THEORETICAL STUDIES ON THE CONFORMATION OF ALDOPYRANOSES

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ABSTRACT

The potential energy of eight aldopentopyranoses in their *C1*(D) and *1C*(D) conformations have been calculated. Minimization of the energies have been studied by suitably tilting the axial –OH groups. A small reduction in the total potential energy is observed when tilts of about 2° are given for the axial –OH groups. Conformational entropies have also been computed for all of the aldohexoses and aldopentoses, and these values have been used to obtain the free energies. The calculated free-energy values agree well with the experimental data on the equilibrium after adding a value of 0.4 kcal.mole^{-1} for the anomeric effect. The calculated values of the percentage of α-anomers present in the equilibrium mixture agree fairly well with those assigned from n.m.r. studies. The present data also indicate that all the aldohexopyranoses except α-D-altrose and α-D-idose exist only in *C1*(D) conformations, whereas all of the aldopentopyranoses except xylose exist in a *C1*(D) ⇄ *1C*(D) equilibrium in solution.

INTRODUCTION

The favoured conformations of aldopyranoses in aqueous solution have been determined from n.m.r. studies[1–11]. Angyal[11,12] has assigned interaction energies for the chair conformations of these molecules from experimental data obtained from the equilibria of cyclitols and from the equilibria of sugars. Recently the authors[13,14] calculated theoretically the potential energies of aldohexoses in the *C1*(D) and *1C*(D) conformations. These results[14] were in accord with the experimentally observed conformations. The same treatment has therefore been extended to calculate the potential energies of the aldopentoses, which differ from aldohexoses only in the nature of the C-5 substituent. The conformational entropies have also been estimated for both aldopentopyranoses and aldohexopyranoses; these values have been added to the corresponding potential energies to obtain the total conformational free-energies, in order to afford a better understanding of the conformations of simple sugars in aqueous solution.

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Theoretical treatment

The potential energy of a molecule was computed by using the expression

$$V = \sum_{i,j} V_{nb}(i,j) + \sum_{i,j} V_{es}(i,j) + \sum V_{\theta} \qquad (I)$$

where the first term represents the contribution from nonbonded interactions, the second term, the contribution from electrostatic interactions, and the third term the deviation of the single-bond angle from tetrahedral values. The expressions for $V_{nb}(i,j)$, $V_{es}(i,j)$ and V_{θ}, and the constants used, are the same as those reported earlier[14]. Deviations in bond lengths have not been considered in the minimization procedure, as they are energetically more expensive.

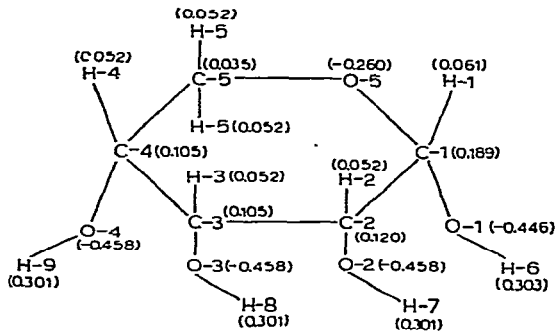

Fig. 1. Distribution of electronic charges in aldopentopyranoses.

The σ-charges on the atoms of the sugar molecule (Fig. 1) have been computed by Sundararajan[15] by using the LCAO-MO method of Del Re[16]. These values differ slightly from the values reported by Zhdanov *et al.*[17] because of the reasons stated earlier. These values have been used in the present study to compute the electrostatic energy.

Energy calculation

The ring atoms and the atoms linked directly to the ring were fixed in the *C1*(D) and *1C*(D) conformations in ideal models by taking the bond angles at the tetrahedrally bonded carbon atom as 109.5°, the divalent oxygen angle as 114°, and the bond lengths C–C = 1.53, C–O = 1.42, C–H = 1.1, and O–H = 1 Å. The hydroxyl hydrogen atoms (denoted H-6, H-7, H-8, and H-9) were fixed by taking the C–O–H angle as 109.5°. These atoms were fixed in the position of minimum energy by an iterative process[14]. After fixing the hydroxyl groups in the position of minimum energy, the total nonbonded and electrostatic energies of the molecule were computed.

