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CHIROPTICAL PROPERTIES OF PYRANOID GLYCOLS IN THE PRESENCE OF $[Mo_2(O_2CCH_3)_4]$*

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ABSTRACT

Bidentate complexes between $[Mo_2(O_2CCH_3)_4]$ and suitable diols from the sugar series show Cotton effects around 500 to 450 (CD band I), 400 (II), 350 (III), and 300 nm (IV), and additional effects at still shorter wavelengths. The sign of Cotton effect IV is identical with the sign of the torsional angle HO–C–C–OH for *vic*-diols. With this rule the absolute configurations of open-chain *vic*-diols of the *threo*-configuration and of vicinal primary–secondary diols can be determined with small amounts of substance; for the application of the rule the torsional angle(s) HO–C–C–C should be fixed at 180°. Cotton effect III is only strong for *vic*-diols having a pyranose ring if no axial RO group is adjacent to the glycol moiety. Complexes of diols of pyranose structure carrying free hydroxyls at C-4 and C-6 show much smaller $\Delta\varepsilon$ values.

INTRODUCTION

The acetate ligands of the complex $[Mo_2(O_2CCH_3)_4]$ (**1**) in solution are kinetically labile and can easily be exchanged for other acyl residues. If these are chiral and all of same handedness the corresponding complexes are optically active and several Cotton effects can be measured[2]. As we have shown, other (nonacidic) bidentate ligands such as glycols[2] or amino alcohols[3] can form optically active complexes, and even some monodentate chiral ligands (thiophosphinic and thiophosphonic acid derivatives[4], not too sterically hindered amines[2]) may complex and

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[¶] Dedicated to Burckhardt Helferich, who in Bonn during 12 years was my admired ideal of a universal scientist, in commemoration of the hundredth anniversary of his birth.

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generate similar c.d. spectra. Summaries of the chiroptical properties of such complexes with **1** and the analogous Rh- or Ru-acylates have recently appeared[5].

The signs of the two or three Cotton effects in the approximate range 400 to 300 nm are particularly suitable for evaluation. Sector rules have been presented for the acyl ligands[2,5], and the usefulness of this *in situ* method for determining the absolute configurations of simple aliphatic glycols, e.g. lipids having a 1-monosubstituted glycerol structure, could be shown[6]. Herein we describe the chiroptical properties of such *in situ* complexes formed from **1** and sugar glycols having a pyranose structure, which actually furnished the basis for the aforementioned rule.

RESULTS

Structure of the complexes. — Although a number of related crystal structures have been determined by X-ray diffraction[7], no structure of a complex with an appropriate glycol or aminoalcohol has been elucidated. Glycols must complex through both oxygen atoms, as optically active monoalcohols or even monoethers of otherwise complexing glycols do not induce Cotton effects. Besides intermolecular binding, which at least in dilute solutions cannot be important, one can envisage the bidentate ligation of a glycol on reaction with **1** in one of three ways: 1) along the Mo≡Mo bond ("parallel"), 2) with two neighbouring oxygen atoms attached to one Mo atom of the original complex ("perpendicular"), and 3) between one of these positions and the axial one of the same Mo atom. The first two structures are illustrated in Fig. 1. The latter structure seems not very probable since (contrary to the situation with complexes containing Rh_2 or Ru_2) axial oxygen is only very weakly bound in an acyl complex of type **1** (ref. 1).

The O····O distance of a *vic*-glycol varies with the torsional angle. As rigid glycols like the cholestane-2,3-diols[2,5] form optically active complexes, and the same is true for our *vic*-glycols of the sugar series, a torsional angle O–C–C–O of about ±60° must be well suited for ligation, leading to $d_{O....O}$ of ~340 to 350 pm, whereas $d_{O....O}$ along the Mo_2 quadruple bond in the "stock" complex **1** is ~220 pm, and between two neighbouring oxygens at one Mo ~300 pm. Either of the two

