[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY,[1] NEW ORLEANS, LA.]

The Infrared Spectra of Ureides of Glucose and Lactose

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Infrared absorption spectra have been obtained for glucose ureide, glucose ureide urea and lactose ureide. Tentative assignments of group vibrations have been made. Some evidence is present in the spectra which suggests that the sugar portion of the ureide molecule may be in the aldehydo-glucose configuration.

The reaction products (ureides) of urea and mono- and disaccharides are crystalline compounds whose preparation and properties have been described by Schoorl[2] and by Helferich and Kosche.[3] As part of a study of the reaction between urea and cellulose, it was desired to obtain the infrared spectra of the ureides of simple sugars closely related to the anhydroglucose unit of cellulose so that infrared spectroscopy could be used in structure studies of cellulose allowed to react with urea. Glucose, cellobiose and lactose were selected for the preparations. Cellobiose ureide, not reported in the literature, could not be isolated in crystalline form, however, and therefore is not included in this paper. Some question exists regarding the stereochemical structure of the ureides of the reducing sugars. In the present study this matter is presented and considered along with tentative band assignments for absorption spectra.

Experimental

The urea, anhydrous glucose and α-lactose hydrate were all reagent grade chemicals and were used without further purification. A sample of purified sodium gluconate was made available and the reason for including this compound will be discussed later.

Glucose ureide and glucose ureide urea were prepared according to the procedure described by Hynd[4] instead of that according to Schoorl[2] because of greater simplicity and higher yield. The procedure of Schoorl, however, was used for lactose ureide. The compounds were isolated in crystalline form and in a high degree of purity. The latter was indicated by the close agreement between the literature values and those found for melting points, optical rotations and analytical results for carbon, hydrogen and nitrogen.

The infrared spectra of the compounds were obtained using the potassium bromide disk technique and the apparatus and procedure described by O'Connor and co-workers.[5]

Results and Discussion

The infrared absorption spectra of glucose ureide, its intermediate glucose ureide urea, and of D-glucose, urea and sodium gluconate, are shown in Fig. 1. The wave length positions of maxima and the relative intensities of the principal bands exhibited in these spectra are given in Table I along with the most probable band assignments. From the data in this table the origin of most of the bands in the spectra of the glucose ureide or glucose ureide urea can be recognized as arising from either the glucose or the urea moiety. More important, a few additional bands which do not pertain to either of the parent compounds can be differentiated.

Bands observed from about 2.90 to 3.10 μ pertain to bonded O–H stretchings and to N–H stretchings, the former from the D-glucose, the latter from the urea. At 3.40 to 3.47 μ, bands from various C–H stretchings are seen in the spectra of the glucose and the reaction products and are, of course, completely absent in the spectrum of urea.

Above 3.50 μ to almost 7.00 μ there is a wide transmission window in the spectrum of D-glucose. Urea, however, exhibits three very strong bands in this region. The infrared spectrum of the urea molecule has been investigated by several workers, the latest work being that reported by Yamaguchi and co-workers.[6] These investigators have assumed the planarity of the urea molecule as established by Waldron and Badger[7] and have calculated the normal modes of vibration for a C_{2v} model. In the region about 6.0 μ three very strong bands have been considered. At 5.93 and 6.24 μ, bands are assigned to a combination of C=O stretching and an NH_2 bending motion with the NH_2 bending contributing to both absorptions. Earlier work[8] had assigned the lower wave length band to a C=O stretching and the longer wave length band to the NH_2 bending mode. A band at 6.14 μ is assigned to a pure NH_2 bending vibration. These assignments agree very well with the bands observed in the spectrum of urea (Fig. 1) obtained in these studies, although the middle and weaker band is poorly resolved from the very strong band observed between 6.18 and 6.27μ. The glucose ureide spectrum also exhibits three bands in this region. The first two agree very well with the bands in urea, but the third appears at a considerably longer wave length, 6.39 μ compared to 6.18–6.27 μ. This band exhibits a definite shoulder at about 6.32 μ, which could be assigned as the longer wave length C=O stretching, —NH_2 bending combination band. The longer wave length component with a maximum at 6.39 μ must be left as a new, and as yet unassigned band. The spectrum of glucose ureide urea somewhat confirms this assignment as three bands are seen which agree rather well with those required for the urea spectrum, and, in addition, a band with maximum from 6.30–6.48 μ is observed. The additional bands observed in this spectrum may arise from different combinations of C=O stretching and NH bending taken in pairs, as assigned by Barlow and Corish[9] for the spectra of some urea complexes.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) N. Schoorl, *Rec. trav. chim.*, **19**, 398 (1900); **22**, 31 (1903).

