125. *Cyclitols. Part II.* Dipole Moments of Some Cyclitol Acetates.*

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The electric dipole moments of several fully acetylated inositols, quercitols, and inositol methyl ethers have been measured in solution. The correlation between configuration and dipole moments is discussed.

The dipole moments of the isomeric benzene hexachlorides have been the subject of much work and discussion in recent years (Melander, *Svensk. Kem. Tids.*, 1946, **58**, 231; Hetland, *Acta Chem. Scand.*, 1948, **2**, 678; Jatkar and Kulkarni, *Science and Culture*, 1949, **14**, 482; Rolla, Fontana, and Marinangeli, *Gazzetta*, 1949, **79**, 491; Bastiansen, Ellefsen, and Hassel, *Research*, 1949, **2**, 248; Lind, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1950, **72**, 4474). It seemed of interest therefore to make similar measurements on the inositols, since they constitute the only other group of hexasubstituted *cyclo*hexanes in which the configuration of a number of isomers is known. Of the eight possible inositols, four (I—IV) † were available for measurements, two others (*allo*- and *muco*-inositol; Dangschat and Fischer, *Naturwiss.*, 1939, **27**, 756) are not well known, and the remaining two are yet unknown. For comparison a number of related compounds (V—VIII) were included in the measurements. Since the cyclitols are completely insoluble in non-polar solvents their fully acetylated derivatives were used.

It was realised that rigorous calculations of the dipole moments from the known structures and configurations would not be possible for two reasons. First, free rotation of acetyl groups around the C–O bond makes the direction of the moment of each acetyl group uncertain; and, secondly, deviations from the tetrahedral angles will occur because of the mutual repulsion of the acetyl groups. The first difficulty only was encountered by Everard and Sutton (*J.*, 1951, 16) in their attempt to evaluate the dipole moment of hexamethoxybenzene, yet the case was regarded as too complicated for rigorous treatment. On the other hand, no difficulty arises from free rotation in the benzene hexachlorides but it has been shown (Bastiansen, Ellefsen, and Hassel, *Acta Chem. Scand.*, 1949, **3**, 918) that

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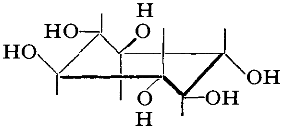
* Part I, preceding paper.

† The formulæ (I—VIII) are approximate perspective representations of chair forms; the heavy lines are to be visualised as in front of the plane of the paper. Slight distortion of the bonds is involved, but polar and equatorial bonds are clearly distinguished. Editors of other journals may like to note that only 45° and 90° angles are involved.—Ed.

the mutual repulsion of chlorine atoms causes deflections from the tetrahedral angles and therefore the actual moments are much smaller than those calculated (Lind *et al.*, *loc. cit.*). Nevertheless it was expected that the dipole moments of the inositol acetates would at least be in the expected sequence and this was verified by the measurements. Thus determinations of the dipole moments may be useful for the establishment of yet unknown configurations; in particular, they were to have been applied in the case of pinitol and quebrachitol, two inositol methyl ethers; but in the meanwhile their configuration was determined by purely chemical methods (cf. preceding paper).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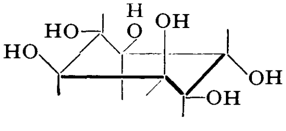
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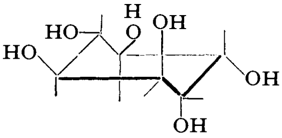
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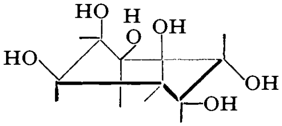
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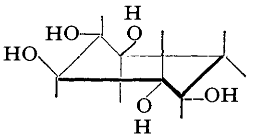
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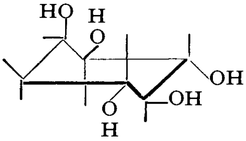
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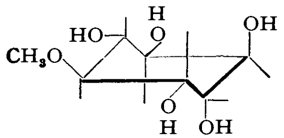
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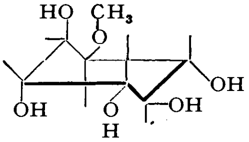
(VIII)

In order to discuss the results it must be realised that in the most stable conformation of the *cyclo*hexane ring—the chair form—the substituent groups are either in " polar " (*p*) or in " equatorial " (*e*) position (cf. the discussion and Fig. 1 in the preceding paper). The formulæ (I—VIII) are written in a way which shows these relations. In the following Table the equatorial-polar disposition † of the acetoxy-groups is given for each cyclitol, together with the measured dipole moment. The nomenclature used is that proposed in the preceding paper.

