Structure of the acetal segment in *O*-glycosides

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The dependence of bond angles and bond lengths of the acetal segment upon its conformation in *O*-glycosides has been studied. For this purpose geometrical parameters of the acetal segment were calculated from X-ray and neutron diffraction structural data for various glycosides and treated statistically. The calculated mean values of geometrical parameters of the individual groups were analyzed from the point of view of their changes resulting from different dihedral angles Θ, Φ, and Ψ, as well as from the type of the glycosidic linkage. The obtained data were compared with those calculated for the most stable conformation of 2-methoxytetrahydropyran by PCILO quantum chemical method. The most significant difference in the geometry of α- and β-glycosides is shortening of the $C(1)$—$O(1)$ bond length by 2 pm in the latter (from 140.9 to 138.9 pm), and contraction of the $O(5)$—$C(1)$—$O(1)$ and $C(5)$—$O(5)$—$C(1)$ bond angle by 4 and 2°, respectively, namely from 111.5 to 107.4° and from 114.1 to 111.8°. The geometrical changes observed for the acetal segment as a result of the changed conformation are interpreted in terms of the mutual equilibrium of steric interactions and delocalization of lone electron pairs at the oxygen atom.

Была изучена зависимость валентных углов и длин связей ацетальных сегментов от их конформаций в *O*-гликозидах. Геометрические параметры были получены на основании структурных данных полученных при помощи рентгеновской и нейтронной диффракции и были обработаны статистически. Средние расчетные значения отдельных групп были анализированы с точки зрения их изменений вследствие различных дигедральных углов Θ, Φ и Ψ и также от типа выстраивания гликозидов. Полученные данные были сравнены с теми, которые были рассчитаны для наиболее устойчивых конформаций 2-метокситетрагидропирана квантово-химическим методом PCILO. Самое существенное различие в геометрии α- и β-гликозидов состоит в сопряжении длины связи $C(1)$—$O(1)$ в последних на 2 пм (от 140,9 до 138,9 пм) и уменьшении углов

O(5)—C(1)—O(1) и C(5)—O(5)—C(1) соответственно на 4 и 2°, а именно с 111,5 до 107,4° и с 114,1 до 111,8°. Геометрические изменения, наблюдаемые для ацетальных сегментов вследствие изменений конформаций, обсуждаются в порядке взаимного равновесия стерических взаимодействий и делокализации свободной электронной пары на атоме кислорода.

In recent years the determination of structural properties of the acetal segment in carbohydrates has been extensively studied [1]. These studies have been prompted by the interest in factors which influence the conformational properties of saccharides, one of the most abundant naturally occurring class of compounds. Also, it is believed, that the biological activity of carbohydrates is related closely to the energetically most favoured conformation of these molecules [2]. In order to study conformational properties of model compounds, mono-, oligo-, and polysaccharides spectral and diffractional methods, as well as theoretical conformational analysis have been applied.

The different C—O bond lengths in the acetal C—O—C—O—C segment have been found [3] in the first crystallographic studies on saccharides. The analysis of the accumulated experimental data confirmed the importance of these differences occurring both in α- and β-glycosides [2, 4, 5]. The shortening of the anomeric C—O bond lengths, accompanied by differences in bond lengths and angles in the acetal segment is one of the means of manifestation of anomeric and exoanomeric effects [6]. Quantum chemical studies on acyclic and cyclic model compounds showed that the changes in the geometry result from conformational dependence of the delocalization interaction of lone electron pairs at the oxygen atom linked to one central atom, namely, the anomeric carbon atom [7—9]. Having analyzed Φ and Ψ experimental data *Perez* and *Marchessault* [5] showed the importance of the exoanomeric effect for the different restriction of the rotation around C(1)—O(1) and O(1)—C(X) bonds in β-glycopyranosides.

During the last three years a number of X-ray and neutron diffraction [10—78] molecular data for alkyl pyranosides and oligosaccharides have appeared. It seemed, therefore, interesting to clarify by statistical analysis of available experimental data and theoretical values for methoxytetrahydropyran (MTHP) the effect of the conformation of the acetal segment upon its geometry.

