Figs. 3 and 4. The mean estimated standard deviations in bond distances are 0·022 Å for Br–C, 0·030 Å for C–C and 0·027 Å for C–O bonds, and those in bond angles are 1·7° for tetrahedral C–C–C bonds and 2·0° for aromatic C–C–C bonds. In Table 4 are listed the bond lengths arranged in groups of similar type, and in Fig. 5 are shown the mean values of the bond distances involved in each of the six kinds of ring *A* to *G*. It is interesting to see the differences existing between the corresponding values in the upper

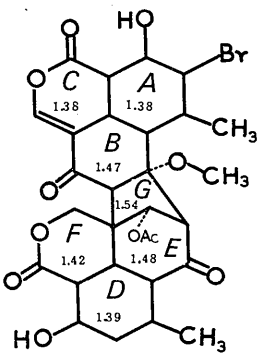

Fig. 5. Mean values of the bond lengths involved in each of the six ring systems (Å).

Table 5. *The perpendicular distances of the atoms from the best planes*

Upper half of the molecule

Plane through *A* and *C* rings (distances from the least-squares plane formed by the following ten atoms)

C(2)	−0·004 Å
C(3)	0·061
C(4)	0·042
C(5)	−0·050
C(6)	−0·012
C(7)	−0·072
C(11)	0·053
C(12)	0·039
O(4)	0·002
C(13)	−0·060

Distances from the least-squares plane formed by the above ten atoms

C(1)	−0·002
Br	0·189
O(1)	0·009
O(5)	−0·012
O(3)	0·613
C(8)	−0·327
C(9)	−0·332
C(10)	0·078

Plane through ketone group at ring *B*

C(9)	0·013
C(10)	−0·038
C(11)	0·011
O(3)	0·014

Plane through *B* ring

C(6)	−0·056
C(7)	0·085
C(8)	−0·016
C(9)	−0·092
C(10)	0·129
C(11)	−0·050

Distances from the above plane

C(2)	0·210
C(5)	−0·224
C(12)	−0·256
O(3)	0·605

Lower half of the molecule

Plane through *D* ring

C(16)	0·029
C(17)	−0·021
C(18)	0·016
C(19)	−0·019
C(20)	0·027
C(21)	−0·033

Distances from the above plane

C(15)	0·054
C(27)	0·092
C(25)	0·101
C(22)	−0·051
O(6)	0·091

Plane through ketone group at ring *E*

C(21)	−0·005
C(22)	0·017
C(23)	−0·005
O(7)	−0·007

Distances from the above plane

C(20)	−0·258
C(25)	−0·472
C(24)	−1·147

Plane through lactone group at ring *F*

C(19)	−0·012
C(27)	0·042
O(10)	−0·014
O(11)	−0·016

Distances from the above plane

C(20)	0·169
C(25)	0·340
C(26)	−0·252

Plane through acetyl group

O(8)	−0·017
C(28)	0·053
C(29)	−0·016
O(9)	−0·020

Distances from the plane through C(8), C(9) and C(23) of *G* ring:

C(24)	0·485
C(25)	−0·345

and lower half of the molecule. The mean values 1·38 Å and 1·39 Å, found in *A* and *D* rings respectively, indicate the aromatic nature of these rings. However, there is a significant difference between the mean values of bond lengths in the rings *C* and *F*. A smaller value of 1·38 Å of the *C* ring as compared with 1·42 Å of the *F* ring should be a consequence of the double bond between C(11) and C(12) and the extension of the resonance structure over the rings *A* and *C*. These values are comparable with those of bromo-3-hydroxy-4-coumarin monohydrate (1·39 Å of the benzene ring and 1·40 Å of the heterocyclic ring, Gaultier & Hauw,

