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CRYSTAL STRUCTURE AND ^{1}H- AND ^{13}C-N.M.R. STUDIES OF 1,4:3,6-DIANHYDRO-α-D-GLUCOPYRANOSE OBTAINED FROM PYROLYSIS OF CELLULOSE

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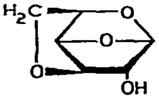
ABSTRACT

The crystal structure of a compound obtained by pyrolysis of cellulose, whose chemical structure has been proposed as 1,4:3,6-dianhydro-α-D-glucopyranose, has been confirmed by X-ray crystallographic analysis. Proton- and ^{13}C-n.m.r. measurements were also made on it and the relationship between n.m.r.-spectroscopic and X-ray crystallographic results is discussed.

INTRODUCTION

1,4:3,6-Dianhydro-α-D-glucopyranose (**1**) was first reported by Tischenko *et al.*[1] in 1948 as one of the gasification products of wood, and its chemical structure was examined by ^{1}H-n.m.r. spectroscopy by Bedford and Gardiner[2]. This is the only example of a 1,4-anhydroaldopyranose except for 1,4:3,6-dianhydro-α-D-mannopyranose, obtained in the same way from D-mannose[2]. Similar crystals were also



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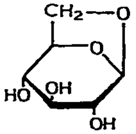

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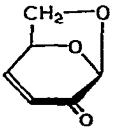

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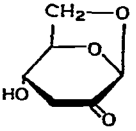

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obtained by the authors as one of the primary pyrolysis products of cellulose[3], and were originally reported[4] to be 1,6-anhydro-3-deoxy-β-D-*erythro*-hex-3-enopyranose. The crystals were recently established by Shafizadeh *et al.*[5] to be identical with **1** from t.l.c., g.l.c., and mixed-m.p. experiments. Interestingly **1** seems to be an intermediate in the conversion of 1,6-anhydro-β-D-glucopyranose (levoglucosan, **2**) into 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone, **3**) during the pyrolysis of cellulose[3,5]. However, no precise mechanism from **2** to **3** *via* **1** has been presented thus far, although a plausible scheme from **1** to **3** has been speculated upon[5].

This paper provides a definitive structure of **1** established by X-ray crystallographic analysis, and the results of ^{1}H- and ^{13}C-n.m.r. measurements.

EXPERIMENTAL

Sample. — Crude crystals were obtained from thermal degradation of cellulose by the procedure already described[4]; m.p. 128° (lit.[1] m.p. 127–128°, lit.[2] 122–123°, and lit.[5] 127.5–128°), $[\alpha]_D^{20}$ +86° (*c* 0.6, ethanol).

Crystal data. — A pure, single crystal (0.4 × 0.4 × 0.4 mm) of **1** was obtained by recrystallization from ethyl acetate, and subjected to a computer-controlled, crystal-structure analysis system, Rigaku RASA-IIF, having a MoKα radiation source (λ = 0.7107 Å), and a four-circle diffractometer with a graphite monochromator. The intensity data of 866 reflections up to 55° (2θ) were collected by using 2θ-ω scan technique at a rate of 2°(ω) min^{-1} and in the range of $\Delta 2\theta = (1.9 + 0.5 \tan\theta)°$. The data are available on demand*.

$C_6H_8O_4$, M = 144.14; space group, $P2_12_12_1$, orthorhombic, $Z = 4$; a = 8,981 ±0.002, b = 10.825 ±0.002, c = 6.282 ±0.001 Å, V = 610.7 Å^3, D_c = 1.57 g/cm^3.

Structure determination. — The molecular structure was solved by the direct method with the computer program MULTAN[6]. The non-hydrogen atoms were first located on the *E*-map and the structure was refined by the block-diagonal, least-square method. Next, the position of each hydrogen atom was determined by differential Fourier synthesis and further refinements (three cycles).