Experimental and theoretical data

In analyzing the experimental data it seemed convenient to sort all glycosides studied into four groups (a—d) according to the arrangement of atoms at the anomeric centre, *i.e.* values of torsional angles Θ, Θ_H (Fig. 1); $\Theta = \Theta[C(5)—O(5)—C(1)—O(1)]$, $\Theta_H = \Theta_H[C(5)—O(5)—C(1)—H(1)]$;
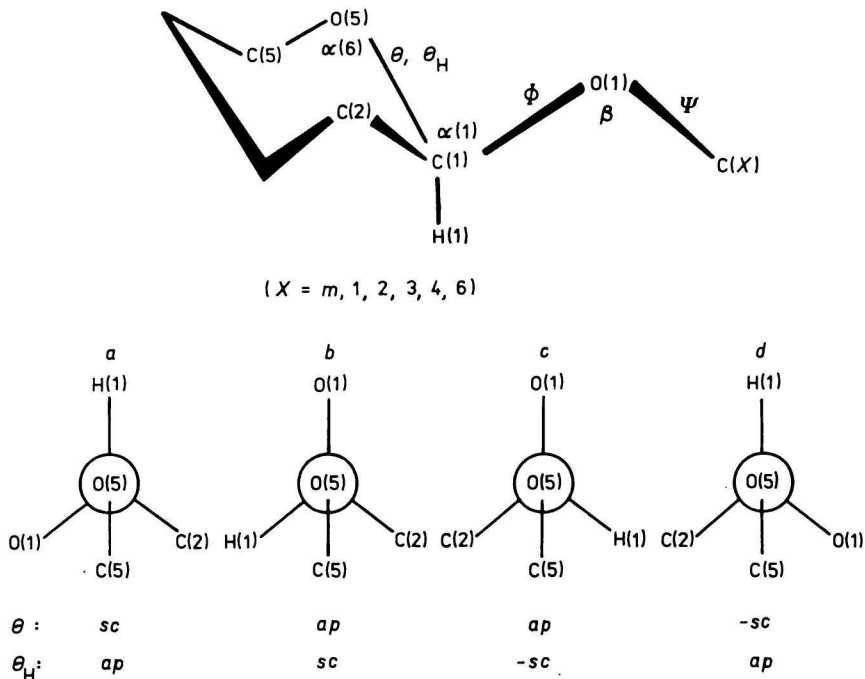
$(X = m, 1, 2, 3, 4, 6)$

Fig. 1. Schematic representation of the acetal segment in saccharides.

a) $\Theta = sc$ (synclinal) $\Theta_H = ap$ (antiperiplanar)
b) $\Theta = ap$ $\Theta_H = sc$
c) $\Theta = ap$ $\Theta_H = -sc$
d) $\Theta = -sc$ $\Theta_H = ap$

When describing the structure of the acetal segment the torsional and bond angles Φ, Ψ, $\alpha(1)$, $\alpha(6)$, and β were defined as $\Phi = \Phi[O(5)\!-\!C(1)\!-\!O(1)\!-\!C(X)]$, $\Psi = \Psi[C(1)\!-\!O(1)\!-\!C(X)\!-\!H(X)]$, $\alpha_1 = \alpha[O(5)\!-\!C(1)\!-\!O(1)]$, $\alpha(6) = \alpha[C(5)\!-\!O(5)\!-\!C(1)]$, $\beta = \beta[C(1)\!-\!O(1)\!-\!C(X)]$ [79].

According to this classification α-D-glycosides belong to the groups a and c when their pyranose ring adopts $^4C_1$ and $^1C_4$ conformation, respectively. The β-D-glycosides are sorted similarly to either the b or d group. The L-glycosides were organized in the same way. After having been analyzed more closely groups a (44 data) and b (25 data) were further divided into subgroups according to the type $(1 \rightarrow X)$ of the glycosidic linkage. The individual subgroups contained, thus, $(1 \rightarrow 1)$-, $(1 \rightarrow 2)$-, $(1 \rightarrow 3)$-, $(1 \rightarrow 4)$-, $(1 \rightarrow 6)$-linked oligosaccharides, and to the last group belonged alkyl derivatives. The group c and d contained only alkyl $(1 \rightarrow m)$ derivatives. Our statistical analysis included data calculated from structures of the following molecules.

Group a

Type of the glycosidic linkage — $(1 \rightarrow 4)$: Maltose monohydrate [10]; methyl β-maltoside [11]; phenyl α-maltoside [12]; β-maltose, monohydrate [13]; α-maltose [14]; methyl 2,3-anhydro-6-bromo-6-deoxy-4-O-(4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-eno-pyranosyl)-α-D-allopyranoside [15]; cyclohexaamylose, hexahydrate [16]; cyclohexa-amylose-1-propanol, 4,8-hydrate [17]; α-cyclodextran, krypton, pentahydrate [18]; α-cyclodextrin-methanol, pentahydrate [19]; α-cyclodextrin-p-iodoaniline, trihydrate [20]; iodine-cyclohexaamylose, tetrahydrate [21].

Type of the glycosidic linkage — $(1 \rightarrow 3)$: Turanose [22, 23]; melezitose [24].

Type of the glycosidic linkage — $(1 \rightarrow 2)$: Raffinose, pentahydrate [25]; 1-kestose [26]; melezitose [24]; sucrose [27, 28]; planteose, dihydrate [29]; O-(4-O-methyl-α-D-glu-copyranosyluronic acid)-$(1 \rightarrow 2)$-O-β-D-xylopyranosyl-$(1 \rightarrow 4)$-D-xylopyranose, trihydrate [30].

Type of the glycosidic linkage — $(1 \rightarrow 1)$: Trehalose·$CaCl_2$, pentahydrate [31]; trehalose, dihydrate [32]; trehalose·$CaBr_2$, monohydrate [33].

Type of the glycosidic linkage — $(1 \rightarrow 6)$: Melibiose, monohydrate [34, 35]; raffinose, pentahydrate [25]; isomaltulose [36]; planteose, dihydrate [29].

