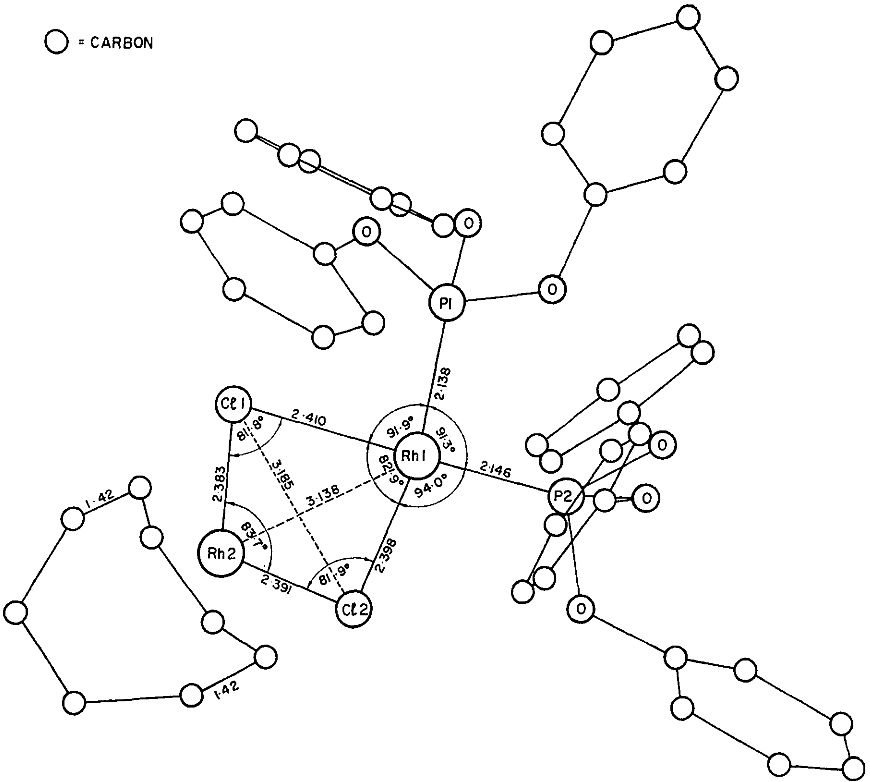


Fig. 3. The principal bond lengths and bond angles.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program.* Report ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.

Dahl, L. F., Martell, C. & Wampler, D. L. (1961). *J. Amer. Chem. Soc.* **83**, 1761.

Davies, W. O. & Stanley, E. (1962). *Acta Cryst.* **15**, 1092.

Dunning, A. J. & Vand, V. (1969). *Acta Cryst.* A**25**, 489.

Haines, L. M. (1969). *Inorg. Nucl. Chem. Letters*, **5**, 399.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Ibers, J. A. & Snyder, R. G. (1962). *Acta Cryst.* **15**, 923.

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

La Placa, S. J. & Ibers, J. A. (1965). *Acta Cryst.* **18**, 511.

Acta Cryst. (1970). B**26**, 991

The Crystal and Molecular Structure of Coriose

By Tooru Taga, Kenji Osaki and Takuo Okuda

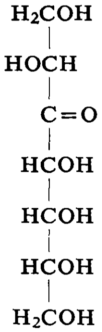
Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan

(*Received* 6 *August* 1969)

The crystal structure of coriose, $C_7H_{14}O_7$, a natural 3-heptulose, has been determined by the use of a symbolic addition procedure. The space group is $P2_1$ with two molecules in the unit cell of dimensions $a=11{\cdot}33$, $b=7{\cdot}460$, $c=5{\cdot}205$ Å and $\beta=90{\cdot}75°$. The molecule is found in a novel α-furanose form with three *cis* hydroxyl groups. Owing to the twist of the five-membered ring, similar to that in adenosine monophosphate, three groups attached to the ring are quasi-equatorial and the other two are quasi-axial.

Introduction

Coriose, $C_7H_{14}O_7$, is a naturally occurring heptulose, extracted from *Coriaria japonica* A. Gray. The crystal of coriose is obtained solvent-free either from aqueous ethanol, methanol or water. The same crystal (m.p. = 169–171 °) is obtained also by evaporation of an aqueous solution to dryness at higher temperature, or by lyophilization of the equilibrated aqueous solution, followed by exposure to the air. This evidence points to the fact that coriose has an unusually stable structure in the crystalline state. Coriose has been shown to be D-*altro*-3-heptulose (I) (Okuda & Konishi, 1968), which forms a hemiketal ring as indicated by the absence of the carbonyl band in the infrared spectrum. As to the hemiketal ring, there are four possible structures, α-pyranose, β-pyranose, α-furanose and β-furanose, of which α-pyranose may be regarded as the most stable on the basis of a conformational analysis (Eliel, Allinger, Angyal & Morrison, 1965). The actual conformation of crystalline coriose, corresponding to one of these, could not be determined by analysis of the proton magnetic resonance spectra, because of the unusually rapid transformation of the ring structure in solution, as shown by the quick mutarotation. The present investigation was carried out in order to determine the molecular and crystal structures, which might provide a basis for an explanation of some remarkable properties of this substance (Okuda, Osaki & Taga, 1969).



$$\begin{array}{c} H_2COH \\ | \\ HOCH \\ | \\ C{=}O \\ | \\ HCOH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array}$$

(I)

Experimental

Crystals were obtained as colourless pentagonal plates by slow evaporation of an aqueous ethanol solution. They were stable in air. The cell dimensions were determined at 24 °C by least-squares calculations including only high-angle reflexions on zero-layer Weissenberg photographs (with $\lambda_{\mathrm{Cu}\,K\alpha_1}=1{\cdot}54051$ Å), calibrated with NaCl ($a_0=5{\cdot}639$ Å). The crystal density was measured at 25 °C by the flotation method in a mixture of chloroform and bromoform. Crystallographic data are as follows: coriose (D-*altro*-3-heptulose), $C_7H_{14}O_7$, monoclinic, $a=11{\cdot}33\pm0{\cdot}01$, $b=7{\cdot}460\pm0{\cdot}005$, $c=5{\cdot}205\pm0{\cdot}005$ Å, $\beta=90{\cdot}75\pm0{\cdot}05$, $V=439{\cdot}99$ Å^3, $D_m=1{\cdot}596$ g.cm^{-3}, $D_x=1{\cdot}584$ g.cm^{-3} (assuming $Z=2$), $\mu=12{\cdot}7$ cm^{-1} (for Cu $K\alpha$). Systematic absences were observed only for $0k0$ reflexions with k = odd. Since coriose crystals are optically active, the space group is $P2_1$ (No. 4).

