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Configurations of Heptitols. The Crystal and Molecular Structure of 1-*O*-(*p*-Bromobenzenesulphonyl)-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*gluco*heptitol

BY A. CAMERMAN AND J. TROTTER

Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada

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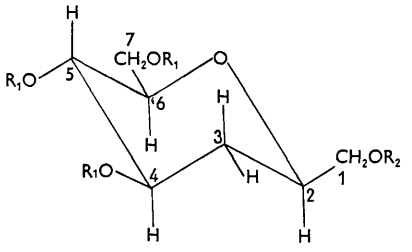
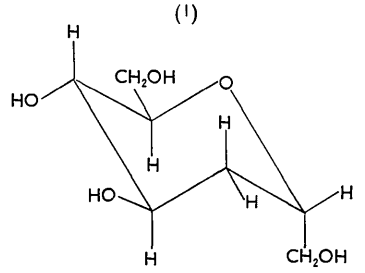
Hydroformylation of tri-*O*-acetyl D-glucal yields two isomeric products, and to establish the configurations X-ray analysis of the *p*-bromobenzenesulphonyl derivative of one of these has been carried out. The crystals of the derivative, $C_{19}H_{23}O_{10}SBr$, are orthorhombic, with four molecules in a unit cell of dimensions $a = 13{\cdot}71$, $b = 29{\cdot}37$, $c = 5{\cdot}79$ Å, space group $P2_12_12$. The intensities of the reflexions were measured with a scintillation counter and Cu $K\alpha$ radiation. The bromine and sulphur positions were determined from the three-dimensional Patterson function, and the carbon and oxygen atoms were located from three successive three-dimensional Fourier summations. The positional and thermal parameters were then refined by seven cycles of differential syntheses, and five cycles of least squares, anisotropic temperature factors being introduced in the final cycles for the bromine atom and for the atoms of the acetyl groups. The final R value was 0·090. The derivative studied is 1-*O*-(*p*-bromobenzenesulphonyl)-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*gluco*-heptitol, and this establishes the structures and configurations of the triacetyl derivatives and of the parent polyols. The sugar ring is in the chair conformation with all the substituent groups in equatorial positions; the absolute configuration is established since the compound is derived from D-glucose. The bond distances and valency angles are all normal, and the intermolecular separations correspond to van der Waals interactions.

Introduction

Hydroformylation of tri-*O*-acetyl-D-glucal yields two isomeric products, which can be deacetylated, and the parent polyols then separated by paper chromatography. The fast running fraction has m.p. 138 °C, $[\alpha]_D^{20} = -1°$, and the other isomer m.p. 153 °C, $[\alpha]_D^{20} = +60°$. Rotation rules and proton magnetic resonance spectra suggest the tentative structures (I) ($R_1 = R_2 = H$) for the lower-melting isomer, and (II) for the higher-melting isomer, that is the compounds are isomeric anhydrodeoxyheptitols which differ only in the configuration of the hydroxymethyl group at C(2) (Rosenthal & Koch, 1964).



(I)



(II)

To establish the structures conclusively an X-ray analysis of the *p*-bromobenzenesulphonyl triacetyl derivative of the lower-melting polyol was undertaken. This derivative was prepared by treatment of the mixture of triacetylanhydrodeoxyheptitols with *p*-bromobenzenesulphonyl chloride, and the required compound preferentially crystallized out of the reaction mixture. It was subsequently deacetylated, and the *p*-bromobenzenesulphonyl group was removed, to yield a pure sample of the lower-melting polyol. The analysis described in this paper shows that the derivative has structure (I) ($R_1 = CH_3.CO-$, $R_2 = BrC_6H_4.SO_2^-$), so that the tentative structural assignment was correct. The systematic name of the derivative examined is 1-*O*-(*p*-bromobenzenesulphonyl)-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*gluco*-heptitol.

Experimental

Crystals of the *p*-bromobenzenesulphonyl triacetyl derivative from methanol–water are needles elongated along *c* with (100) and (010) developed. The unit-cell dimensions and space group were determined from rotation, Weissenberg and precession films, and the density was measured by flotation in aqueous caesium bromide.

Crystal data

(λ(Cu $K\alpha$) = 1·5418 Å, λ(Mo $K\alpha$) = 0·7107 Å)

$C_{19}H_{23}O_{10}SBr$.

M = 523·4, m.p. 104 °C.
Orthorhombic,

$a = 13{\cdot}71 \pm 0{\cdot}03$, $b = 29{\cdot}37 \pm 0{\cdot}08$, $c = 5{\cdot}79 \pm 0{\cdot}01$ Å.

U = 2331 Å^3.
$D_m \sim 1{\cdot}5$ g.cm^{-3}, $Z = 4$, $D_x = 1{\cdot}49$ g.cm^{-3}.
Absorption coefficients for X-rays,

$\lambda = 1{\cdot}5418$ Å, $\mu = 39$ cm^{-1},
$\lambda = 0{\cdot}7107$ Å, $\mu = 20$ cm^{-1}.

$F(000) = 1072$.
Absent spectra: $h00$ when h is odd, $0k0$ when k is odd.
Space group $P2_12_12$.

The intensities of all reflexions with 2θ(Cu $K\alpha$) $\leq 90°$ (corresponding to a minimum interplanar spacing $d = 1{\cdot}09$ Å) were measured on a G.E. XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, Cu $K\alpha$ radiation (nickel filter and pulse height analyser), and the moving-crystal moving-counter technique (Furnas, 1957). All the intensities were corrected for background, Lorentz and polarization factors were applied, and the structure amplitudes were derived. The crystal used was mounted with c parallel to the φ axis of the goniostat, and had a small uniform cross-section, so that absorption corrections were not considered necessary. 851 reflexions were observed, 74% of the total number in the range $0 < 2\theta$(Cu $K\alpha$) $\leq 90°$.

Structure analysis

The bromine and sulphur atom positions were determined from the three-dimensional Patterson function, and a three-dimensional Fourier series was summed with phases based on the Br and S atoms. On the resulting electron-density distribution fourteen peaks, in addition to the bromine and sulphur peaks, were chosen as atomic sites without any regard for chemical considerations. A second Fourier synthesis, phased on these sixteen atoms, revealed positions for 24 atoms in all, the general structure of the molecule now being clear, and a third Fourier showed all 31 atoms in