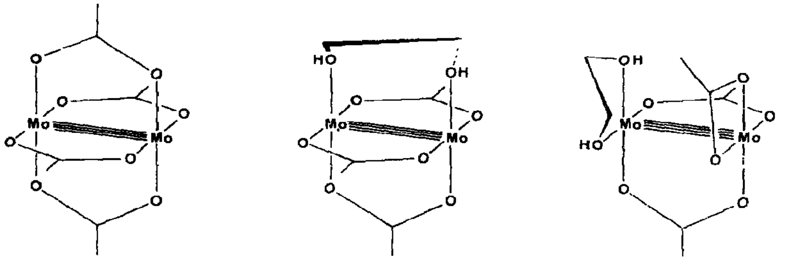


Fig. 1. Structure of complex **1** (left), and schematic drawings of possible bidentate ligations of an α-glycol in the "parallel" (middle) and "perpendicular" mode (right). In both cases a negative torsional angle (HO–)C–C(–OH) is assumed. If the alcoholic hydrogen atoms of the glycol are retained then these complexes would have charge +1. If in the perpendicular mode instead of one cyclic acetate moiety two are bound in a unidentate fashion to the right Mo, then this complex would be neutral.

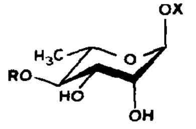
mentioned ligation modes thus necessitates some deviation from the original geometry, which could most easily be achieved by changing somewhat the C–O–Mo bond angles. Ligation of the second type is found in the related complex $[ReCl_4ReCl(H_3CSCH_2CH_2SCH_3)_2]$ (ref. 8); the torsional angle S–C–C–S is 61.1°.

In such complexes there is usually no differentation possible between the directions of the two nonbonding electron pairs of different MO-energies on oxygen; for two somewhat related copper–aminoalcohol complexes the Cu–O bond is inclined by 146° and 132°, respectively, in relation to the C–O–H plane[9], and molecular models show that similar angles could easily be possible in the glycolomolybdenum complexes. In a "parallel" complex the Mo_2O_8 moiety may also become inherently chiral by changing its "inner" torsional angle O–Mo≡Mo–O from the original value of 0° and thereby reducing its symmetry from D_{4h} to D_4. Such a twist has recently been found in a complex with chiral acylate ligands, but it was very small[10]. For complexes with a glycol as ligand this should become noticeable only if several acetates are replaced by glycol moieties, because such a twist will at the same time weaken the bonding to the still present acetate residues. Thus the most probable structures remain the "parallel" complex having a chiral six-membered ring, or the "perpendicular" one having a chiral five-membered ring, both containing a (practically) achiral chromophore (Fig. 1). In such molecules it is mainly the helicity of the ring that determines the signs of the Cotton effects, and this in turn is determined by the absolute configuration of the glycol moiety.

In the complexes each glycol replaces one acyl moiety, which dissociates into solution, rendering the complex positively charged, although in the "perpendicular" complex one end of each of two acetate residues replaced, the complex neutral (see Fig. 1). As we have to work in dimethyl sulfoxide (DMSO) solution because of solubility problems the solvent could, however, set the acetate residue(s) completely free, giving rise to a charged cluster; axially solvated complexes with DMSO are known for similar Rh compounds[11]. No dramatic differences in the u.v.-visible spectra were caused by the replacement of acylate ligands by glycol moieties. This proves that no great changes of the chromophoric system Mo_2O_8 accompany such a ligand exchange; one could take this as an indication that, predominantly, only one glycol moiety is entering the complex.

It was observed, however, that band shapes and band positions in the c.d. spectra depend somewhat on the type of the glycol (*pri-sec, sec-sec, or sec-tert*). Results obtained for one class should not be transfered uncritically to another class for the determination of absolute configuration. Also the magnitude of the torsional angle plays some role, as was found out by measuring the c.d., in presence of **1**, of a few furanosidic glycols. Here we confine ourselves to pyranosides.

For *sec-sec vic*-glycols we did not notice a marked dependence of the c.d. curve on either the concentration ratio ("stock complex": glycol) or on time. Only for ligands containing a primary CH_2OH moiety did the c.d. in a few cases change shape and magnitude after the solution had stood for several hours at room temperature. Such solutions give final c.d. readings more quickly if the solution is warmed to ~50° for 30 to 50 min. Such a change of the c.d. may be caused by the existence of an equilibrium between different structures (e.g. between the "perpendicular" and the "parallel" one), both containing only one glycol residue or between the mono- and some oligo-glycolo complexes. Because of the several different complexes that might be present in solution and the unknown stability constant of each, Job's method[12] cannot be applied. What is needed is to isolate a complex crystalline in order to have its structure determined by X-ray diffraction.