Hexa-acetate of	Acetoxy-groups	μ, D	Penta-acetate of	Acetoxy-groups	μ, D
*scyllo*Inositol (I)	*e e e e e e*	2·3	*scyllo*Quercitol (V)......	*e e e e e* –	2·3
*meso*Inositol (II)	*e p e e e e*	2·8	(–)-*vibo*Quercitol (VI)	*p e e e e* –	2·3
(±)-Inositol (III)	*p e e e e p*	3·0	Pinitol (VII)	*p e e* e e p*	4·1
*epi*Inositol (IV)	*e p e p e e*	4·1	Quebrachitol (VIII) ...	*p e* e e e p*	3·3

* Methoxy-group.

Discussion.—*scyllo*Inositol, being centrosymmetrical, should have no moment but for the free rotation of the acetoxy-groups; the corresponding benzene hexachloride (β) has a moment of zero. It is interesting to compare our result with the value of 2·05 observed for hexamethoxybenzene (Everard and Sutton, *loc. cit.*). Introduction of one group into the polar position increases the moment; two acetoxy-groups in polar positions on the opposite sides of the ring cause a further slight increase. The corresponding benzene hexachlorides (δ and α) both have moments of 2·2 D. Introduction of two polar groups on the same side of the ring results in a further considerable increase in polarity; the corresponding benzene hexachloride is not known.

It is remarkable that the quercitols, though less symmetrical, have moments not larger

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† The *e*-*p* disposition is readily obtained from the conventional planar formulæ (as shown in the preceding paper) if it is realised that two adjacent " *trans* "-groups are both *e* or both *p*, and of two adjacent " *cis* "-groups one is *e* and one is *p*. For each molecule two chair forms are possible of which the one containing fewer substituents in polar positions is regarded as the more stable (Hassel and Ottar, *Acta Chem. Scand.*, 1947, **1**, 929) and is given here.

than that of *scyllo*inositol. This probably indicates that the acetoxy-groups orient themselves so as to fill in the space available near the methylene group. Replacement of an acetoxy- by a methoxy-group reduces the symmetry of the molecule and therefore increases the polarity but the influence of the position of the group is not understood.

EXPERIMENTAL

Materials.—The cyclitols were obtained as described in the preceding paper. They were acetylated by heating them with acetic anhydride containing a trace of sulphuric acid. Their m. p.s were in agreement with the values recorded in the literature. Hexa-acetyl (±)-inositol was obtained by mixing equal parts of the (+)- and the (−)-compound, made from pinitol and quebrachitol, respectively.

Measurements.—Details of procedure and calculation were as recorded by Calderbank and Le Fèvre (*J.*, 1948, 1949; cf. also Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1). Benzene was used as a solvent except for hexa-acetyl *scyllo*inositol. Some of the compounds (II, IV, V) are insufficiently soluble in cold benzene; they were dissolved by warming them and then remained in solution at 25°. Hexa-acetyl *scyllo*inositol is insoluble in benzene; it dissolved in warm dioxan but tended to crystallise slowly at 25°, thereby reducing the accuracy of the determination. The measurments, made at 25°, are tabulated below under the usual headings (Calderbank and Le Fèvre, *loc. cit.*).