N.m.r. spectroscopy. — Proton- and ^{13}C-n.m.r. spectra were recorded in D_2O solution (4 mg/25 μL) at 23° with a JEOL FX-100 instrument equipped with a 1-mm diam. ^{1}H–^{13}C dual probe in the pulsed Fourier-transform mode operating in the time domain with 8192 data points at 99.55 and 25.00 MHz, respectively. Chemical shifts refer to an internal standard of methanol (δ 3.35 and 49.80 p.p.m. for ^{1}H and ^{13}C, respectively). Signal assignments for each proton and carbon atom were established by proton-selective, homo- and hetero-nuclear decoupling methods, respectively.

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*The table of structure factors can be obtained from Elsevier Scientific Publishing Company, BBA Deposition, P. O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/189/*Carbohydr. Res.*, 96 (1981) 161–166.

TABLE I

NON-HYDROGEN ATOMIC POSITIONAL PARAMETERS (× 10^4) (E.S.D. VALUES IN PARENTHESES) AND THERMAL PARAMETERS (× 10^5)

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O-1	4849(3)	7796(2)	−916(5)	1446	429	2996	231	317	74
O-2	6675(3)	6760(2)	−4191(5)	1329	798	2569	286	704	509
O-3	5979(3)	4816(2)	394(5)	827	551	3078	147	29	401
O-5	3269(3)	6209(3)	−1273(5)	637	1041	2667	62	−72	198
C-1	4326(4)	6926(4)	−2416(7)	803	813	2187	260	−82	259
C-2	5962(4)	6114(3)	−2814(6)	793	567	1983	144	32	36
C-3	6278(4)	5999(3)	−524(6)	604	448	2235	−23	−62	145
C-4	5258(5)	6910(3)	662(7)	1276	462	2051	22	−62	−96
C-5	3872(4)	6089(4)	852(6)	880	731	2071	124	344	136
C-6	4471(4)	4801(3)	1262(7)	1076	594	2759	−39	200	191

TABLE II

HYDROGEN POSITIONAL PARAMETERS (× 10^3) (E.S.D. VALUES IN PARENTHESES) AND THERMAL PARAMETERS (× 10^2)

Atom	*x*	*y*	*z*	β_{iso}
H-0	754(5)	616(4)	−431(7)	386
H-1	372(5)	731(4)	−366(7)	295
H-2	538(5)	522(4)	−343(7)	248
H-3	744(4)	619(4)	−46(7)	189
H-4	562(5)	729(4)	222(8)	311
H-5	306(5)	634(4)	188(7)	234
H-6^1	391(5)	402(4)	59(7)	259
H-6^2	456(5)	471(4)	302(8)	366

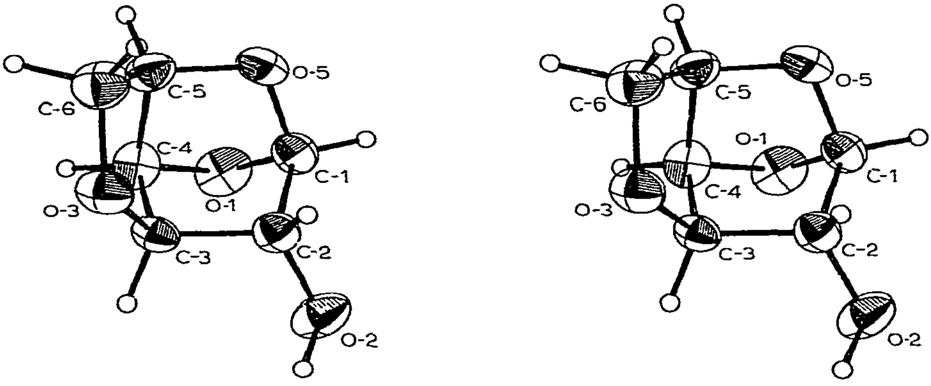

Fig. 1. Stereoscopic view of 1,4:3,6-dianhydro-α-D-glucopyranose (1).

