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1,2,3,5-Tetra-O-acetyl-β-D-ribofuranose

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Abstract. C₁₃H₁₈O₉, orthorhombic, $P2_12_12_1$, $a=7.501$ (1), $b=13.665$ (1), $c=15.337$ (1) Å, $Z=4$, $D_m=1.345$ g cm⁻³. The acetyl groups each adopt the expected planar conformation with the carbonyl and acetyl CO bonds in an eclipsed disposition; in addition, for three of the four methyl groups, one CH bond is *cis* to the carbonyl bond. The furanose ring has the ³T₂ twist conformation, with normal bond lengths and angles except for the C(5)C(4) bond which is 1.508 (3) Å. Final *R* value was 0.052 with 1891 observed reflections. The structure agrees well with that determined by James & Stevens [*Cryst. Struct. Commun.* (1973), **2**, 609–612].

Introduction. The title compound is reported to crystallize in two forms: *A*, m.p. 58°C, and *B*, m.p. 85°C (Brown, Davoll & Lowy, 1955). Form *B* will catalyze the transformation of *A* to *B* in both the liquid and solid state (Davoll, Brown & Visser, 1952). A preliminary X-ray investigation of the solid-state transformation gave the cell parameters of Table 1 for the two forms (Patterson & Groshens, 1954), which imply

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Table 1. Cell parameters

	Form <i>A</i>	Form <i>B</i>
<i>a</i>	12.49 Å	7.50 Å
<i>b</i>	5.58	13.66
<i>c</i>	11.12	15.33
β	97.75°	
<i>Z</i>	2	4
<i>V</i>	767.9 Å ³	1570.6 Å ³
Space group	$P2_1$	$P2_12_1$
	Monoclinic	Orthorhombic

an increase of the molecular volume by about 2% in passing from *A* to the more stable *B* form. The mechanism of the transformation is unknown and if the reported loss of acetic acid (Davoll, Brown & Visser, 1952) is indeed associated with the change then the system is most unusual.

An attempt to produce the rare *A* form by application of high pressure, based on the assumption that the transformation was conformational rather than chemical, was not successful. The infrared spectrum and polarization in visible light were followed up to a pressure of 4.2 GPa, but no variations attributable to the desired change were noted (Linton, 1973).

In an initial step to resolve this unusual behavior the structure determination of the title compound was undertaken. Subsequently a report of an independent determination appeared (James & Stevens, 1973). The present paper reports the results of our analysis and briefly compares the two structure analyses.

Structure analysis

A crystal was ground approximately spherical to a radius of 0.21 (1) mm from a sample supplied by Dr C. M. Stewart of the CSIRO Division of Chemical Technology, Melbourne. The unit-cell parameters were derived by least-squares refinement against 2θ values for 15 reflections ($45^\circ \leq 2\theta \leq 90^\circ$) determined on a Nonius CAD-4 diffractometer with graphite-monochromated Cu radiation ($\lambda=1.5418$ Å). A total of 1871 integrated intensities were measured with an ω - 2θ scan; of these reflections 140 were less than $3\sigma_I$. The usual Lorentz and polarization corrections were applied in addition to an absorption correction based on a spherical crystal.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and completed with, initially, the system of Shiono (1971) and later the X-RAY

system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) modified to operate on a PDP10 computer (Ernst & Poppleton, 1974). All H atoms were located and the final least-squares cycle was blocked, through core limitations, into two groups comprising 19 and 21 atoms. In this final cycle all positional parameters

Table 2. Atomic fractional coordinates ($\times 10^5$)
Estimated standard deviations are in parentheses.

	x	y	z
C(1)	4777 (35)	-33329 (17)	1595 (16)
C(2)	12594 (37)	-43185 (17)	-943 (16)
C(3)	-1505 (34)	-49962 (16)	2936 (14)
C(4)	-18856 (32)	-44448 (17)	1290 (15)
C(5)	-33667 (37)	-46238 (20)	7743 (18)
C(6)	-31364 (45)	-37267 (22)	21108 (19)
C(7)	-23255 (81)	-37184 (52)	29775 (26)
C(8)	8544 (41)	-66315 (18)	2164 (18)
C(9)	8269 (54)	-75459 (23)	-3179 (30)
C(10)	23707 (48)	-49730 (23)	-14222 (20)
C(11)	23090 (87)	-48262 (40)	-23884 (25)
C(12)	8662 (39)	-22258 (20)	13336 (19)
C(13)	17791 (72)	-20973 (38)	22089 (32)
O(1)	11061 (28)	-31567 (12)	10270 (12)
O(2)	12091 (26)	-43528 (13)	-10253 (11)
O(3)	-2274 (23)	-59390 (11)	-1147 (10)
O(4)	-13750 (24)	-34291 (12)	1410 (12)
O(5)	-27051 (28)	-45342 (15)	16514 (12)
O(6)	-41238 (53)	-31066 (21)	18112 (20)
O(1)	17375 (47)	-65123 (18)	8600 (15)
O(10)	32830 (40)	-55483 (17)	-10426 (16)
O(12)	635 (32)	-16209 (14)	9560 (14)