Type of the glycosidic linkage — $(1 \rightarrow m)$: 1-Decyl α-D-glucopyranoside [37]; methyl α-D-altropyranoside [38]; methyl α-D-glucopyranoside [39]; methyl α-D-galactopyranosi-de [40]; methyl α-D-altropyranoside [41]; methyl 2,3,4-tri-O-acetyl-6-deoxy-6-methylsul-finyl (S)-α-D-glucopyranoside [42]; methyl β-L-arabinopyranoside [43]; methyl α-D-xylo-pyranoside [44]; methyl 3,4-O-isopropylidene-β-L-*erythro*-pentopyranosid -2-ulose [45]; methyl 2,3-anhydro-6-bromo-6-deoxy-4-D-(4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro*--hex-2-enopyranosyl)-α-D-allopyranoside [15]; 7-(methyl-2-acetamido-6-O-acetyl-2,3,4--trideoxy-α-D-*threo*-hex-2-enopyranosid-4-yl)theophylline [46]; methyl 4,6-O-ben-zylidene-2,3-dideoxy-2,3-diphenylazo-α-D-mannopyranoside [47].

Group b

Type of the glycosidic linkage — $(1 \rightarrow 4)$: 1,2,3,2',3',4'-hexa-O-Acetyl-β--D-xylobiose [48]; lactose·$CaCl_2$, heptahydrate [49]; β-cellobiose octaacetate [50]; β-lacto-se [51]; lactose·$CaBr_2$, heptahydrate [52]; 4-O-β-D-glucopyranosyl-D-glucitol [53]; 4-O-β-D-galactopyranosyl-L-rhamnitol [54]; β-N,N'-diacetylchitobiose [55]; α-N,N'--diacetylchitobiose, monohydrate [56]; β-cellotriose [57]; aldotriouronic acid [30]; α-lac-tose, monohydrate [58]; cellobiose [59]; methyl β-cellobioside [60].

Type of the glycosidic linkage — $(1 \rightarrow 3)$: β-Laminarabiose [61]; methyl 2,3,4,6,2',4',6'-hepta-O-acetyl-β-laminarabioside [62].

Type of the glycosidic linkage — $(1 \rightarrow 2)$: Sophorose [63].

Type of the glycosidic linkage — $(1 \rightarrow 6)$: Gentiobiose [64].

Type of the glycosidic linkage — $(1 \rightarrow m)$: Methyl 2,3,4,6-tetra-O-acetyl-β--D-glucopyranoside [65]; methyl-3,4-O-ethylidene-β-D-galactopyranoside [66]; methyl 6-O-acetyl-β-D-glucopyranoside [67]; methyl 6-O-acetyl-β-D-galactopyranoside [68];

methyl β-D-xylopyranoside [69]; methyl β-D-galactopyranoside [40]; methyl α-L-arabinopyranoside [43]; methyl 3,6-dideoxy- β-D-ribohexopyranoside, monohydrate [75].

Group c

Type of the glycosidic linkage — (1→2): 3,6-Anhydro-α-D-glucopyranosyl-1,4:3,6-dianhydro-β-D-fructoside [70].

Type of the glycosidic linkage — (1→m): Methyl 2,4-bis(N-acetylbenzamido)--3,6-di-O-benzoyl-2,4-dideoxy-α-D-idopyranoside [71]; 4,6-dideoxy-4-N,N-dimethylamino-α-D-talopyranoside methiodide [72]; methyl 3,6-anhydro-α-D-galactopyranoside [73]; Apterine [74].

Group d

Type of the glycosidic linkage — (1→m): 1-Naphthyl 2',3',4',6'-tetra-O-acetyl-β--D-glucopyranoside [76]; methyl β-D-ribopyranoside [77]; 7-(methyl 2-acetamido--6-O-acetyl-2,3,4-trideoxy-β-D-erythro-hex-2-enopyranosid-4-yl)theophylline [78].

For comparison with mean values obtained from statistical analysis geometrical parameters for MTHP, a model of glycosides, in the individual conformations have been calculated by quantum chemical PCILO method while optimization of the geometry has been taken into account.