Since an axially oriented, hydroxyl oxygen atom may approach close to other *syn*-axial atoms or groups, the overall minimum-energy conformations of the sugar molecules were studied by tilting the axially oriented C–O bond suitably, according to the procedure described in the earlier paper[14]. The angles that deviate in the mini-

TABLE I

BOND ANGLES IN THE MINIMUM-ENERGY CONFORMATION[a] AT THE RING-CARBON ATOMS HAVING AXIAL SUBSTITUENTS

Aldopyranose	*Bond angles deviated from ideal values in the minimum-energy conformation (in degrees)*			
	C1 *Conformation*		1C *Conformation*	
	Bond angle	*Value*	*Bond angle*	*Value*
α-D-Arabinose	[O-5–C-1–O-1 / C-2–C-1–O-1]	111		
	[C-2–C-3–O-3 / C-4–C-3–O-3]	111		
β-D-Arabinose	[C-1–C-2–O-2 / C-3–C-2–O-2]	111		
	[C-2–C-3–O-3 / C-4–C-3–O-3]	111		
α-D-Lyxose	[O-5–C-1–O-1 / C-2–C-1–O-1]	111	[C-2–C-3–O-3 / C-4–C-3–O-3]	111
	[C-1–C-2–O-2 / C-3–C-2–O-2]	111	[C-3–C-4–O-4 / C-5–C-4–O-4]	111
β-D-Lyxose			[O-5–C-1–O-1 / C-2–C-1–O-1]	111
			[C-2–C-3–O-3 / C-4–C-3–O-3]	111
α-D-Ribose	[O-5–C-1–O-1 / C-2–C-1–O-1]	111	[C-1–C-2–O-2 / C-3–C-2–O-2]	112
	[C-2–C-3–O-3 / C-4–C-3–O-3]	111	[C-3–C-4–O-4 / C-5–C-4–O-4]	112
β-D-Ribose	[C-2–C-3–O-3 / C-4–C-3–O-3]	111	[C-1–C-2–O-2 / C-3–C-2–O-2]	112
			[C-3–C-4–O-4 / C-5–C-4–O-4]	112
α-D-Xylose	[O-5–C-1–O-1 / C-2–C-1–O-1]	111	[C-1–C-2–O-2 / C-3–C-2–O-2]	112
			[C-3–C-4–O-4 / C-5–C-4–O-4]	112
β-D-Xylose			[O-5–C-1–O-1 / C-2–C-1–O-1]	111
			[C-1–C-2–O-2 / C-3–C-2–O-2]	111
			[C-2–C-3–O-3 / C-4–C-3–O-3]	111
			[C-3–C-4–O-4 / C-5–C-4–O-4]	111

[a]When the axial substituents were tilted, the hydrogen atoms attached to these ring-carbon atoms were re-fixed by following Hendrickson's method[18] to minimize the total energy of angle strain in the five angles involved. These bond angles are not shown in the Table.

mum energy conformations, from those in the ideal models, are shown in Table I.

As it is known from n.m.r.-spectral studies of free sugars in solution[1–11,19] that the pyranoid ring normally favors one or the other chair conformation, the

relative stability of the *C1*(D) and *1C*(D) conformations alone were considered in the present calculations.

Percentage of anomers in the equilibrium mixture

The percentage proportion (p) of α- and β-anomers in the *C1*(D) and *1C*(D) conformations present in equilibrium mixtures were computed by using the expression

$$p_i = 100.\ e^{-F_i/RT} / \sum_i e^{-F_i/RT} \qquad (2)$$

where the summation is over all of the four states, namely, the α-anomer in the *C1*(D) and *1C*(D) conformations and the β-anomer in the *C1*(D) and *1C*(D) conformations. F_i is the free energy of the component i.

RESULTS AND DISCUSSION

The results of the energy calculations on ideal and distorted models (minimum-energy conformations) are given in columns 2 and 3 and columns 4 and 5 of Table II.

It can be seen from Table I that the bond-angle distortions in the minimum-energy conformations are in most cases only 1.5°. Deviations of this magnitude from tetrahedral angles have also been reported in the solid state in the angle O-1–C-1–O-5 for the anomers having O-1 axial[20]. Whenever *syn*-axial hydroxyl groups come into interaction, the angular distortion is about 2°. Similar deviations in bond angles have also been observed in cyclitols in the solid state[21].