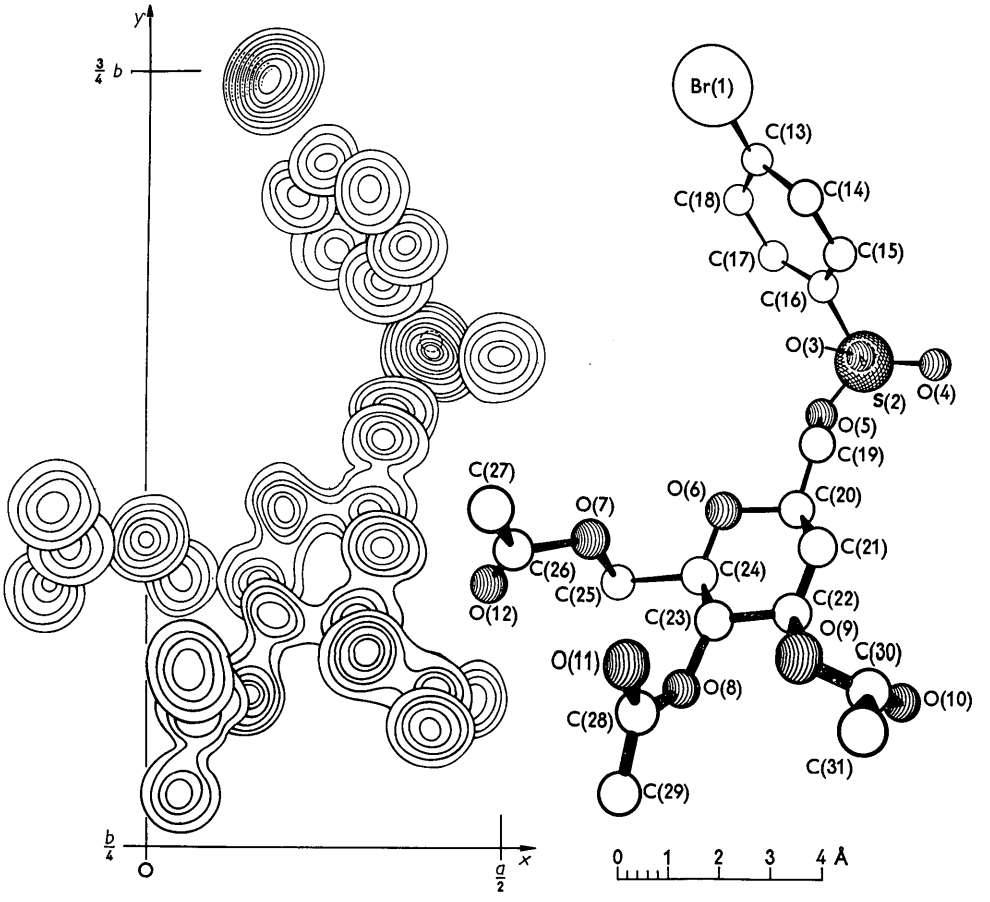


Fig. 1. Superimposed sections of the three-dimensional electron-density distribution, taken through the atomic centres parallel to (001). Contours start at 2 e.Å^{-3} and are at intervals of 1 e.Å^{-3}, except for Br(1) and S(2) which start at zero and are at intervals of 2·5 e.Å^{-3}. A perspective drawing of the molecule is also shown.

Table 1. *Measured and calculated structure amplitudes*

Unobserved reflexions, which are listed as 0·0, have threshold values in the range 5–17

