Carbohydrate Research, 90 (1981) 319–325
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

The crystal structure of 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose

THOMAS T STEVENSON*,
Department of Botany University of Washington Seattle Washington 98195 (U S A)
RONALD E STENKAMP, LYLE H JENSEN,
Department of Biological Structure, University of Washington Seattle, Washington 98195 (U S A)
TODD G COCHRAN,
School of Pharmacy, University of Montana Missoula Montana 59812 (U S A)
FRED SHAFIZADEH AND RICHARD H FURNEAUX
Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula Montana 59812 (U S A)

(Received September 15th 1980 accepted for publication October 30th 1980)

The potential for conversion of biomass residues into useful, chemical intermediates has stimulated research into the mechanism and products of the pyrolytic decomposition of cellulosic materials[1–3] Additional interest has arisen from the fact that many volatile, cellulose-pyrolysis products are introduced into the environment through tobacco- and wood-smoke[4] The title compound, 1,5-anhydro-4-deoxy D-*glycero*-hex-1-en-3-ulose (**1**), is a newly identified product obtained from the pyrolysis of cellulose and other D-glucans[5]. A characteristic feature of this molecule is its stable enol function, the presence of which has been confirmed by the single-crystal X-ray diffraction study reported here

A stereochemical drawing of **1** from the X-ray data is shown in Fig 1 This model is consistent with the results of the chemical-structure determination[5] From ^{1}H-n m r spectroscopy, it was concluded that **1** adopts the $^4H_5$ conformation in solution, with the 5-(hydroxymethyl) substituent in a quasi-equatorial position[5] The coupling observed between the two protons on C-4 and H-5 indicated that one of the proton dihedral-angles is large ($J_{4,5}$ 13 Hz), and the other small ($J_{4,5}$ 5 Hz) Fig 2 shows that this interpretation is consistent with the conformation adopted by **1** in the solid state, where the C-3–C-4–C-5–C-6 dihedral angle of 175° results in proton dihedral-angles of 193 and 65°

The conformation of **1** in the crystalline state can be accurately assessed from

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*Address correspondence to this author, at the Wood Chemistry Laboratory, University of Montana, Missoula MT 59812, U S A

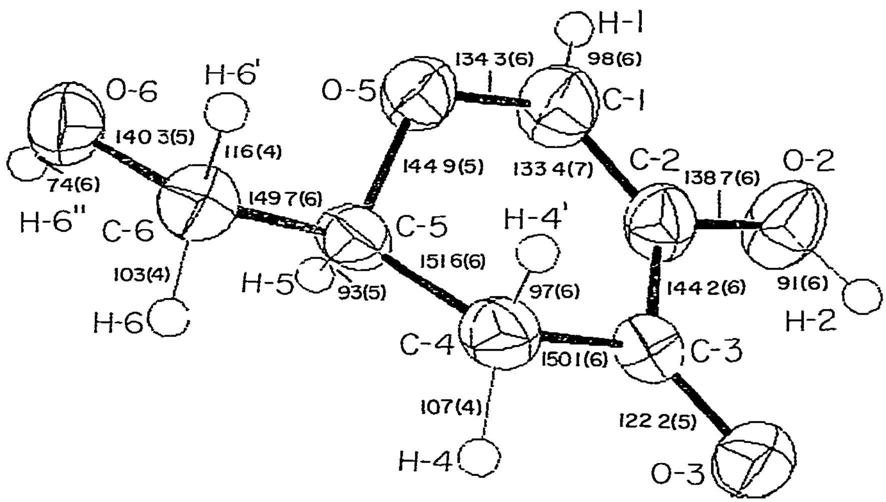


Fig 1 ORTEP[14] drawing of **1**, showing bond lengths (pm) with standard deviations in parentheses Thermal parameters for hydrogen are not depicted