As a consequence of distortions from ideal-chair conformations, there results a small decrease in the total potential energy of aldopentoses (Table II); it is less than 0.5 kcal.mole^{-1} in most examples except for the *1C* conformations of α- and β-D-

TABLE II

POTENTIAL ENERGIES CALCULATED FOR ALDOPENTOPYRANOSES[a]

Aldopyranose	*Calculated energy-values (kcal.mole^{-1})*			
	Ideal		*Distorted*	
	C1	1C	C1	1C
α-D-Arabinose	1.92	0.68	1.56	0.68
β-D-Arabinose	1.03	1.13	0.99	1.13
α-D-Lyxose	1.04	0.44	0.93	0.42
β-D-Lyxose	1.00	2.04	1.00	1.68
α-D-Ribose	2.27	2.74	1.91	2.30
β-D-Ribose	0.56	2.26	0.53	1.81
α-D-Xylose	0.60	2.10	0.50	1.41
β-D-Xylose	0.00	2.91	0.00	1.86

[a]The excess energy of a particular conformation in each set, over that of β-D-xylose in the *C1* conformation in that set, is given.

xylopyranoses. Even in these situations, the potential-energy difference between ideal and distorted conformations is less than 1.0 kcal.mole^{-1}, which is much less than that estimated in the *1C*(D) conformations of aldohexopyranoses[14].

It can be seen from Tables II and IV that, in general, the favoured conformation assigned by n.m.r. spectroscopy has the lower potential energy. However, if a strict explanation of the experimental results in solution is sought, the conformational entropy, which arises because of the different possible arrangements of the O–H bonds, has to be computed in order to obtain the free energies, since the calculated energies shown in Table II are enthalpies. Also, the calculated potential-energy values correspond to the conformation of minimum energy, and the experimental values correspond to average conformation in solution arising through the possible rotations of the O–H bonds around the corresponding C–O bonds. Since the favoured conformation is the one having the minimum energy, any change in the orientation of one of the O–H bonds may affect the orientation of others in such a way that the total energy of the molecule as a whole may not be much different from the minimum energy. Hence it can be assumed, to a first approximation, that the potential energy of the average conformation $\Sigma N_i V_i$ (N_i is the mole fraction and V_i is its potential energy) is very close to the minimum potential-energy. Hence $\Sigma N_i V_i \simeq V_{min}$. Even if there is a small error in this approximation, it cancels out when the relative energies of various molecules are considered.

Thermodynamic studies of glucose and sucrose in aqueous solution[22] indicated that the sugars are extensively hydrated, presumably by hydrogen bonding between hydroxyl groups and water molecules. In water, the relatively weak, intramolecular hydrogen-bonds are, in all probability, replaced by stronger hydrogen bonds with the oxygen atoms of the surrounding water molecules. It is therefore highly probable that, in aqueous solution, the sugar hydroxyl groups are directed outwards to the oxygen atoms of the adjacent water molecules.

The conformational entropy that arises because of the various possible orientations of the O–H bonds can be calculated to a first approximation by assuming that the O–H bond will favour one of the three staggered conformations. Examination of models indicates that, in chair conformations, all of the three staggered dispositions of the O–H bond appear equally favoured if the corresponding C–O bond is equatorially oriented, whereas only two positions appear possible when the C–O bond is axially oriented; in the latter orientation, one of the rotamers would cause the hydroxyl hydrogen atom (directed inwards) to interact with the axially oriented atoms or groups on the same side of the ring as the OH group. In fact, Rader[23] has observed, from p.m.r. studies of epimeric, substituted cyclohexanols in methyl sulfoxide, that an equatorial alcohol exhibits a larger coupling-constant than an axial one; he attributed this difference to a greater contribution of the anti conformer relative to the gauche conformers in the equatorial epimer. Thus, the number of possible hydroxyl-group orientations for β-D-xylopyranose in the *C1* chair form is about 81, whereas in the *1C* conformation there are about 16 orientations possible. Certain of these combinations might be less probable, because of possible interactions

between hydroxyl hydrogen atoms of adjacent hydroxyl groups. Further refinement of the entropy calculations has not been attempted as we are primarily interested in the relative stabilities, and such effects may cancel when the excess energies are expressed. The conformational entropy (S) is therefore given by

$$S = 2.3\ R \log P$$

where R is the gas constant and P is the number of possible conformations differing in the orientations of the O–H bonds for the same ring conformation. The values so obtained for the aldopentopyranoses are shown in Table III.