Intensities were recorded for layers 0 to 6 about the *b* axis and 0 to 4 about the *c* axis of equi-inclination Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation. The crystals used for the intensity measurement were approximately cylindrical with mean diameters of 0·35 mm both for the *b* and *c* axes. The relative intensities were estimated visually by comparison with a standard scale, and corrected for Lorentz and polarization factors and for absorption effects. They were correlated and reduced to structure factors $|F_o|$ and normalized structure factors $|E|$ for 1046 independent reflexions (Rollett, 1965).

The values of the statistical averages for $|E|$ and $|E^2-1|$ were 0·887 and 0·775 compared with the theoretical values, 0·886 and 0·736, for a noncentrosymmetric space group.

Structure determination

The structure was determined directly by the application of the symbolic addition procedure (Karle & Karle, 1966*a*, *b*).

Initially three phases to specify the origin, and three symbols, were assigned (Hauptman & Karle, 1956), as listed in Table 1; symbols *a* and *b* must be 0 or π, but *p* lies somewhere in the range $0<p<\pi$.

Table 1. *Phase assignments for specifying the origin and implementing equation* (1)

h			$\varphi_{\mathbf{h}}$	$\lvert E_{\mathbf{h}}\rvert$
−9	1	5	0	3·00
5	0	1	0	2·54
2	0	1	0	2·20
−5	0	1	*a*	2·07
9	0	0	*b*	2·97
1	3	1	*p*	2·03

The phase determining procedure, using the formula

$$\varphi_{\mathbf{h}}=\langle\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}_r}\,, \qquad (1)$$

was applied first to $h0l$ reflexions with $|E|>1{\cdot}5$, since there are a relatively large number of $h0l$ reflexions with large enough $|E|$ values. During this stage 28 phases were determined in terms of *a* and *b*, and it became apparent that the symbols *a* and *b* should be 0 and π respectively. The next step was to apply formula (1) to general hkl reflexions, and 106 phases with $|E|>1{\cdot}5$ were determined in terms of the symbol *p* and it seemed likely that *p* was near 0 or π. Since *p* cannot be exactly 0 or π for a noncentrosymmetric crystal, *p* was initially assigned the value $\frac{1}{2}\pi$, and 117 phases with $|E|>1{\cdot}4$ were determined and refined by the use of the tangent formula (Karle & Karle, 1966*a*). An *E* map computed with these phases provided a reasonable structure, which gave an *R* value of 0·24 for reflexions with $\sin\theta<0{\cdot}8$.

Refinement

The refinement of the positional and thermal parameters was carried out first by four cycles of isotropic diagonal least-squares calculations, which reduced the *R* value to 0·13 for all the observed reflexions. A difference Fourier synthesis was then computed and all the hydrogen atoms were revealed at reasonable positions with respect to the carbon and oxygen atoms. Inclusion of the hydrogen atoms and three more cycles of anisotropic block-diagonal refinement reduced the R index to 0·08, at which stage the refinement was terminated. The last shift of any parameter was less than the corresponding estimated standard deviation.

The final positional and thermal parameters are given in Tables 2 and 3. Parameters of the thermal ellipsoids are illustrated in Fig. 1. Observed and calculated values of the structure factors are listed in Table 4, the scattering factor values being taken from *International Tables for X-ray Crystallography* (1962).

Table 2. *Positional parameters in fractional coordinates*

The estimated standard deviations given in parentheses refer to the last decimal positions of the respective values.

	x/a	*y/b*	*z/c*
C(1)	0·4877 (6)	0·7860 (12)	0·2863 (16)
C(2)	0·4012 (6)	0·2454 (12)	0·8634 (14)
C(3)	0·2885 (6)	0·2638 (11)	0·6899 (14)
C(4)	0·1744 (6)	0·2404 (10)	0·8486 (14)
C(5)	0·1305 (6)	0·4365 (12)	0·8700 (14)
C(6)	0·1654 (7)	0·5158 (11)	0·6145 (14)
C(7)	0·1691 (4)	0·7184 (12)	0·6062 (16)
O(1)	0·3841 (4)	0·7385 (10)	0·1287 (12)
O(2)	0·3950 (5)	0·3657 (10)	0·0759 (10)
O(3)	0·2971 (4)	0·1389 (9)	0·4894 (10)
O(4)	0·0928 (4)	0·1370 (9)	0·6993 (10)
O(5)	0·0075 (4)	0·4501 (9)	0·9203 (10)
O(6)	0·2847 (4)	0·4448 (9)	0·5875 (11)
O(7)	0·1750 (5)	0·7929 (9)	0·3591 (11)
H(1)	0·491 (10)	0·901 (17)	0·357 (21)
H(2)	0·487 (10)	0·694 (18)	0·479 (25)
H(3)	0·393 (10)	0·110 (18)	0·935 (21)
H(4)	0·189 (10)	0·169 (18)	0·065 (22)
H(5)	0·162 (10)	0·488 (18)	0·033 (21)
H(6)	0·118 (10)	0·455 (18)	0·422 (21)
H(7)	0·238 (10)	0·751 (19)	0·752 (22)
H(8)	0·113 (10)	0·739 (19)	0·688 (22)
H(9)	0·382 (10)	0·646 (17)	0·097 (21)
H(10)	0·355 (10)	0·323 (18)	0·203 (22)
H(11)	0·334 (11)	0·092 (17)	0·341 (21)
H(12)	0·057 (11)	0·076 (18)	0·801 (21)
H(13)	−0·006 (13)	0·407 (16)	0·002 (26)
H(14)	0·173 (11)	0·912 (17)	0·365 (22)

Description and discussion

The conventional numbering and identification of the atoms are shown in Fig. 1. The molecule is the α-anomer with a furanose ring.

