Tetrahedron, 1964, Vol. 20, pp. 647 to 653. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF ASSOCIATION FEATURES, CONFIGURATION AND NUMBER OF RING MEMBERS IN ANHYDRO SUGAR ALCOHOLS AND THEIR PARTIALLY DEUTERATED DERIVATIVES BY MEANS OF THE INFRARED SPECTRA*

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(*Received* 8 *July* 1963; *in revised form* 11 *October* 1963)

Abstract—The structure of new anhydro sugar alcohols can be determined without an interpretation of the bands below 1600 cm^{-1}, and solely on a basis of the multiplicity of the CH stretching vibrational frequencies. In cases where spectra cannot be taken in solution, the features of the associations within the molecules can be clarified by means of IR spectra of partially deuterated derivatives, and the assignation of the stretching vibration bands of the hydroxyl groups becomes possible. The torsional vibrations of the OH groups hindered in their rotation are also identifiable in the spectra.

INTRODUCTION

THE elaboration of an IR spectroscopic method for the structure verification of anhydro sugar alcohols is the subject of this investigation. The problem is complicated as complex in the region below wave number 1500 cm^{-1} the assignation of bands based on a few model compounds is unreliable because of the number of functional groups. Unequivocal interpretation in this spectral range can only be achieved by investigation of a large number of substances of this type, or by spectral comparison of compounds deuterated in the skeleton. Any attempt to determine the number of the ring members based upon the ether frequencies of the anhydro ring had to be abandoned—because the deformation frequencies of OH and CH, and the stretching vibration frequency of $>$C—O—(H) all fall within the same range.

RESULTS AND DISCUSSION

The structure verification (determination of the number of ring members) can be achieved by the stretching vibration frequencies of CH.

The spectra of the following compounds are discussed: 1,5-anhydro-D-sorbitol (I)[1], 1,6-anhydro-D-sorbitol (II),[2] 2,6-anhydro-D-sorbitol (III) structure originally unknown, 1,6-anhydro-L-iditol (IV),[2] and the partially deuterated derivatives of I, II and IV. The designation of the spectra is, in the same order: Figs. 1–7 respectively.

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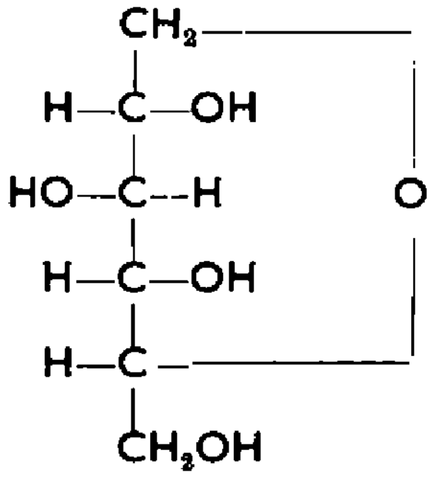
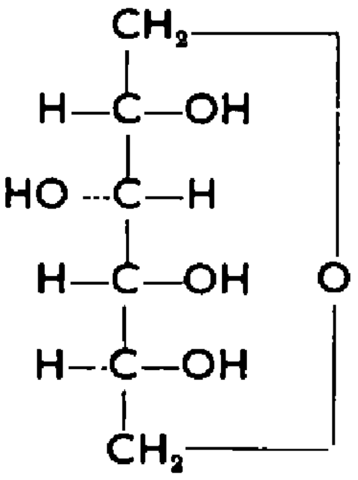
* The paper was given in abbreviated form at the VII$^{\text{th}}$ European Congress on Molecular Spectroscopy, Budapest. 22–27 July 1963.

[1] A. Ashahina. *Arch. Pharm.* **2-7**, 157 (1909).

[2] L. Vargha and E. Kasztreiner, *Chem. Ber.* **93**, 1608 (1960).


I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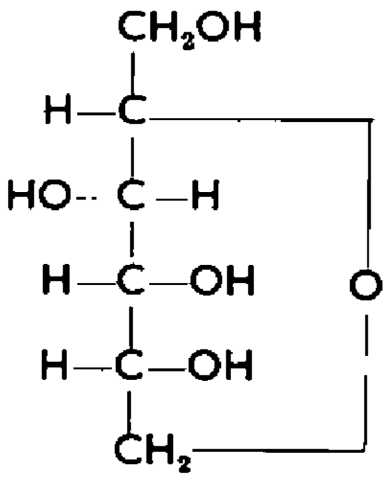
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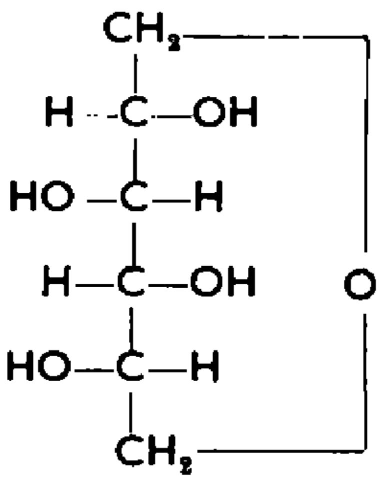