Results and discussion

Bond lengths

The average values of the calculated bond lengths in acetal segments for substances belonging to groups a and b are in Figs. 2 and 3. The type of the glycosidic linkage that determines the subgroup is denoted by the symbol X; for alkyl derivatives black colour is used; the number of data from which the mean values were calculated is denoted by N. The resulting mean values within the group are depicted by a dashed line. For the sake of comparison of the effect of the shape of the pyranose ring upon the geometrical parameters of the acetal segment data for alkyl pyranosides, present in all groups, are shown separately in Fig. 4. While group a contains all types of glycosidic linkage in the same measure, group b mainly contains alkyl derivatives and (1→4)-linked oligosaccharides. Consequently, there are only small differences between the mean values in the individual
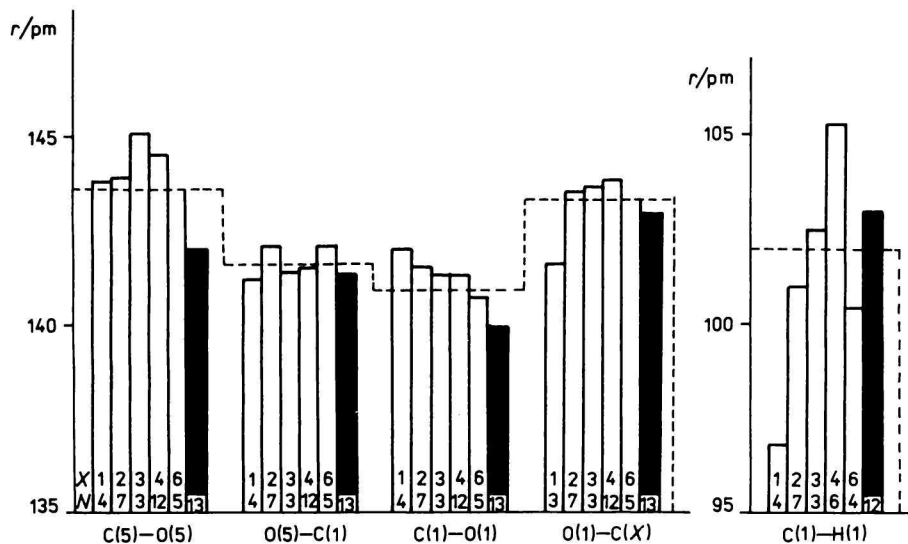
Fig. 2. Calculated mean bond length values for the acetal segment in saccharides in group a.
X — type of the glycosidic linkage, N — the number of data from which the mean value was calculated;
the data for methoxy derivatives are in black and the overall mean values are denoted by dashed lines.
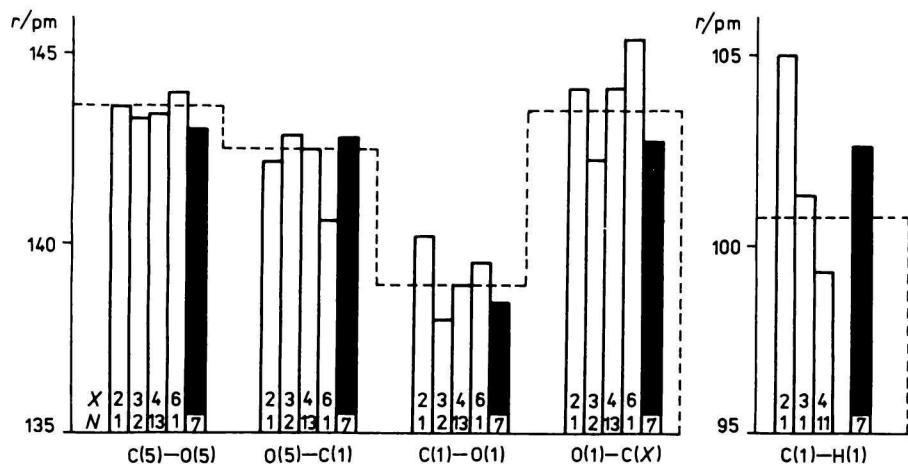

Fig. 3. Calculated mean bond length values for the acetal segment in saccharides in group b.
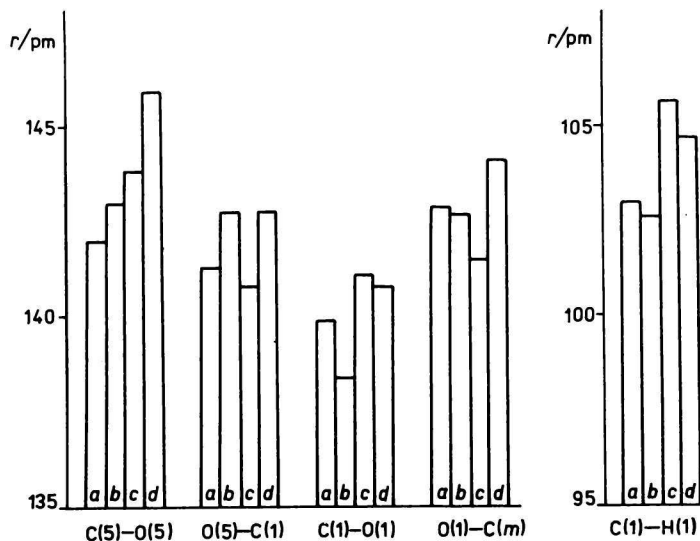For symbols see Fig. 2.

Fig. 4. Calculated mean bond length values for the individual groups of methoxy derivatives.

subgroups and the overall mean value in the group *a*, while in the group *b* the differences are larger. In average, alkyl derivatives show smaller values, an exception being the O(5)—C(1) linkage in the group *b*. Compared to β-pyranosides, the most significant difference in α-pyranosides is shortening of the C(1)—O(1) linkage by 2 pm, lengthening of the O(5)—C(1) linkage by 0.9 pm and shortening of the C(1)—H(1) linkage. The shortening of the latter is significant but it must be considered with care since the determination of the position of hydrogen atoms is obscure. The effect of the change of the shape of the ring upon the geometry of the acetal segment in pyranosides is shown in Fig. 4. The mean bond length values in alkyl derivatives belonging to the individual subgroups are rather different, particularly in the part of the acetal segment that forms a part of the pyranose ring. This should not be surprising when one considers the nonflexibility of the chair forms. Consequently, every conformational change of the chair form results necessarily in a change of the corresponding bond lengths and angles. These differences indicate that it is not quite correct to convert saccharides in groups *c* and *d* into their mirror images and include them into groups *a* and *b*, although the Θ, Φ values seem to justify such a transformation. Nevertheless, the configuration of the anomeric carbon atom seems to be important and, thus, also the value of Θ_H.

