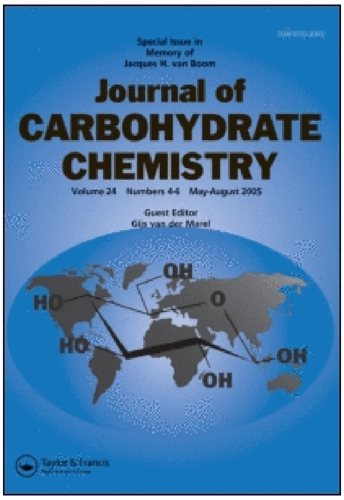


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Circular Dichroism of Transition Metal Complexes and Sugar Derivatives Having a Free 1,3-Diol System or "Isolated" Hydroxyl Group

Jadwiga Frelek[a]; Zbigniew Pakulski[a]; Aleksander Zamojski[a]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland

To cite this Article Frelek, Jadwiga , Pakulski, Zbigniew and Zamojski, Aleksander(1993) 'Circular Dichroism of Transition Metal Complexes and Sugar Derivatives Having a Free 1,3-Diol System or "Isolated" Hydroxyl Group', Journal of Carbohydrate Chemistry, 12: 4, 625 — 639

To link to this Article: DOI: 10.1080/07328309308019412

URL: http://dx.doi.org/10.1080/07328309308019412

J. CARBOHYDRATE CHEMISTRY, 12(4&5), 625-639 (1993)

CIRCULAR DICHROISM OF TRANSITION METAL COMPLEXES AND SUGAR DERIVATIVES HAVING A FREE 1,3-DIOL SYSTEM OR "ISOLATED" HYDROXYL GROUP[1]

Jadwiga Frelek, Zbigniew Pakulski, and Aleksander Zamojski*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44,
01-224 Warszawa, Poland

Received September 1, 1992 - Final Form April 8, 1993

ABSTRACT

Heptofuranose derivatives **1-6** having free 1,3-diol systems form *in situ* complexes with $Mo_2(OAc)_4$ whose CD spectra permit the assignment of absolute configuration at C-5 using a sector rule proposed by G. Snatzke.[2-6] The interpretation of CD spectra of analogous complexes formed from derivatives **7-12** was more complicated and did not lead to direct configurational conclusions. CD spectra of complexes formed from $Rh_2(CF_3COO)_4$ and sugar derivatives **13-21**, containing an "isolated" hydroxyl group, permit the assignment of absolute configuration. Conclusions were corroborated by the investigation of CD spectra of rhodium complexes with compounds **22-27**.

INTRODUCTION

In recent years circular dichroism (CD) has been successfully employed for determination of absolute configuration of UV-transparent molecules as complexes with some transition metals.[2-6] In this "in situ" method, elaborated by the late G. Snatzke, an optically active compound is added to a CD-inactive transition metal complex; exchange of ligands induces circular dichroism within the absorption bands of the metal. Coordination to the axial position of the cluster or exchange of ligands depends on the nature of the metal and of the potential ligands. For example, dimolybdenum tetraacetate gives strong Cotton effects with chiral bidendate ligands such as diols, amino alcohols, diamines or carboxylic acids via exchange of one or more of the acetate ligands.[2] On the other hand, complexes of rhodium tend to bind ligands at the axial position.[7] This property was exploited by Snatzke and Gerards[8] for the determination of configuration of monodendate ligands such as optically active secondary alcohols or monoolefins using an achiral dirhodium tetrakis(trifluoroacetate) complex. In this paper the use of molybdenum and rhodium complexes of sugar derivatives containing "1,3-diol" and "monoalcohol" systems is described.

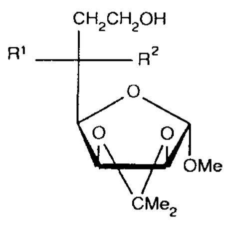
RESULTS AND DISCUSSION

It has been shown earlier[3,5,6] that 1,3-diols, in the presence of $Mo_2(OAc)_4$, form chiral complexes showing Cotton effects within absorption bands of molybdenum clusters. The exchange of an acetyl group for the HO-C-C-C-OH (1,3-diol) system occurs only when both hydroxyl groups attain a *syn*-parallel orientation and the molecule adds to the cluster as a bidendate ligand parallel to the Mo-Mo axis (Mo-O-C-C-C-O-Mo).[3,5] Cotton effects thus obtained are dependent on the chirality of the optically active ligand.