IV

The CH *stretching vibrations*

In these compounds CH groups of four different types are present: —CH_2—(OH), —CH_2—(O—), >CH—(OH) and >CH—(O—), where, in every case, the free valencies form bonds with carbon atoms.

The vibration frequency of the CH and CH_2 residues linked to an ether-oxygen is lower, and its intensity less, than the frequencies of CH and CH_2 groups linked to OH since the C—H bond near the ether-oxygen is less polarized than in the vicinity of the negative OH group. The asymmetric, and the symmetric stretching vibration bands of both types of CH_2 groups can be identified and the above holds for both types. It should be noted that the wave number values of the CH group frequencies are greater than that of the CH_2 groups. Based upon spectra of model compounds, it can be stated that no coupling between CH-vibrations takes place—this is to be expected because molecular models show that the angles enclosed by the groups are smaller than 90°. Groups, identically directed and in the same spatial position, absorb at the same frequencies. In the substances investigated, there are axial, and equatorial CH groups both "above" and "below" the anhydro ring. Taking all these into account the number of ring members in unknown anhydro sugar alcohols can be determined from the multiplicity of the CH vibrations. The band which follows the CH group of the >CH—(OH) type appears between wave numbers 3000–2960 cm^{-1}. In I the molecular model indicates three such axial groups, two of them are above, one is below the plane of the ring. The more intensive band at 2985 cm^{-1}, and the less intensive band at 2998 cm^{-1} can be assigned to these (Fig. 1). In II, four such axial groups can be found of which three have the same spatial position and one is in the opposite direction. The corresponding wave numbers are 2990 cm^{-1} and 2975 cm^{-1} respectively (Fig. 2). The latter is very intensive and can be, therefore, assigned to the three groups of the same spatial position. In IV there are again four axial >CH—(OH) groups with two pairs in identical spatial position. The two bands of equal intensity are found at 2998 cm^{-1} and 2960 cm^{-1}, respectively (Fig. 4).

The band of the CH group of the >CH—(O—) type is very weak, and in the spectrum of the one model compound containing such a group, it coalesces with the asymmetric CH_2 stretching vibration band of the —CH_2—OH group. This is shown by a weak shoulder at 2943 cm^{-1} in this band.

The group of the —CH_2—(OH)— type can also only be found in I, and on the basis of greater intensity and higher wave numbers, the bands at 2940 cm^{-1} and 2885 cm^{-1} can be assigned to it.