Bond lengths in the molecule are given in Table 5. The C–C bond lengths range from 1·510 to 1·560 Å with mean value 1·539 Å and the C–OH bond lengths range from 1·403 to 1·467 Å with mean value 1·425 Å. No bond length differs from the corresponding mean value by more than 2σ except C(1)–O(1), 1·467 Å, which is greater than any C–OH bond length ever reported in pyranose sugars (Kim & Rosenberg, 1967) or than the corresponding C–OH bond length in L-ascorbic acid (Hvoslef, 1968). The ring C–O distances are 1·458 and 1·452 Å, which may be compared with the mean values of 1·455 and 1·426 Å derived from the furanose rings in nucleic acids (Sundaralingam & Jensen, 1965). The average values of C–H and O–H bond lengths are 1·07 and 0·87 Å respectively.

Valence angles are given in Table 6. The carbon valence angles inside the ring range from 101·6 to 106·2° with mean value 102·9°, and those outside the ring range from 108·0 to 113·7° with mean value 110·4°. The oxygen valence angle in the ring is 108·7° which may be compared with the mean value of 109·3° from the furanose rings in nucleic acids (Sundaralingam & Jensen, 1965).

With respect to the conformation of the furanose structure, the hydroxyl groups O(3)H, O(4)H and O(5)H are *cis* to each other and C(2) and C(7) are *trans* to these hydroxyl groups. The O(3)–O(4) and O(4)–O(5) distances are 2·573 and 2·783 Å respectively. These oxygen atoms are pushed away from each other. The five-membered ring is not strictly planar, but the four atoms other than C(5) are approximately in the same plane. The equation of the best plane through these four atoms is expressed as follows:

$$0{\cdot}3603X+0{\cdot}4528Y+0{\cdot}8156Z=5{\cdot}060\,,$$

where the orthogonal axes of X and Y were chosen to coincide with the a and b axes respectively of the crys-

Table 3. *Thermal parameters of non-hydrogen atoms*

β as given here is defined by:

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·0007 (3)	0·0093 (14)	0·0200 (28)	−0·0004 (6)	−0·0021 (8)	−0·0026 (17)
C(2)	0·0009 (3)	0·0079 (13)	0·0144 (24)	−0·0003 (6)	−0·0002 (7)	0·0013 (16)
C(3)	0·0006 (3)	0·0069 (13)	0·0140 (24)	0·0004 (6)	0·0001 (7)	0·0008 (15)
C(4)	0·0010 (3)	0·0059 (13)	0·0137 (24)	−0·0019 (6)	0·0000 (7)	−0·0008 (15)
C(5)	0·0009 (3)	0·0080 (13)	0·0148 (24)	−0·0009 (6)	−0·0002 (8)	−0·0026 (16)
C(6)	0·0010 (3)	0·0061 (12)	0·0135 (24)	0·0002 (6)	0·0005 (7)	−0·0002 (15)
C(7)	0·0025 (4)	0·0056 (13)	0·0218 (29)	0·0003 (7)	0·0000 (9)	0·0015 (17)
O(1)	0·0009 (2)	0·0133 (13)	0·0256 (23)	−0·0007 (5)	−0·0025 (6)	−0·0040 (15)
O(2)	0·0018 (3)	0·0141 (12)	0·0125 (18)	−0·0002 (5)	0·0002 (6)	−0·0023 (14)
O(3)	0·0021 (3)	0·0086 (10)	0·0143 (18)	0·0001 (5)	0·0009 (6)	−0·0022 (13)
O(4)	0·0018 (2)	0·0058 (9)	0·0180 (19)	−0·0024 (5)	−0·0004 (6)	−0·0010 (12)
O(5)	0·0007 (2)	0·0094 (10)	0·0187 (19)	0·0003 (5)	0·0025 (6)	−0·0040 (12)
O(6)	0·0011 (2)	0·0068 (9)	0·0205 (19)	0·0006 (5)	0·0009 (6)	0·0044 (12)
O(7)	0·0015 (2)	0·0093 (10)	0·0207 (21)	0·0019 (5)	0·0007 (6)	0·0047 (13)

tal lattice. The displacements of the atoms from the best plane are given in Table 7. Of the five atoms in the ring, the biggest deviation is 0·62 Å for C(5) which is on the same side of the plane as C(2) and C(7). Among the atoms attached to the ring, O(3) and O(4) are regarded as quasi-axial and O(5), C(2) and C(7) are quasi-equatorial. This conformation of the ring most closely resembles that of ribofuranose in adenosine monophosphate (AMP) of all the furanosides in nucleic acids (Sundaralingam, 1965). The bond lengths and angles in coriose, except C(3)–C(4), are in good agreement with those in AMP (Kraut & Jensen, 1963), as shown in Table 8. The C(3)–C(4) distance of 1·554 Å in coriose is much larger than 1·509 Å in AMP, and even larger than 1·53 Å in sucrose (Brown & Levy, 1963) in which the anomeric carbon atom, corresponding to C(3) in coriose, is bonded with carbon and oxygen atoms as in the case of coriose.

Table 4. *Observed and calculated structure factors*

The columns in each group headed by the values of k and l give h, $10|F_o|$, and $10|F_c|$.