$10^6 w_1$	ε^{25}	d_4^{25}	$\alpha\varepsilon_2$	β
0	2·2725	0·87378	—	—
Hexa-acetyl meso*inositol.*				
8 831	2·2888	0·87602	1·846	0·2902
12 269	2·2947	0·87692	1·809	0·2929
13 980	2·2978	0·87738	1·810	0·2947
Whence $\alpha\varepsilon_2 = 1·82$ (mean); $\beta = 0·293$ (mean).				
Hexa-acetyl (±)-inositol.				
10 624	2·2953	0·87649	2·146	0·2919
15 612	2·3063	0·87768	2·165	0·2859
21 169	2·3190	0:87914	2·192	0·2898
Whence $\alpha\varepsilon_2 = 2·17$ (mean); $\beta = 0·289$ (mean).				
Penta-acetyl (−)-vibo*quercitol.*				
11 410	2·2880	0·87621	1·358	0·2437
17 001	2·2953	0·87677	1·341	0·2020
22 759	2·3026	0·87880	1·323	0·2524
Whence $\alpha\varepsilon_2 = 1·34$ (mean); $\beta = 0·233$ (mean).				
Penta-acetyl quebrachitol.				
10 495	2·3027	0·87639	2·877	0·2846
14 924	2·3156	0·87751	2·888	0·2860
20 832	2·3323	0·87868	2·871	0·2692
Whence $\alpha\varepsilon_2 = 2·88$ (mean); $\beta = 0·280$ (mean).				

$10^6 w_1$	ε^{25}	d_4^{25}	$\alpha\varepsilon_2$	β
Hexa-acetyl epi*inositol.*				
10 692	2·3174	0·87655	4·199	0·2965
14 092	2·3310	0·87757	4·151	0·3077
17 949	2·3460	0·87834	4·095	0·2907
Whence $\alpha\varepsilon_2 = 4·15$ (mean); $\beta = 0·298$ (mean).				
Penta-acetyl scyllo*quercitol.*				
3466	2·2377	0·87477	1·486	0·3268
5194	2·2798	0·87517	1·405	0·3063
7193	2·2823	0·87564	1·362	0·2960
Whence $\alpha\varepsilon_2 = 1·42$ (mean); $\beta = 0·310$ (mean).				
Penta-acetyl pinitol.				
9 926	2·3164	0·87622	4·423	0·2813
14 884	2·3385	0·87727	4·435	0·2684
19 377	2·3584	0·87858	4·433	0·2835
Whence $\alpha\varepsilon_2 = 4·43$ (mean); $\beta = 0·278$ (mean).				
Hexa-acetyl scyllo*inositol (in dioxan).*				
0	2·2184	1·0296	—	—
1468	2·2202	1·0297	1·226	0·068
3021	2·2221	1·0301	1·225	0·115
4205	2·2235	—	1·213	—
6086	2·2259	1·0300	1·232	0·064
Whence $\alpha\varepsilon_2 = 1·22$ (mean); $\beta = 0·08$ (mean).				

Calculation of results.

Acetate of	*M.*	$\alpha\varepsilon_2$	β	${}_{\infty}P_{\mathrm{T}}$	$[R_L]_{\mathrm{D}}$	μ, D
*meso*Inositol	432·4	1·82	0·293	252·4	93·0	2·79
*epi*Inositol	432·4	4·15	0·298	440·8	93·0	4·12
(±)-Inositol	432·4	2·17	0·289	281·1	93·0	3·03
*scyllo*Quercitol	374·3	1·42	0·310	188	82·1	2·28
(−)-*vibo*Quercitol	374·3	1·34	0·233	192·3	82·1	2·32
Pinitol	404·4	4·43	0·278	436·5	88·4	4·13
Quebrachitol	404·4	2·88	0·280	318·2	88·4	3·35
*scyllo*Inositol	432·4	1·22	0·08	198	93·0	2·3

The authors are indebted to Dr. Arthur B. Anderson, Oregon Lumber Co., Portland, U.S.A., and to Mr. M. W. Philpott, The Rubber Research Institute of Malaya, Kuala Lumpur, for samples of pinitol and quebrachitol, respectively. One of them (C. L. A.) thanks Professor R. J. W. Le Fèvre for helpful discussions. Financial assistance from the Commonwealth Science Fund is gratefully acknowledged.

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