Finally, the asymmetric and symmetric stretching vibration bands of the CH_2

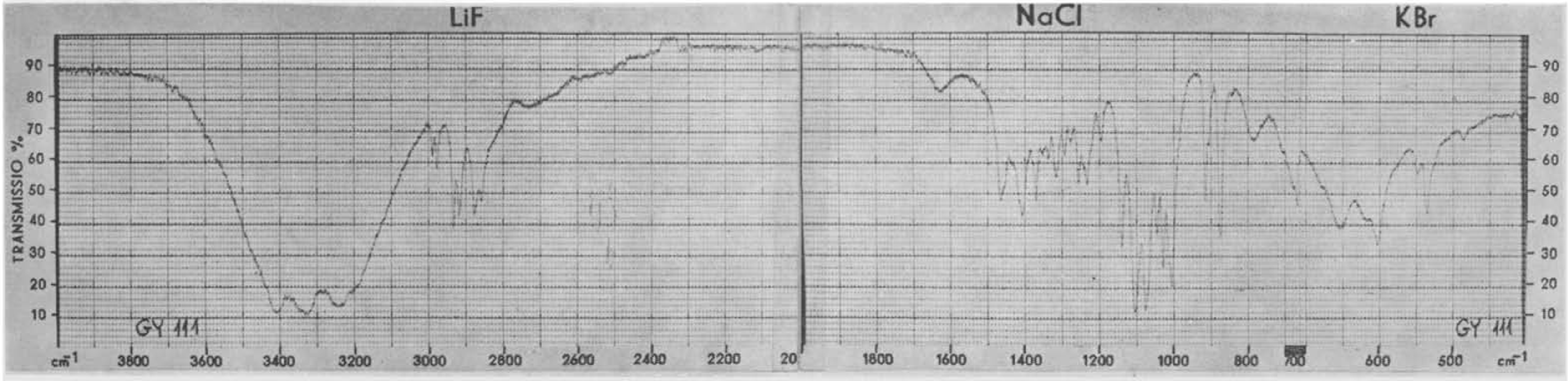


FIG. 1. Spectrum of 1,5-anhydro-D-sorbitols

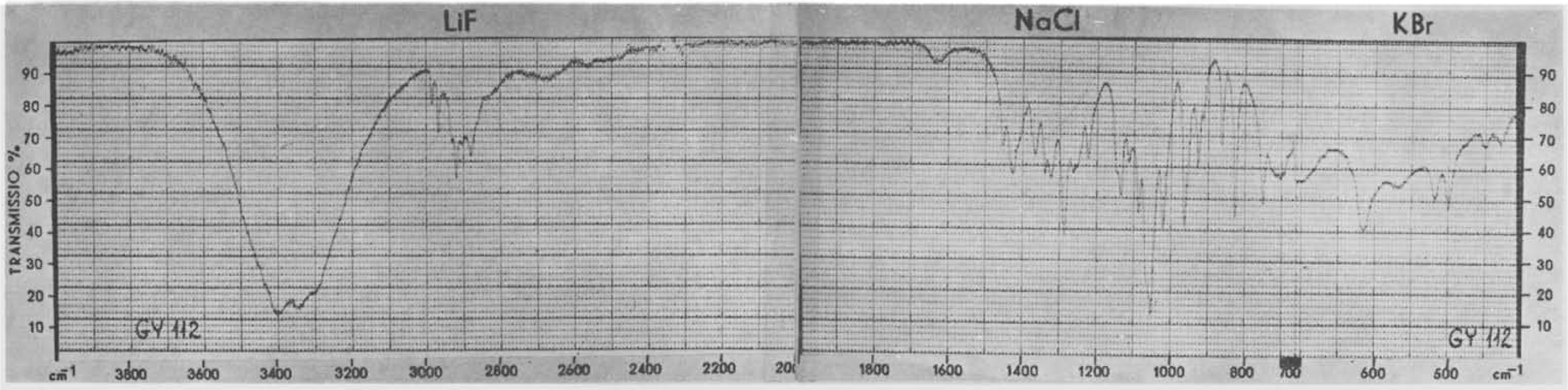


FIG. 2. Spectrum of 1,6-anhydro-D-sorbitols

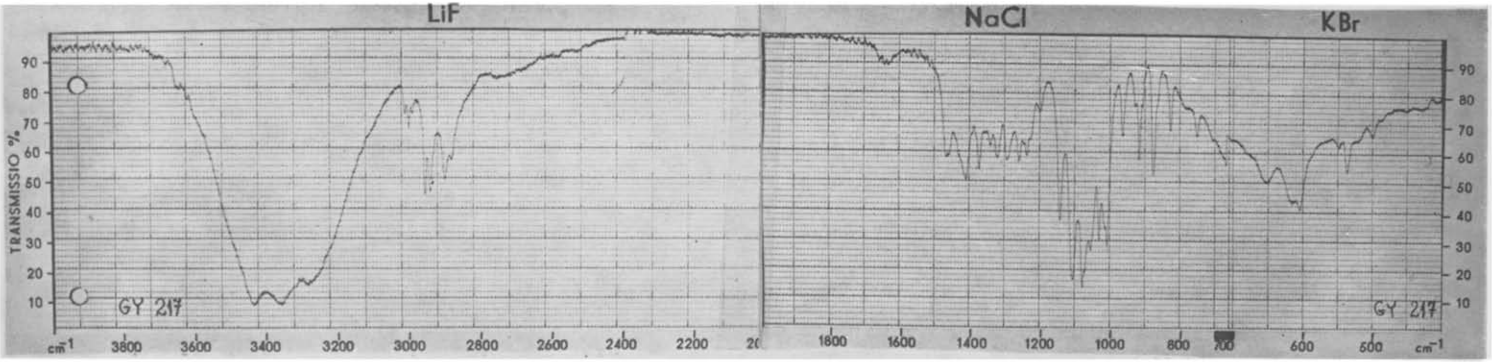


FIG. 3. Spectrum of 2,6-anhydro-D-sorbitols

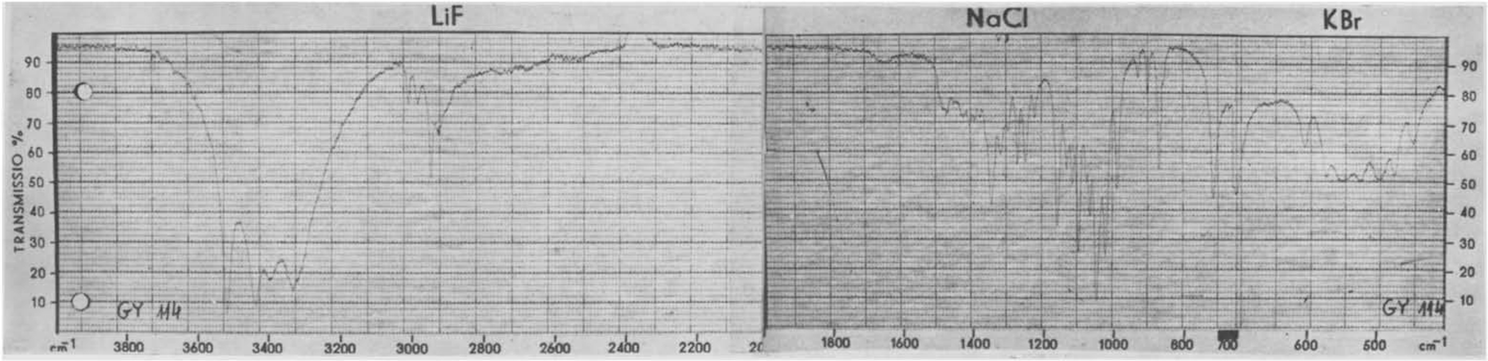


FIG. 4. Spectrum of 1,6 anhydro-L-iditols

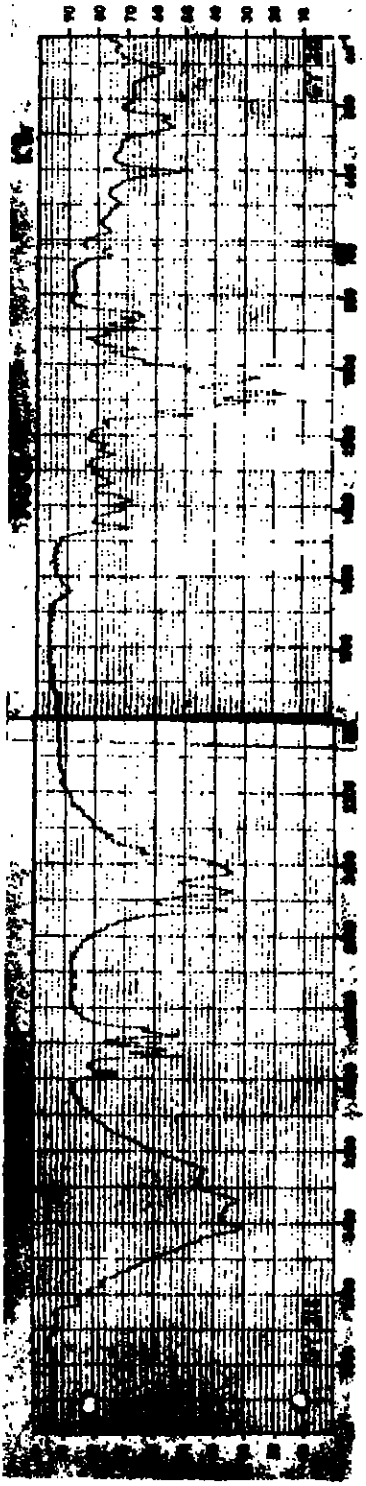


FIG. 5. Spectrum of deuterated derivatives of 1,5-anhydro-D-sorbitols

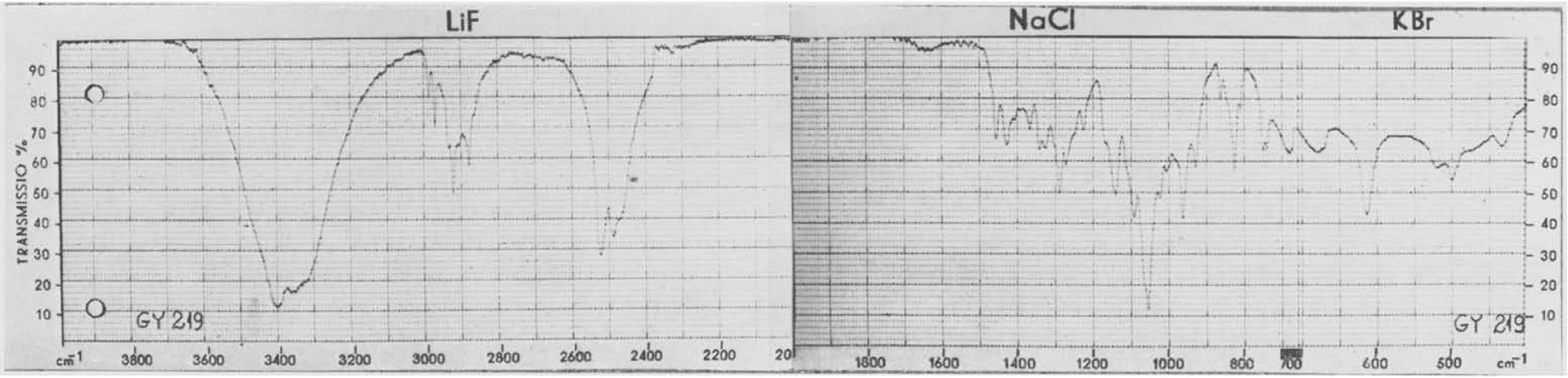