	$x(\times 10^4)$	$y(\times 10^4)$	$z(\times 10^4)$	$u(\times 10^3)$
H(O1)	866 (52)	-2813 (25)	-201 (20)	54 (8)
H(O2)	2208 (74)	-4408 (27)	45 (22)	70 (10)
H(O3)	364 (40)	-5040 (21)	869 (18)	34 (6)
H(O4)	-2225 (43)	-4647 (21)	-405 (18)	42 (7)
H(O51)	-4252 (59)	-4090 (30)	749 (24)	68 (10)
H(O52)	-3958 (54)	-5346 (28)	707 (23)	47 (10)
H(O71)	-2819 (218)	-4258 (88)	3296 (73)	378 (40)
H(O72)	-2879 (128)	-3106 (59)	3246 (50)	116 (23)
H(O73)	-1290 (147)	-3773 (65)	2896 (52)	178 (22)
H(O91)	1448 (98)	-7758 (48)	-883 (34)	166 (17)
H(O92)	-523 (85)	-7540 (38)	-477 (29)	101 (13)
H(O93)	1819 (67)	-8064 (27)	123 (21)	64 (10)
H(111)	1131 (318)	-4142 (108)	-2393 (131)	258 (67)
H(112)	1784 (97)	-5460 (42)	-2547 (32)	76 (14)
H(113)	3201 (154)	-4882 (65)	-2535 (67)	130 (27)
H(131)	1602 (119)	-2693 (60)	2574 (45)	104 (20)
H(132)	1486 (57)	-1510 (29)	2457 (23)	57 (9)
H(133)	2720 (225)	-2209 (80)	2228 (64)	103 (36)

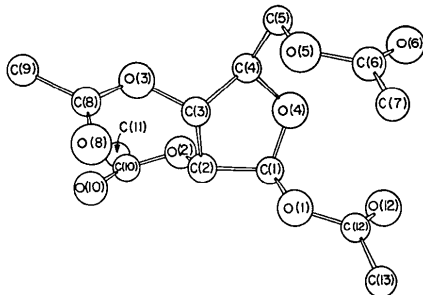


Fig. 1. Numbering of the C and O atoms. H atoms are given the same number as the C atom to which they are attached together with an additional numeral to differentiate where necessary between H atoms attached to the same C atom.

were varied with anisotropic temperature factors for C and O, and isotropic temperature factors for H. Also included was an overall scale factor, while weights were assigned from counting statistics; R was 0.052. The final atomic fractional coordinates and thermal parameters* with their estimated standard deviations are given in Table 2, and the atom numbering is in Fig. 1.

Structure assessment

The final electron-density difference map calculated using all reflections showed no variations greater than $0.2 e \text{ \AA}^{-3}$. However, R deteriorated significantly at low angle with F_c commonly calculating greater than F_o . This suggested that extinction might be significant, but two cycles of least-squares refinement of an isotropic extinction coefficient, g , showed little improvement: $g = (37 \pm 33) \times 10^{-6} \text{ cm}$.

A qualitative assessment is provided by the H atom bond lengths and angles, particularly those of the methyl groups. The estimated standard deviations are high and there is clearly some distortion, but for the most part they are within reasonable limits. Similar remarks apply to the structure determination by James & Stevens (1973).

A quantitative comparison of the two structures can be made using a half-normal probability plot (Abrahams & Keve, 1971). This plot is shown in Fig. 2 for the positional parameters of the non-H atoms [an error of sign in the James & Stevens z coordinate of C(12) was corrected before plotting]. The plot is linear, with perhaps a tendency to turn up at the higher quantile values which would indicate some systematic error. The curvature is much more pronounced if the H coordinates are included in the analysis. The slope of the plot suggests that the computed least-squares standard deviations need to be multiplied by approximately 1.9 to provide true estimates of the errors. This factor is in good agreement with that derived from other comparisons of a similar kind (Hamilton & Abrahams, 1970; De Camp, 1973).