H.	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
0	2	0	74·8	62·0	4	22	0	0·0	14·2	10	1	0	0·0	13·1	2	22	1	21·5	16·3
0	4	0	53·6	51·8	4	23	0	0·0	1·6	10	2	0	44·6	41·8	2	23	1	0·0	11·2
0	6	0	97·2	103·7	4	24	0	22·4	22·5	10	3	0	16·0	20·8	2	24	1	0·0	7·5
0	8	0	40·4	35·7	4	25	0	0·0	4·9	10	4	0	0·0	0·2	2	25	1	20·5	21·4
0	10	0	210·9	226·7	5	1	0	9·9	6·0	10	5	0	16·7	14·7	2	26	1	0·0	10·8
0	12	0	52·0	54·3	5	2	0	30·5	32·8	10	6	0	16·7	16·6	3	0	1	44·3	44·0
0	14	0	20·2	12·9	5	3	0	0·0	11·1	10	7	0	23·1	23·1	3	1	1	38·2	35·2
0	16	0	61·9	64·2	5	4	0	25·0	19·4	10	8	0	48·4	48·5	3	2	1	71·9	73·4
0	18	0	27·9	31·0	5	5	0	0·0	7·9	10	9	0	22·1	26·0	3	3	1	51·7	50·3
0	20	0	0·0	6·6	5	6	0	36·6	35·6	10	10	0	37·2	34·3	3	4	1	94·0	92·0
0	22	0	39·5	37·9	5	7	0	59·4	60·0	10	11	0	26·0	26·7	3	5	1	38·8	39·0
0	24	0	17·6	21·4	5	8	0	17·9	20·2	10	12	0	24·4	18·5	3	6	1	129·4	126·8
0	26	0	16·7	17·5	5	9	0	52·3	52·9	10	13	0	22·4	21·0	3	7	1	13·8	15·6
1	1	0	41·7	39·4	5	10	0	62·9	67·2	10	14	0	18·6	15·2	3	8	1	31·1	27·6
1	2	0	4·5	1·3	5	11	0	11·5	9·9	10	15	0	27·2	23·4	3	9	1	83·1	79·7
1	3	0	21·5	20·4	5	12	0	16·3	17·7	10	16	0	22·8	22·8	3	10	1	80·6	75·3
1	4	0	14·7	11·4	5	13	0	32·4	32·0	11	1	0	32·7	32·0	3	11	1	42·3	39·4
1	5	0	17·9	16·7	5	14	0	70·3	72·2	11	2	0	0·0	1·1	3	12	1	30·5	26·8
1	6	0	90·8	92·1	5	15	0	0·0	5·6	11	3	0	0·0	0·3	3	13	1	14·1	43·4
1	7	0	57·1	49·7	5	16	0	16·0	21·3	11	4	0	0·0	3·4	3	14	1	21·8	22·3
1	8	0	40·4	46·2	5	17	0	29·8	28·8	11	5	0	0·0	6·1	3	15	1	49·7	53·1
1	9	0	75·4	70·4	5	18	0	24·0	28·8	11	6	0	0·0	5·3	3	16	1	53·3	54·6
1	10	0	19·2	13·5	5	19	0	0·0	3·3	11	7	0	26·0	23·8	3	17	1	24·4	24·6
1	11	0	31·7	32·4	5	20	0	0·0	15·1	11	8	0	0·0	0·1	3	18	1	27·2	25·5
1	12	0	24·4	31·4	5	21	0	17·6	15·6	11	9	0	25·6	25·4	3	19	1	45·6	46·1
1	13	0	31·7	29·6	5	22	0	0·0	10·7	11	10	0	39·8	39·5	3	20	1	21·1	26·0
1	14	0	28·2	30·0	5	23	0	29·5	26·0	11	11	0	0·0	2·5	3	21	1	18·3	16·0
1	15	0	62·2	59·9	5	24	0	19·5	17·0	11	12	0	22·1	21·8	3	22	1	17·6	18·3
1	16	0	45·6	23·9	6	0	0	112·0	99·0	11	13	0	19·2	13·9	3	23	1	28·2	26·9
1	17	0	35·9	35·7	6	1	0	18·3	19·5	12	0	0	38·8	36·3	3	24	1	0·0	8·2
1	18	0	107·2	107·3	6	2	0	11·8	2·3	12	1	0	0·0	2·6	3	25	1	18·9	19·3
1	19	0	27·6	27·4	6	3	0	0·0	1·3	12	2	0	14·1	5·5	4	0	1	0·0	9·0
1	20	0	14·1	8·7	6	4	0	60·3	67·0	12	3	0	15·7	12·0	4	1	1	22·4	21·9
1	21	0	43·6	44·1	6	5	0	36·6	35·1	12	4	0	15·7	15·1	4	2	1	56·8	57·1
1	22	0	36·9	37·5	6	6	0	69·6	71·0	12	5	0	30·8	25·5	4	3	1	90·8	88·6
1	23	0	16·0	18·9	6	7	0	12·5	6·9	12	6	0	20·8	18·6	4	4	1	27·2	25·4
1	24	0	0·0	5·5	6	8	0	92·4	99·2	12	7	0	19·2	16·4	4	5	1	72·2	70·0
1	25	0	29·8	30·2	6	9	0	24·0	20·8	12	8	0	0·0	8·3	4	6	1	16·0	16·9
1	26	0	21·1	15·2	6	10	0	18·3	14·0	0	0	1	112·7	103·7	4	7	1	69·3	67·1
2	0	0	103·7	96·2	6	11	0	31·1	29·9	0	1	1	0·0	5·7	4	8	1	67·7	66·0
2	1	0	44·9	43·9	6	12	0	0·0	12·3	0	2	1	29·8	31·1	4	9	1	82·5	74·8
2	2	0	62·9	64·9	6	13	0	0·0	6·5	0	3	1	73·5	71·5	4	10	1	35·0	35·7
2	3	0	169·5	181·4	6	14	0	47·2	46·5	0	4	1	113·0	119·0	4	11	1	11·8	13·6
2	4	0	32·1	34·1	6	15	0	18·9	21·8	0	5	1	67·1	66·2	4	12	1	53·3	52·2
2	5	0	50·4	56·1	6	16	0	0·0	0·4	0	6	1	121·0	118·4	4	13	1	52·0	49·1
2	6	0	8·3	1·6	6	17	0	18·6	16·2	0	7	1	50·0	53·2	4	14	1	32·7	34·5
2	7	0	65·5	81·7	6	18	0	25·3	25·0	0	8	1	38·5	34·4	4	15	1	26·9	27·3
2	8	0	142·5	142·3	6	19	0	0·0	6·5	0	9	1	41·7	43·2	4	16	1	22·4	21·7
2	9	0	46·5	48·8	6	20	0	0·0	13·2	0	10	1	12·8	13·2	4	17	1	20·2	20·1
2	10	0	34·6	37·1	6	21	0	28·5	33·4	0	11	1	22·1	20·1	4	18	1	20·2	21·4
2	11	0	43·0	40·7	6	22	0	0·0	2·4	0	12	1	62·6	63·6	4	19	1	31·7	30·2
2	12	0	0·0	5·5	6	23	0	0·0	7·9	0	13	1	0·0	1·5	4	20	1	18·3	21·4
2	13	0	58·1	66·4	7	1	0	15·0	11·9	0	14	1	61·9	58·8	4	21	1	0·0	6·8
2	14	0	115·6	115·1	7	2	0	100·1	86·2	0	15	1	17·6	23·7	4	22	1	34·0	34·3
2	15	0	57·8	57·4	7	3	0	22·8	27·8	0	16	1	17·3	22·7	4	23	1	0·0	10·2
2	16	0	0·0	0·4	7	4	0	99·2	92·4	0	17	1	42·3	40·4	4	24	1	26·9	24·0
2	17	0	13·1	13·0	7	5	0	24·0	21·8	0	18	1	28·9	29·2	4	25	1	0·0	5·8
2	18	0	46·2	45·1	7	6	0	16·0	14·8	0	19	1	78·0	81·1	5	0	1	47·2	44·4
2	19	0	35·9	38·8	7	7	0	33·3	32·1	0	20	1	29·5	31·6	5	1	1	38·2	37·8
2	20	0	0·0	7·8	7	8	0	0·0	6·8	0	21	1	0·0	12·5	5	2	1	39·8	42·0
2	21	0	20·8	22·7	7	9	0	0·0	3·2	0	22	1	18·3	25·7	5	3	1	0·0	8·7
2	22	0	0·0	9·2	7	10	0	26·6	27·4	0	23	1	0·0	8·9	5	4	1	0·0	5·7
2	23	0	0·0	5·9	7	11	0	19·2	16·5	0	24	1	20·8	21·8	5	5	1	45·9	47·1
2	24	0	21·5	22·1	7	12	0	27·6	29·9	0	25	1	0·0	11·8	5	6	1	0·0	8·9
2	25	0	0·0	8·5	7	13	0	31·1	31·9	0	26	1	22·4	22·2	5	7	1	65·1	60·6
2	26	0	0·0	13·2	7	14	0	69·6	71·0	1	0	1	76·7	65·2	5	8	1	49·7	45·2
3	1	0	78·9	66·9	7	15	0	22·1	21·2	1	1	1	218·3	210·0	5	9	1	82·5	78·3
3	2	0	38·2	31·0	7	16	0	18·9	20·5	1	2	1	88·3	88·9	5	10	1	19·2	22·5
3	3	0	43·3	39·8	7	17	0	0·0	17·3	1	3	1	35·9	41·1	5	11	1	41·4	39·7
3	4	0	239·2	233·6	7	18	0	0·0	10·8	1	4	1	139·3	129·2	5	12	1	29·5	29·9
3	5	0	23·7	26·8	7	19	0	0·0	3·5	1	5	1	71·9	61·6	5	13	1	31·1	30·6
3	6	0	80·6	86·3	7	20	0	17·6	17·5	1	6	1	43·3	44·6	5	14	1	29·2	26·9
3	7	0	75·7	74·8	7	21	0	19·9	19·0	1	7	1	137·4	136·6	5	15	1	24·7	22·9
3	8	0	54·9	55·4	7	22	0	18·3	12·4	1	8	1	65·1	66·8	5	16	1	23·7	23·1
3	9	0	0·0	3·1	8	0	0	48·1	46·5	1	9	1	80·2	82·7	5	17	1	24·0	27·3
3	10	0	31·1	31·7	8	1	0	10·9	13·8	1	10	1	22·4	20·1	5	18	1	36·6	41·3
3	11	0	0·0	5·8	8	2	0	25·3	28·6	1	11	1	27·9	28·0	5	19	1	26·9	28·4
3	12	0	18·3	22·7	8	3	0	32·4	30·4	1	12	1	47·5	52·3	5	20	1	0·0	16·4
3	13	0	91·8	91·4	8	4	0	13·4	13·6	1	13	1	56·8	60·0	5	21	1	21·1	23·4
3	14	0	59·7	61·9	8	5	0	54·5	58·1	1	14	1	46·5	45·5	5	22	1	0·0	6·8
3	15	0	89·9	91·0	8	6	0	10·9	4·5	1	15	1	17·9	20·5	5	23	1	0·0	11·2
3	16	0	15·4	9·6	8	7	0	22·8	25·8	1	16	1	15·0	12·6	5	24	1	0·0	10·7
3	17	0	0·0	6·1	8	8	0	48·4	48·2	1	17	1	45·2	43·5	6	0	1	149·9	147·5
3	18	0	23·7	21·7	8	9	0	0·0	2·0	1	18	1	45·9	47·2	6	1	1	36·2	31·3
3	19	0	31·4	32·5	8	10	0	13·4	6·2	1	19	1	15·0	19·6	6	2	1	17·3	18·7
3	20	0	18·3	13·3	8	11	0	47·8	53·4	1	20	1	33·0	32·1	6	3	1	38·2	39·1
3	21	0	46·8	47·9	8	12	0	16·7	13·7	1	21	1	32·1	33·3	6	4	1	17·3	27·0
3	22	0	18·9	26·2	8	13	0	28·9	31·9	1	22	1	15·4	15·4	6	5	1	45·6	46·5
3	23	0	30·5	25·9	8	14	0	40·4	41·9	1	23	1	32·4	34·8	6	6	1	43·6	46·9
3	24	0	0·0	5·8	8	15	0	20·8	21·1	1	24	1	0·0	14·0	6	7	1	25·6	24·8
3	25	0	40·1	38·7	8	16	0	0·0	9·7	1	25	1	0·0	8·1	6	8	1	17·6	11·3
3	26	0	21·1	20·5	8	17	0	0·0	11·4	1	26	1	33·0	36·7	6	9	1	51·3	49·1
4	0	0	168·9	155·9	8	18	0	0·0	8·3	2	0	1	108·2	106·8	6	10	1	71·9	67·1
4	1	0	102·7	99·0	8	19	0	0·0	13·0	2	1	1	54·2	62·1	6	11	1	24·7	27·4
4	2	0	16·0	11·7	8	20	0	0·0	6·2	2	2	1	46·2	53·5	6	12	1	41·4	40·3
4	3	0	50·0	49·1	9	1	0	0·0	4·7	2	3	1	30·5	30·3	6	13	1	28·5	28·7
4	4	0	22·4	19·8	9	2	0	20·2	18·8	2	4	1	137·1	119·7	6	14	1	19·9	18·9
4	5	0	130·3	126·6	9	3	0	18·3	20·1	2	5	1	184·3	176·6	6	15	1	30·1	30·6
4	6	0	41·4	43·6	9	4	0	17·0	16·6	2	6	1	35·6	34·3	6	16	1	23·1	24·4
4	7	0	95·6	101·4	9	5	0	31·4	30·9	2	7	1	72·8	63·1	6	17	1	15·7	11·0
4	8	0	24·4	24·1	9	6	0	16·7	14·5	2	8	1	48·8	44·3	6	18	1	0·0	10·4
4	9	0	19·2	15·2	9	7	0	45·9	49·4	2	9	1	19·9	20·2	6	19	1	31·7	29·9
4	10	0	36·6	39·5	9	8	0	0·0	0·4	2	10	1	41·7	39·9	6	20	1	0·0	10·6
4	11	0	87·3	87·9	9	9	0	13·4	8·0	2	11	1	66·7	63·5	6	21	1	0·0	5·1
4	12	0	48·8	45·4	9	10	0	50·0	51·9	2	12	1	52·3	49·2	6	22	1	0·0	5·1
4	13	0	48·1	48·1	9	11	0	17·9	22·9	2	13	1	22·4	19·6	6	23	1	17·0	15·3
4	14	0	28·9	27·9	9	12	0	38·8	38·7	2	14	1	46·2	45·7	7	0	1	37·8	35·0
4	15	0	54·9	55·2	9	13	0	42·7	41·3	2	15	1	47·8	50·9	7	1	1	50·7	50·4
4	16	0	0·0	5·3	9	14	0	13·8	10·5	2	16	1	40·7	40·2	7	2	1	42·0	42·2
4	17	0	48·4	45·6	9	15	0	17·0	12·9	2	17	1	26·6	22·4	7	3	1	23·7	24·7
4	18	0	0·0	1·2	9	16	0	0·0	15·8	2	18	1	14·7	11·2	7	4	1	35·9	35·6
4	19	0	0·0	5·2	9	17	0	0·0	17·3	2	19	1	22·8	20·7	7	5	1	17·9	24·4
4	20	0	0·0	11·3	9	18	0	0·0	8·2	2	20	1	34·6	35·2	7	6	1	47·2	27·2
4	21	0	0·0	14·2	10	0	0	27·9	23·0	2	21	1	32·7	34·3	7	7	1	28·2	28·8