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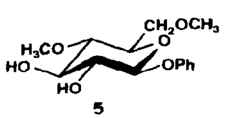
3 R = Bzl, X = Me
4 R = All, X = Bzl



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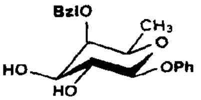

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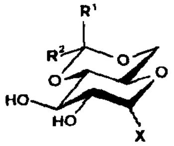
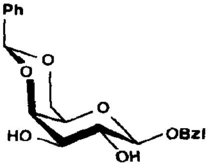


	X	R¹	R²
7	β- OBzl	H	Ph
8	α - OBzl	H	Ph
9	β- SPh	H	Ph
10	α- OMe	Me	Ph
11	α - OMe	Ph	Me



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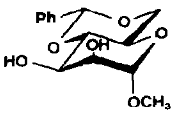

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Correlation between absolute conformation and c.d. — *A.* vic-*Glycols.* The three related rhamnopyranosides **2–4**, having the 2a, 3e conformation, in the presence of **1** give the strongest Cotton effect around 300 nm (band IV), of positive sign, corresponding to the sign of the respective torsional angle (Table I; see Fig. 2 for the c.d. of **4**). A Cotton effect of about 1/4 the magnitude and the same sign is recognized around 400 nm (band II), and between these two a negative band (III) can just be detected. This is the typical picture found for *sec-sec* 1,2-glycols having a torsional angle of about +60°. Additional c.d. bands appear between 500 and 450 nm (very small, band I) and below 270 nm (strong, maximum not reached), and they are also positive.

The diequatorial 2,3-diols **5–11** (positive torsional angle) all show similar c.d. curves between 550 and 280 nm, with Cotton effect IV always being the largest

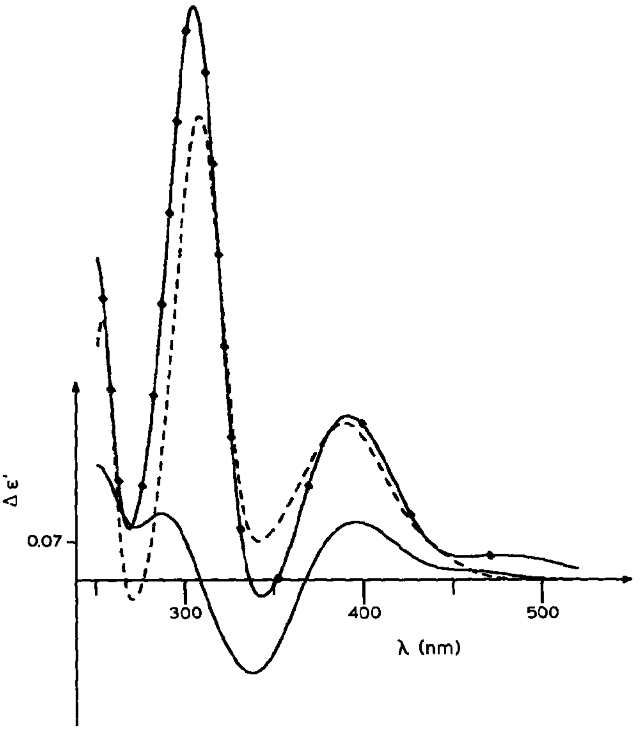


Fig. 2. C.d. of the complexes of **1** with **4** (—◆—), **7** (——), and **8** (------) in DMSO.

positive one in this wavelength range (Table I; see Fig. 2 for the c.d. of **7** and **8**). The magnitudes of the other effects vary appreciably from compound to compound however, for **5**, **7**, and **9** the negative Cotton effect III is even stronger than Cotton effect IV, whereas for **6** this same c.d. band is barely recognized and appears in the spectrum only as a positive minimum instead of a negative maximum. Whenever there is at least one axial C–O bond next to the glycol moiety then this 340 nm Cotton effect becomes quite small. This regularity holds also for **2**–**4**, whereas no simple correlation between structure and the Cotton effect around 500 nm could be found. The additional c.d. bands observed below 280 nm cannot be taken as characteristic for the glycol complex because of the presence of one or more benzenoid chromophores in the molecules studied.