Bond angles

Figs. 5—7 show mean values of bond angles treated in the same manner as bond lengths. The mean C(5)—O(5)—C(1) angle value in β-pyranosides (group b) is smaller by 2°, as compared with α-pyranosides (group a). The change of the conformation of the acetal segment manifests itself in an even more pronounced way in the case of the O(5)—C(1)—O(1) bond angle, the mean value of which in β-pyranosides is smaller by 4°; conversely, in the case of angle O(5)—C(1)—H(1) it is larger by 4°. The mean value of the glycosidic C(1)—O(1)—C(X) angle, β, is almost the same for both groups. The difference of the mean values becomes noticeable when the values in the individual subgroups are compared according to the type of the glycosidic linkage. Owing to the great number of items in the individual subgroups alkyl derivatives and $(1\rightarrow 4)$-linked glycosides can be compared best. For $(1\rightarrow 4)$-linked oligosaccharides belonging to groups a and b the mean value of the glycosidic angle is 117.14 and 116.24°, respectively. For methyl derivatives the mean values are smaller, and identical for both groups, namely, 113.4°.
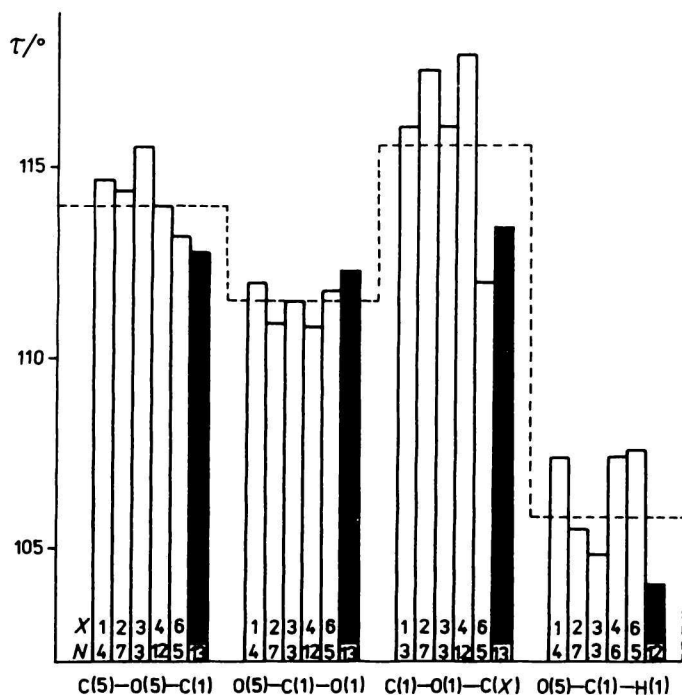

Fig. 5. Calculated mean bond angle values for the acetal segment in group a.
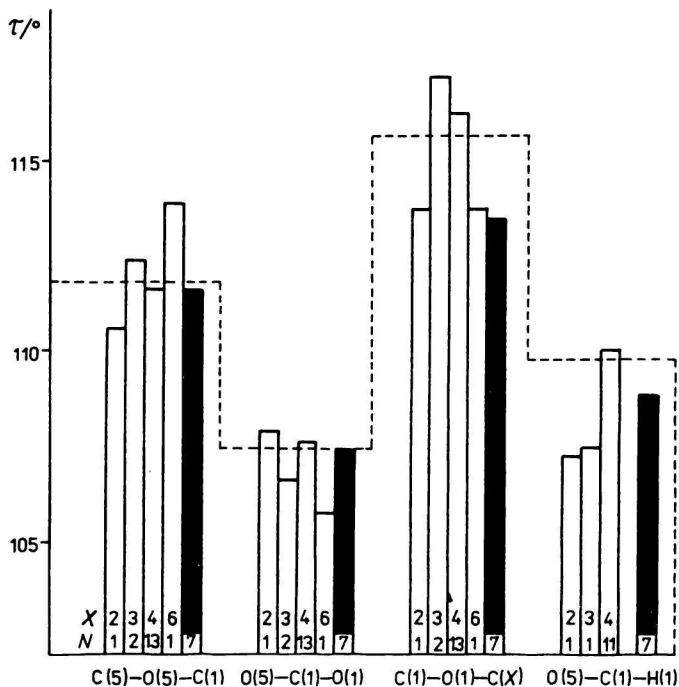For symbols see Fig. 2.