Table 1 (*cont.*)

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
7	8	1	16.3	14.3	0	24	2	0.0	13.6	5	14	2	13.1	12.2	0	6	3	25.3	26.0
7	9	1	44.3	37.8	1	0	2	82.2	66.0	5	15	2	0.0	0.5	0	7	3	30.5	32.1
7	10	1	14.7	12.7	1	1	2	78.3	71.9	5	16	2	0.0	3.0	0	8	3	31.7	32.4
7	11	1	0.0	1.0	1	2	2	45.2	41.2	5	17	2	22.8	20.5	0	9	3	19.2	10.5
7	12	1	42.3	41.2	1	3	2	109.5	104.4	5	18	2	29.2	27.2	0	10	3	17.9	19.2
7	13	1	27.2	27.3	1	4	2	53.9	52.5	5	19	2	0.0	8.2	0	11	3	0.0	4.1
7	14	1	0.0	8.4	1	5	2	33.7	32.5	5	20	2	23.7	21.0	0	12	3	0.0	8.5
7	15	1	35.3	36.5	1	6	2	54.2	57.8	5	21	2	0.0	11.2	0	13	3	32.7	31.8
7	16	1	0.0	4.7	1	7	2	60.0	69.5	5	22	2	16.3	18.3	0	14	3	0.0	1.0
7	17	1	0.0	5.4	1	8	2	23.1	17.9	6	0	2	0.0	2.3	0	15	3	22.8	27.3
7	18	1	43.0	42.2	1	9	2	31.1	28.1	6	1	2	15.0	16.2	0	16	3	18.3	17.1
7	19	1	0.0	4.1	1	10	2	21.5	20.5	6	2	2	34.6	28.4	0	17	3	19.5	21.2
7	20	1	0.0	8.3	1	11	2	41.1	40.7	6	3	2	27.2	27.3	0	18	3	0.0	0.2
7	21	1	24.4	21.8	1	12	2	38.2	36.9	6	4	2	19.5	17.3	0	19	3	20.8	22.2
8	0	1	30.5	29.4	1	13	2	38.8	42.2	6	5	2	39.1	40.0	0	20	3	25.6	25.2
8	1	1	0.0	7.9	1	14	2	21.8	20.3	6	6	2	22.4	18.5	0	21	3	0.0	12.9
8	2	1	14.4	10.9	1	15	2	29.8	28.0	6	7	2	20.5	21.4	0	22	3	0.0	8.2
8	3	1	65.8	66.2	1	16	2	15.4	12.3	6	8	2	18.3	16.4	1	0	3	41.1	37.2
8	4	1	29.5	38.6	1	17	2	0.0	11.5	6	9	2	26.3	24.5	1	1	3	74.5	63.3
8	5	1	18.3	14.0	1	18	2	0.0	14.1	6	10	2	13.8	7.6	1	2	3	54.2	45.4
8	6	1	19.5	22.3	1	19	2	0.0	10.4	6	11	2	18.6	16.2	1	3	3	12.5	21.0
8	7	1	0.0	7.8	1	20	2	25.0	30.2	6	12	2	20.8	16.5	1	4	3	53.3	51.1
8	8	1	18.6	20.0	1	21	2	23.7	24.9	6	13	2	26.3	24.7	1	5	3	13.1	9.2
8	9	1	27.9	27.3	1	22	2	0.0	17.1	6	14	2	28.2	26.2	1	6	3	24.4	22.5
8	10	1	25.6	28.0	1	23	2	19.9	23.2	6	15	2	0.0	10.7	1	7	3	38.5	41.1
8	11	1	19.9	16.8	1	24	2	0.0	8.6	6	16	2	16.3	17.0	1	8	3	27.6	28.8
8	12	1	33.0	32.7	2	0	2	50.7	49.5	6	17	2	35.0	33.8	1	9	3	36.6	37.1
8	13	1	39.1	37.4	2	1	2	34.6	30.9	6	18	2	0.0	7.0	1	10	3	18.6	23.8
8	14	1	31.1	30.7	2	2	2	13.4	12.8	6	19	2	36.9	36.5	1	11	3	17.0	38.6
8	15	1	18.3	15.1	2	3	2	43.3	42.0	6	20	2	0.0	9.8	1	12	3	24.4	25.3
8	16	1	14.4	16.2	2	4	2	13.1	11.5	6	21	2	0.0	14.1	1	13	3	0.0	11.8
8	17	1	19.5	20.9	2	5	2	35.0	32.9	7	0	2	0.0	3.3	1	14	3	15.7	16.0
8	18	1	0.0	3.6	2	6	2	11.8	9.0	7	1	2	38.2	34.5	1	15	3	0.0	14.0
8	19	1	17.0	14.7	2	7	2	50.4	45.6	7	2	2	15.0	12.7	1	16	3	0.0	18.1
8	20	1	17.0	14.8	2	8	2	0.0	7.7	7	3	2	32.4	34.8	1	17	3	27.6	29.3
9	0	1	27.2	25.6	2	9	2	36.2	35.0	7	4	2	45.9	47.7	1	18	3	27.6	31.1
9	1	1	21.1	17.3	2	10	2	83.8	81.3	7	5	2	27.2	31.1	1	19	3	21.8	24.7
9	2	1	0.0	9.3	2	11	2	43.6	46.2	7	6	2	27.2	23.4	1	20	3	22.1	22.0
9	3	1	15.0	12.8	2	12	2	32.1	32.6	7	7	2	42.0	42.1	1	21	3	27.6	29.2
9	4	1	37.5	35.1	2	13	2	18.6	19.9	7	8	2	0.0	4.0	1	22	3	0.0	7.0
9	5	1	13.4	11.1	2	14	2	28.5	25.9	7	9	2	17.0	9.4	2	0	3	28.2	29.8
9	6	1	32.1	39.2	2	15	2	0.0	11.1	7	10	2	0.0	2.1	2	1	3	29.5	28.0
9	7	1	24.0	27.0	2	16	2	25.6	29.8	7	11	2	58.1	57.6	2	2	3	55.8	43.7
9	8	1	21.8	19.6	2	17	2	32.7	37.4	7	12	2	0.0	4.2	2	3	3	37.2	33.7
9	9	1	41.1	42.1	2	18	2	16.3	9.9	7	13	2	0.0	11.9	2	4	3	74.5	62.6
9	10	1	43.0	42.3	2	19	2	18.9	18.1	7	14	2	21.5	20.6	2	5	3	65.8	59.2
9	11	1	0.0	4.2	2	20	2	16.0	15.9	7	15	2	24.7	21.3	2	6	3	21.1	20.8
9	12	1	0.0	14.7	2	21	2	16.3	19.6	7	16	2	0.0	11.4	2	7	3	0.0	2.6
9	13	1	0.0	11.6	2	22	2	33.7	34.8	7	17	2	0.0	6.9	2	8	3	0.0	3.6
9	14	1	0.0	8.5	2	23	2	0.0	7.3	7	18	2	0.0	3.8	2	9	3	0.0	11.0
9	15	1	37.5	38.5	2	24	2	39.8	39.7	7	19	2	0.0	6.4	2	10	3	24.4	23.1
9	16	1	27.6	23.2	3	0	2	43.6	44.2	8	0	2	0.0	8.1	2	11	3	27.6	28.0
9	17	1	15.0	9.7	3	1	2	18.3	18.3	8	1	2	24.7	19.1	2	12	3	0.0	7.3
9	18	1	0.0	3.2	3	2	2	18.6	26.4	8	2	2	0.0	13.8	2	13	3	16.7	14.3
10	0	1	27.9	30.7	3	3	2	33.3	31.0	8	3	2	29.2	23.7	2	14	3	25.6	27.1
10	1	1	15.4	16.1	3	4	2	83.8	119.0	8	4	2	33.7	31.5	2	15	3	28.2	30.6
10	2	1	0.0	3.9	3	5	2	13.4	14.5	8	5	2	0.0	14.8	2	16	3	28.2	32.6