(3) B. Helferich and W. Kosche, *Ber.*, **59B**, 69 (1926).

(4) A. Hynd, *Biochem. J.*, **20**, 205 (1926).

(5) R. T. O'Connor, E. F. DuPré and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).

(6) A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957).

(7) R. D. Waldron and R. M. Badger, *J. Chem. Phys.*, **18**, 566 (1950).

(8) J. E. Stewart, *ibid.*, **26**, 248 (1957).

(9) G. B. Barlow and P. J. Corish, *J. Chem. Soc.*, 1706 (1959).

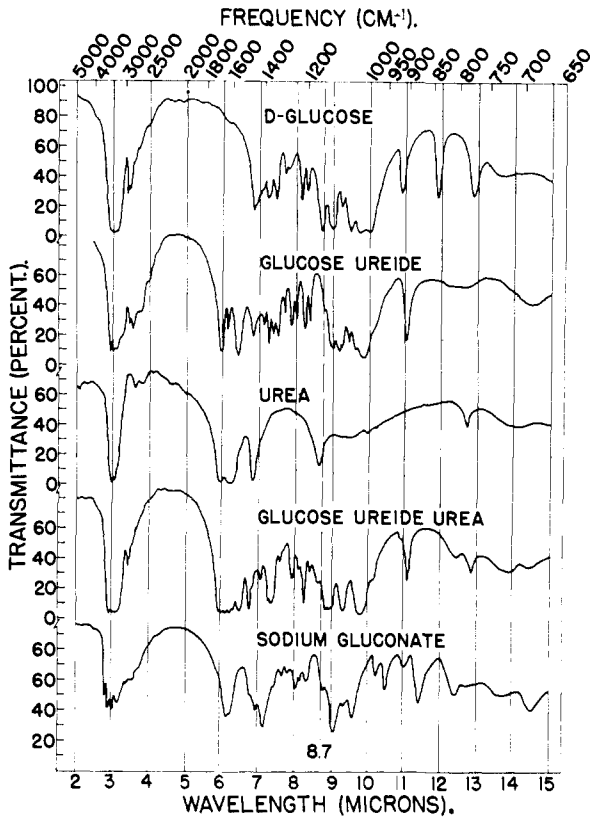
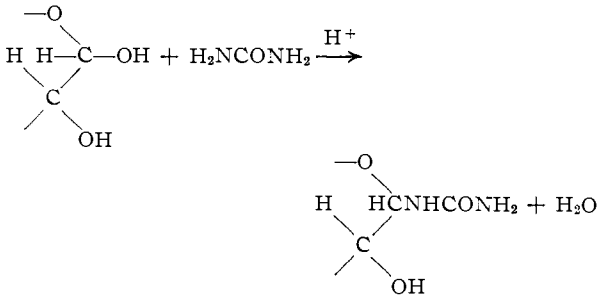


Fig. 1.—Infrared absorption spectra of glucose ureide and glucose ureide urea compared with those for glucose, urea and sodium gluconate.

Schoorl[2] postulated that the ureide is formed by reaction of the carbonyl group of glucose and other reducing sugars in the aldehyde form, according to the equation

$$\begin{matrix} HC{=}O \\ | \end{matrix} + H_2NCONH_2 \xrightarrow{H^+} \begin{matrix} HC{=}NCONH_2 \\ | \end{matrix} + H_2O$$

Helferich and Kosche,[3] however, held that the ureide retains the ring structure according to the reaction



Benn and Jones[10] have recently presented some chemical evidence pointing to a ring structure in the ureide. Their work involved oxidation with periodate and degradation of acetylated compounds.