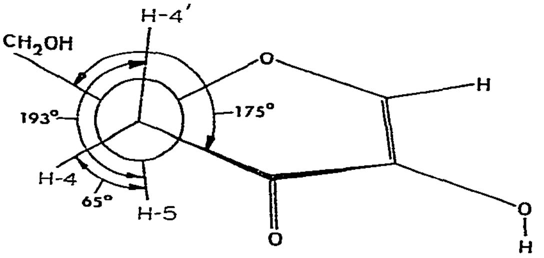


Fig 2 Projection of **1**, viewed along the C-4–C-5 axis, with dihedral angles from X-ray data

the atomic parameters obtained in the X-ray study The conformation can be described in terms of the deviation of atoms from a plane through the ring, or, more precisely, by ring-puckering parameters Both of these methods show that **1** adopts a sofa$_5$ conformation[6] (five ring-atoms coplanar) that is strongly distorted towards the $^{4}H_{5}$ conformation Table I lists deviations of ring atoms from several, least-squares planes calculated for **1** Plane I shows that five ring-atoms are nearly coplanar, none being displaced more than 6 1 pm from the plane, and that C-5 lies well below the plane, at —63.0 pm The distortion towards the $^{4}H_{5}$ conformation is evident from plane II, defined by the four ring-atoms required to be coplanar in this conformation, where C-5 again lies well below the plane, at —55 1 pm, and C-4 lies above the plane, at 12 3 pm The ring-puckering parameters, calculated according to Cremer and Pople[7] ($Q = 46\ 3$ pm, $\theta = 59\ 8°$, and $\phi = 286\ 7°$), and plotted on a stereogram[8], show that **1** adopts a conformation lying between sofa$_5$ (where $\phi = 300°$) and $^{4}H_{5}$ (where $\phi = 270°$) The sofa$_5$ and $^{4}H_{5}$ conformations both possess one large and one small dihedral angle between the protons on C-4 and C-5, and thus are not readily differentiated by ^{1}H-n m r spectroscopy

TABLE I

LEAST-SQUARES PLANES FOR **1**

Atom	Plane I	Plane II	Plane III
	Deviations of atoms from plane (pm)		
C-1	6.1[a]	4.2[a]	10.4
C-2	−2.3[a]	−4.0[a]	0.09[a]
C-3	−2.1[a]	1.8[a]	−0.09[a]
C-4	3.2[a]	12.3	7.1
C-5	−63.0	−55.1	−57.3
O-5	−4.7[a]	−2.0[a]	1.3
O-2	−0.8	−7.6	−0.04[a]
O-3	−0.3	4.1	0.05[a]
H-1	11.8	6.1	16.4
H-2	11.9	5.7	11.5
[O-3][b]			116.3
	Coefficients of equations for planes[c]		
m	−3.384	−3.411	−3.435
n	11.067	11.377	10.912
r	−2.698	−2.412	−2.646
s	3.067	3.156	2.952

[a] An atom defining the plane [b] O-3 at $3/2 - x$, $1 - y$, $-1/2 + z$ [c] $mx - ny + rz = s$

TABLE II

HYDROGEN-BOND DISTANCES AND ANGLES FOR **1**

Atom			Distance (pm)				Angle	Acceptor
Donor (D)	*H*	Acceptor (A)	D-*H*	*H*···A	*H*···A[a]	D···A	D-*H*···A (degrees)	symmetry
O-6	H-6″	O-6	74	208	187	275.1	152	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
O-2	H-2	O-3	91	210	206	287.8	142	$3/2 - x, 1 - y, -1/2 + z$
O-2	H-2	O-3	91	243	242	279.1	103	x, y, z

[a] *D*-H bond-length normalized to 97 pm

Hydrogen bonding plays an important role in the crystal structure of **1**, with both hydroxyl groups forming hydrogen bonds (see Table II). Intermolecular hydrogen-bonding between O-6 atoms of adjacent molecules forms an infinite chain running along the x axis of the crystal, with each O-6 atom serving as a hydrogen-bonding donor (*D*) and acceptor (*A*). This type of interaction is common in carbohydrate crystals, although the H···*A* distance of 208 pm is somewhat longer than the values obtained by neutron diffraction for infinite-chain hydrogen-bonding in other carbohydrates[9]. However, when the *D*–H-6″ bond-length is normalized to the mean, neutron-diffraction value[9] of 97 pm. the H-6″ *A* distance becomes 187 pm, which is consistent with values reported for this type of bonding

The enolic H-2 forms an intermolecular hydrogen-bond with the carbonyl O-3, linking the crystal lattice in the *z* direction The H *A* distance of 210 pm, which is essentially unchanged upon normalization of the *D*–H bond-length, indicates that this bond is weaker than the hydrogen bonding of the aliphatic hydroxyl H-6″ which is of the donor–acceptor type.