10	3	1	0.0	11.8	3	6	2	91.8	99.0	8	6	2	0.0	3.9	2	17	3	0.0	6.0
10	4	1	16.0	12.1	3	7	2	30.8	34.2	8	7	2	0.0	10.3	2	18	3	17.6	14.4
10	5	1	21.1	27.9	3	8	2	0.0	16.9	8	8	2	0.0	1.3	2	19	3	17.3	17.4
10	6	1	17.9	13.6	3	9	2	52.6	50.4	8	9	2	20.8	19.9	2	20	3	30.1	26.4
10	7	1	0.0	2.5	3	10	2	43.0	44.9	8	10	2	33.3	33.4	2	21	3	23.4	21.5
10	8	1	27.2	25.1	3	11	2	31.1	35.3	8	11	2	22.4	24.3	3	0	3	27.9	31.6
10	9	1	37.5	36.4	3	12	2	14.4	13.4	8	12	2	0.0	7.3	3	1	3	12.2	8.9
10	10	1	0.0	9.8	3	13	2	0.0	9.7	8	13	2	17.6	17.5	3	2	3	40.4	38.6
10	11	1	18.6	19.8	3	14	2	56.8	56.4	8	14	2	26.0	23.5	3	3	3	44.3	46.4
10	12	1	30.1	26.6	3	15	2	15.0	18.6	8	15	2	0.0	10.1	3	4	3	14.1	22.3
10	13	1	0.0	2.1	3	16	2	15.7	14.6	8	16	2	40.7	39.3	3	5	3	23.7	30.5
10	14	1	44.9	38.7	3	17	2	17.3	20.3	8	17	2	0.0	6.5	3	6	3	30.8	28.9
10	15	1	0.0	14.8	3	18	2	0.0	9.6	8	18	2	0.0	8.9	3	7	3	34.0	32.8
11	0	1	16.3	17.6	3	19	2	14.7	16.5	9	0	2	26.9	25.5	3	8	3	26.3	24.9
11	1	1	28.9	28.3	3	20	2	0.0	13.3	9	1	2	20.8	19.2	3	9	3	30.5	29.7
11	2	1	15.0	14.4	3	21	2	35.3	34.3	9	2	2	22.1	22.6	3	10	3	34.3	35.7
11	3	1	0.0	11.6	3	22	2	15.4	16.0	9	3	2	18.3	19.2	3	11	3	0.0	6.7
11	4	1	15.7	12.9	3	23	2	0.0	1.6	9	4	2	18.6	19.1	3	12	3	0.0	5.6
11	5	1	19.2	15.8	3	24	2	0.0	13.5	9	5	2	13.8	6.1	3	13	3	35.0	37.2
11	6	1	24.0	25.6	4	0	2	11.5	11.4	9	6	2	23.0	23.3	3	14	3	21.8	21.3
11	7	1	0.0	15.1	4	1	2	24.7	19.7	9	7	2	29.8	30.9	3	15	3	32.4	30.2
11	8	1	25.6	27.4	4	2	2	41.4	37.8	9	8	2	16.0	16.7	3	16	3	18.3	20.4
11	9	1	24.0	24.9	4	3	2	11.5	11.9	9	9	2	23.1	23.1	3	17	3	0.0	8.5
11	10	1	14.7	8.4	4	4	2	24.4	32.0	9	10	2	21.5	22.9	3	18	3	0.0	6.8
11	11	1	25.3	20.6	4	5	2	12.8	9.8	9	11	2	0.0	9.6	3	19	3	0.0	10.3
11	12	1	0.0	12.3	4	6	2	24.4	24.6	9	12	2	19.2	15.0	3	20	3	0.0	11.6
12	0	1	0.0	8.2	4	7	2	21.1	10.2	9	13	2	36.2	33.4	3	21	3	0.0	10.2
12	1	1	0.0	8.3	4	8	2	39.8	38.0	9	14	2	17.6	7.1	4	0	3	11.5	10.4
12	2	1	16.7	14.7	4	9	2	29.2	26.7	9	15	2	0.0	2.0	4	1	3	30.8	31.4
12	3	1	0.0	4.9	4	10	2	49.1	48.9	10	0	2	18.6	20.8	4	2	3	25.0	22.6
12	4	1	0.0	15.6	4	11	2	37.8	39.5	10	1	2	0.0	11.5	4	3	3	16.3	17.3
12	5	1	16.7	20.5	4	12	2	20.5	21.0	10	2	2	0.0	9.2	4	4	3	25.6	23.1
12	6	1	0.0	3.8	4	13	2	22.4	20.1	10	3	2	0.0	6.0	4	5	3	14.7	23.1
0	0	2	28.9	28.5	4	14	2	31.4	30.0	10	4	2	15.0	13.7	4	6	3	31.1	34.7
0	1	2	13.4	20.2	4	15	2	19.2	17.0	10	5	2	15.7	11.9	4	7	3	30.8	33.4
0	2	2	20.8	28.5	4	16	2	17.9	20.2	10	6	2	22.1	20.2	4	8	3	26.0	32.3
0	3	2	10.6	26.9	4	17	2	19.9	20.6	10	7	2	34.6	38.4	4	9	3	0.0	14.8
0	4	2	0.0	10.8	4	18	2	19.9	18.8	10	8	2	17.0	10.3	4	10	3	30.1	25.7
0	5	2	66.4	61.8	4	19	2	0.0	6.4	10	9	2	14.4	12.4	4	11	3	0.0	11.9
0	6	2	28.2	30.8	4	20	2	22.4	27.0	10	10	2	29.2	28.6	4	12	3	29.5	31.3
0	7	2	35.6	32.2	4	21	2	20.2	21.6	10	11	2	17.6	12.0	4	13	3	25.6	25.3
0	8	2	17.9	8.9	4	22	2	0.0	5.8	10	12	2	0.0	6.4	4	14	3	14.7	19.9
0	9	2	76.4	70.4	4	23	2	0.0	6.8	11	0	2	0.0	5.9	4	15	3	24.4	25.5
0	10	2	22.1	22.7	5	0	2	0.0	5.4	11	1	2	19.5	14.5	4	16	3	15.0	18.2
0	11	2	55.8	55.0	5	1	2	66.7	71.2	11	2	2	0.0	9.0	4	17	3	32.4	34.5
0	12	2	0.0	0.8	5	2	2	18.9	20.7	11	3	2	0.0	14.5	4	18	3	0.0	8.4
0	13	2	24.0	29.7	5	3	2	39.5	38.7	11	4	2	14.7	9.7	4	19	3	0.0	7.4
0	14	2	12.8	10.5	5	4	2	25.6	28.6	11	5	2	17.9	9.8	4	20	3	15.7	12.1
0	15	2	34.0	35.3	5	5	2	27.2	27.0	11	6	2	0.0	8.1	5	0	3	48.1	50.9
0	16	2	17.3	17.5	5	6	2	37.8	39.8	11	7	2	0.0	8.5	5	1	3	38.5	37.8
0	17	2	12.8	16.6	5	7	2	43.6	41.7	11	8	2	14.7	5.1	5	2	3	22.8	23.0
0	18	2	23.4	23.7	5	8	2	42.0	41.4	0	0	3	16.0	19.6	5	3	3	18.3	23.0
0	19	2	68.7	76.0	5	9	2	45.6	44.6	0	1	3	50.0	44.9	5	4	3	0.0	15.8
0	20	2	0.0	9.7	5	10	2	23.4	20.3	0	2	3	41.4	40.0	5	5	3	0.0	1.9
0	21	2	32.7	33.5	5	11	2	58.7	54.4	0	3	3	17.3	10.2	5	6	3	31.1	39.0
0	22	2	0.0	15.9	5	12	2	0.0	14.3	0	4	3	14.1	1.5	5	7	3	0.0	4.2
0	23	2	27.9	33.2	5	13	2	17.3	13.1	0	5	3	40.4	40.8	5	8	3	16.0	15.1