On the basis of results obtained for structurally rigid 1,3-diols of the cholestane series a simple sector rule was proposed correlating the sign of the Cotton effect (at *ca.* 400 nm) with stereochemistry of the ligand.[9] Up to now only a few sugar 1,3-diols have been investigated.[5,6] All of them were hexopyranoses having free hydroxyl groups at C-4 and C-6. We have investigated furanoses having free primary-secondary or

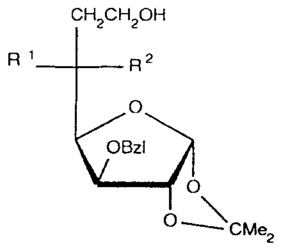
Table 1. Δε' - values for the *in situ* complexes of 1,3-diols with $Mo_2(OAc)_4$ in DMSO.

Compound No.	λ_{max} [nm]	Δε'	Other bands λ [nm] (Δε')
1	431	-0.067	
2	410	+0.059	
3	433	-0.074	
4	427	+0.095	
5	418	-0.109	
6	415	+0.067	
7	no Cotton effect		
8	406	-0.043	
9	381	-0.121	
10	no Cotton effect		
11	411	+0.836	547 (+0.073) 338 (+0.757) 299 (-0.463) 268 (+1.588)
12	394	-0.234	332 (+0.219) 300 (positive minimum) 271 (+0.415)