The postulation of Schoorl requires the appearance of a C=N stretching band. This band is somewhat stronger than the C=C stretching, and the observed band at 6.39 μ might be assigned to this vibrational mode. Against such an assignment is the argument that C=N stretching vibrations are reported for acyclic compounds as occurring from 5.92 to 6.14 μ,[11] and Bellamy has reported that, except in cyclic systems, the effect of conjugation on the wave length position of the C=N stretching band is very small; hence the band would not be expected to be found at a wave length as long as 6.39 μ. These arguments can be countered, probably, by the fact that in the molecule postulated by Schoorl the C=N group is conjugated to the C=O, and no model compounds with this combination appear to have been investigated. Furthermore, unless an unlikely postulation is valid, *i.e.*, that in the spectra of the reaction products the C=O stretching, $-NH_2$ bending combination band has been shifted to a considerably longer wave length than that found for the parent compound urea, the band with the maxima at 6.39 μ must be accounted for by some new group, by a group not found in the urea moiety. It may be concluded, probably, without study of additional model compounds that the bands in this region do not confirm the C=N stretching required by Schoorl's postulation, but, on the other hand, they do not entirely rule out this possibility.

The strong C–N stretching band in urea at 6.83 μ is probably unresolved from the C–H deformations of the glucose in the spectra of the reaction products, and a series of bands in the 7μ region probably arises from C–H deformations originating in the D-glucose moiety.

Bands at 8.18 and 8.32 μ in the spectrum of glucose, arising from C–O stretching, are seen at slightly longer wave lengths in the spectra of the reaction products. Bands in the spectra of the ureides at 8.75 and 8.65 μ are probably incompletely resolved components from both the 8.72 μ band of the glucose and the 8.66 band of urea. The band in urea has been assigned to an NH_2 rocking. In the spectrum of cellulose a band at 8.55–8.70 μ has been assigned by Rowen and coworkers[12] to a vibration of the glucopyranose ring.

Rowen, Forziati and Reeves[13] studied periodate-oxidized cellulose where it is known that the anhydroglucose ring suffers cleavage, and they observed that the change in the 8–10 μ region is probably caused in part by cleavage of the ring. Any other product from glucose where a straight chain configuration results should also show a similar effect in this region. Such is indeed seen in the curve for sodium gluconate in Fig. 1. Gluconic acid is a straight chain glyconic acid produced by mild oxidation of glucose where only the aldehydic group is oxidized. Use of the sodium salt assures absence of a lactone ring. The presence of only a very weak absorption at 8.75 μ is indicative of lack of ring structure. In light of the preceding, the virtual disappearance of the 8.7 μ band in the

(10) M. H. Benn and A. S. Jones, *Chemistry & Industry*, 997 (1959).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1954.

(12) F. H. Forziati and J. W. Rowen, *J. Research Natl. Bur. Standards*, **46**, 38 (1951); J. W. Rowen, C. M. Hunt and E. K. Plyler, *ibid.*, **39**, 133 (1947).

(13) J. W. Rowen, F. H. Forziati and R. E. Reeves, THIS JOURNAL, **73**, 4484 (1951).