RESULTS

The final positional and thermal parameters for each atom of the crystal are listed in Tables I (non-hydrogen) and II (hydrogen). The final R-index for 641 reflections having $I > 2\sigma(I)$ was 0.040. A sterescopic view of the molecule is shown in Fig. 1. Bond lengths and bond angles are summarized in Table III.

Proton and ^{13}C chemical shifts are summarized in Table IV. Coupling constants between vicinal protons were measured and the proton–proton dihedral angles

TABLE III

BOND LENGHTS (Å) AND BOND ANGLES (°) (E.S.D. VALUES IN PARENTHESES)

Bond	*Length*	*Bond*	*Angle*	*Bond*	*Angle*
C-1–C-2	1.529(5)	O-1–C-1–O-5	104.4(3)	O-1–C-4–H-4	116.0(2)
C-2–C-3	1.536(5)	O-1–C-1–C-2	103.0(3)	C-5–C-4–C-3	98.6(3)
C-3–C-4	1.538(5)	O-1–C-1–H-1	114.3(2)	C-5–C-4–H-4	112.4(2)
C-4–C-5	1.534(5)	O-5–C-1–C-2	107.7(3)	C-3–C-4–H-4	119.5(2)
C-5–C-6	1.517(5)	O-5–C-1–H-1	104.1(2)	O-5–C-5–C-4	100.4(3)
C-1–O-5	1.421(5)	C-2–C-1–H-1	121.9(2)	O-5–C-5–C-6	111.8(3)
C-5–O-5	1.446(5)	O-2–C-2–C-1	108.4(3)	O-5–C-5–H-5	107.3(3)
C-1–O-1	1.412(5)	O-2–C-2–C-3	113.4(3)	C-4–C-5–C-6	104.9(3)
C-4–O-1	1.427(5)	O-2–C-2–H-2	112.8(2)	C-4–C-5–H-5	118.7(2)
C-3–O-3	1.430(4)	C-1–C-2–C-3	99.7(3)	C-6–C-5–H-5	113.0(2)
C-6–O-3	1.460(5)	C-1–C-2–H-2	111.3(2)	O-3–C-6–C-5	104.8(3)
C-2–O-2	1.420(5)	C-3–C-2–H-2	110.5(2)	O-3–C-6–H-6^1	107.2(2)
C-1–H-1	1.048(4)	O-3–C-3–C-2	112.7(3)	O-3–C-6–H-6^2	107.6(2)
C-2–H-2	1.078(4)	O-3–C-3–C-4	105.5(3)	C-5–C-6–H-6^1	119.5(2)
C-3–H-3	1.072(4)	O-3–C-3–H-3	110.2(2)	C-5–C-6–H-6^2	105.8(2)
C-4–H-4	1.110(5)	C-2–C-3–C-4	101.4(3)	H-6^1–C-6–H-6^2	111.2(3)
C-5–H-5	1.010(4)	C-2–C-3–H-3	110.7(2)	C-1–O-1–C-4	95.8(3)
C-6–H-6^1	1.067(4)	C-4–C-3–H-3	116.1(2)	C-2–O-2–H-0	101.9(3)
C-6–H-6^2	1.110(5)	O-1–C-4–C-5	103.6(3)	C-3–O-3–C-6	109.6(3)
O-2–H-0	1.021(5)	O-1–C-4–C-3	104.3(3)	C-1–O-5–C-5	105.4(3)

TABLE IV

PROTON AND CARBON CHEMICAL SHIFTS (δ, P.P.M.) AT 23°

Atom	δ	*Multiplicity*	*Atom*	δ	*Multiplicity*
H-1	5.52	d	C-1	101.63	d
H-2	3.74	s	C-2	78.93	d
H-3	4.15	dd	C-3	82.68	d
H-4	5.36	dd	C-4	80.10	d
H-5	4.30	td	C-5	76.77	d
H-6^1 H-6^2	3.98	d	C-6	72.15	t