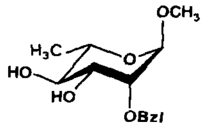
The torsional angle in the axial–equatorial diol **13** is negative, and the c.d. spectrum of its complex with **1** is indeed enantiomorphous to that of the hitherto described curves (Table I). With the axial methoxy group at C-1 the magnitude of the positive 350 nm Cotton effect is, as expected, less than 20% of that of band IV. The c.d. of the diequatorial glycol **14** in presence of **1** is somewhat anomalous, as Cotton effect II is very small and negative, but the strong positive band IV has as usual the same sign as the torsional angle of the diol moiety. A c.d. band III cannot

TABLE I

C.D. MAXIMA OF COMPLEXES BETWEEN **1** AND GLYCOLS IN DMSO SOLUTION

Glycol	*Position and conformation of hydroxyls (at least one OH on ring)*	*Sign of torsional angle (vic-glycols only)*	λ_{max} ($\Delta\varepsilon'$)
2 Methyl 4-*O*-allyl-α-L-rhamnopyranoside[14]	2*a*,3*e*	+	440sh (+0.05), 394 (+0.25), 349 (−0.19), 306 (+1.21), 272 (−0.06), 250 (+0.50)
3 Methyl 4-*O*-benzyl-α-L-rhamnopyranoside[15]	2*a*,3*e*	+	450 (+0.03), 390 (+0.20), 349 (−0.09), 306 (+0.98)
4 Benzyl 4-*O*-allyl-α-L-rhamnopyranoside[16]	2*a*,3*e*	+	480 (+0.04), 390 (+0.30), 348 (−0.14), 305 (+1.07), 250 (+0.60)
5 Phenyl 4,6-di-*O*-methyl-β-D-glucopyranoside[17]	2*e*,3*e*	+	454sh (+0.02), 394 (+0.07), 343 (−0.16), 298 (+0.15)
6 Phenyl 4-*O*-benzyl-β-D-fucopyranoside[18]	2*e*,3*e*	+	476 (+0.08), 380 (+0.31), 312 (+1.73), 276 (−1.02)
7 Benzyl 4,6-*O*-benzylidene-β-D-glucopyranoside[19]	2*e*,3*e*	+	459 (+0.02), 395 (+0.11), 340 (−0.19), 290 (+0.14)
8 Benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside[20]	2*e*,3*e*	+	388 (+0.28), 308 (+0.86), 275 (−0.08)
9 Phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[22]	2*e*,3*e*	+	468 (+0.02), 392 (+0.20), 342 (−0.32), 298 (+0.39), 279 (−0.32), 250 (+0.70)
10 Methyl 4,6-*O*-[(1*R*)-1-phenylethylidene]-α-D-glucopyranoside[23]	2*e*,3*e*	+	448sh (+0.06), 392 (+0.23), 351 (−0.12), 309 (+0.82), 276 (−0.04)
11 Methyl 4,6-*O*-[(1*S*)-1-phenylethylidene]-α-D-glucopyranoside[23]	2*e*,3*e*	+	460 (+0.04), 384 (+0.49), 310 (+1.40), 274 (−0.51)
12 Benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside[21]	2*e*,3*e*	+	385 (+0.26), 309 (+0.78), 275 (−0.15)

13 Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside[24]	2*a*,3*e*	−	460 (−0.02), 395 (−0.32), 353 (+0.39), 308 (−1.97), 273 (+0.10), 250 (−0.70)
14 Methyl 2-*O*-benzyl-α-L-rhamnopyranoside[14]	3*e*,4*e*	+	463 (+0.04), 386 (−0.12), 310 (+1.10)
15 Benzyl 2,6-di-*O*-methyl-β-D-galactopyranoside[25]	3*e*,4*a*	+	393 (+0.32), 340 (−0.30), 286 (+0.56)
16 Benzyl 2,6-di-*O*-benzyl-β-D-galactopyranoside[25]	3*e*,4*a*	+	446 (−0.03), 395 (+0.29), 343 (−0.67), 291 (+0.99)
17 Methyl 2-*O*-methyl-α-D-xylopyranoside[26]	3*e*,4*e*	−	523 (+0.06), 405 (+0.61), 367 (+0.30), 302 (−0.39), 250 (+0.70)
18 Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside[24]	4*e*,6		510sh (−0.03), 418 (−0.13), 284 (+0.07)
19 Phenyl 2-*O*-benzyl-3-*O*-methyl-β-D-glucopyranoside[27]	4*e*,6		540 (−0.01), 427 (−0.04), 347 (+0.01)
20 Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[28]	4*e*,6		520 (−0.04), 415 (−0.13), 280 (+0.14)
21 Phenyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[17]	4*e*,6		521 (−0.04), 416 (−0.20), 286 (+0.04), 250 (−0.20)
22 Phenyl 2,3-di-*O*-benzyl-β-D-galactopyranoside[29]	4*a*,6		400, weakly positive
23 2,5-Di-*O*-benzyl-1-*O*-methyl-D-xylitol[30]		−	536 (+0.02), 430sh (−0.11), 370 (−0.23), 310 (−1.01), 274 (+0.32)
24 1,2,4-Tri-*O*-benzyl-3-*O*-methyl-D-glucitol[31]		+	532sh (+0.02), 466 (+0.05), 408 (−0.07), 311 (+0.54), 275 (−0.25)
25 1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose[32]		+	459 (+0.02), 348 (−0.12), 303 (+0.26), 250 (+0.30)