FIG. 6. Spectrum of deuterated derivatives of 1,6-anhydro-D-sorbitols

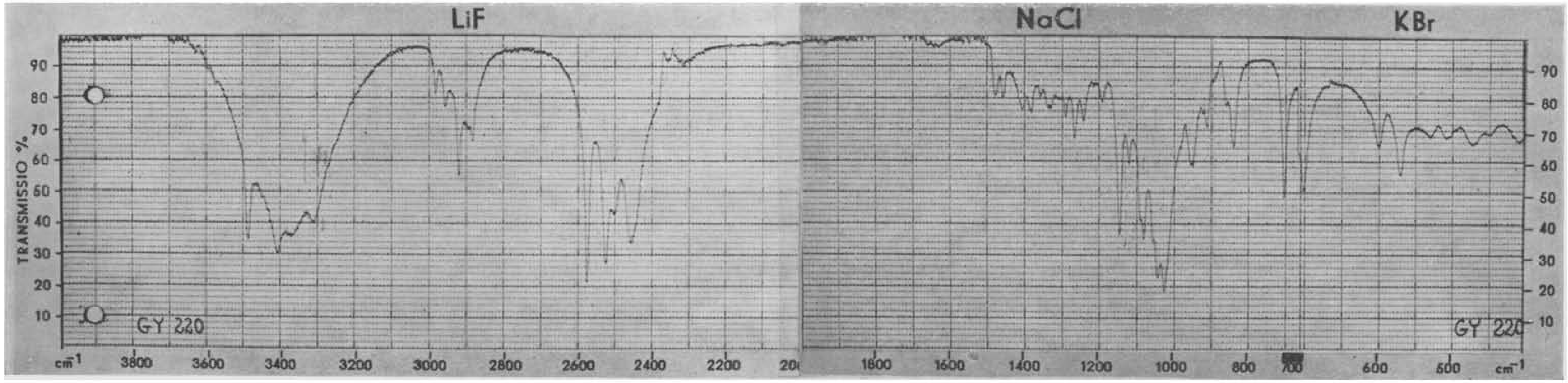


FIG. 7. Spectrum of deuterated derivatives of 1,6-anhydro-L-idits

group of the —CH_2—(O—)— type in I were found at 2925 cm^{-1} and 2862 cm^{-1}; in II at 2928 cm^{-1} and 2888 cm^{-1}; in IV at 2925 cm^{-1} and 2886 cm^{-1}, respectively.

TABLE 1. CH-STRETCHING VIBRATIONS*

	1,5-anhydro-D-sorbitol (I)			1,6-anhydro-D-sorbitol (II)			1,6-anhydro-L-iditol (IV)			2,6-anhydro-D-sorbitol (III)		
>CH—(OH)										2992	*a*↑	*w*
	2998	a↑	*w*	2990	a↑	*w*	2998	a↑a↑	*s*	2980	*e*↗	*s*
	2985	a↓a↓	*s*	2975	a↓a↓a↓	*s*	2960	a↓a↓	*s*	2970	*e*↘	*w*
>CH—(O—)	2940		*w*	—			—			2938		*w*
—CH_2—(OH)	2940		*s*							2938		*s*
	2885		*s*	—			—			2880		*s*
—CH_2—(O—)	2925		*w*	2928		*w*	2925		*w*	2920		*w*
	2862		*w*	2888		*w*	2886		*w*	2860		*w*

* In this table, *a* means axial, *e* means equatorial, the arrows pointing upwards, or downwards, indicate the relative position of the >CH—(OH) groups; *s* is the mark of a stronger, and *w* that of a weaker band. All the figures in the table represent wave numbers in cm^{-1}.