Fig. 6. Calculated mean bond angle values for the acetal segment in group b.
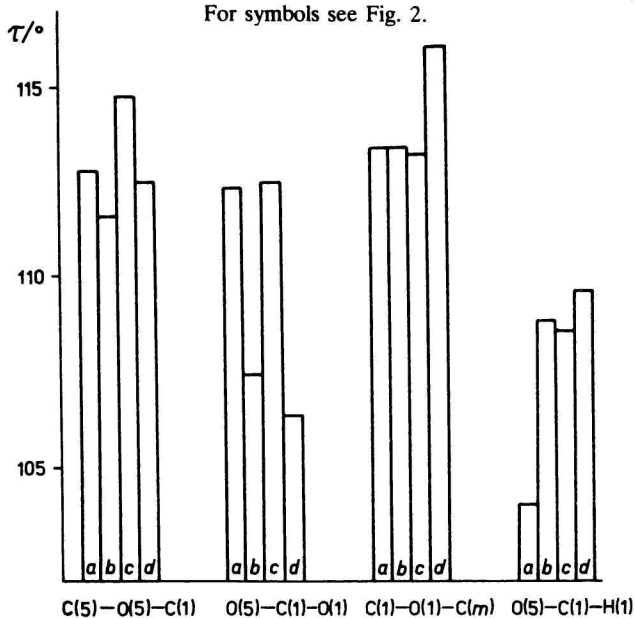For symbols see Fig. 2.

Fig. 7. Calculated bond angle values for the individual groups of methoxy derivatives.

Dihedral glycosidic angles

The mutual position of the two adjacent sugar units in oligo- and polysaccharides is determined by angles Φ and Ψ, which characterize the rotation around the glycosidic linkages C(1)—O(1) and O(1)—C(X). It is therefore extremely important in the determination of detailed structure of oligo- and polysaccharides to understand correctly the principles that govern the conformational properties
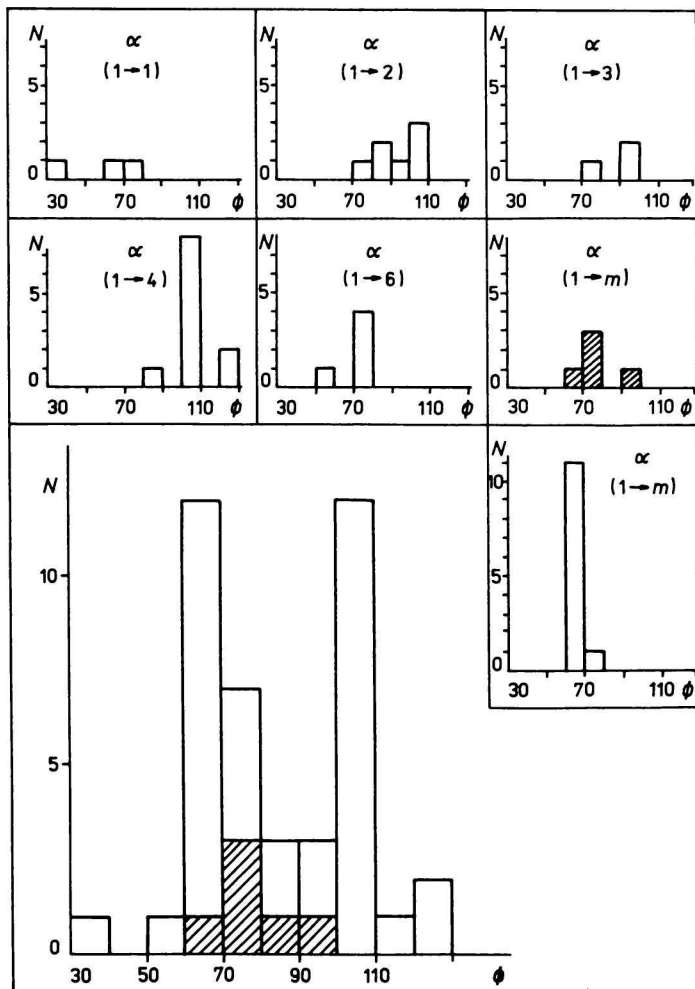

Fig. 8. Histograms of the distribution of Φ for saccharides in group a.

around these linkages. One of the most important effects that influences the conformational behaviour of glycosidic linkages is the exoanomeric effect (EAE) [5, 80]. It expresses the preference of the *sc* over the *ap* conformation during the rotation around the C(1)—O(1) linkage. The histograms of Φ angle values are in Figs. 8 and 9 for individual types of the glycosidic linkage in derivatives belonging to groups *a* and *b*. Here are also shown histograms for alkyl derivatives listed in groups *c* and *d*, *i.e.* for $^1C_4$ conformation of the pyranose ring. The values for angles Φ and compounds belonging to groups *b* and *d* vary from -50 to $-110°$, with a mean value in the groups *b* and *d* of -79.4 and $-68.4°$, respectively. The values in the groups *a* and *c* lie within 30 and 130°, with a mean value of 84.5 and
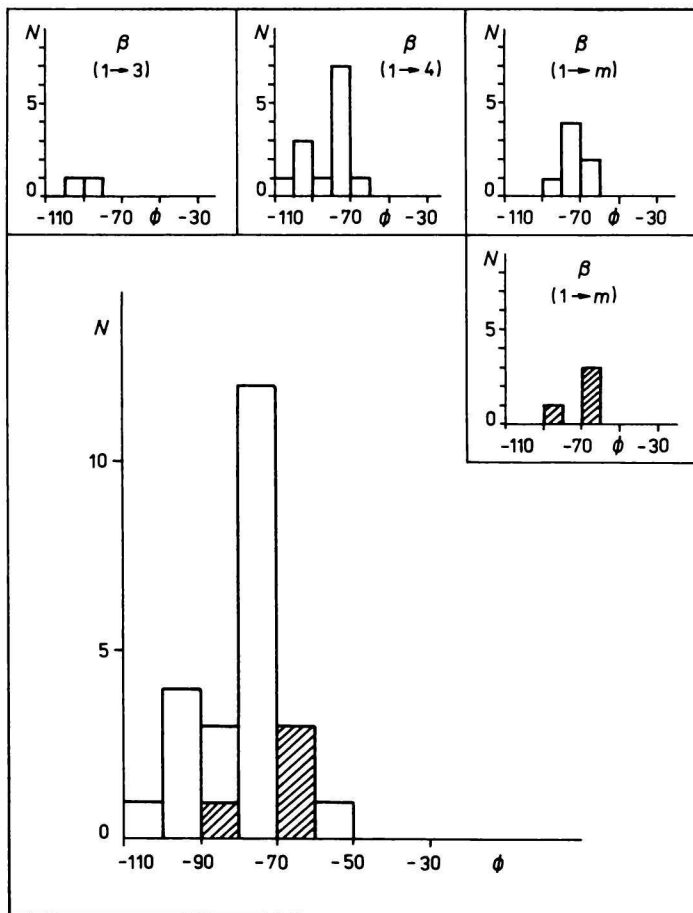