H	FO	FC
K,L= 0 0		
2	211	205
3	105	86
4	236	242
5	117	96
6	181	185
7	273	261
8	58	52
9	310	326
10	264	271
11	106	118
12	41	44
13	109	97
14	40	29
K,L= 0 1		
0	58	52
K,L= 0 -1		
1	319	358
2	130	121
3	221	225
4	354	357
5	416	405
6	104	84
7	55	45
8	168	169
9	177	166
10	19	26
11	53	57
12	53	55
13	43	52
14	89	86
K,L= 0 1		
1	220	229
2	648	790
3	192	176
4	74	50
5	502	473
6	328	286
7	79	72
8	325	307
9	18	9
10	48	49
11	94	99
12	76	75
13	21	29
14	7	9
K,L= 0 2		
0	40	49
K,L= 0 -2		
1	118	114
2	268	281
3	214	222
4	180	186
5	125	125
6	35	30
7	21	16
8	39	45
9	71	58
10	83	86
11	24	23
12	48	53
13	12	3
14	0	87
K,L= 0 2		
1	203	177
2	114	126
3	188	183
4	107	74
5	100	79
6	38	34
7	305	277
8	68	55
9	46	39
10	130	131
11	47	47
12	26	29
13	84	93
K,L= 0 3		
0	28	29
K,L= 0 -3		
1	97	98
2	95	78
3	28	16
4	84	71
5	50	45
6	132	132
7	163	155
8	111	97
9	66	66
10	10	16
11	101	98
12	54	43
13	31	30
K,L= 0 3		
1	142	120
2	134	126
3	250	224
4	53	45
5	63	60
6	44	48
7	83	82
8	14	13
9	55	60
10	0	3
11	52	41
12	87	91
K,L= 0 4		
0	196	210
K,L= 0 -4		
1	11	12
2	14	0
3	76	93
4	8	9
5	226	233
6	28	24
7	51	50
8	49	46
9	114	107
10	54	51
11	63	58
K,L= 0 4		
1	105	96
2	78	76
3	84	83
4	278	275
5	150	132
6	96	96
7	98	96
8	78	85
9	86	92
10	54	53
11	10	21
K,L= 0 5		
0	124	117
K,L= 0 -5		
1	84	81
2	69	68
3	45	47
4	35	25
5	24	11
6	28	23
7	21	28
8	45	31
9	49	41
K,L= 0 5		
1	12	6
2	71	70
3	121	113
4	45	39
5	69	60
6	93	76
7	11	14
8	125	104
9	8	7
K,L= 0 6		
0	0	1
K,L= 0 -6		
1	41	29
2	25	15
3	13	5
4	13	11
5	49	49
6	21	13
K,L= 0 6		
1	28	26
2	90	68
3	60	47
4	41	20
5	37	38
6	14	16
K,L= 1 0		
2	160	169
3	35	35
4	309	325
5	158	146
6	177	161
7	131	125
8	205	201
9	172	167
10	58	58
11	81	80
12	19	12
13	54	45
14	12	3
K,L= 1 1		
0	479	592
K,L= 1 -1		
1	122	114
2	266	276
3	114	106
4	358	408
5	160	150
6	267	258
7	120	113
8	76	70
9	97	105
10	103	109
11	68	75
12	30	29
13	121	120
14	59	62
K,L= 1 1		
1	128	125
2	192	180
3	328	298
4	338	303
5	96	80
6	176	160
7	201	182
8	34	35
9	145	140
10	156	147
11	122	127
12	22	28
13	104	109
14	30	49
K,L= 1 2		
0	125	135
K,L= 1 -2		
1	234	247
2	257	275
3	151	143
4	147	148
5	197	178
6	45	34
7	76	69
8	134	132
9	189	186
10	30	23
11	24	22
12	45	41
13	63	62
K,L= 1 2		
1	161	149
2	210	211
3	105	93
4	131	120
5	182	165
6	39	42
7	28	26
8	103	94
9	175	171
10	31	31
11	81	75
12	62	58
13	63	62
K,L= 1 3		
0	176	182
K,L= 1 -3		
1	198	197
2	147	147
3	105	111
4	142	148
5	147	150
6	99	85
7	180	186
8	81	80
9	27	40
10	18	10
11	87	87
12	9	11
K,L= 1 3		
1	192	182
2	72	66
3	103	90
4	149	149
5	59	57
6	75	80
7	159	163
8	98	100
9	33	33
10	45	48
11	75	71
12	44	47
K,L= 1 4		
0	70	83
K,L= 1 -4		
1	129	127
2	49	50
3	43	44
4	82	85
5	154	149
6	143	140
7	42	45
8	28	35
9	54	55
10	19	18
11	43	37
K,L= 1 4		
1	135	141
2	82	78
3	20	21
4	102	97
5	64	57
6	30	25
7	29	31
8	70	77
9	56	58
10	74	75
11	37	40
K,L= 1 5		
0	109	113
K,L= 1 -5		
1	87	84
2	31	35
3	12	18
4	112	111
5	54	51
6	58	55
7	36	37
8	39	33
9	145	127
K,L= 1 5		
1	118	113
2	62	61
3	91	84
4	108	100
5	83	85
6	57	53
7	40	35
8	69	62
9	47	48
K,L= 1 6		
0	7	87
K,L= 1 -6		
1	74	63
2	12	11
3	10	14
4	53	49
5	12	11
6	33	25
K,L= 1 6		
1	92	71
2	45	40
3	46	35
4	38	25
5	23	18
K,L= 2 0		
1	314	332
2	153	130
3	191	176
4	200	194
5	236	225
6	94	86
7	161	154
8	145	135
9	210	214
10	79	75
11	28	29
12	33	31
13	34	22
14	87	100
K,L= 2 1		
0	257	233
K,L= 2 -1		
1	225	218
2	208	208
3	307	295
4	223	201
5	15	17
6	136	125
7	61	60
8	16	14
9	29	38
10	25	17
11	43	42
12	40	46
13	143	147
14	46	46
K,L= 2 1		
1	266	248
2	107	97
3	47	29
4	102	91
5	105	88
6	161	150
7	93	97
8	97	97
9	200	198
10	125	129
11	45	51
12	5	7
13	37	32
K,L= 2 2		
0	232	208
K,L= 2 -2		
1	113	113
2	141	155
3	115	102
4	68	40
5	141	140
6	73	80
7	151	159
8	129	131
9	100	113
10	27	26
11	69	78
12	35	26
13	84	80
K,L= 2 2		
1	143	143
2	350	359
3	142	130
4	245	228
5	39	16
6	132	125
7	96	82
8	26	26
9	64	64
10	119	120
11	89	94
12	68	60
13	78	93
K,L= 2 3		
0	46	61
K,L= 2 -3		
1	192	199
2	120	116
3	117	114
4	122	125
5	121	117
6	145	147
7	43	37
8	62	62
9	83	82
10	31	33
11	55	53
12	58	55
K,L= 2 3		
1	94	85
2	12	5
3	49	43
4	195	188
5	129	127
6	64	59
7	44	49
8	101	108
9	57	53
10	42	50
11	43	40
12	44	38
K,L= 2 4		
0	90	106
K,L= 2 -4		
1	44	56
2	52	57
3	69	70
4	24	27
5	156	158
6	79	85
7	132	136
8	19	24
9	98	91
10	80	79
11	45	44
K,L= 2 4		
1	108	109
2	72	67
3	87	87
4	178	180
5	101	105
6	49	46
7	10	7
8	37	41
9	50	54
10	20	20
K,L= 2 5		
0	64	70
K,L= 2 -5		
1	73	73
2	62	67
3	82	70
4	8	8
5	110	123
6	34	35
7	50	46
8	74	63
9	54	55
K,L= 2 5		
1	61	69
2	61	61
3	19	20
4	25	25
5	66	65
6	53	49
7	49	43
8	34	42
K,L= 2 6		
0	99	96
K,L= 2 -6		
1	80	66
2	25	13
3	68	61
4	34	26
5	28	23
K,L= 2 6		
1	18	16
2	41	33
3	52	46
4	20	29
K,L= 3 0		
1	368	367
2	245	242
3	133	135
4	96	91
5	37	48
6	153	144
7	128	124
8	31	31
9	73	68
10	68	67