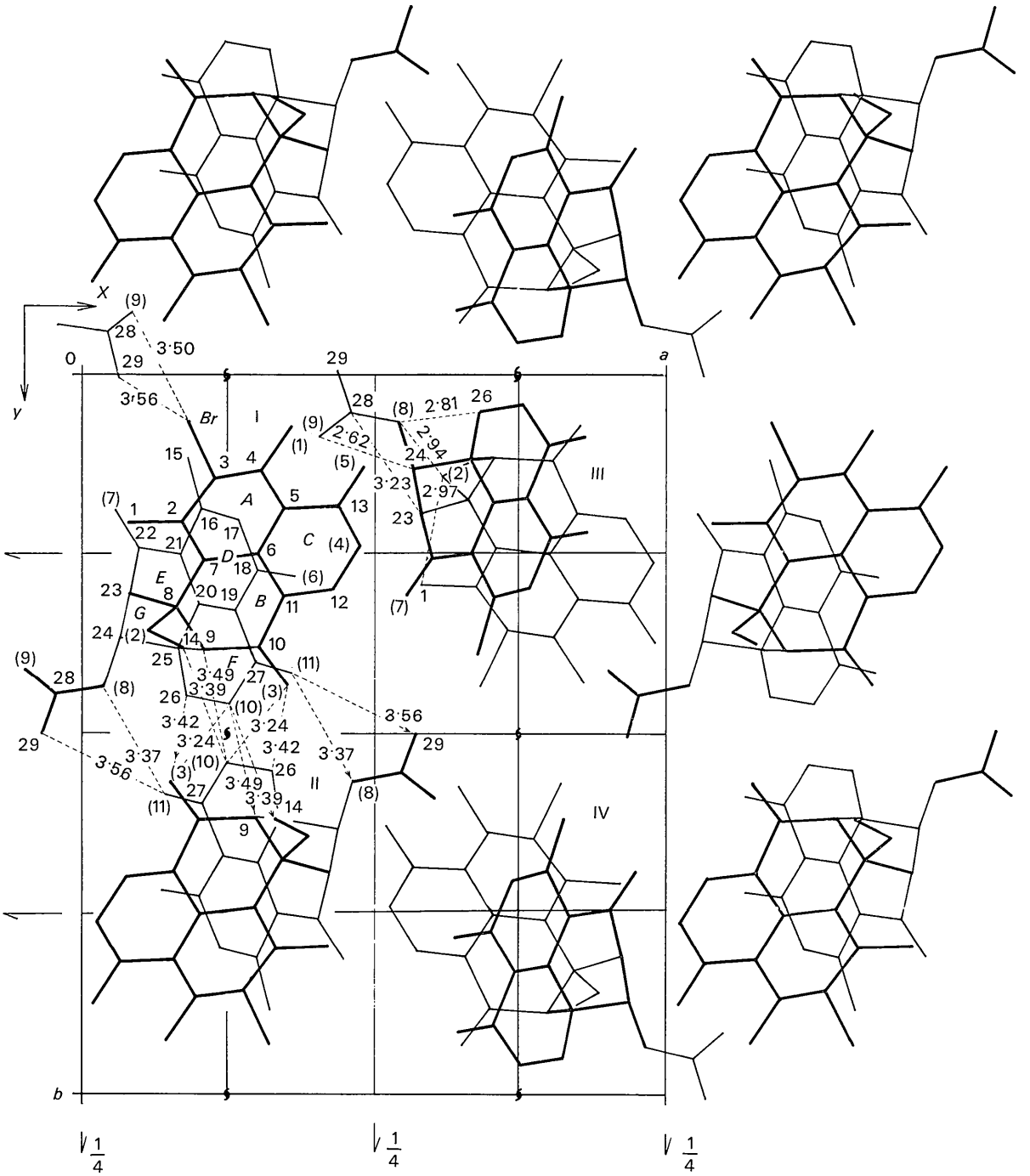

Fig. 6. Crystal structure of monobromoduclauxin projected along the *c* axis. To represent the correct absolute configuration the positive direction of **c** should be taken as upwards, towards the observer. Intramolecular short contacts less than or equal to 3·30 Å are shown for molecule III. Intermolecular short contacts less than or equal to 3·60 Å from molecule I are also shown.

1965). It should be noted in this connexion that every skeletal chemical reaction investigated is found to take place mainly in *A*, *B* and *C* rings.

The eighteen atoms comprising the main part of the upper half of the molecule (C(1)~C(13), O(1), O(3), O(4), O(5) and Br: see Fig. 2 or 7) lie roughly in a plane.