Discussion. The bond lengths and angles listed in Table 3 show no unexpected variations (Kennard *et al.*, 1972), and are in good agreement with those reported by James & Stevens. Of the minor variations the short anomeric CO bond is well known, as are the short C(4)C(5) bond and the disproportionation of the ring CO bonds (Arnott & Hukins, 1972). For the acetyl groups the various bond lengths are close to the mean observed for a number of other sugar acetates

* The U_{ij} values for the non-hydrogen atoms, a table of least-squares planes, a figure showing the packing of the molecules and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31780 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond lengths and angles

C(1)—C(2)	1.520 Å	C(7)—H(O71)	0.96 Å
—O(1)	1.432	—H(O72)	1.02
—O(4)	1.396	—H(O73)	0.79
—H(O1)	0.95	C(8)—C(9)	1.494
C(2)—C(3)	1.526	—O(3)	1.346
—O(2)	1.429	—O(8)	1.200
—H(O2)	0.75	C(9)—H(O91)	1.03
C(3)—C(4)	1.524	—H(O92)	1.04
—O(3)	1.433	—H(O93)	1.23
—H(O3)	0.96	C(10)—C(11)	1.496
C(4)—C(5)	1.507	C(10)—O(2)	1.360
—O(4)	1.440	—O(10)	1.193
—H(O4)	0.90	C(11)—H(111)	1.29
C(5)—O(5)	1.439	—H(112)	0.98
—H(O51)	0.99	—H(113)	0.71
—H(O52)	1.09	C(12)—C(13)	1.517
C(6)—C(7)	1.461	—O(1)	1.368
—O(5)	1.348	—O(12)	1.175
—O(6)	1.216	C(13)—H(131)	1.00
		—H(132)	0.91
		—H(133)	0.72

Central atom	Con-tiguous atoms	Angle	Central atom	Con-tiguous atoms	Angle
C(1)	O(4), C(2)	107.2°	C(8)	O(3), O(8)	123.2°
	—O(4), O(1)	111.2		—O(3), O(9)	111.9
	—O(1), C(2)	105.1		—O(8), C(9)	124.9
C(2)	C(1), C(3)	99.8	C(10)	O(2), O(10)	124.0
	—C(1), O(2)	105.9		—O(2), C(11)	109.9
	—O(2), C(3)	110.6		—O(10), C(11)	126.1
C(3)	C(2), C(4)	103.1	C(12)	O(1), O(12)	123.5
	—C(2), O(3)	113.8		—O(1), C(13)	110.6
	—O(3), C(4)	109.7		—O(12), C(13)	125.9
C(4)	C(3), C(5)	116.1	O(1)—C(1), C(12)		115.6
	—C(3), O(4)	104.3	O(2)—C(2), C(10)		116.8
	—O(4), C(5)	110.1	O(3)—C(3), C(8)		116.3
C(5)	C(4), O(5)	110.2	O(4)—C(4), C(1)		110.8
C(6)	O(5), O(6)	121.3	O(5)—C(5), C(6)		118.4
	—O(5), C(7)	112.4			
	—O(6), C(7)	126.3			

Table 4. Torsion angles (°)

C(1)C(2)C(3)C(4)	+37.3	C(3)O(3)C(8)O(8)	+6.0
C(2)C(3)C(4)O(4)	−29.6	C(4)C(5)O(5)C(6)	+105.7
C(3)C(4)O(4)C(1)	+9.1	C(5)O(5)C(6)O(6)	+3.3
C(4)O(4)C(1)C(2)	+15.6	C(12)O(1)C(1)H(O1)	+46
O(4)C(1)C(2)C(3)	−33.0	C(10)O(2)C(2)H(O2)	+33
C(1)O(1)C(12)O(12)	+6.6	C(8)O(3)C(3)H(O3)	−19
C(2)O(2)C(10)O(10)	+7.7	C(6)O(5)C(5)H(O51)	−12
C(2)C(1)O(1)C(12)	+167.6	O(2)C(2)C(3)O(3)	+44.8
C(3)C(2)O(2)C(10)	−95.6	O(4)C(4)C(5)O(5)	−69.8
C(4)C(3)O(3)C(8)	−156.7		

(Leung & Marchessault, 1974, and references therein; James & Stevens, 1974*a, b, c*).

The torsion angles of Table 4 show that the furanose ring has the twist conformation, 3T_2 .

For each of the acetate groups the plane comprising O—CO—CH₃ is planar to within 0.006 Å, whilst the remaining C is invariably *cis* to the carbonyl bond and within 0.15 Å of the same plane. Similarly each methyl group, with the possible exception of C(11), is disposed so that one CH is planar with and *cis* to the C=O. This approximate coplanarity of CH₃—CO—O—C allows the disposition of the acetate groups

with respect to the furanose ring to be visualized readily using the HCOC torsion angles, where the H is attached to the ring (Table 4). They reveal a bias toward coplanarity of the ring CH and the acetate C=O; Mathieson (1965) has discussed in some detail this preferred conformation of the acetate group.