11	81	89
12	52	50
13	41	32
K,L= 3 1		
0	177	172
K,L= 3 -1		
1	165	165
2	138	138
3	191	186
4	151	135
5	138	125
6	67	73
7	63	68
8	27	31
9	230	253
10	103	109
11	41	47
12	45	55
13	51	50
K,L= 3 1		
1	430	436
2	138	117
3	141	141
4	82	84
5	121	105
6	195	180
7	132	128
8	114	113
9	83	82
10	104	116
11	58	64
12	16	27
13	36	47
K,L= 3 2		
0	161	164
K,L= 3 -2		
10	248	90
2	55	49
3	167	157
4	185	177
6	87	87
7	99	95
8	161	165
10	64	90
11	20	29
12	12	13
13	59	75
K,L= 3 2		
1	96	88
2	183	179
3	137	136
4	125	126
5	165	160
6	188	175
7	37	39
8	89	100
9	147	153
10	43	41
11	54	57
12	12	12
13	37	61
K,L= 3 3		
0	96	95
K,L= 3 -3		
1	89	85
2	129	137
3	120	132
4	42	45
5	106	109
6	151	157
7	131	131
8	21	29
9	31	29
10	35	30
11	57	53
12	18	17
K,L= 3 3		
1	86	84
2	101	96
3	22	34
4	260	256
5	95	89
6	31	38
7	57	58
8	90	99
9	61	71
10	77	82
11	73	67
12	31	35
K,L= 3 4		
0	41	49
K,L= 3 -4		
1	43	51
2	43	49
3	51	56
4	22	21
5	109	107
6	56	50
7	30	34
8	12	4
9	39	39
10	39	43
K,L= 3 4		
1	106	115
2	119	135
3	25	30
4	78	89
5	19	14
6	26	34
7	45	47
8	43	46
9	104	120
10	20	28
K,L= 3 5		
0	57	67
K,L= 3 -5		
1	17	12
2	39	35
3	42	45
4	45	42
5	78	74
6	23	22
7	47	43
8	41	44
K,L= 3 5		
1	0	3
2	23	30
3	79	20
4	36	44
5	55	66
6	33	43
7	0	6
8	49	76
K,L= 3 6		
0	34	35
K,L= 3 -6		
1	75	78
2	21	24
3	31	37
4	31	35
K,L= 3 6		
1	51	57
2	16	15
3	15	21
K,L= 3 5		
4	43	44
K,L= 4 0		
1	128	126
2	75	61
3	105	196
4	30	29
5	172	165
6	175	166
7	142	142
8	64	55
9	144	152
10	51	50
11	50	49
12	69	62
13	31	34
K,L= 4 1		
0	49	50
K,L= 4 -1		
1	104	94
2	41	58
3	105	197
4	83	83
5	158	144
6	121	121
7	67	65
8	127	132
9	72	81
10	62	71
11	17	14
12	38	34
13	29	27
K,L= 4 1		
1	231	233
2	182	188
3	34	29
4	61	64
5	119	117
6	58	68
7	68	70
8	151	153
9	58	55
10	51	53
11	18	19
12	53	57
K,L= 4 2		
0	162	155
K,L= 4 -2		
1	148	135
2	64	55
3	140	141
4	75	80
5	38	27
6	91	101
7	91	88
8	45	44
9	128	134
10	78	85
11	28	21
12	42	45
K,L= 4 2		
1	133	125
2	94	90
3	96	91
4	125	130
5	51	53
6	63	59
7	83	90
8	18	14
9	45	48
10	135	132
11	43	42
12	42	41
K,L= 4 3		
0	80	91
K,L= 4 -3		
1	97	104
2	113	117
3	84	93
4	138	136
5	78	72
6	67	68
7	74	74
8	116	116
9	44	39
10	24	19
11	17	17
K,L= 4 3		
1	112	119
2	86	84
3	58	60
4	59	64
5	102	105
6	97	106
7	69	74
8	68	72
9	60	66
10	56	50
11	24	30
K,L= 4 4		
0	138	158
K,L= 4 -4		
1	21	16
2	138	142
3	53	54
4	27	30
5	67	65
6	56	65
7	38	41
8	26	26
9	72	66
K,L= 4 4		
1	41	44
2	36	34
3	40	47
4	70	76
5	40	35
6	33	32
7	72	83
8	93	102
9	76	89
K,L= 4 5		
0	41	44
K,L= 4 -5		
1	49	54
2	14	15
3	35	35
4	71	66
5	69	64
6	23	24
7	36	33
K,L= 4 5		
1	65	75
2	81	87
3	19	17
4	49	52
5	12	11
6	12	13
7	17	20
K,L= 4 6		
0	18	24
K,L= 4 -6		
1	32	39
K,L= 4 6		
1	14	22
K,L= 5 0		
1	26	36
2	28	22
3	106	104
4	59	62
5	37	43
6	63	71
7	39	36
8	82	78
9	36	33
10	53	52
11	24	24
12	44	49
K,L= 5 1		
0	211	204
K,L= 5 -1		
1	63	56
2	96	99
3	124	126
4	18	14
5	33	25
6	80	81
7	173	171
8	71	77
9	95	99
10	85	89
11	53	56
12	61	70
K,L= 5 1		
1	146	142
2	152	157
3	82	85
4	30	29
5	110	111
6	83	81
7	17	16
8	44	46
9	97	103
10	41	32
11	29	25
12	56	62
K,L= 5 2		
0	223	224
K,L= 5 -2		
1	59	57
2	181	177
3	96	99
4	135	140
5	188	188
6	96	97
7	32	31
8	25	35
9	76	81
10	44	46
11	49	49
K,L= 5 2		
1	112	110
2	41	46
3	157	161
4	186	181
5	138	137
6	85	79
7	75	79
8	126	132
9	72	66
10	41	37
11	29	34
K,L= 5 3		
0	136	146
K,L= 5 -3		
1	30	33
2	87	88
3	28	23
4	73	74
5	90	98
6	65	66
7	62	63
8	81	79
9	44	39
10	85	85
K,L= 5 3		
1	33	26
2	150	153
3	164	172
4	118	119
5	85	84
6	61	59
7	50	54
8	61	60
9	30	25
10	67	79
K,L= 5 4		
0	56	56
K,L= 5 -4		
1	60	66
2	23	29
3	31	35
4	16	13
5	42	44
6	109	102
7	27	27
8	11	13
K,L= 5 4		
1	49	50
2	39	39
3	11	10
4	63	69
5	57	73
6	20	21
7	23	21
8	43	53
K,L= 5 5		
0	23	23
K,L= 5 -5		
1	39	37
2	48	47
3	51	55
4	100	100
5	31	27
K,L= 5 5		
1	46	41
2	42	42
3	22	23
4	32	34
5	33	42
K,L= 5 0		
1	78	36
2	21	17
3	49	49
4	99	101
5	158	161
6	33	33
7	78	85
8	56	54
9	64	66
10	101	86
11	38	42
K,L= 6 1		
0	110	113
K,L= 6 -1		
1	63	78
2	116	116
3	77	83
4	104	100
5	52	51
6	100	111
7	91	100
8	66	70
9	89	85
10	96	100
K,L= 6 1		
1	128	125
2	59	42
3	45	41
4	143	134
5	120	106
6	21	24
7	106	107
8	78	76
9	68	65
10	34	31
11	44	55
K,L= 6 2		
0	47	40
K,L= 6 -2		
1	35	34
2	83	85
3	62	59
4	156	159
5	96	101
6	43	43
7	27	34
8	66	63
9	48	40
10	32	21
K,L= 6 2		
1	75	74
2	104	104
3	144	142
4	97	86
5	65	67
6	71	63
7	93	92
8	38	41
9	68	66
10	15	18
K,L= 6 3		
0	65	58
K,L= 6 -3		
1	43	44
2	93	99
3	50	51
4	80	79
5	73	70
6	28	22
7	32	26
8	32	30
9	60	64
K,L= 6 3		
1	19	14
2	58	59
3	60	58
4	83	80
5	60	68
6	12	10
7	68	75
8	12	13
9	11	13
K,L= 6 4		
0	62	67
K,L= 6 -4		
1	61	65
2	28	31
3	42	46
4	34	35
5	8	9
6	17	19
7	17	11
K,L= 6 4		
1	14	7
2	13	13
3	26	30
4	44	42
5	12	11
6	24	20
7	28	47
K,L= 6 5		
0	60	65
K,L= 6 -5		
1	52	57
2	26	28
3	25	31
K,L= 6 5		
1	11	14
2	11	13