TABLE V

PROTON COUPLING-CONSTANTS AT 99.55 MHz, DIHEDRAL ANGLES, AND TORSION ANGLES

Coupling constants (Hz)		*Dihedral angles (°)*[a]	*Torsion angles (°)*[b]	
$J_{1,2}$	<0.1 (<0.4)[c]	85 (75)[c]	H-1–C-1–C-2–H-2	107.7
$J_{2,3}$	<0.1 (<0.4)	85 (105)	H-2–C-2–C-3–H-3	111.6
$J_{3,4}$	5.0 (4.5)	40 (25)	H-3–C-3–C-4–H-4	39.2
$J_{4,5}$	3.2 (3.0)	52 (40)	H-4–C-4–C-5–H-5	38.6
$J_{5,6^1}$	1.2 (1~2)	102 (70)	H-5–C-5–C-6–H-6^1	94.8
$J_{5,6^2}$		66 (50)	H-5–C-5–C-6–H-6^2	41.1
$J_{1,3}$	1.3 (1.0)			

[a]Calculated by the Karplus equation[7]. [b]Observed from the X-ray analysis. [c]The values in parentheses were obtained by Bedford and Gardiner[2] at 60 MHz.

calculated according to the Karplus equation[7], as shown in Table V. In Table V, the results of Bedford and Gardiner[2] and the torsion angles along C–C bonds obtained from the X-ray analysis (corresponding to the respective proton dihedral angles) are also shown.

DISCUSSION

The results of X-ray crystallographic analysis clearly indicate the structure of the compound to be **1** (Fig. 1). The pyranose ring has the $B_{4,1}$(D) conformation, but is considerably strained by the 1,4-anhydro linkage. Formation of such a 1,4-anhydro linkage in the pyranose ring is usually very difficult, because it requires a boat conformation ($B_{4,1}$ or $^{4,1}B$) of high energy. Examples of this have been reported only for two compounds; **1** and 1,4:3,6-dianhydro-α-D-mannopyranose[2]. Both of them have the 3,6-anhydro- as well as the 1,4-anhydro-linkage, which suggests that formation of the 1,4-linkage requires a somewhat rigid $B_{4,1}$ conformation achieved by prior formation of the 3,6-linkage. The squares defined by the atoms C-2–C-3–C-5–O-5 and C-3–C-5–C-6–O-3 are almost flat planes (deviations are <0.003 and <0.007 Å, respectively), and the angle relating these two planes is 113.00°.

The n.m.r. signal for H-2 is unusual in being almost a singlet, as shown in Table IV. Both $J_{1,2}$ and $J_{2,3}$ are very small (Table V). According to the Karplus equation, the respective dihedral angles are both ~85° (Table V, second column). On the other hand, the proton–proton torsion angles along C–C bonds obtained from the X-ray analysis are 107.7 and 111.6°, respectively (Table V, third column). Although the Karplus equation is only an approximation, the difference between these two results is substantial. As **1** seems to have a rigid, multi-cyclic structure, the difference between conformations in the crystal and in the solution is expected to be small. Thus, the Karplus equation fits poorly for this compound. The observed torsion angles H-1–C-1–C-2–H-2 and H-2–C-3–C-3–H-3 are quite similar (Table V, third column), indicating that H-1 and H-3 are almost symmetrically disposed with respect to C-2 or H-2. The appearance of the H-2 signal as a singlet may be caused, perhaps, by this symmetry.

Now that structure **1** has been confirmed, the most acceptable structure for the compound intermediate between **2** and **3** would appear to be 1,6-anhydro-3-deoxy-β-D-*erythro*-hexopyranos-2-ulose (**4**), according to general principles of carbohydrate chemistry. However, no direct proof has yet been obtained for the existence of **4** during pyrolysis of cellulose or other carbohydrates.

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