Based upon findings of spectral analysis of model compounds, the structure of anhydro-D-sorbitol (III), for instance, wherein the number of ring members is unknown, can be elucidated as follows. In the spectrum of III (Fig. 3) several stretching vibration bands are observed, i.e. three sharp bands of medium intensity at 2992 cm^{-1}, 2980 cm^{-1} and 2970 cm^{-1}, two pairs of bands at 2938–2920 and at 2880–2860 cm^{-1}, respectively. In both pairs the band of higher frequency is the more intensive one. There is a very weak shoulder in the 2938 cm^{-1} band at the side towards the higher wave numbers. On this basis, the compound is 2,6-anhydro-D-sorbitol for the following reasons:

(a) There are four bands of CH_2 groups, consequently the molecule contains both —CH_2—(OH) and —CH_2—(O—) type groups.

(b) There are three >CH—(OH) type bands in the spectrum and this excludes the possibility of an anhydro ring having less than six members. (In similar cases not more than two cyclic >CH—(OH) type groups, therefore not more than two corresponding bands, are possible on the one hand, on the other hand the wave number of the band must shift towards higher values because the corresponding vibrations are more strongly valency-directed in case of greater number of ring members; the electron cloud forced towards the perifery rises the bond order.)

(c) The shoulder in the band at 2938 cm^{-1} is, presumably, due to the weak coalescent absorption caused by the >CH—(O—) group.

(d) The spectrum is not identical with that of I, therefore only the III structure is possible.

(e) The molecular model shows that structure III contains one axially, and deviates in two equatorially arranged >CH—(OH) groups. This explains the presence of three such bands in the spectrum.

(f) The supposition is strengthened by the considerations, to be evolved later about the features of association, and about the OH-torision vibration band.

OH *stretching vibrations*

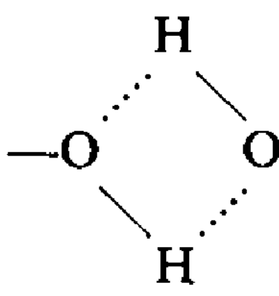
The elucidation of the association features (formation of hydrogen bonds) should establish the configurations. As, however, these compounds are insoluble in the customary solvents and their only common solvent, i.e. water, is not applicable in the range of the OH-frequencies which is of interest in the spectrum, the following method was applied. By partial deuteration a number of the OH groups were converted into OD groups. Deuteration takes place first on the free OH groups, or on those involved in loose intermolecular associations, and, therefore, a greater proportion of these groups becomes deuterated than of the groups in more stable intramolecular association. Since the stability of the association in otherwise completely similar substances is dependent on the configuration alone, in the spectrum of deuterated derivatives conclusions as to configuration can be drawn from the relative intensities of the OH/OD stretching vibration bands.[3,4]

The structure of hydrogen bonds existing in model compounds was established by means of molecular models. It must be added that several confirmations are possible for anhydro rings of 6 or 7 members. Those only were considered in which the substituents on the ring occupy the most advantageous steric positions, i.e. in which the substituents do not mutually hinder their rotation about the valency axis. This selection is justified because conformational isomers are freely interchangeable and thus the most stable form is the more probable one.

Based upon the evidence furnished by molecular models, in compound I one intramolecular hydrogen bond can be formed between the primary hydroxyl and the neighbouring secondary hydroxyl group, whereas the other two such groups can associate only intermolecularly. In the unknown derivative III the situation is similar and a separate discussion is, therefore, unnecessary. The complete congruence in this part of their spectra and the same degree of deuteration in both compounds are additional evidence for the validity of the established structure. In II two pairs of the secondary hydroxyl groups can each form an intramolecular hydrogen bond, finally, in IV the hydroxyl groups are arranged in a Seegner-wheel pattern, and three of them are mutually associated, whilst the fourth, somewhat shielded (with a weak tendency to form a hydrogen bond owing to its fixed spatial position), is free.

Accordingly, five OH stretching vibration frequencies are to be expected in I, and in III, which, arranged in a falling order of wave number values are the following:

(a) $—\overset{\cdot^{\cdot^{\cdot}}}{\mathrm{O}}—\mathrm{H}$, or (b) $—\mathrm{O}—\overset{\cdot^{\cdot^{\cdot}}}{\mathrm{H}}$ type groups present in intramolecular hydrogen bonds,

(c)  , or (d) $—\overset{\cdot^{\cdot^{\cdot}}}{\mathrm{O}}—\mathrm{H}$, and (e) $—\mathrm{O}—\overset{\cdot^{\cdot^{\cdot}}}{\mathrm{H}}$ type groups present in intermolecular hydrogen bonds. The OH stretching vibration band is tripartite, because

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[3] G. H. Beawen, E. A. Johnson, H. A. Willis and R. G. J. Miller, *Molecular Spectroscopy*. Heywood, London (1961).