Table 4 (*cont.*)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
K,L=	6	0	7	25	24	4	52	50	3	47	45	4	62	53	3	29	32	4	21	17	3	21	26	K,L=	9	2
1	72	78	8	17	13	5	43	36	4	21	22	K,L=	7	4	4	47	43	5	47	36	4	70	57	0	87	85
2	18	17	9	77	81	6	31	30	5	80	72	1	17	21	5	58	54	6	10	7	K,L=	9	0	K,L=	9	-2
3	14	49	K,L=	7	1	7	81	79	6	42	38	2	35	32	6	40	31	K,L=	8	2	1	73	67	1	35	34
4	142	137	1	74	86	8	96	89	7	56	53	3	15	14	7	52	56	1	68	62	2	12	10	K,L=	9	2
5	38	35	2	44	44	K,L=	7	2	K,L=	7	3	4	34	37	K,L=	8	1	2	59	50	3	13	13	1	47	28
6	96	97	3	59	61	1	25	31	1	51	53	K,L=	8	0	1	21	22	3	51	40	4	16	15	K,L=	2	0
7	58	47	4	60	63	2	65	63	2	25	30	1	44	39	2	21	31	4	39	36	K,L=	9	1	0	372	390
8	34	31	5	33	31	3	75	81	3	30	28	2	21	21	3	0	5	5	43	39	0	40	35	0	250	251
9	57	55	6	25	18	4	25	26	4	70	68	3	25	29	4	67	62	K,L=	8	3	K,L=	9	-1	0	190	196
K,L=	7	1	7	17	14	5	47	47	5	33	28	4	72	77	5	36	38	0	58	50	1	27	19	0	70	66
0	113	124	8	56	46	6	38	40	6	11	11	5	94	81	6	33	35	K,L=	8	-3	2	53	44	1	71	51
K,L=	7	-1	9	86	80	7	45	36	7	65	73	6	46	41	7	61	56	1	77	65	3	70	64	1	289	328
1	35	36	K,L=	7	2	8	22	28	K,L=	7	4	7	29	20	K,L=	8	2	2	36	31	4	60	65	K,L=	4	-4
2	68	73	0	59	62	K,L=	7	3	0	78	71	K,L=	8	1	0	48	40	3	49	44	K,L=	9	1	10	59	61
3	10	18	K,L=	7	-2	0	49	37	K,L=	7	-4	0	47	58	K,L=	8	-2	4	48	36	1	21	27	K,L=	2	4
4	68	76	1	71	70	K,L=	7	-3	1	32	32	K,L=	8	-1	1	27	24	K,L=	8	3	2	41	34	11	26	38
5	76	91	2	39	45	1	28	26	2	52	51	1	83	89	2	50	36	1	21	18	3	23	22	K,L=	6	-1
6	38	41	3	22	20	2	0	6	3	15	12	2	52	53	3	42	39	2	33	28	4	29	22	11	53	62