TABLE III

CONFORMATIONAL ENTROPIES OF ALDOPENTOPYRANOSES RESULTING FROM VARIOUS POSSIBLE ORIENTATIONS OF O–H BONDS

Aldopyranose	*Calculated conformational entropy* (S) *in cal.mole*$^{-1}$*.deg*$^{-1}$	
	C1	1C
α-D-Arabinose	6.32	7.93
β-D-Arabinose	7.12	7.12
α-D-Lyxose	7.12	7.12
β-D-Lyxose	7.93	6.32
α-D-Ribose	7.12	7.12
β-D-Ribose	7.93	6.32
α-D-Xylose	7.93	6.32
β-D-Xylose	8.73	5.51

The contributions of entropy ($-TS$) to the free energy have been estimated for various molecules in the *C1*(D) and *1C*(D) chair forms, and these values have been added to the corresponding potential energies given in columns 4 and 5 of Table II, to give the total conformational-energy at 300°K. The conformational free-energy values thus estimated are shown in columns 2 and 3 of Table IV.

The estimated free-energy difference between the α- and β-anomers of D-xylose in the *C1* conformation (columns 2 and 3 of Table IV) is 0.74 kcal.mole^{-1}, as compared with the value of 0.35 kcal.mole^{-1} determined from the equilibrium composition. The difference of 0.4 kcal.mole^{-1} between the calculated and the observed value may be due to the anomeric effect, which was not taken into account in the present calculations. Accordingly, this value has been added whenever the anomeric hydroxyl group is equatorially disposed.

The conformational free-energies, as corrected for the anomeric effect, are shown in columns 4 and 5 of Table IV. The free-energy values assigned by Angyal[11] are given in columns 6 and 7. The favoured conformations determined from n.m.r. studies are shown in columns 8 and 9.

Table IV shows that, in those aldopentopyranoses for which a single conforma-

TABLE IV

CALCULATED FREE-ENERGY VALUES FOR ALDOPENTOPYRANOSES[a]

Aldopyranose	*Calculated free energies* (*kcal.mole*$^{-1}$)		*Free energies calculated after correcting for anomeric effect* (*kcal.mole*$^{-1}$)		*Angyal's values*[11] (*kcal.mole*$^{-1}$)		*Favoured conformations assigned from n.m.r. studies by*	
	C1	1C	C1	1C	C1	1C	*Rudrum and Shaw*[4]	*Lemieux and Stevens*[1]
α-D-Arabinose	2.28	0.92	1.88	0.92	1.60	0.45	1C	1C
β-D-Arabinose	1.47	1.61	1.47	1.21	1.30	0.80	1C	
α-D-Lyxose	1.41	0.90	1.01	0.90	0.45	1.00	C1, 1C	C1, 1C
β-D-Lyxose	1.24	2.40	1.24	2.00	0.90	1.95	C1	C1
α-D-Ribose	2.39	2.78	1.99	2.78	1.85	1.95	1C	1C
β-D-Ribose	0.77	2.53	0.77	2.13	0.90	1.50	C1, 1C	C1
α-D-Xylose	0.74	2.13	0.34	2.13	0.35	2.00	C1	C1
β-D-Xylose	0.00	2.83	0.00	2.43	0.00	2.30	C1	C1

[a]The excess free-energy of a particular conformation in each set, over that of β-D-xylose in the *C1* conformation in that set, is given.

TABLE V

CONFORMATIONAL ENTROPIES OF ALDOHEXOPYRANOSES RESULTING FROM VARIOUS POSSIBLE ORIENTATIONS OF O–H BONDS AND THE $-CH_2OH$ GROUP