TABLE I

INFRARED ABSORPTION BANDS OF D-GLUCOSE, UREA, SODIUM GLUCONATE AND REACTION PRODUCTS

Tentative assignment	Location of band maxima (μ) and relative intensity[a]				
	D-Glucose, anhydrous	Glucose ureide	Urea	Glucose ureide urea	Sodium gluconate
O—H, N—H stretching	....	2.90vs	2.92vs	2.90vs	2.85s
	2.95–3.10vs	2.98vs	3.00vs	3.00–3.12vs	2.93s
	....	3.05vs	3.05vs	....	3.03–3.08s
C—H stretching	3.40s	....	....	3.40w	3.38w
	3.43s	3.43m	....	3.43m	3.44w
	3.47s	....	....	....	....
Comb. C=O stretching and NH_2 bending	....	5.93vs	5.90–5.95vs	5.90–5.95vs	....
COO^- stretching	....	....	....	....	6.15s
NH_2 bending	....	6.12s	6.10–6.18vs	6.10vs	....
Comb. C=O stretching and NH_2 bending	....	6.32sh	6.18-6.27vs	6.20–6.30vs	....
C=N stretching (?)	....	6.39vs	....	6.48vs	....
C—N stretching	6.84s	6.82s	6.83vs	6.76vs	6.93s
C—H deformation	7.05w	7.10m	....	7.06m	7.15vs
	7.22m	7.22s	....	7.28s	....
	7.28m	7.36m	....	7.38s	....
	7.45m	7.49m	....	7.59w	7.65m
	7.72m	7.68m	....	....	....
	7.80w	7.86s	....	7.93w	7.83m
	....	7.99s	....	8.13w	8.04m
C—O stretching	8.18s	8.22s	....	8.25s	8.15m
	8.32s	8.37s	....	8.41m	8.33m
C—O stretch, O—H bend, NH_2 rocking and glucopyranose ring (?)	8.72vs	8.75w	8.66s	8.65w	....
C—O stretch and O—H bend, or comb. of these two	8.99vs	8.98vs	....	8.95vs	8.84s
	9.28s	9.18vs	....	....	9.15s
	....	9.43s	....	9.35vs	9.45w
	9.52vs	9.58w	....	....	9.63s
	9.75vs	....	....	....	....
C—N stretching	....	9.83vs	9.95w	9.83vs	....
Glucopyranose ring (?)	10.02vs	....	....	....	10.28m
C_1—H deformation	10.92vs	11.00vs	....	11.12s	10.53s
Glucopyranose ring (?)	11.92vs	....	....	....	11.45s
NH_2 wagging and C=O out-of-plane bending	....	12.70w	12.68m	12.88m	....
Glucopyranose ring (?)	12.88w	....	....	....	12.44m
NH_2 wagging and C=O out-of-plane bending	....	14.50w	14.00w	13.90w	....

[a] vs = very intense, s = intense, m = medium, w = weak, sh = shoulder.

glucose ureide and ureide urea spectra strongly suggests that the sugar has reacted with urea while in the aldehydo or open chain form. Higgins,[14] however, has shown that decline in intensity of this band does not necessarily imply ring cleavage as he observed that this band can be displaced by deuteration. This observation confirms the assignment of O'Connor, DuPré and McCall[5] who attributed the band to a C–O stretching or an O–H bending of the C–O–H group. No bands are found in the region above 8.66 to 10 μ in the spectrum of urea. In this region three or four bands are found in the spectrum of the ureides and parallel those found in the spectrum of glucose. These undoubtedly arise from C–O stretching and/or O–H deformations (or, more likely, to combinations of these two modes).

Above about 10μ, the spectrum of urea exhibits three weak to medium intensity bands at 9.95, 12.68 and 14.00 μ. The first of these bands has been assigned to a C–N stretching and the latter two to a combination of NH_2 wagging and C=O out-of-plane bending.[6] In the region above 10μ, glucose exhibits four very strong bands. Of these four, only that at 10.92 μ in glucose is seen as a band at 11.00 and 11.12 μ in the spectra of the glucose ureide and of the glucose ureide urea, respectively. This band has been assigned by Barker, *et al.*,[15] to a C–H deformation on the C_1-carbon atom of glucose and related sugars, although Stacey[16] has claimed that the absorptions in the 10.4–13.7 μ region are due to a C_1-group vibration. Higgins and McKenzie[17] have shown that the 10.92 μ band shifts to longer wave lengths upon oxidation of cellulose, and they account for this shift as arising from a change in the bending force constant accompanying ring scission. Thus, the shift in the wave length position of this band in the spectra of the ureides, as compared to D-glucose, may likewise be considered as arising from ring scission. Furthermore, Barker, *et al.*,[15] have assigned strong bands in this region of the spectra of glucose and

(14) H. G. Higgins, *J. Polymer Sci.*, **23**, 645 (1958).

(15) S. A. Barker, E. J. Bourne and D. H. Whiffen in "Methods of Biochemical Analysis," D. Glick, Ed., Vol. III, Interscience Publishers, Inc., New York, N. Y., 1956.