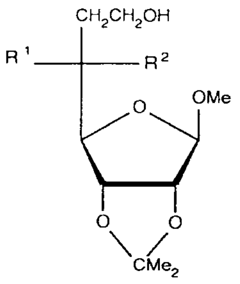
1 $R^1 = OH$, $R^2 = H$

2 $R^1 = H$, $R^2 = OH$



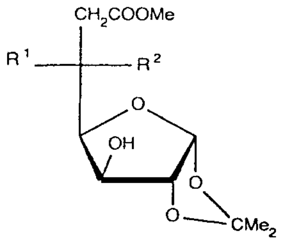
3 $R^1 = OH$, $R^2 = H$

4 $R^1 = H$, $R^2 = OH$



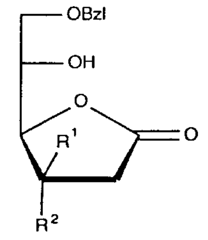
5 $R^1 = OH$, $R^2 = H$

6 $R^1 = H$, $R^2 = OH$



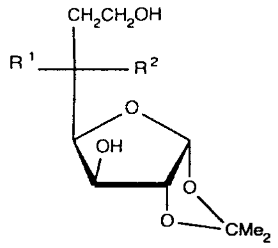
7 $R^1 = OH$, $R^2 = H$

8 $R^1 = H$, $R^2 = OH$



9 $R^1 = OH$, $R^2 = H$

10 $R^1 = H$, $R^2 = OH$



11 $R^1 = OH$, $R^2 = H$

12 $R^1 = H$, $R^2 = OH$

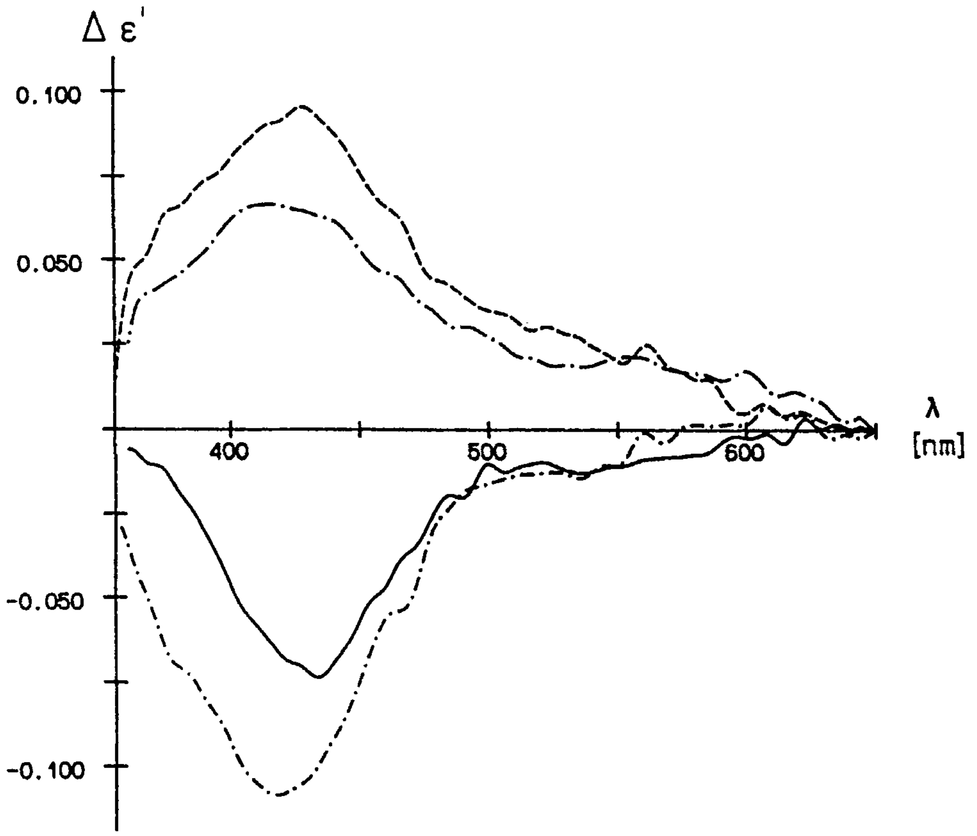


Figure 1. CD spectra of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-heptofuranose (3) ———————, 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranose (4)-----, methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-*allo*-heptofuranoside (5) -.-.-.-.-.-.-., and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*talo*-heptofuranoside (6) __.__.__.__. with $\mathrm{Mo_2(OAc)_4}$.

secondary-secondary diol systems. We have also examined two sugar derivatives containing two 1,3-diols capable of forming different complexes. The results obtained are collected in **Table 1.**

Primary-secondary diols (**1-6**).

In the CD spectra of compounds **1-6** prepared *in situ* with $\mathrm{Mo_2(OAc)_4}$ only one Cotton effect within 433-415 nm can be observed. Furanoses of **D** configuration (**1**, **3**, and **5**) display a negative Cotton effect and those of **L** configuration (**2**, **4**, and **6**) enantiomorphic

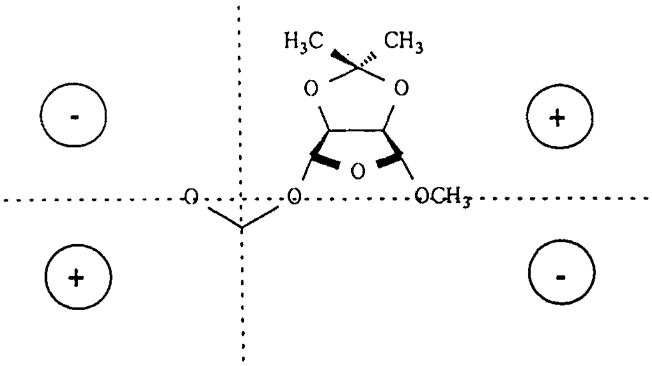


Figure 2. Sector rule for methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*talo*-heptofuranoside (**6**). Carbon atoms C-5 and C-7 are located behind the oxygen atoms.

curves (**Figure 1**). Signs of Cotton effects for the **D** and **L** series are in accord with predictions based on the sector rule proposed for cholestane 1,3-diols.[9] According to this rule the sign of the Cotton effect should be the same as the sign of the sector where the majority of the molecule is located (**Figure 2**).

The results obtained demonstrated the validity of the CD method employing molybdenum complexes and confirmed the assignment of absolute configuration of the secondary alcohol center (C-5) in **1**-**6**.

Secondary-secondary diols (**7**-**10**).

Derivatives **8** and **9** give negative Cotton effects and for **9** this effect is *ca.* three times larger than for **8**. This observation can be explained by the sector rule (**Figure 2**). In **9** the majority of the molecule is in the negative sector whereas in **8** both sectors are occupied. The Cotton effect for **7** should be positive; however, none was observed. Also, for **10**, no Cotton effect could be measured. In this case, a complex with $Mo_2(OAc)_4$ probably could not be formed because both hydroxyl groups (at C-3 and C-5) were too distant.

The lack of complexation can be also explained by deviation from the *syn*-parallel orientation of hydroxyl groups caused by the presence of the furanose ring or by the proximity of large substituents to the metal cluster. In such a case, interaction between large substituents and the acetate ligands present in the cluster may prevent the exchange of ligands and formation of optically active complexes. On the other hand, it is also possible that the substituents present in the chiral ligand may provide a compensating contribution to the CD spectrum. The limited number of compounds available in this study does not allow us to draw definite conclusions regarding the structure of the diol and the CD spectrum. It may be added that for primary-secondary 1,3-diols, having one hydroxyl group within a six-membered ring, difficulties arise in the interpretation of data. Thus, (2*R*,3*R*)-2-hydroxymethyltetrahydropyran-3-ol and its (2*R*,3*S*) stereoisomer both show negative Cotton effects at 415 and 413 nm, respectively.[6] Certainly, further CD investigation of molybdenum complexes of cyclic 1,3-diols should be continued until a rule enabling assignment of absolute configuration to such alcohols is found.