Table 6. *Shortest approaches less than or equal to* 3·6 Å *of atoms between the confronted aromatic rings*

Between ring atoms

C(6)—C(20)	3·56 Å	C(7)—C(22)	2·80
C(6)—C(21)	3·38	C(7)—C(25)	3·57
C(7)—C(21)	3·25	C(8)—O(7)	3·42
C(11)–C(19)	3·55	C(8)—C(20)	3·04
C(11)–C(20)	3·21	C(8)—C(21)	3·06
C(11)–C(21)	3·58	C(9)—C(19)	3·44
		C(9)—C(21)	3·22
Including exocyclic atoms		C(9)—C(22)	3·29
C(1)–C(22)	3·56	C(10)–C(19)	3·29
C(1)–C(23)	3·22	C(10)–O(10)	3·20
C(1)–O(7)	3·41	C(10)–C(20)	2·84
C(2)–O(7)	3·31	C(10)–C(23)	3·60
C(2)–C(22)	3·20	C(10)–C(27)	3·37
C(2)–C(23)	3·13	C(11)–C(25)	3·41
C(6)–C(22)	3·53		
C(7)–O(7)	3·39		

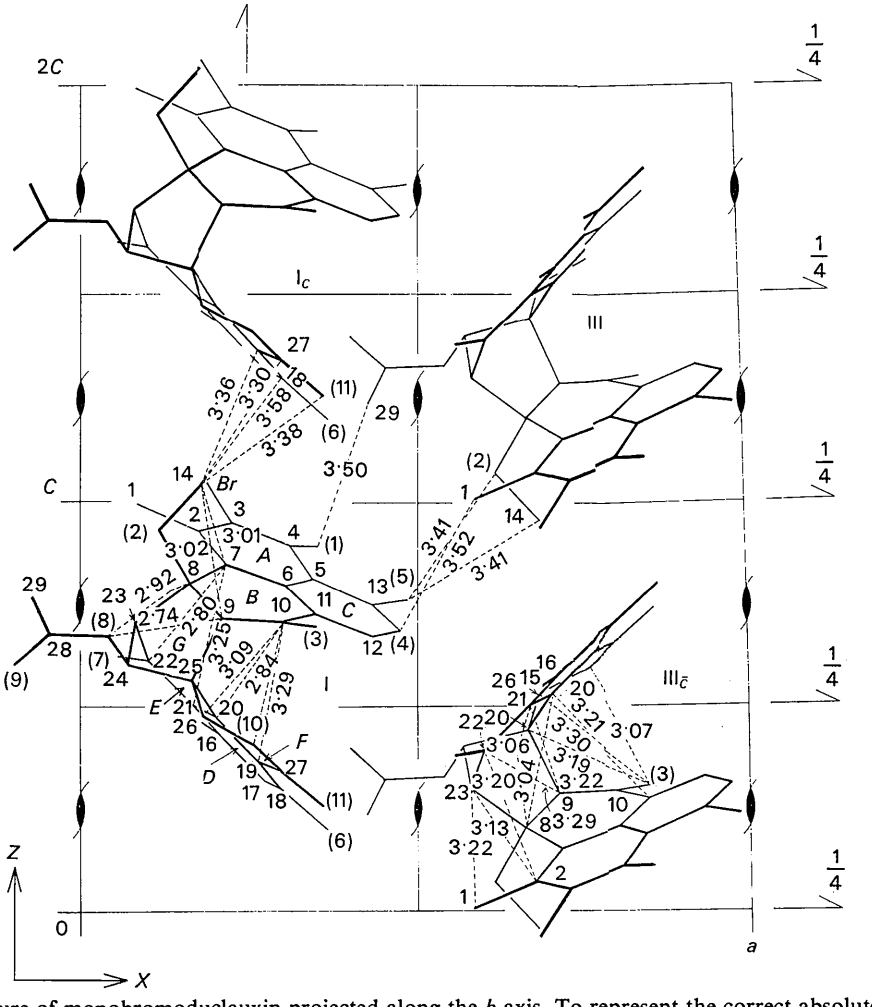

Fig. 7. Crystal structure of monobromoduclauxin projected along the *b* axis. To represent the correct absolute configuration the positive direction of **b** should be taken as upwards towards the observer. Molecules II and IV of Fig. 6 are omitted for the sake of simplicity. Intramolecular contacts are shown for molecules I, III and III$\bar{c}$. Intermolecular contacts from molecule I are also shown.