[4] D. H. Whiffen and H. W. Thompson. *J. Chem. Soc.* 1420 (1948).

the absorption appertaining to each of the last three types coalesces in the spectrum, therefore this is the most intensive one. As anticipated, after deuteration the intensity of this band is greatly reduced, and the corresponding OD band is the stronger.

In the spectrum of II the OH stretching vibration band has two maxima, and here deuteration proceeds to a lesser extent than in I and III; however, the ratio of the intensities of the two maxima is the same for the OH and the OD bands. This is in complete accordance with the statements based upon molecular models, consequently there are two types possible here: (a) $—\overset{\cdot\cdot\cdot}{\mathrm{O}}—\mathrm{H}$, and (b) $—\mathrm{O}—\overset{\cdot\cdot\cdot}{\mathrm{H}}$ type, intramolecularly associated groups. The lower degree of deuteration, other experimental conditions being equal, is evident because of the great stability of intramolecular hydrogen bonds, and also the similar changes in intensity of the (a) and (b) type bands are in keeping with the facts.

In IV a quadripartite structure of the OH stretching vibration band is anticipated, and is registered, in the spectrum, to which (a) the free OH group, further the groups involved in (b) the$—\overset{\cdot\cdot\cdot}{\mathrm{O}}—\mathrm{H}$ type, (c) the$—\mathrm{O}—\overset{\cdot\cdot\cdot}{\mathrm{H}}$ type, and (d) the$—\overset{\cdot\cdot\cdot}{\mathrm{O}}—\overset{\cdot\cdot\cdot}{\mathrm{H}}$ type intramolecular bonds correspond. Accordingly, deuteration proceeds to a greater extent partly in the (a) type band, and to about the same degree as in I and III.

TABLE 2. OH AND OD-STRETCHING VIBRATIONS*

	OH stretching vibration	OH stretching vibration	OD stretching vibration	Degree of deuteration
	I and III	deuterated I		
(a)	3410 s	3410 m	2530 m	37%
(b)	3340 s	3330 m	2475 m	
(c), (d), (e)	3250 vs	3260 w	2410 s	
	II	deuterated II		
(a)	3410 vs	3410 s	2520 m	25%
(b)	3350 vs	3350 s	2480 m	
	IV	deuterated III		
(a)	3490 vs	3490 w	2576 vs	40%
(b)	3410 vs	3410 m	2524 m	
(c)	3370 s	3370 w	2500 w	
(d)	3310 vs	3310 m	2455 m	

* The experimental frequencies are shown together with relative intensities. The percentage of deuteration is given, as the integral value of the OD band of the deuterated derivative if the area below the OH band of the reference compound is taken as 100 per cent. *s* means a strong, *vs* a very strong, *m* a medium, and *w* a weak band. All the figures in the tables represent wave numbers in cm^{-1}.

In spite of the relatively few models investigated, the results fully substantiate our views and their general application. Several other sorbitol-, iditol- and mannitol derivatives, similar to those mentioned, have been investigated but the spectra of these do not add to the facts reported. The structures suggested by the multiplicity of the CH stretching frequencies can be confirmed through the association features determined by partial deuteration.

The assignation of the C—O—(H) and C—O—(C) stretching and of the OH and CH deformation frequencies, respectively, in the 1500 to 800 cm^{-1} spectrum interval is uncertain because of the many bands with commensurable intensity in this region, but this assignation, as has been demonstrated, is not necessary for the elucidation of the structures. It is noteworthy that the deformation vibration perpendicular to the OH plane, at least with some groups, can be identified. In the literature, the data given on this vibration is scant,[5–12] perhaps because, on the one hand, the correlated absorption band appears at low wave numbers and, on the other hand, this band is rather diffuse and stretches out over a broad wave number range (whenever the OH groups can freely rotate around the C—O—(H) bond, because in this case, torsion vibration is converted into internal movement). For example, in methanol the very broad and diffuse band system corresponding to torsional vibrations falls between 800 cm^{-1} and 270 cm^{-1}. If internal rotation is hindered (e.g. by a potential minimum caused by a stable intramolecular association, or by steric hindrance owing to neighbouring substituents) the otherwise diffuse band can appear with a comparatively sharp frequency most probably in the region below 700 cm^{-1}.