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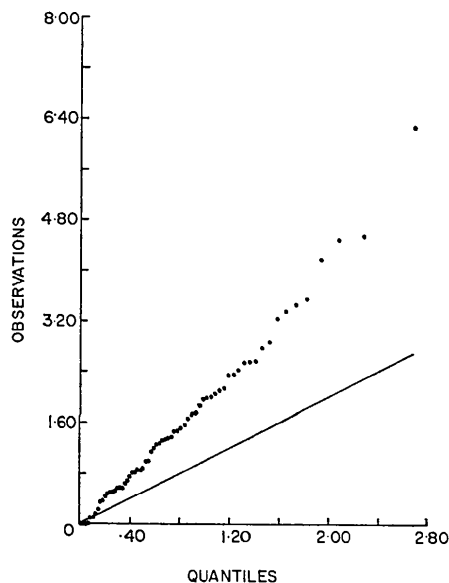


Fig. 2. Half-normal probability plot: the vertical axis is the statistic δp_i ; the horizontal axis is the expected δp_i (Abrahams & Keve, 1971). $\delta p_i = |P_i| - |P_i'| / (\sigma^2 P_i + \sigma^2 P_i')^{1/2}$ where P_i, P_i' are the atom coordinates of the two independent structure determinations and $\sigma^2 P_i, \sigma^2 P_i'$ are the associated variances in the parameters.

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Le Sulfure Mixte d'Uranium et de Scandium U_3ScS_6

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Abstract. Orthorhombic, space group $Pnmm$, $a = 16.355$ (8), $b = 13.472$ (7), $c = 3.823$ (2) Å; $Z = 4$. The crystal structure was determined from single-crystal Enraf-Nonius CAD-4 diffractometer data, with Patterson and Fourier syntheses, and refined by full-matrix least-squares calculations. $R = 0.054$.

Introduction. Ce composé a été rencontré dans une préparation réalisée en chauffant le mélange $3UO_2 \cdot Sc_2O_3$ dans un courant d'hydrogène sulfuré, pendant 4 h, vers $1350^\circ C$. Afin d'obtenir des monocristaux, le produit ainsi obtenu a été fondu dans une atmosphère d'argon, puis refroidi lentement. La température de fusion n'est pas connue avec précision mais paraît se situer aux environs de $1800^\circ C$.

Le monocristal utilisé, prélevé dans la préparation grossièrement écrasée, a sensiblement la forme d'un parallélépipède et mesure approximativement $30 \times 40 \times 120 \mu m$. Les diagrammes d'oscillation et de Weissenberg, obtenus en l'irradiant avec le rayonnement X $K\alpha$ du cuivre, révèlent un réseau de symétrie orthorhombique. Les dimensions de la maille, déterminées d'abord à partir des diagrammes précédents, puis confirmées et précisées à l'aide d'un diffractomètre automatique Enraf-Nonius CAD-4, ont les valeurs suivantes: $a = 16,355$ (8), $b = 13,472$ (7), $c = 3,823$ (2) Å. On observe toutes les réflexions avec les seules restrictions: $h0l$: $h+l=2n$ et $0kl$: $k+l=2n$. Le symbole de diffraction du réseau est donc $mmmPnn$; il lui correspond deux groupes spatiaux, $Pnn2$ et $Pnmm$ (n° 34 et 58 dans

International Tables for X-ray Crystallography). La valeur du paramètre c permet de penser que les positions les plus vraisemblables, au moins pour une partie des atomes, sont les positions $4(g)$ du groupe $Pnmm$ dont les coordonnées sont de la forme: $\pm(x, y, 0)$, $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2})$. Cette remarque, admise comme hypothèse de travail, a été confirmée par la détermination de la structure.

Les intensités des réflexions, obtenues avec le rayonnement $K\alpha$ du molybdène isolé par un monochromateur à lame de graphite, ont été mesurées à l'aide du diffractomètre déjà cité, dans les conditions suivantes: Balayage $\omega/2\theta$ d'amplitude s ($^\circ$) = $0,60 + 0,30 \operatorname{tg} \theta$. Domaine de mesures: $0 \leq \theta \leq 35^\circ$, $0 \leq h \leq 26$, $0 \leq k \leq 21$, $0 \leq l \leq 6$. Indices des réflexions choisies pour contrôler la stabilité des mesures: $\bar{6}31, 270, 360$. Ecart-type relatif moyen sur les facteurs de structure correspondant à ces trois réflexions: 0,018. Chacune de ces trois réflexions a été mesurée 21 fois au cours de l'enregistrement. Nombre de réflexions mesurées: 2073. Nombre de réflexions nulles: 350. Nombre de réflexions conservées pour la résolution de la structure: 1681. Les intensités de ces dernières vérifient la relation: $I < 2\sigma(I)$. Elles ont été corrigées des facteurs de Lorentz et de polarisation.

Dans l'hypothèse envisagée précédemment, les maximums de la fonction de Patterson $P(u, v, w)$ sont situés dans les plans $w=0$ et $w=\frac{1}{2}$. L'étude de ces deux sections a permis de déterminer les valeurs approchées des coordonnées de deux atomes d'uranium. Les autres