Fig. 9. Histograms of the distribution of Φ for saccharides in group *b*.

80.4° for groups *a* and *c*, respectively. The average values for the individual types of glycosidic linkage in α- and β-pyranosides are 110.3 and $-81.9°$ for $(1\rightarrow4)$-linked, 92.1 and $-88.4°$ for $(1\rightarrow3)$-linked, and 66.9 and $-75.4°$ for alkyl derivatives. A comparison of absolute values shows that for methyl pyranosides $\Phi_{Me}(ax) < \Phi_{Me}(eq)$ and in oligosaccharides as well as for the mean value $\Phi(eq) < \Phi(ax)$. Fig. 10 shows histograms for the second dihedral glycosidic angle Ψ. The data show that values for Ψ are scattered in a wider range than are those for Φ.

Theoretical conformational analysis of the two forms of A-MTHP and E-MTHP by PCILO method with the inclusion of the optimization of the geometry showed that the geometry changes continuously with the change of angle Φ (change of the conformation around the C(1)—O(1) linkage) [81]. The most stable conformations in both A- and E-MTHP were those having the angle close to the ideal *sc* position, namely, $\Phi = 63$ and 66° for A-MTHP and E-MTHP, respectively. In agreement
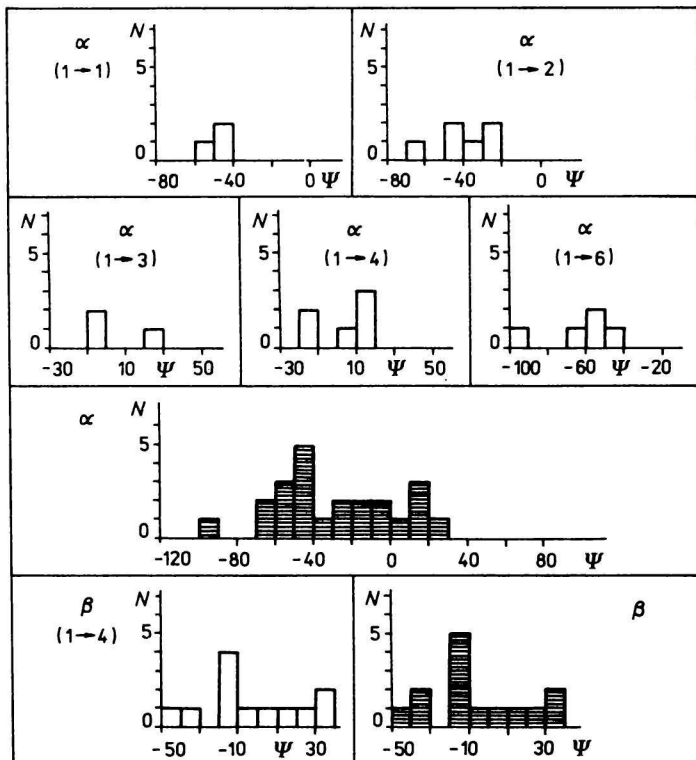

Fig. 10. Histograms of the distribution of Ψ in saccharides.