Primary-secondary-secondary triols (**11** and **12**)

6-Deoxy-1,2-*O*-isopropylidene-α-D-*gluco*- and β-L-*ido*-heptofuranoses (**11** and **12**) contain two 1,3-diol systems each. Their CD spectra contain five Cotton effects at *ca.* 550, 400, 340, 300 and 270 nm. The sign of the Cotton effect at 400 nm is positive for **11** and negative for **12**. However, for diols **1**, **3** and **5** having the same C-5 - C-7 structural fragment as **11**, the Cotton effect at 400 nm is negative. Similarly, the Cotton effect at the same wavelenght for **2**, **4** and **6** is positive, in contrast to the CD spectrum of **12**. A possible explanation for this discrepancy is that **11** and **12** form complexes with $Mo_2(OAc)_4$ with both 1,3-diol systems and, in the CD spectra contributions from different complexes are present. Both 1,3-diol systems, capable of forming complexes, possess one hydroxyl group (at C-5) in common, therefore the CD curve obtained cannot be a simple summation of curves stemming from complexes obtained from C-3, C-5 and C-5, C-7 diols measured separately. Addition of CD curves used earlier[10] for non-interfering 1,2-diols cannot be applied here. It appears that the CD spectra of **11** and **12**, displaying enantiomorphism for **D** and **L** configurations, should be treated as specific for the triol system in question (**Figure 3**).

Secondary alcohols (**13-21**).

Rhodium tetracarboxylates, in contrast to molybdenum tetracarboxylates, are capable of binding ligands at the axial position.[7] This is especially pronounced in the case of dirhodium tetrakis(trifluoroacetate) in which the presence of strongly electron-withdrawing

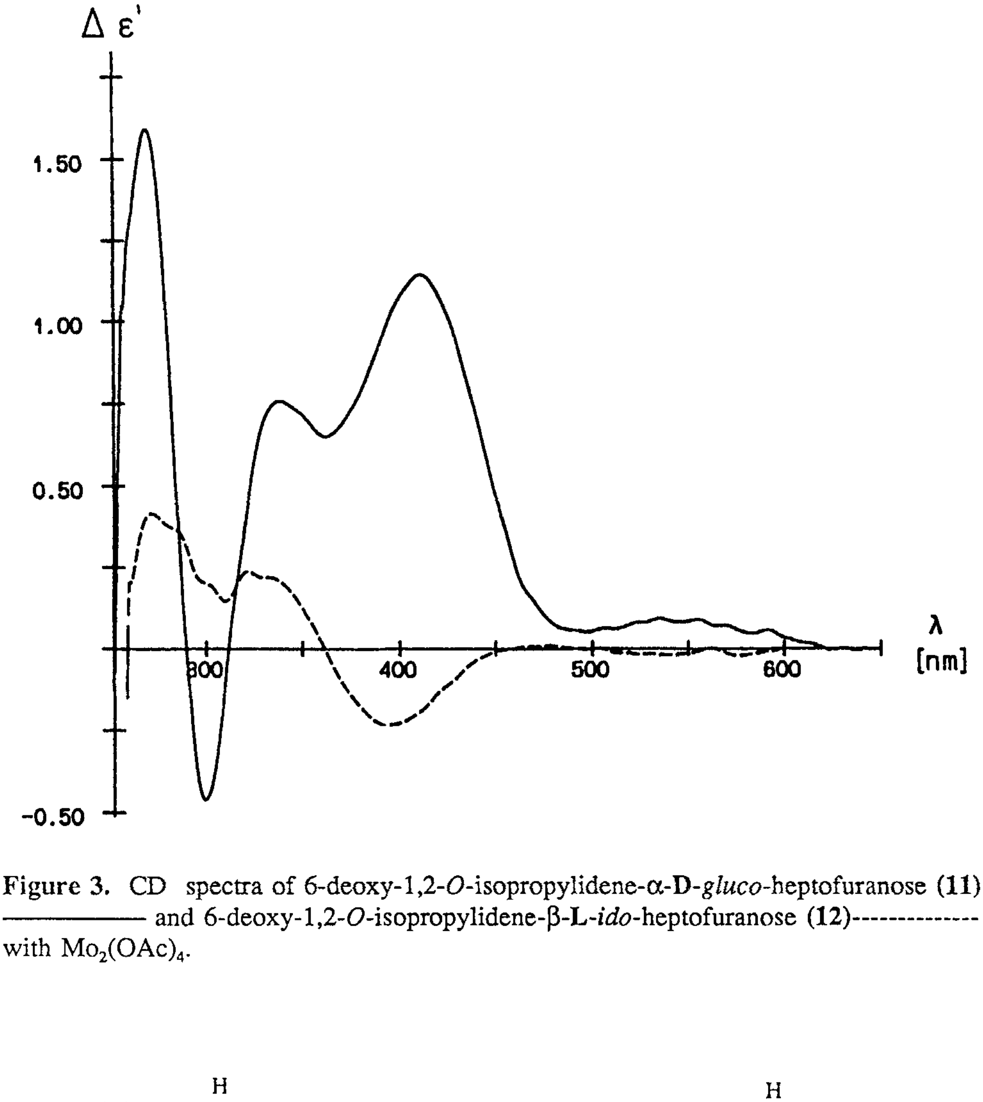
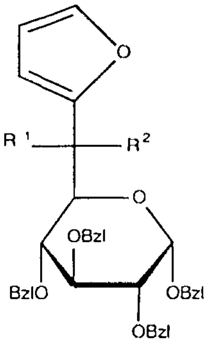