Aldopyranose	*Calculated conformational entropy* (S) *in cal.mole*$^{-1}$*.deg*$^{-1}$	
	C1	1C
α-D-Allose	9.30	8.50
β-D-Allose	10.11	7.70
α-D-Altrose	8.50	9.30
β-D-Altrose	9.30	8.50
α-D-Galactose	9.30	8.50
β-D-Galactose	10.11	7.70
α-D-Glucose	10.11	7.70
β-D-Glucose	10.93	6.90
α-D-Gulose	8.50	9.30
β-D-Gulose	9.30	8.50
α-D-Idose	7.70	10.11
β-D-Idose	8.50	9.30
α-D-Mannose	9.30	8.50
β-D-Mannose	10.11	7.70
α-D-Talose	8.50	9.30
β-D-Talose	9.30	8.50

tion has been assigned from n.m.r. studies[1,4] (by two groups of workers), namely α-D-arabinose, β-D-lyxose, α-D- and β-D-xylose, the calculated energy difference between the *C1* and *1C* conformations is in agreement, being 0.7–2.4 kcal.mole^{-1}. The free-energy calculations predict that the two chair forms of α-D-lyxopyranose have equal energy and should exist as a conformational mixture in aqueous solution, also in good agreement with the n.m.r. observations[1,4]. Although the *1C* conformation has been assigned for β-D-arabinopyranose by Rudrum and Shaw[4], Lemieux and Stevens[1] have stated that the n.m.r. spectrum of this compound does not differentiate the *C1* and *1C* conformations. The free-energy calculations indicate that it should contain both chair forms in equilibrium, differing in free energy by about 0.3 kcal.mole^{-1}. From n.m.r. studies, a *1C* conformation has been assigned for α-D-ribopyranose in aqueous solution, whereas the free-energy calculations suggest a *C1* conformation for this molecule. The calculated energy-difference of 1.3 kcal. mole^{-1} between the *C1* and *1C* conformations of β-D-ribopyranose indicates that it exists preponderantly in the *C1* conformation in aqueous solution, in accord with n.m.r.-spectral evidence[1].

The conformational free-energies of aldohexopyranoses also have been computed similarly. In computing the conformational entropy of aldohexopyranoses, we have distinguished the conformations that result from the different orientations of the O–H bonds at C-1, C-2, C-3, and C-4, and the possible orientations of the $-CH_2OH$ group around the C-5–C-6 bond, but the conformations resulting from the various

TABLE VI

FREE-ENERGY VALUES CALCULATED FOR ALDOHEXOPYRANOSES[a]

Aldopyranose	*Calculated free energies* (*kcal.mole*$^{-1}$)		*Free energies calculated after correcting for anomeric effect* (*kcal.mole*$^{-1}$)		*Angyal's values*[11] (*kcal.mole*$^{-1}$)		*Favoured conformations assigned from n.m.r. studies.*[1,4,11]
	C1	1C	C1	1C	C1	1C	
α-D-Allose	2.29	4.63	1.89	4.63	1.85	3.30	C1
β-D-Allose	0.72	4.82	0.72	4.42	0.90	4.0	C1
α-D-Altrose	2.01	2.67	1.61	2.67	1.60	1.80	C1, 1C
β-D-Altrose	1.28	3.80	1.28	3.40	1.30	3.30	C1
α-D-Galactose	1.27	3.49	0.87	3.49	0.80	4.25	C1
β-D-Galactose	0.72	5.23	0.72	4.83	0.45	5.7	C1
α-D-Glucose	0.69	4.74	0.29	4.74	0.35	4.5	C1
β-D-Glucose	0.00	6.37	0.00	5.97	0.0	5.95	C1
α-D-Gulose	2.22	3.24	1.82	3.24	1.95	2.7	
β-D-Gulose	0.84	4.10	0.84	3.70	1.00	3.4	C1
α-D-Idose	2.54	2.12	2.14	2.12	2.30	1.80	C1, 1C
β-D-Idose	2.13	3.43	2.13	3.03	2.00	3.30	
α-D-Mannose	1.30	3.40	0.90	3.40	0.45	3.50	C1
β-D-Mannose	1.18	5.45	1.18	5.05	0.90	5.60	C1
α-D-Talose	2.30	3.84	1.90	3.84	1.50	3.85	C1
β-D-Talose	2.67	6.33	2.67	5.93	1.95	5.95	

[a]The excess energy of a particular conformation in each set over that of β-D-glucose in the *C1* conformation in that set, is given.

possible orientations of the O–H bond of the $-CH_2OH$ group were neglected. The conformational-entropy values calculated for aldohexopyranoses are shown in Table V.