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with EAE the next most stable were *ap* conformations. We have explained [81] the calculated changes of the MTHP geometry resulting from the changes of Φ values on the basis of simultaneous effect of nonbonding interactions and delocalization of lone electron pairs on oxygen atoms. The Ψ value was determined only by nonbonding interactions. An analysis of experimental data supports this interpretation. It indicates that, as in pyranosides, the orientation around the O(1)—C(X) linkage (*i.e.* angle Ψ) is determined mainly by nonbonding interactions. A thorough examination of histograms reveals that for the determination of Φ in crystalline state, besides the influence of the crystal fields, two additional forces determine the final value of Φ, namely, exoanomeric effect — as a result of which there is a tendency for the aglycon to take the *sc* position, and nonbonding interactions — which are responsible for a shift from this ideal position. This can be demonstrated by several facts. For example, the smallest deviations from the ideal value of $\Phi = 60°$ were found for methyl pyranosides and $(1\rightarrow6)$-linked oligosaccharides, where the nonbonding interactions of the C(X) substituents with the nonreducing residue are least pronounced and, as a result, EAE predominates. As the most bulky substituent (CH_2OH) gets closer to the glycosidic linkage, *i.e.* in the order $1\rightarrow1$, $1\rightarrow2$, $1\rightarrow3$, and $1\rightarrow4$ (in the latter case CH_2OH being at the vicinal position), the nonbonding interactions become more pronounced and, in turn, also the deviation from the value 60°. The calculated mean geometrical parameters of the glycosidic linkage for compounds belonging to the four groups are in Table 1. The values for groups *a* and *b* are close to those reported by *Perez* and *Marchessault* [5] for the so-called *gauche-gauche* and *trans-gauche* classes of

Table 1

Experimental mean bond length values (in pm) and bond angles (in degrees) of the acetal segment compared with theoretical data calculated for the most stable conformations of MTHP

	Mean values obtained from experimental data				MTHP	
	a	*b*	*c*	*d*	GG	TG$_1$
Θ	62.4	177.7	177.1	−69.4	66.0	178.5
Φ	84.5	−79.4	80.4	−68.4	63.0	−58.2
r[C(5)—O(5)]	143.6	143.6	145.9	143.8	139.6	139.5
r[O(5)—C(1)]	141.6	142.5	142.9	140.9	139.9	140.0
r[C(1)—O(1)]	140.9	138.9	141.2	141.1	139.4	139.2
r[O(1)—C(X)]	143.3	143.5	143.0	141.4	139.1	139.1
$\alpha(1)$	111.5	107.4	112.4	114.8	110.5	106.6
$\alpha(6)$	114.1	111.8	106.1	112.4	111.9	112.4
β	115.6	115.5	116.2	113.2	108.8	108.5

glycosides, and by *Jeffrey* [4] and *Gorenstein* [7] for α- and β-glycosides. For the sake of comparison Table 1 includes also values for the most stable A-MTHP and E-MTHP conformations calculated with the inclusion of the optimization of the geometry by the PCILO method. The data in Table 1 show a close connection between the value Φ and the geometrical structure of the glycosidic linkage, a fact that has already been demonstrated [7—9] for dimethoxymethane, the simplest acyclic model for the glycosidic linkage.

In comparing the theoretical values of the individual parameters and mean values obtained from experimental data the different values for Φ should not be overlooked. While in MTHP the values Φ are close to the ideal ones, in glycosides, as a result of effects that had already been discussed, the mean values differ somewhat. Owing to the connection of the geometry of the acetal segment with the value Φ this difference manifests itself also in other geometrical parameters. The mean Φ values do not correspond to the minima on the energy curve of the rotation around the C(1)—O(1) bond in MTHP. The MTHP conformations with such Φ values are energetically less stable (by about 4 kJ mol^{-1}) [81]. As examples, values for $\alpha(1)$, $\alpha(6)$, and β in MTHP for $\Phi = 90°$ are given below. The values for $\alpha(1)$ are 111.7 and 112.4°, values for $\alpha(6)$ are 109.1 and 104.9°, and values for β are 108.8 and 108.7° for A-MTHP and E-MTHP, respectively. The structure of a molecule in the crystalline state is given by the equilibrium between inter- and intramolecular interactions. Thus, the loss of energy resulting from the change of Φ in an isolated molecule is easily compensated by an energy gain from intermolecular interactions (packing energies); based on an analogy with MTHP this energy amounts to about 4 kJ mol^{-1}.

The results of statistical analysis of various experimental glycoside structures presented here support the conclusions arrived at in theoretical studies on dimethoxymethane [7—9] and MTHP [81], dealing with the effect of the conformation of the acetal segment upon its structure in glycosides. With the differences of the configuration of the acetal segment are connected differences in bond lengths (in pm) and angles (in degrees); the differences lie in the following intervals: C(5)—O(5) 142.0—145.9, O(5)—C(1) 140.6—142.9, C(1)—O(1) 138.0—142.0, O(1)—C(X) 141.6—145.5, $\alpha(6)$ 110.6—115.6, $\alpha(1)$ 105.7—112.3, β 112.0—118.0. The most significant change between geometry of the α- and β-glycosides is the shortening of C(1)—O(1) linkage by 2 pm in the latter (from 140.9 to 138.9) and a contraction of $\alpha(1)$ and $\alpha(6)$ by 4 and 2° (from 111.5 to 107.4° and from 114.1 to 111.8°), respectively. These changes do not exceed 5 pm and 6° and do not affect much the overall size of a monosaccharide. However, when the geometrical differences are multiplied, as in a linear polysaccharide, they may result in significant changes in models used in the interpretation of X-ray diffraction data and, consequently in ambiguous interpretation of fibre diagrams. The use of constant geometry of a monosaccharide residue is an even

more rough approximation in structural studies on polysaccharides in solution, since in this case one deals with a dynamic equilibrium of great number of conformations having different values of Φ and Ψ.

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Translated by P. Kováč