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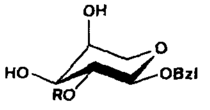
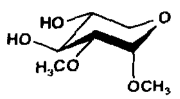


15: R = Me

16: R = Bzl



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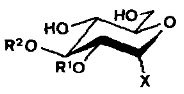
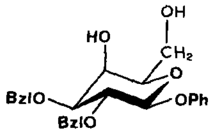


	X	R¹	R²
18	α-OMe	Me	Me
19	β-OPh	Bzl	Me
20	α-OMe	Bzl	Bzl
21	β-OPh	Bzl	Bzl



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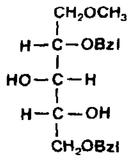

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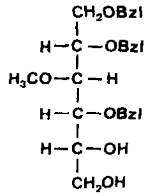

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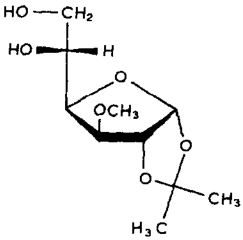

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be recognized in the spectrum, in agreement with the presence of an axial RO group at C-2. In both the equatorial–axial diols **15** and **16** the determining torsional angle is positive, and so are the signs of Cotton effects II and IV. C.d. band III, of negative sign, is also distinctly visible, again in agreement with the general findings. For **16** Cotton effect I is, on the contrary, negative; as in the case of complexes between **1** and chiral acids[5] a more complicated sector rule may govern this Cotton effect.

The c.d. of the complex with the diequatorial diol **17** (Fig. 3) of negative torsional angle HO–C–C–OH shows an anomaly similar to that of **14**, although again the sign of the c.d. band IV reflects correctly the absolute helicity of the diol moiety. Also Cotton effect III is present with the correct (positive) sign and of magnitude comparable to that of Cotton effect IV, although in the presence of an unusually strong positive Cotton effect II it is observed only as a shoulder.

In each of these glycols the absolute conformation of the *vic*-diol moiety can be determined unequivocally from the sign of Cotton effect IV; Cotton effect III gives additional information about the presence or absence of an axial RO group next to the diol structure.

B. 1,3-Glycols. All the available 1,3-glycols were 4,6-diols in the sugar series,

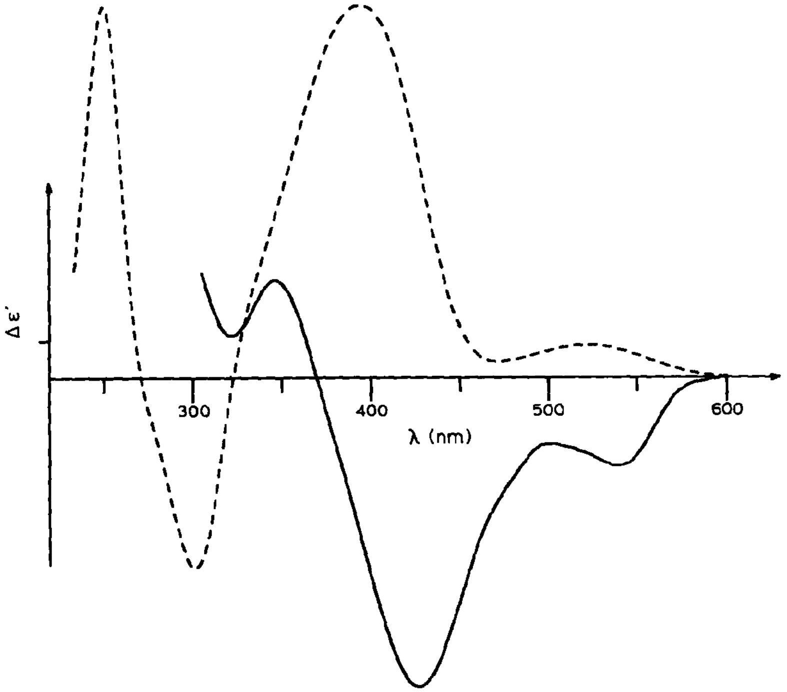

Fig. 3. C.d. of the complexes of **1** with **17** (------) and **19** (——) in DMSO. The mark on the Δε' scale is at 0.07 for **17** and 0.005 for **19**.