(16) M. Stacey, paper presented at the 135th National Meeting of the American Chemical Society, Division of Cellulose Chemistry, Boston, Mass., April, 1959.

(17) H. G. Higgins and A. W. McKenzie, *Australian J. Appl. Sci.*, **8**, 197 (1958).

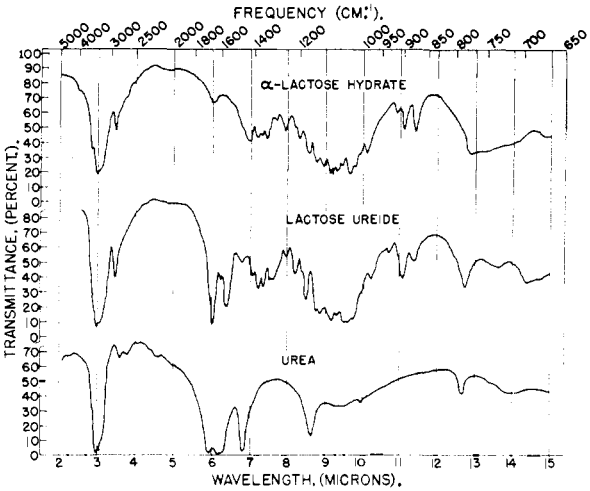


Fig. 2.—Infrared absorption spectrum of lactose ureide compared to those of α-lactose hydrate and urea.

other sugars to vibrations associated with the glucopyranose ring. Tipson, Isbell and Stewart[18] have made similar assignments in their investigations of the β-glycopyranosides. The absence of any of these strong bands in the spectra of the ureides can be accounted for nicely by the postulation of Schoorl that the ureide is formed by reaction of the carbonyl group of the glucose in the aldehyde form. This postulation could also account for the shift of the 10.92 μ band to longer wave lengths. Absence in the spectra of the reaction products of these strong bands observed in the spectrum of glucose is difficult to interpret on the basis of the reaction as postulated by Helferich and Kosche, involving merely the replacement of an O–H group by the urea moiety.

Any other product from glucose where a straight chain configuration results should exhibit in its spectrum a similar disappearance of the three strong glucose bands with maxima at 10.02, 11.92 and 12.88 μ, considered in Table I as arising from some vibration of the glucopyranose ring. The bands in the spectrum of sodium gluconate, given in the table, resemble those of glucose very closely below 10 μ, with the exception of the very characteristic maximum at 6.15 μ, arising from the COO^- stretching mode. Above 10 μ, however, the three strong bands of glucose are absent; only two or three bands of moderate intensity at considerably different wave lengths are observed.

The spectrum of glucose ureide urea contains both urea and ureide absorption modes. The urea bands are located at 2.9, 3.0, 5.9, 6.2, 6.8, 8.65 and 12.85 μ, but the bands at 2.9, 3.0 and 5.9 μ are also ureide absorptions. The broad band from 6.0 to 6.3 includes the 6.2 μ amide I band of urea. The urea $-NH_2$ rocking mode at 12.75 has apparently shifted to 12.85 μ—the shift to a longer wave length signifying restrictions on the urea $-NH_2$ groups in the same manner that shifts of the –OH stretching band to longer wave lengths signify changes from free –OH to bonded –OH groups. Restrictions on the movements of the $-NH_2$ groups would naturally result with the urea molecule being associated through these groups to the ureide molecule by hydrogen bonding. The sites for this particular bonding have not been visualized yet. Upon removal of the urea molecule by boiling the ureide urea in absolute alcohol to give the free ureide, the urea bands disappear, specifically the bands at 8.65 and 12.85μ. Since the ureide contains the group $-CNH_2$, several of the urea bands seem to remain, but naturally these are bands common with the ureide amide group.

(18) R. S. Tipson, H. S. Isbell and J. E. Stewart, *J. Research Natl. Bur. Standards*, **62**, 257 (1959).