Table 1 (*cont.*)

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
5	9	3	20.5	22.1	9	0	3	26.3	22.0	2	8	4	25.0	27.1	6	4	4	18.3	9.7
5	10	3	26.6	27.0	9	1	3	17.6	17.8	2	9	4	0.0	15.3	6	5	4	0.0	6.7
5	11	3	0.0	7.7	9	2	3	0.0	4.4	2	10	4	23.4	24.2	6	6	4	0.0	12.9
5	12	3	18.6	23.1	9	3	3	14.4	6.8	2	11	4	0.0	13.7	6	7	4	18.3	20.1
5	13	3	0.0	9.8	9	4	3	15.7	14.9	2	12	4	34.6	35.0	6	8	4	27.9	34.5
5	14	3	0.0	7.7	9	5	3	0.0	9.5	2	13	4	0.0	8.0	6	9	4	15.0	13.0
5	15	3	0.0	3.3	9	6	3	40.7	41.5	2	14	4	29.2	26.9	6	10	4	18.3	17.2
5	16	3	30.1	32.3	9	7	3	22.4	20.9	2	15	4	23.7	24.8	6	11	4	0.0	6.4
5	17	3	0.0	3.1	9	8	3	24.0	20.2	2	16	4	0.0	15.4	6	12	4	0.0	9.7
5	18	3	0.0	13.0	9	9	3	31.1	28.3	2	17	4	0.0	7.3	7	0	4	21.1	25.0
5	19	3	0.0	10.7	9	10	3	17.6	18.0	3	0	4	0.0	1.7	7	1	4	16.0	12.7
6	0	3	0.0	1.4	9	11	3	24.4	24.7	3	1	4	35.3	33.7	7	2	4	24.7	23.3
6	1	3	23.4	17.5	10	0	3	19.5	19.5	3	2	4	17.3	17.4	7	3	4	20.5	9.1
6	2	3	35.6	36.5	10	1	3	0.0	11.4	3	3	4	20.8	19.8	7	4	4	30.1	31.6
6	3	3	14.1	11.0	10	2	3	17.9	16.8	3	4	4	0.0	18.3	7	5	4	21.8	19.6
6	4	3	24.4	21.3	10	3	3	0.0	9.2	3	5	4	14.4	23.7	7	6	4	18.6	19.9
6	5	3	24.4	30.2	10	4	3	16.7	6.8	3	6	4	19.9	25.4	7	7	4	16.7	11.2
6	6	3	16.0	8.6	10	5	3	0.0	10.6	3	7	4	0.0	10.1	7	8	4	0.0	6.4
6	7	3	23.4	25.5	0	0	4	109.1	105.7	3	8	4	22.8	22.0	7	9	4	0.0	6.9
6	8	3	0.0	14.6	0	1	4	13.1	20.0	3	9	4	0.0	10.5	8	0	4	16.0	12.9
6	9	3	34.6	36.3	0	2	4	26.0	22.9	3	10	4	19.9	27.2	8	1	4	25.3	25.2
6	10	3	20.2	20.3	0	3	4	0.0	4.1	3	11	4	27.9	31.5	8	2	4	32.1	29.5
6	11	3	0.0	3.3	0	4	4	0.0	11.5	3	12	4	0.0	7.4	8	3	4	21.8	20.8
6	12	3	30.1	29.9	0	5	4	0.0	2.2	3	13	4	23.4	21.2	8	4	4	29.5	27.4
6	13	3	0.0	9.4	0	6	4	22.1	22.8	3	14	4	21.5	20.2	0	0	5	24.4	23.2
6	14	3	0.0	6.6	0	7	4	33.7	32.1	3	15	4	27.2	22.2	0	1	5	28.2	25.6
6	15	3	33.3	33.4	0	8	4	0.0	8.0	3	16	4	0.0	7.2	0	2	5	15.0	12.6
6	16	3	0.0	6.4	0	9	4	32.4	27.2	4	0	4	49.1	44.5	0	3	5	0.0	3.5
6	17	3	19.5	17.6	0	10	4	32.4	32.9	4	1	4	23.4	21.0	0	4	5	19.9	17.7
6	18	3	0.0	4.3	0	11	4	0.0	6.2	4	2	4	29.2	29.4	0	5	5	19.9	16.5
7	0	3	0.0	7.4	0	12	4	0.0	0.6	4	3	4	0.0	14.3	0	6	5	0.0	11.8
7	1	3	14.4	17.7	0	13	4	0.0	13.9	4	4	4	16.3	16.6	0	7	5	23.4	16.3
7	2	3	27.9	31.7	0	14	4	0.0	13.3	4	5	4	20.0	20.5	0	8	5	0.0	12.2
7	3	3	39.5	39.6	0	15	4	28.2	26.7	4	6	4	18.6	22.9	1	0	5	17.3	5.8
7	4	3	0.0	0.6	0	16	4	15.7	16.2	4	7	4	19.5	29.0	1	1	5	0.0	15.0
7	5	3	16.7	8.5	0	17	4	21.1	17.1	4	8	4	17.3	18.6	1	2	5	0.0	2.5
7	6	3	17.3	12.3	1	0	4	12.8	1.9	4	9	4	0.0	17.4	1	3	5	0.0	13.8
7	7	3	26.0	26.2	1	1	4	22.4	17.2	4	10	4	25.0	26.9	1	4	5	0.0	14.5
7	8	3	20.2	15.6	1	2	4	23.7	26.0	4	11	4	14.7	23.4	1	5	5	0.0	0.4
7	9	3	22.1	24.4	1	3	4	26.9	39.5	4	12	4	0.0	3.1	1	6	5	31.4	29.7
7	10	3	0.0	10.1	1	4	4	0.0	4.5	4	13	4	0.0	12.7	1	7	5	19.9	19.1
7	11	3	18.6	18.0	1	5	4	18.6	16.0	4	14	4	0.0	5.7	1	8	5	14.7	10.1
7	12	3	0.0	9.2	1	6	4	32.1	31.0	4	15	4	20.2	20.7	2	0	5	0.0	5.6
7	13	3	27.2	26.5	1	7	4	14.7	17.1	5	0	4	36.9	31.9	2	1	5	19.5	16.6
7	14	3	0.0	5.5	1	8	4	17.3	10.2	5	1	4	14.7	9.6	2	2	5	0.0	10.1
7	15	3	25.6	24.1	1	9	4	0.0	15.6	5	2	4	34.0	33.3	2	3	5	20.0	20.1
7	16	3	15.0	10.3	1	10	4	16.0	14.3	5	3	4	0.0	13.8	2	4	5	0.0	7.7
8	0	3	0.0	8.1	1	11	4	14.1	13.7	5	4	4	0.0	10.3	2	5	5	28.2	25.1
8	1	3	24.0	23.3	1	12	4	0.0	8.2	5	5	4	0.0	16.5	2	6	5	16.3	9.3
8	2	3	24.0	23.4	1	13	4	18.6	15.1	5	6	4	0.0	18.9	2	7	5	0.0	7.9
8	3	3	16.7	17.8	1	14	4	21.8	22.4	5	7	4	0.0	9.7	3	0	5	0.0	3.0
8	4	3	0.0	7.1	1	15	4	16.3	13.4	5	8	4	26.6	39.5	3	1	5	0.0	10.8
8	5	3	25.6	25.4	1	16	4	17.6	13.6	5	9	4	17.3	19.0	3	2	5	16.0	10.2
8	6	3	22.4	22.9	1	17	4	0.0	3.0	5	10	4	24.4	25.2	3	3	5	25.0	25.2
8	7	3	0.0	16.9	2	0	4	30.5	24.1	5	11	4	0.0	11.2	3	4	5	16.3	16.6
8	8	3	16.3	10.6	2	1	4	30.8	27.9	5	12	4	15.0	8.9	3	5	5	0.0	17.4
8	9	3	26.0	26.2	2	2	4	0.0	9.4	5	13	4	0.0	15.7	3	6	5	0.0	10.5
8	10	3	0.0	2.0	2	3	4	40.4	38.7	5	14	4	17.6	17.5	4	0	5	0.0	7.5
8	11	3	0.0	4.7	2	4	4	21.1	15.2	6	0	4	36.2	39.5	4	1	5	16.7	13.9
8	12	3	36.6	35.3	2	5	4	0.0	9.5	6	1	4	40.4	41.8	4	2	5	19.5	16.1
8	13	3	0.0	9.9	2	6	4	18.3	21.9	6	2	4	0.0	6.9					
8	14	3	0.0	7.4	2	7	4	18.6	13.0	6	3	4	15.7	9.0					