The position of H-2 in the crystal structure indicates that it is also involved in an intramolecular interaction with O-3, forming a bifurcated, hydrogen-bonding system Although the H *A* distance of 243 pm and the *D*–H *A* angle of 103° are not within the range generally accepted for isolated hydrogen-bonds, there is substantial evidence suggesting that a weak, intramolecular hydrogen-bond occurs between H-2 and O-3 in this structure The intermolecular, hydrogen-bond distance and angle between H-2 and O-3 of 210 pm and 142°, respectively, are much more typical of values reported for bifurcated, hydrogen-bonding systems than for isolated hydrogen-bonds[9] As may be seen from plane III in Table I, H-2 lies very close to the plane defined by O-2–C-2–C-3–O-3 In the absence of an intramolecular hydrogen-bond, the hydroxyl group could, presumably, rotate, thereby allowing H-2 to approach O-3 of the adjacent molecule more closely In actuality, H-2 deviates from this plane only very slightly in the direction of the adjacent O-3 Although the bond distance and angle for this intramolecular interaction between H-2 and O-3 indicate that it is very weak, they are not inconsistent with values reported for other weak, hydrogen-bonding interactions, especially in bifurcated systems[9] As noted by Jeffrey[10], vicinal, intramolecular hydrogen-bonding is necessarily weak, due to the geometric restrictions of the five-membered ring-system that is formed, and unambiguous examples of this type of interaction in carbohydrate crystals are rare

The bifurcated system of **1** is quite similar to that reported for 1,2-dihydroxy-

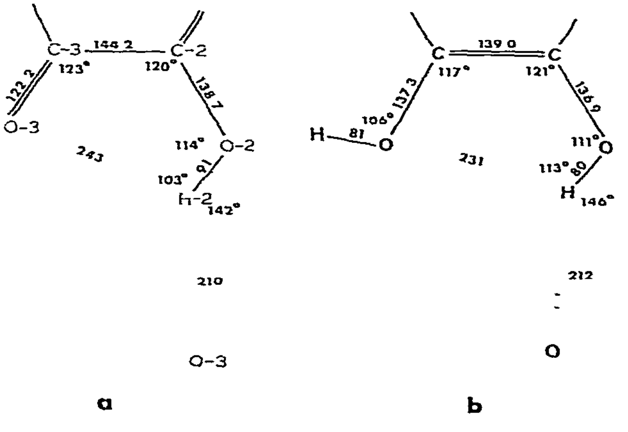
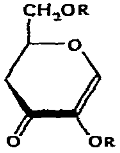


Fig 3 Bifurcated, hydrogen-bonding systems in (a) **1**, and (b) 1,2-dihydroxybenzene[11]

benzene (see Fig 3), which is also a planar, five-membered ring-system having adjacent, sp^2-hybridized carbon atoms Intramolecular hydrogen-bonding has been suggested in the crystalline state of 1,2-dihydroxybenzene, based on its X-ray crystal structure[11], and demonstrated in solution by infrared spectroscopy[12]

The presence of an intramolecular hydrogen-bond in **1** in the crystalline state had been suggested[5] from infrared spectroscopy (KBr pellet), where the carbonyl absorption of O-3 shifts from 1663 cm^{-1} for **1** to 1680 and 1690 cm^{-1} for its dibenzoate (**2**) and diacetate (**3**), indicating that the 2-hydroxyl group decreases the carbonyl force-constant, presumably through an intramolecular interaction



1 R = H
2 R = Bz
3 R = Ac

EXPERIMENTAL

Crystals of **1** ($C_6H_8O_4$ m p 98 5–99 0°) suitable for crystallographic work were obtained from a previous study[5] in which the spectral properties were reported By Weissenberg and precession photography, the unit cell was found to be orthorhombic, in space group $P2_12_12_1$ (systematic absences at h00,0k0, and 00l when h, k, or l is odd), $z = 4$ Intensity data were collected from a single crystal mounted on a computer-controlled, four-circle diffractometer for 590 unique reflections to $2\theta = 120°$, using CuKα radiation Cell parameters were found to be a = 477 65(6), b = 1853 15 (27), and c = 717.33(6) pm The intensities of standard reflections did not decrease during the data collection, and no decomposition correction was applied An empirical, absorption correction was applied