TABLE II

INFRARED ABSORPTION BANDS OF α-LACTOSE HYDRATE, UREA AND LACTOSE UREIDE

Tentative assignment	Location of band maxima (μ) and relative intensity[a] α-Lactose hydrate	Urea	Lactose ureide
O—H, N—H stretching	2.85w	2.92vs	2.87w
	2.99vs	3.00vs	2.95vs
	3.05w	3.05w	3.00–3.03vs
C—H stretching	3.35w	....	....
	3.42w	....	3.43m
	3.46m	....	3.47m
Comb. C=O stretching and NH_2 bending	....	5.90–5.95vs	6.03vs
Water band	6.00w	....	....
NH_2 bending	....	6.10–6.18vs	6.22w
Comb. C=O stretching and NH_2 bending	....	6.18–6.27vs	....
C=N stretching (?)	....	....	6.37s
C—N stretching	....	6.83vs	6.85–6.87w
C—H deformation	7.00m	....	7.10w
	7.22m	....	7.24m
	7.35m	....	7.37m
	7.45m	....	....
	7.52w	....	7.55m
	7.72w	....	7.65w
	7.90m	....	7.98w
C—O stretching	8.32m	....	8.22m
	8.57s	....	8.51s
C—O stretching, O—H bending, NH_2 rocking, glucopyranose ring (?)	8.75s	8.66s	8.77m
C—O stretching and O—H bending or comb. of these	8.95m	....	8.89s
	9.14m	....	9.18s
	9.22m	....	....
	9.32m	....	9.33w
	9.45w	....	....
	9.68s	....	9.52–9.65s
C—N stretching	9.95w	9.95w	9.76w
Glucopyranose ring (?)	10.12m	....	10.25w
C_1—H deformation	10.92w	....	10.75w
Glucopyranose ring (?)	11.12s	....	11.12m
	11.43s	....	11.43w
NH_2 wagging and C=O out-of-plane bending	....	12.68m	12.75m
	....	14.00w	13.63w

[a] vs = very intense, s = intense, m = medium, w = weak.

The spectra of lactose ureide and α-lactose hydrate with that of urea are shown in Fig. 2. The wave length positions and relative intensities of the principal absorption bands in these spectra are listed in Table II along with the most probable band assignments. The product from reaction of urea with lactose, lactose ureide, has a spectrum much as might be expected, where most of the absorption bands are similar to those of the product from reaction of urea with D-glucose. Evidence for the aldehyde configuration is not quite so obvious as in the case of the reaction products with urea and D-glucose. The long wave length bands

in the spectrum of lactose do not disappear in the spectrum of the ureide but are considerably weaker and somewhat shifted in wave length position. This is, upon reflection, the effect to be expected. Lactose (glucose–β-galactoside) is a disaccharide containing 2 pyranose rings. Urea can react only with the glucose portion since only that part of the molecule has a free reducing group. There is little doubt from the spectrum that an amide group is present in the ureide. The changes at the longer wave lengths can be explained by the fact that the bands arising from the glucopyranose ring disappear as the reaction proceeds. The galactose portion, however, still remains in the ring form regardless of what happens to the glucose portion and, hence, the absorption bands associated with the ring vibrations can only be expected to become weaker. But, as these bands are now resolved from the glucopyranose ring bands, their exact wave length positions would be expected to exhibit slight shifts in position. These are exactly the changes observed. On the basis of these data, the spectrum can most readily be explained as arising from an aldehydo-glucose configuration in the lactose ureide molecule.

Conclusions

The tentative infrared band assignments for glucose ureide, glucose ureide urea and lactose ureide indicate the presence of an amide group in the respective molecules. In the glucose ureide and glucose ureide urea molecules there is evidence to suggest that the glucose is apparently in the aldehydo configuration. There is some evidence in the spectrum of lactose ureide to suggest that the glucose portion of the molecule is in the aldehydo form.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND NUTRITION, GRADUATE SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF PITTSBURGH]

The Conformations of Methyl Idopyranosides[1]