Table 2. *Final positional (fractional) and thermal parameters*

Atom	x	y	z	B (Å^2)
Br(1)	0·1680	0·7398	0·3841	—
S(2)	0·4027	0·5633	0·0728	2·89
O(3)	0·4032	0·5624	−0·1658	4·63
O(4)	0·4935	0·5620	0·1894	4·26
O(5)	0·3378	0·5231	0·1556	3·22
O(6)	0·1981	0·4635	0·4232	3·13
O(7)	0·0093	0·4453	0·5960	3·33
O(8)	0·1464	0·3490	0·6387	4·22
O(9)	0·3165	0·3729	0·8797	3·93
O(10)	0·4513	0·3406	0·7308	—
O(11)	0·0573	0·3604	0·9489	—
O(12)	−0·1373	0·4161	0·5335	—
C(13)	0·2424	0·6844	0·3009	4·40
C(14)	0·3135	0·6714	0·4465	4·55
C(15)	0·3664	0·6321	0·3931	3·28
C(16)	0·3363	0·6121	0·1639	2·57
C(17)	0·2676	0·6285	0·0085	4·13
C(18)	0·2150	0·6691	0·0828	5·36
C(19)	0·3393	0·5099	0·3942	2·99
C(20)	0·3042	0·4604	0·4035	2·21
C(21)	0·3356	0·4397	0·6429	3·73
C(22)	0·2952	0·3920	0·6588	1·88
C(23)	0·1808	0·3967	0·6470	2·96
C(24)	0·1563	0·4184	0·4240	3·06
C(25)	0·0480	0·4230	0·3852	4·08
C(26)	−0·0865	0·4417	0·6564	4·03
C(27)	−0·1166	0·4646	0·8576	—

Table 2 (*cont.*)

Atom	x	y	z	B (Å^2)
C(28)	0·0915	0·3360	0·8141	4·93
C(29)	0·0595	0·2844	0·7754	—
C(30)	0·4009	0·3457	0·8857	3·30
C(31)	0·4080	0·3243	1·1279	—

Anisotropic thermal parameters ($\times 10^4$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Br(1)	136	20·0	861	2	240	44
O(10)	57	16·9	353	47	80	13
O(11)	128	25·3	420	−45	178	−18
O(12)	84	27·2	453	15	−19	−14
C(27)	41	21·3	398	−48	43	18
C(29)	102	9·4	604	13	−51	−17
C(31)	77	10·4	258	−19	−62	9

the molecule, although the acetyl groups were rather poorly resolved at this stage. Throughout this structure determination, the scattering factors of *International Tables for X-ray Crystallography* (1962) were used, with $B=4·5$ Å^2 for all atoms, and oxygen atoms were distinguished at the final stage; R, the usual discrepancy index, decreased from 0·46 for Br and S only to 0·26 for all 31 atoms.

Refinement of the positional and isotropic thermal parameters then proceeded by computing successive

Table 3. *Bond lengths* (Å) *and standard deviations, and valency angles*

σ varies from 0·9° for O–S–O angles to 2·6° for angles in the acetyl groups

Bond	*l*	σ	Bond	*l*	σ
Br(1)–C(13)	1·980	0·027	O(5)–C(19)	1·44	0·029
S(2)–C(16)	1·777	0·021	O(6)–C(20)	1·46	0·026
S(2)–O(3)	1·381	0·019	O(6)–C(24)	1·44	0·024
S(2)–O(4)	1·416	0·018	O(7)–C(25)	1·48	0·033
Mean S=O	1·399	0·013	O(8)–C(23)	1·48	0·025
			O(9)–C(22)	1·43	0·028
S(2)–O(5)	1·553	0·015	Mean O–C_{sp^3}	1·45	$0·01_1$
C(13)–C(14)	1·34	0·039			
C(14)–C(15)	1·40	0·033	O(7)–C(26)	1·36	0·030
C(15)–C(16)	1·51	0·036	O(8)–C(28)	1·32	0·036
C(16)–C(17)	1·39	0·034	O(9)–C(30)	1·41	0·026
C(17)–C(18)	1·46	0·037	Mean O–C_{sp^2}	1·36	$0·01_8$
C(18)–C(13)	1·39	0·044			
Mean C_{ar}–C_{ar}	1·41	$0·01_5$	O(10)–C(30)	1·14	0·032
			O(11)–C(28)	1·16	0·038
C(19)–C(20)	1·53	0·027	O(12)–C(26)	1·25	0·034
C(20)–C(21)	1·57	0·036	Mean C=O	1·18	$0·02_0$
C(21)–C(22)	1·51	0·030			
C(22)–C(23)	1·58	0·030	C(26)–C(27)	1·41	0·042
C(23)–C(24)	1·48	0·034	C(28)–C(29)	1·59	0·038
C(24)–C(25)	1·51	0·033	C(30)–C(31)	1·54	0·040
Mean C_{sp^3}–C_{sp^3}	1·53	$0·01_3$	Mean C_{sp^2}–C_{sp^3}	1·51	$0·02_3$