An initial phase-set, determined by direct methods using GENTAN[13], revealed the position of all non-hydrogen atoms, these were refined by CRYLSQ, the least-squares program of the X-RAY system[14] Thermal parameters for carbon and oxygen atoms were refined anisotropically, and hydrogen atoms were refined isotropically Weights of $1/\sigma$ were applied, and the stereochemistry of C-5 was assigned, based on the known, D configuration of the precursor cellulose The final refinement yielded values having all shift/errors <0 2, and R ($= \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) equal to 0 048 for 577 reflections having F_o greater than 4 times $\sigma(F_o)$ At this point, the Fourier-difference map showed no points having a density greater than 2×10^{-7}e-/pm^3, and the isotropic thermal parameters (U) for all hydrogen atoms averaged 560(195) pm^2, where the temperature factor is of the form $\exp[-2\pi^2(Uh^2a^{*2} + Uk^2b^{*2} + Ul^2c^{*2})]$

TABLE III

BOND ANGLES FOR **1**

Bond	*Angle (degrees)*	*Bond*	*Angle (degrees)*
H-1–C-1–C-2	119(4)	H-4′–C-4–C-5	98(3)
H-1–C-1–O-5	115(4)	C-4–C-5–O-5	110 5(3)
C-2–C-1–O-5	125 3(4)	C-4–C-5–H-5	116(3)
C-1–C-2–O-2	119 6(4)	C-4–C-5–C-6	113 1(4)
C-1–C-2–C-3	120 6(4)	O-5–C-5–H-5	99(3)
O-2–C-2–C-3	119 6(4)	O-5–C-5–C-6	107 4(4)
C-2–O-2–H-2	114(4)	H-5–C-5–C-6	110(3)
C-2–C-3–O-3	122 7(4)	C-1–O-5–C-5	114 1(4)
C-2–C-3–C-4	114 7(4)	C-5–C-6–O-6	114 3(4)
O-3–C-3–C-4	122 6(4)	C-5–C-6–H-6	99(2)
C-3–C-4–H-4	104(2)	C-5–C-6–H-6′	115(2)
C-3–C-4–H-4′	106(3)	O-6–C-6–H-6′	101(2)
C-3–C-4–C-5	111 0(4)	O-6–C-6–H-6	117(2)
H-4–C-4–H-4′	116(4)	H-6–C-6–H-6′	111(3)
H-4–C-4–C-5	121(2)	C-6–O-6–H-6″	120(4)

TABLE IV

FRACTIONAL ATOMIC-COORDINATES[a] [b] FOR **1**

Atom	x	y	z
C-1	2583(13)	3388(3)	−0935(7)
C-2	4612(11)	3873(2)	−1176(6)
C-3	5205(9)	4403(2)	0244(6)
C-4	3451(10)	4335(2)	1971(6)
C-5	2598(9)	3558(2)	2305(6)
C-6	0635(10)	3471(2)	3917(7)
O-2	6019(9)	3905(2)	−2865(5)
O-3	6908(7)	4887(2)	0026(4)
O-5	1219(8)	3265(2)	0672(4)
O-6	−0086(8)	2754(2)	4310(5)
H-1	213(16)	305(3)	−195(9)
H-2	709(14)	431(3)	−302(8)
H-4	460(9)	463(2)	299(6)
H-4′	161(13)	452(3)	165(8)
H-5	406(11)	323(2)	239(7)
H-6	175(10)	374(2)	492(6)
H-6′	−155(8)	373(2)	370(6)
H-6″	101(12)	249(3)	459(8)

[a] $a = 477\ 65(6)$, $b = 1853\ 15(27)$, $c = 717\ 33(6)$ pm, $\alpha = \beta = \gamma = 90°$ [b] $\times 10^4$ for C and O, $\times 10^3$ for H (standard deviations in parentheses)

Interatomic bond-angles and fractional atomic-coordinates are reported in Tables III and IV, respectively ‡

ACKNOWLEDGMENT

This work was supported, in part, by Research Grant GM 10828 from the National Institutes of Health

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‡Supplementary data Hydrogen and non-hydrogen thermal parameters (Table V) and a listing of observed and calculated structure factors (Table VI) 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/00/*Carbohydr Res*, 00 (1981) 000–000