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Complex formation with cuprammonium solutions was studied with methyl α- and β-D-idopyranoside (compensating complexes), methyl 2-methyl-β-D-idopyranoside (levorotatory complex), methyl 3-methyl-β-D-idopyranoside (1*a*,3*a*-complex) and methyl 2,3-dimethyl-β-D-idopyranoside (no complex). The oxidation of methyl β-D-idoside by chlorine was more rapid than that of the α-anomer. Possible conformations for idose derivatives are based on these observations and results already in the literature. α-Idosides are assigned a 1C conformation. The closest representation of the β-idosides is believed to be a half-chair structure, HC3, with deviations from this ideal representation either toward the chair conformation C1 or the skew conformation 1B3. Methyl 2-methyl-β-D-idopyranoside and methyl 3-methyl-β-D-idopyranoside were prepared in the form of sirups and were characterized by means of optical rotations. The structures of these two compounds were confirmed by periodate oxidation experiments.

In his classic studies of the conformations of pyranose rings, Reeves[2] investigated the reactions of a number of idose derivatives with cuprammonium solutions. The following conformational assignments were made: 1C conformation, methyl α-D-idoside,[3] methyl 2-methyl-α-D-idoside, methyl 4,6-benzylidene-α-D-idoside. Of the two β-idosides examined, methyl 3-methyl-β-D-idoside was assigned the C1 conformation and methyl 4,6-benzylidene-β-D-idoside, a 1C conformation. In the latter case, complex formation with the cuprammonium reagent was very poor. It was concluded that the β-idosides could react in both chair conformations. Consideration of the "instability factors"[2] also suggested a C1 ⇄ 1C equilibrium for the β-idosides. With the realization that other stable conformations participate in the interconversion of the two chair forms,[4] the description of a compound as a C1 ⇄ 1C mixture is unsatisfactory unless it is established that the theoretical intermediates in this interconversion have no stable existence. In two other instances, lyxose and altrose, where C1 ⇄ 1C interconversions were originally postulated, Reeves has suggested[4] a stable shape in the flexible cycle of the six boat forms. The present paper describes experiments designed to provide more information about the possible conformations of idose derivatives.

Experimental

Methyl 4,6-benzylidene-α- and β-D-idosides were prepared from methyl α- and β-D-galactosides as described by Sorkin and Reichstein.[5] Removal of the benzylidene group was accomplished by catalytic hydrogenation[6] as follows: methyl 4,6-benzylidene-β-D-idoside (535 mg.) in glacial acetic acid (32 ml.) was shaken with 10% palladium–charcoal catalyst (450 mg.) in a hydrogen atmosphere. After about 2.5 hours no more hydrogen was taken up. The solution was filtered and evaporated to a sirup. The sirup was taken up in water (10 ml.) and extracted three times with chloroform (15 ml. in all). The aqueous solution was treated with a small amount of Amberlite MB 2, then Norite A. Filtration and evaporation gave methyl β-D-idoside as a sirup, $[\alpha]^{24}D$ −48.5° (*c* 1.39, H_2O). Sorkin and Reichstein[5] quote the specific rotation of this compound as $[\alpha]^{20}D$ −95.0° (*c* 3.799 in methanol) and $[\alpha]^{20}D$ −81.1° (*c* 3.265 in H_2O). However, in describing the conversion of this compound to D-idosan, they quote a specific rotation $[\alpha]^{18}D$ −47° for a 2.5% solution in 2.5% sulfuric acid after 3 minutes at room temperature. Wiggins[7] later reported $[\alpha]^{20}D$ −40.8° (*c* 10 in H_2O) for this compound.

(1) This work was supported in part by a Research Grant (A-725) from the National Institutes of Health, United States Public Health Service.

(2) R. E. Reeves, THIS JOURNAL, **72**, 1499 (1950).

(3) The abbreviated form, idoside, used in this paper, refers throughout to idopyranoside structures.

(4) R. E. Reeves, *Ann. Rev. Biochem.*, **27**, 15 (1958).

(5) E. Sorkin and T. Reichstein, *Helv. Chim. Acta*, **28**, 1 (1945).

(6) R. E. Reeves, THIS JOURNAL, **71**, 2116 (1949).

(7) L. F. Wiggins, *J. Chem. Soc.*, 1590 (1949).