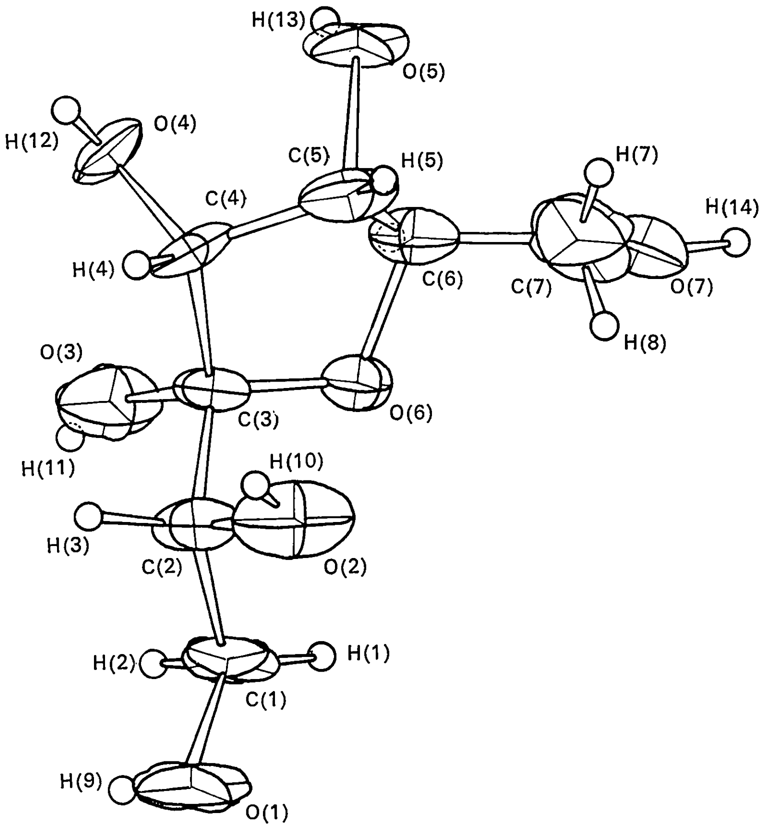


Fig. 1. Identification and numbering of the atoms in the molecule.

Table 5. *Bond lengths*

The estimated standard deviations given in parentheses refer to the last desimal positions of the respective values.

	Length		Length
C(1)-C(2)	1·520 (13) Å	C(1)-H(1)	0·93 (13) Å
C(2)-C(**3**)	1·560 (13)	C(1)-H(2)	1·21 (14)
C(3)-C(4)	1·554 (12)	C(2)-H(3)	1·08 (13)
C(4)-C(5)	1·550 (13)	C(4)-H(4)	1·25 (14)
C(5)-C(6)	1·510 (13)	C(5)-H(5)	1·00 (13)
C(6)-C(7)	1·521 (13)	C(6)-H(6)	1·21 (14)
C(1)-O(1)	1·467 (12)	C(7)-H(7)	1·11 (15)
C(2)-O(2)	1·427 (12)	C(7)-H(8)	0·80 (15)
C(3)-O(3)	1·403 (11)	O(1)-H(9)	0·71 (13)
C(4)-O(4)	1·427 (11)	O(2)-H(10)	0·87 (14)
C(5)-O(5)	1·425 (12)	O(3)-H(11)	0·95 (13)
C(6)-O(6)	1·458 (11)	O(4)-H(12)	0·81 (14)
C(7)-O(7)	1·404 (12)	O(5)-H(13)	0·95 (14)
C(3)-O(6)	1·452 (11)	O(7)-H(14)	0·89 (13)

The O(1)-C(1)-C(2)-O(2) dihedral angle is 68·7° and the O(1)-O(2) bond is *gauche*. O(2)-C(2)-C(3)-O(3) is *trans* and accordingly the atom O(2) is stretched over the furanose ring. The distance from O(2) to O(6) in the ring is 2·85 Å, but O(2)-O(6) is not an intramolecular hydrogen bond, since the hydrogen atom attached to O(2) is not found in the appropriate position. The O(7)-C(7)-C(6)-O(6) dihedral angle is 111·8°, and the orientation of the C(7)-O(7) part with regard to the ring is stereochemically unstable. This might be the consequence of the three hydrogen bonds from hydroxyl groups in the neighboring molecule.

The crystal structure is illustrated in Fig. 2, as viewed in orthographic projection along the *c* axis. The crystal is composed of a three-dimensional hydrogen bond network, as can be seen in the Figure. It should be

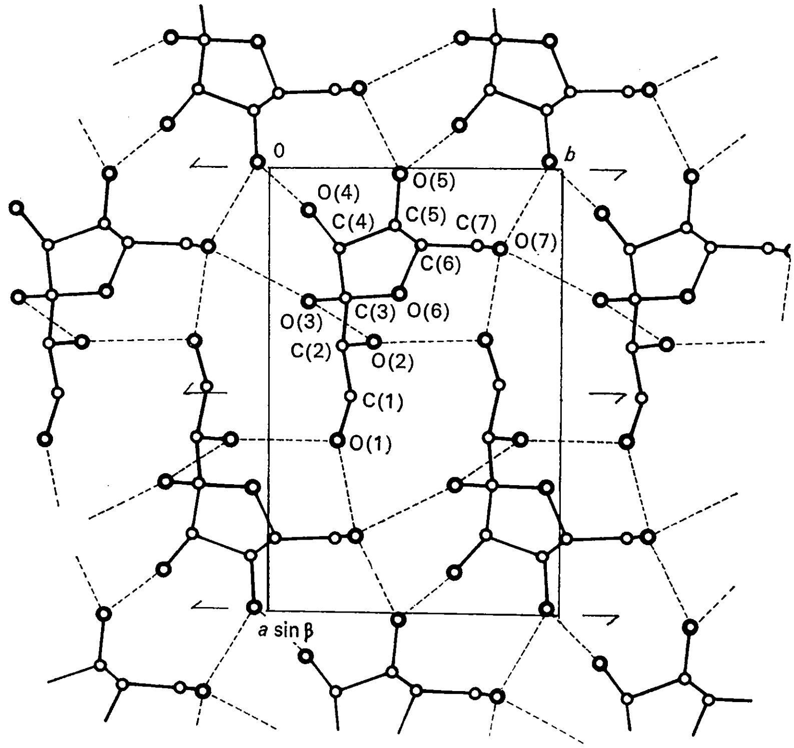


Fig. 2. Projection of the atomic positions along the c axis; hydrogen bonds are shown by dashed lines.