Br–C_{ar}–C_{ar}	Range	C(25)–O(7)–C(26)	121·5
S–C_{ar}–C_{ar}	110·0–132·4	C(23)–O(8)–C(28)	115·6
C_{ar}–C_{ar}–C_{ar}	(10 angles)	C(22)–O(9)–C(30)	114·4
	Mean 117·8	Mean C_{sp^3}–O–C_{sp^2}	117·2
O(3)–S(2)–O(4)	118·2	O(7)–C(26)–O(12)	116·0
O(3)–S(2)–O(5)	107·3	O(8)–C(28)–O(11)	124·7
O(3)–S(2)–C(16)	108·3	O(9)–C(30)–O(10)	123·6
O(4)–S(2)–O(5)	109·6	Mean O–C=O	121·4
O(4)–S(2)–C(16)	109·3		
O(5)–S(2)–C(16)	103·2	O(7)–C(26)–C(27)	117·3
Mean at S	109·3	O(8)–C(28)–C(29)	108·9
		O(9)–C(30)–C(31)	107·8
S(2)–O(5)–C(19)	119·6	Mean O–C–CH_3	111·3
C(20)–O(6)–C(24)	109·9		
	Range	O(12)–C(26)–C(27)	126·6
O–C_{sp^3}–C_{sp^3}	103·1–113.1	O(11)–C(28)–C(29)	124·9
C_{sp^3}–C_{sp^3}–C_{sp^3}	(15 angles)	O(10)–C(30)–C(31)	128·6
	Mean 107·2	Mean O=C–CH_3	126·7

observed and calculated differential syntheses, and after seven cycles R was reduced to 0·183. At this stage a three-dimensional Fourier series was summed, and superimposed sections of the resulting electron-density distribution taken through the atomic centres are shown in Fig. 1. There was no spurious detail, so that the structure appeared to be essentially correct.

Refinement of the atomic parameters, and an overall scale factor, was completed by (block-diagonal) least squares. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, with $\sqrt{w}=|F_o|/40$ when $|F_o|<40$, and $\sqrt{w}=40/|F_o|$ when $|F_o| \geq 40$. Refinement was complete in five cycles, during which R was reduced from 0·183 to 0·090, and $\Sigma w.\Delta F^2$ from 26×10^3 to 6×10^3. In the final cycles anisotropic thermal parameters were introduced for the bromine atom and for the outer atoms of the acetyl groups (our 40K IBM 1620 could not accommodate all the atoms anisotropically, and the atoms treated were those whose thermal vibration seemed most anisotropic).

The measured structure amplitudes are compared in Table 1 with the values calculated from the final parameters, those from the fifth least-squares cycle ($R=0·090$ for the 851 observed reflexions).

Atomic parameters and molecular dimensions

The final positional and thermal parameters are given in Table 2. x, y and z are fractional coordinates referred to the crystal axes, B are isotropic temperature factors and b_{ij} are the anisotropic thermal parameters in the expression:

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

A perspective drawing of the molecule, with the atom numbering used, is shown in Fig. 1, and the bond distances and valency angles are given in Table 3, together with their standard deviations calculated from the least-squares residuals. All the intermolecular distances less than 4·0 Å were calculated, and the shorter contacts are listed in Table 4.

Table 4. *Shorter intermolecular distances*

All contacts ≤ 4·0 Å between a standard molecule (1) and neighbouring molecules were calculated, but only the most significant crystallographically independent separations are listed

Atom (Molecule 1)	to Atom	in Molecule	*d*
Br(1)	O(10)	6	3·45 Å
Br(1)	C(30)	6	3·61
O(4)	O(5)	11	3·41
O(4)	C(19)	11	3·34
O(4)	C(20)	11	3·11
O(4)	C(21)	11	3·52
O(10)	C(15)	11	3·27
O(11)	C(24)	7	3·51
O(11)	C(25)	7	3·13
C(15)	O(3)	7	3·31
C(19)	O(3)	7	3·10
C(31)	O(10)	7	3·57
C(14)	C(17)	7	3·55

Molecule				
	1	x	y	z
	6	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$
	7	x	y	$1+z$
	11	$1-x$	$1-y$	z

Discussion

The analysis has established that the derivative investigated is 1-*O*-(*p*-bromobenzenesulphonyl)-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*gluco*heptitol. The tentative assignment of structures to the two anhydro-deoxyheptitols is therefore correct; the lower-melting isomer is 2,6-anhydro-3-deoxy-D-*gluco*heptitol (I, $R_1=R_2=H$), and the higher-melting isomer is 2,6-anhydro-3-deoxy-D-*manno*heptitol (II).

The sugar ring is in the chair conformation with all substituent groups in equatorial positions, as is clear

from Fig. 1. Since the compound is derived from D-glucose the absolute configuration is established: the parameters of Table 2 referred to a right-hand set of axes give the true absolute configuration. Fig. 1 also depicts the correct absolute configuration.

The bond distances and valency angles in the molecule (Table 3) are all quite normal, and require no special comment.

All the intermolecular separations (Table 4) correspond to normal van der Waals interactions. The shortest distances are three C · · · O contacts of 3·1 Å, equal to the sum of the van der Waals radii of carbon and oxygen (Pauling, 1960). The shortest Br–O and Br–C contacts are 3·45 Å and 3·61 Å respectively (sum of van der Waals radii 3·35 Å and 3·65 Å respectively). The shortest O–O contact is 3·41 Å, and the shortest C–C separation is 3·55 Å.

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The Crystal and Molecular Structure of 5-Iodo-2′-deoxyuridine

BY N. CAMERMAN AND J. TROTTER

Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada

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Crystals of 5-iodo-2′-deoxyuridine and 5-bromo-2′-deoxyuridine are isomorphous; the compounds are triclinic with one molecule in the unit cell, space group $P\bar{1}$, with dimensions $a=4{\cdot}98$, $b=6{\cdot}83$, $c=9{\cdot}60$ Å, $\alpha=101°40'$, $\beta=109°18'$, $\gamma=98°20'$ for the iodo-compound, and $a=4{\cdot}87$, $b=6{\cdot}72$, $c=9{\cdot}56$ Å, $\alpha=100°10'$, $\beta=107°24'$, $\gamma=98°31'$ for the bromo-derivative. The detailed structure of 5-iododeoxyuridine was determined from Mo $K\alpha$ scintillation counter data. A three-dimensional Fourier synthesis with all phases zero (based on the I atom), although it contained a false centre of symmetry, revealed all the atoms in the molecule. The positional and isotropic thermal parameters were refined by least squares to an R value of 0·142; further refinement with anisotropic temperature factors indicated no further significant shifts in positional parameters, but reduced R to 0·054.

The atoms attached to the pyrimidine ring show small deviations from exact planarity. The deoxyribose ring is puckered with C(2′) displaced 0·59 Å from the plane of the other four atoms. The angle between the planes of the two rings is 81°; the conformation about the glycosidic C–N bond, as defined by the angle formed by the trace of the plane of the base with the projection of the C–O bond, is −67°. The bond distances indicate that the pyrimidine base is in the keto form (both carbon-oxygen distances 1·22 Å); the C(4)–C(5) bond (1·34 Å) is a double bond, C(5)–C(6) is a single bond (1·49 Å), and the C–N distances in the pyrimidine ring all measure 1·37 Å. The glycosidic C–N bond length is 1·49 Å. The distances and angles in the deoxyribose ring are all normal.

The most significant intermolecular distance is an I · · · O (carbonyl) separation of 2·96 Å; this is very considerably shorter than the usual van der Waals contact (3·55 Å), and suggests charge transfer bonding involving donation of oxygen lone-pair electrons to vacant 5*d* orbitals of the iodine atom. A strong intermolecular attraction of this type may be the explanation for the antiviral activity of 5-iodo-2′-deoxyuridine. The other short intermolecular separations correspond to O–H · · · O and O · · · H–N hydrogen bonds.

Introduction

5-Iodo-2′-deoxyuridine (IDU) (Fig. 2) has been used in the treatment and cure of *herpes simplex* keratitis (Kaufman, Nesburn & Maloney, 1962; Kaufman, 1962), and this is the first clear-cut demonstration that true viral disease can be effectively treated without obvious harm to the host. It is postulated