The free energies calculated for the aldohexopyranoses are shown in columns 2 and 3 of Table VI. The potential-energy terms were those used earlier[14], and the free energies, corrected for the anomeric effect, are given in columns 4 and 5 of the table. The table shows that the favoured conformations assigned from n.m.r. studies have the lower calculated energy, but these results do not affect significantly the conclusions already drawn[14] on the basis of the potential energies alone about the favoured ring-conformations.

When aldopyranoses mutarotate in aqueous solution the configuration at C-1 undergoes change and, whenever the difference in energy between the *C1*(D) and *1C*(D) conformations is small, there may also result changes in the conformation of the pyranoid ring. Hence, an aqueous solution at equilibrium may contain mixtures of α and β-pyranose anomers in their *C1* and *1C* conformations. The percentages of the α- and β-D-anomers in their *C1* and *1C* conformations present in the equilibrium mixture can be computed by using the expression (*2*) in conjunction with the calculated free-energy values given in columns 4 and 5 of Tables IV and VI. The results of such

TABLE VII

PERCENTAGE OF α- AND β-ANOMERS IN *C1*(D) AND *1C*(D) CONFORMATIONS PRESENT IN EQUILIBRIUM MIXTURES OF ALDOPYRANOSES

Aldopyranose	*α Anomer (percent)*		*β Anomer (percent)*		*Total percentage of α-anomer present*	
	C1(D)	1C(D)	C1(D)	1C(D)	*From calculations*	*From n.m.r. data*[11]
Arabinose	9	45	18	28	54	63
Lyxose	33	39	22	6	72	71
Ribose	10	2.6	79	8.2	12.6	26
Xylose	34	2	63	1.0	36	33
Allose	12	0	88	0	12	20
Altrose	29	21	49	1	50	44
Galactose	44	0	56	0	44	27
Glucose	38	0	62	0	38	36
Gulose	16	1	83	0	17	<22
Idose	30.5	31.6	31	7	62	46
Mannose	61	1	38	0	62	67
Talose	76	3	21	0	79	58

calculations are given in Table VII. It is seen that all of the pentopyranoses except α- and β-D-xylose are predicted to be present in to a considerable extent in the *1C*(D) conformation in the equilibrium mixture, but the proportions of α- and β-D-xylose, β-D-lyxose, and α-D-ribose present in the *1C* conformation at mutarotational equilibrium should be small. Table VII also shows that, for the aldohexopyranoses, the

proportion of sugar existing in the *1C*(D) conformation in the equilibrium mixture is negligible except with α-D-altropyranose and α-D-idopyranose.

Table VII shows that the percentages of α-D-pyranose form present at equilibrium, determined by these energy calculations, agree fairly well with those determined by n.m.r. spectroscopy[11], except for D-ribose.

Tables IV and VI show that the free-energy values calculated after correcting for the anomeric effect agree fairly well with those assigned by Angyal[11,12], considering the approximations involved in both the procedures. In assigning energy values, Angyal[12] added to the interaction energies, energy values for the anomeric effect of about 0.55 kcal.mole^{-1} or 0.1 kcal.mole^{-1}, depending upon the orientation of the C-2 hydroxyl group, to afford agreement with experimental results. The agreement observed between the percentages of α-anomer present in the equilibrium mixture (for D-allose, D-glucose, D-mannose, and D-talose), as calculated from the conformational free-energy values corrected for the anomeric effect, with those percentages determined from n.m.r. studies, indicate that the anomeric effect is small (about 0.4 kcal.mole^{-1}) and does not depend on the configuration of the OH group at C-2. It is also seen from Table VII that α-D-lyxopyranose and α-D-mannopyranose, which have the C-2 hydroxyl group axially disposed in the *C1*(D) conformation, are predicted to have 0.25–0.28 kcal.mole^{-1} lower energy than the corresponding β-anomer in the *C1*(D) conformation; this difference is small compared with the value of 0.45 kcal.mole^{-1} assigned by Angyal. In view of the approximations involved in these calculations, better agreement than this cannot be anticipated at this stage. The extent of agreement between these values estimated by theoretical calculation and those assigned by Angyal suggest that the behaviour of simple sugars in aqueous solution can be explained well by adding to the calculated free-energies a small value for the anomeric effect of about 0.4 kcal.mole^{-1}, independent of the orientation of the OH group at C-2.

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