Table 6. *Bond angles for covalent bonds of non-hydrogen atoms*

The estimated standard deviation is less than 0·7° for all angles.

C(1)–C(2)–C(3)	111·3°	C(5)–C(4)–O(4)	110·1°
C(2)–C(3)–C(4)	111·3	C(4)–C(5)–O(5)	113·3
C(3)–C(4)–C(5)	101·7	C(6)–C(5)–O(5)	113·7
C(4)–C(5)–C(6)	102·3	C(5)–C(6)–O(6)	101·6
C(5)–C(6)–C(7)	114·8	C(7)–C(6)–O(6)	109·2
C(2)–C(1)–O(1)	109·1	C(6)–C(7)–O(7)	115·0
C(1)–C(2)–O(2)	108·8	C(3)–O(6)–C(6)	108·7
C(3)–C(2)–O(2)	110·2	O(3)–C(3)–O(6)	110·3
C(2)–C(3)–O(3)	107·9	C(2)–C(3)–O(6)	108·3
C(4)–C(3)–O(3)	112·8	C(4)–C(3)–O(6)	106·2
C(3)–C(4)–O(4)	108·0		

Table 7. *Deviations* (Å) *of the atoms from the best plane**

Atoms marked † were included in the least-squares calculation of the best plane.

C(1)	1·009	O(1)	1·937
C(2)	1·050	O(2)	2·328
C(3)†	−0·080	O(3)	−1·312
C(4)†	0·045	O(4)	−1·268
C(5)	0·619	O(5)	0·375
C(6)†	−0·053	O(6)†	0·084
C(7)	0·616	O(7)	−0·152

* See text.

noted here that the hydrogen bond O(2)---O(3) is actually an intermolecular hydrogen bond between two molecules separated by a translation along the c axis.

All the hydroxyl groups in the structure contribute their hydrogen atoms to a hydrogen bond. O(7) accepts two hydrogen bonds and O(4) accepts none. All other oxygen atoms accept one hydrogen bond.

Hydrogen-bond lengths are given in Table 9. O(2)---O(3) and O(7)---O(3) lengths may be rather great, but the positions of the hydrogen atoms attached to these oxygen atoms indicate that they are hydrogen bonds.

The coriose studied here is the first case where a furanose structure has been established in a crystal of a monosaccharide, although such a structure has often been found among the sugar derivatives. All other monosaccharides hitherto analysed have a pyranose form. In the case of D-*manno*-3-heptulose, another member of 3-heptulose, the furanose forms may be

Table 8. *Bond lengths and angles of coriose and* AMP

C–C bond lengths

	Coriose	AMP
C(3)–C(4)	1·554 Å	1·509 Å
C(4)–C(5)	1·550	1·544
C(5)–C(6)	1·510	1·520
C(6)–C(7)	1·521	1·525

C–O bond lengths

	Coriose	AMP
C(3)–O(6)	1·452 Å	1·445 Å
C(6)–O(6)	1·458	1·476
C(4)–O(4)	1·427	1·438
C(5)–O(5)	1·425	1·400

Internal angles of the ring

	Coriose	AMP
C(3)–O(6)–C(6)	108·7°	108·3°
C(4)–C(3)–O(6)	106·2	106·7
C(5)–C(6)–O(6)	101·6	104·0
C(3)–C(4)–C(5)	101·7	101·7
C(6)–C(5)–C(4)	102·3	99·9

External angles of the ring

	Coriose	AMP
C(3)–C(4)–O(4)	108·0°	107·0°
C(5)–C(4)–O(4)	110·1	110·0
C(4)–C(5)–O(5)	113·3	115·4
C(6)–C(5)–O(5)	113·7	115·6
C(5)–C(6)–C(7)	114·8	119·1
O(6)–C(6)–C(7)	109·2	107·9

Table 9. *Hydrogen bond lengths*

The estimated standard deviation is 0·012 Å for all bond lengths in the Table.

Bond	Length
O(1)---O(2)	2·798 Å
O(2)---O(3)	2·964
O(3)---O(7)	3·002
O(4)---O(5)	2·686
O(5)---O(7)	2·773
O(7)---O(1)	2·700

regarded as being less unfavourable than that of coriose, since the number of *cis* substituents is less in the former. Even in this case the actual form found in the monohydrate crystal is β-pyranose (Taga & Osaki, 1969). Thus the furanose form in crystalline coriose is a novel one and might be a consequence of the possible stabilizing effect due to the elaborate three-dimensional network of hydrogen bonds.

The authors wish to thank Dr T. Ashida for the use of the block-diagonal least-squares program *HBLS*. All other computations were made using the programs written by one of the authors, T. Taga. We are indebted to the Kyoto University Computation Centre for the use of KDC II computer, and also to the Computer Centre of the University of Tokyo for the use of a HITAC 5020E.

References

Brown, G. M. & Levy, H. A. (1963). *Science*. **141**, 921.
Eliel, E. L., Allinger, N. L., Angyal, S. J. & Morrison, G. A. (1965). *Conformational Analysis*, p. 351. New York: John Wiley.
Hauptman, H. & Karle, J. (1956). *Acta Cryst.* **9**, 45.
Hvoslef, J. (1968). *Acta Cryst.* B**24**, 1431.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Karle, I. L. & Karle, J. (1966*a*). *Acta Cryst.* **21**, 849.
Karle, I. L. & Karle, J. (1966*b*). *Acta Cryst.* **21**, 860.
Kim, S. H. & Rosenberg, R. D. (1967). *Acta Cryst.* **22**, 648.
Kraut, J. & Jensen, L. H. (1963). *Acta Cryst.* **16**, 79.
Okuda, T., Osaki, K. & Taga, T. (1969). *Chem. Comm.* p. 851.
Okuda, T. & Konishi, K. (1968). *Chem. Comm.* p. 553.
Rollett, J. S. (1965). In *Computing Methods in Crystallography*. Oxford: Pergamon Press.
Sundaralingam, M. (1965). *J. Amer. Chem. Soc.* **87**, 599.
Sundaralingam, M. & Jensen, L. H. (1965). *J. Mol. Biol.* **13**, 930.
Taga, T. & Osaki, K. (1969). *Tetrahedron Letters*. No 51, p. 4433.