TABLE 3. OH AND OD OUT OF PLANE DEFORMATION VIBRATIONS

I	deuterated I	
$670\ \mathrm{cm}^{-1}$ *s*	$670\ \mathrm{cm}^{-1}$ *w*	$460\ \mathrm{cm}^{-1}$ *s*
II	deuterated II	
$590\ \mathrm{cm}^{-1}$ *s*	$590\ \mathrm{cm}^{-1}$ *w*	$425\ \mathrm{cm}^{-1}$ *m*
IV	deuterated III	
$560\ \mathrm{cm}^{-1}$ *s*	$560\ \mathrm{cm}^{-1}$ *m*	$410\ \mathrm{cm}^{-1}$ *m*

Therefore, in the spectra of the partially deuterated derivatives of the compounds investigated, such frequencies seem to be identifiable by the change of their intensity and by the shift of their frequency. Table 3 shows the shift of the bands of this region in the spectra of the three models with different association structures. It is obvious that these bands can be assigned to the OH groups involved in intramolecular hydrogen bonding, and this explains why in I the absorption is the sharpest (a primary hydroxyl forms the most stable hydrogen bond).

[5] D. Hadzi, *Hydrogen Bonding* pp. 99, 139. Pergamon, London (1959).

[6] D. Hadzi and N. Sheppard, *Trans. Farad. Soc.* **50**, 911 (1954).

[7] H. J. Becher, *Chem. Ber.* **89**, 1593, 1951 (1956).

[8] A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.* **20**, 1977 (1952).

[9] P. C. Cross, J. Burnham and P. A. Leighton, *J. Amer. Chem. Soc.* **59**, 1134 (1937).

[10] H. K. Kessler and G. B. B. M. Sutherland, *J. Chem. Phys.* **21**, 570 (1953).

[11] C. L. Angel, N. Sheppard, A. Yamaguchi, T. Shimanouchi, T. Miyazarva and S. Mizushima, *Trans. Farad.* **53**, 589 (1957).

[12] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* pp. 334, 498. Van Nostrand, New York (1945).

Further evidence for structure III is provided by the band system below 600 cm^{-1} which has the same course in I and III.

These problems require far more detailed investigation, but the observations recorded may point the way to a study of the hitherto neglected subject of OH-torsional vibrations.

EXPERIMENTAL

Spectra were determined with a Zeiss UR-10 type spectrometer by means of KBr pellets.

Deuteration. The anhydro compound (0·5 g) was heated with heavy water (8 ml) for 2 hr at 95°, the solution evaporated (red. press.) and the residue dried *in vacuo* at 75° (P_2O_5).

1,3,4,5-Tetra-acetyl-2,6-anhydro-D-sorbitol (tetraacetate of III). The mother liquors from the recrystallization of 1,6-anhydro-D-sorbitol[3] (II) were evaporated *in vacuo* and the residue boiled for 3 hr with acetic anhydride (420 ml) and anhydrous sodium acetate (42 g). After cooling the mixture was poured into water (500 ml) and, after addition of chloroform (200 ml), neutralized (Na_2CO_3), The organic layer was washed (water and $NaHCO_3$ aq.), dried and evaporated. The residue was distilled fractionally *in vacuo* to give the oily, colorless tetraacetate of III (32·53 g), b.p. 156–158° at 0·03 mm, $[\alpha]_D^{20}$ +20·38° (*c* 2, chloroform). (Found: C, 50·2; H, 6·4; saponification number, 661; $C_{14}H_{20}O_9$ requires: C, 50·6; H, 6·1%; saponification number, 674).

2,6-*Anhydro*-D-*sorbitol* (III). The tetraacetate of III (30·08 g) was boiled with 0·1 N sodium methoxide solution (80 ml) in dry methanol (200 ml), evaporated *in vacuo* and the residue recrystallized first from dry ethanol, then from 95% aqueous ethanol and finally from 95% aqueous methanol to give III (7·4 g), m.p. 115–118°, $[\alpha]_D^{20}$ + 15·4° (*c* 2, water). The mixed m.p. was 116° with II, 104–106° with 1,6-anhydro-D-mannitol[3] and 104–106° with IV. (Found: C, 43·7; H, 7·1; $C_6H_{12}O_5$ requires: C, 43·0; H, 7·4%). When III was oxidized with periodic acid and then with hypobromite[3] no diglycolic acid was obtained which was isolated during similar oxidations of II, IV, and I-anhydro-D-mannitol.[3] This fact, together with the mixed m.p. and optical rotation data confirm that III cannot contain an 1,6-anhydro ring, a conclusion which is in accordance with the result of the spectral investigations.