being thus of the *pri-sec* type. Irrespective of the configuration at C-4 the ligating unit HO–C-6–C-5–C-4–OH, including even the ring oxygen, is locally achiral. The measured Δε' values (Table I) are therefore relatively small, and the appearance of the c.d. spectra in the presence of **1** differs appreciably from that of the complexes with the *vic*-glycols. For the four related compounds **18** to **21** c.d. band I is always distinctly observable and negative, Cotton effect II around 420 nm is the strongest and is also negative, and the quite small and positive c.d. band IV appears around 284 nm. Except in the c.d. of **19** (Fig. 3) no band III was found, not even as shoulder. Only a very small amount of benzyl 3-*O*-benzyl-2-*O*-methyl-α-D-mannopyranoside was at hand, but above 350 nm the same Cotton effects could be detected for its complex with **1** as with **18–21**.

The OH at C-4 is axially arranged in **22**, and only a very weak positive Cotton effect II could be observed for its complex with **1**. The reversal of sign with respect to the corresponding band of **18–21** might be due to the opposite configurations and conformations at C-4, but with only a single example available we would not like to generalize this observation.

C. Some other related diols. Open chain *sec-sec vic*-diols can adopt two conformations having a torsional angle HO–C–C–OH of ±60°; in one the torsional angle C–C–C–C is 180°, in the other ±60°. It is the latter, which is preferred in complexes with **1** as has been found experimentally[6]. that seems reasonable when deducing steric interactions in the complex from molecular models. With the xylitol derivative **23** this preferred conformation leads to a negative torsional angle HO–C–C–OH, and in accord with this Cotton effects II and IV are negative, and III (observed only as a minimum) is positive (Table I). C.d. band I is negative for this complex.

Also *pri-sec* chiral *vic*-diols give c.d. effects in presence of **1**, and again it is Cotton effect IV from which the stereochemistry can be deduced[6]. The preferred conformation in the complex is the one for which the torsional angle HO–CH$_2$–C–C is about 180°. For both diols **24** and **25** the configuration at C-5 is *R*. The conformational requirements select a positive torsional angle HO–C–C–OH, and the positive Cotton effect IV is in agreement with this. C.d. bands II are for both complexes of negative sign. A c.d. band III cannot be identified in the spectrum of the complex from **25**; in case of **24** a positive band III might perhaps be present as indicated by a shoulder.

In conclusion, the circular dichroism of complexes between **1** and glycols in the pyranoside series is a very useful tool for the determination of stereochemistry with small amounts of substance.

EXPERIMENTAL

C.d. measurements and presentation of results. — The c.d. spectra were measured between 800 and 230 nm with a dichrograph Mark III (ISA-Jobin-Yvon), connected on-line to a PDP-8/e computer (computer resolution 1 data point per nm). To a stock solution of ~6.4 mg of **1** in 10 mL of DMSO (stable at least 3 days when stored at 4°) solid sugar was added so that the molar ratio of the stock complex to the glycol was ~1:0.8 to 1:2.5. As the true concentrations of the individual optically active complexes are not known we give here apparent $\Delta\varepsilon'$ values, calculated for the total ligand concentration. Severely sterically hindered glycols or those which for other reasons complex only weakly will show much smaller $\Delta\varepsilon'$ values than the better complex formers. Quantitative interpretation of these $\Delta\varepsilon'$ values is anyway not necessary for the purpose of determining absolute configuration, but semiquantitative correlations are possible for glycols of very similar structures. The values are summarized in Table I.

Comparison of c.d. curves of related compounds reveals that occasionally a maximum between two others of opposite sign appears only as a c.d. minimum. Interpretation of a c.d. curve in such cases is often assisted by concomitant inspection of its first derivative (*cf.* Fig. 4 of ref. 6). This was obtained with the help of the Golay–Savitzky algorithm (*cf.* e.g. ref. 13), which was also used for curve smoothing.

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