Deviations from the least-squares plane formed by the thirteen atoms C(1)~C(7), C(11)~C(13), O(1), O(4) and O(5) are found to be 0·19 Å for Br, −0·33 Å for C(8), −0·33 Å for C(9), 0·08 Å for C(10), and 0·61 Å for O(3). The seventeen atoms comprising the main part of the lower half of the molecule [C(15)~C(27), O(6), O(7), O(10) and O(11)] also lie roughly in a plane. Deviations from the least-squares plane formed by the eleven atoms C(15)~C(22), C(25), C(27), and O(10) are found to be 0·14 Å for C(23), −0·76 Å for C(24), −0·50 Å for C(26), 0·15 Å for O(6), −0·40 Å for O(7) and 0·18 Å for O(11). The dihedral angle between these two planes is 34°25′. The planarity may well be described by dividing the ring systems as shown in Table 5. It is seen from Table 5 that the isocoumarin nucleus in the upper part of the molecule is slightly bent so as to bring the bromine and the C(11), C(12) atoms away from the lower part of the molecule. The atoms comprising ring *B* do not lie in a plane; the fact that the atoms C(7), C(10), C(2) and O(3) lie respectively 0·09 Å, 0·13 Å, 0·21 Å and 0·61 Å above the mean plane indicates the deformation to a boat conformation. In ring *D*, on the other hand, a slight deformation to the chair conformation is observed. Ring *G* which connects the upper and lower half of the molecule takes a so-called 2-*endo* and 3-*exo* conformation; the atoms C(24) and C(25) are displaced 0·49 Å and 0·35 Å, respectively, above and below the plane passing through the atoms C(8), C(9) and C(23).

The atoms O(1), C(4), C(5), C(13) and O(5) form a six membered ring together with the hydrogen atom attached to O(1) or O(5). The distance between O(1) and O(5), 2·62 Å, suggests a strong intramolecular hydrogen bond. Only a small shift of the hydrogen atom would cause the conversion of the structure to another tautomeric form. However, the assignment of the tautomeric form shown in Fig. 3 is made on the basis of the difference between the two C–O distances such that C(4)–O(1) = 1·36 Å and C(13)–O(5) = 1·31 Å. The same argument is also applied to the corresponding part [O(6), C(18), C(19), C(27), O(11)] of the lower half of the molecule. Here, the intramolecular hydrogen bond distance between O(6) and O(11) is 2·56 Å.

Several very close approaches of the atoms are observed between the upper and the lower parts of the molecule. Some of the atoms are forced to come to very short distances on account of the peculiar structure of the molecule. Those which are less than or equal to 3·30 Å are shown for molecule III in Fig. 6 and for molecule I, III and $III_{\bar{c}}$ in Fig. 7. In these Figures, contacts of the atoms at the second next positions are not shown. It is seen that the shortest approaches down to 2·84 Å are found for the distances from O(3), C(10) and C(11) of ring *B* to the atoms of ring *F*. The maximum overlap of the upper and the lower halves of the molecule takes place mostly in this part. The shortest approaches found between the aromatic rings (*AC*) and *D* are listed in Table 6.

The crystal structure

Two projections of the structure viewed along the *c* and *b* axes are shown in Figs. 6 and 7 respectively. The shortest intermolecular distances less than or equal to 3·60 Å, from molecule I to the surrounding molecules, are also shown in these Figures. Although the molecules possess a strange structure resembling a hinge with flapping wings, there is no peculiar feature in the packing of the molecules. They are packed together mainly through van der Waals forces as if the molecule possessed a massive structure. Close contacts are observed among the molecules I and II and their translation equivarents along the *c* axis.

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References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

GAULTIER, J. & HAUW, C. (1965). *Acta Cryst.* **19**, 927.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

OGIHARA, Y., IITAKA, Y. & SHIBATA, S. (1965). *Tetrahedron Letters*, No. 18, 1289.

SHIBATA, S., OGIHARA, Y., TOKUTAKE, N. & TANAKA, O. (1965). *Tetrahedron Letters*, No. 18, 1287.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

VAN DEN HENDE, J. H. (1961). *Crystallographic Structure Factor and Least-Squares Refinement Program for the IBM 7090 Computer*. Esso Research and Engineering Co.