Figure 3. CD spectra of 6-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-heptofuranose (11) ———————— and 6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranose (12)-------------- with $Mo_2(OAc)_4$.

Figure 4. An empirical rule for the E band (350 nm) for secondary alcohols in the presence of $Rh_2(CF_3COO)_4$.[8] Definition of configuration bR and bS. M and L - medium and large substituents.

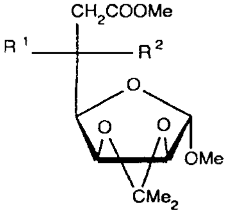
Table 2. Δε' - values for the *in situ* complexes of "monoalcohols" **13-21** with $Rh_2(CF_3COO)_4$ in hexane.

Comp. No.		Band E λ [nm] (Δε')	Band D λ [nm] (Δε')	Band C λ [nm] (Δε')	Band B λ [nm] (Δε')	Band A λ [nm] (Δε')
13	286 (+0.156)	352 (+0.042)	399 (+0.013)	453 (-0.015)	507 (+0.006)	573 (-0.013)
14	291 (-0.320)	347 (-0.078)		442 (-0.022)	521 (+0.004)	
15	305 (-0.259)	355 (+0.162)	407 (+0.105)		540 (+0.015)	619 (-0.015)
16	282 (+0.099)	346 (-0.063)	413 (-0.033)	446 (-0.024)	511 (+0.014)	573 (-0.016)
17	304 (-0.858)	358 negative maximum		441 (-0.031)	512 (+0.015)	582 (-0.005)
18		346 (-0.031)	418 (-0.037)		516 (+0.012)	570 (-0.017)
19	298 (-0.048)	350 (+0.003)	385 (-0.020)	447 (-0.019)		
20	no Cotton effects					
21	274 (-0.057)	347 (+0.100)	403 (+0.034)		497 (-0.024)	602 (+0.004)



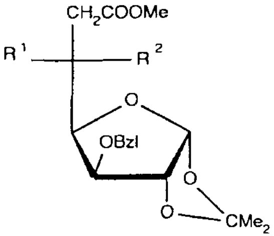
13 R^1 = OH, R^2 = H

14 R^1 = H, R^2 = OH



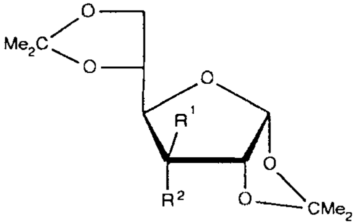
15 R^1 = OH, R^2 = H

16 R^1 = H, R^2 = OH



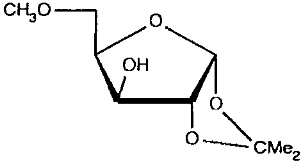
17 R^1 = OH, R^2 = H

18 R^1 = H, R^2 = OH

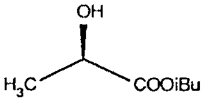


19 R^1 = H, R^2 = OH

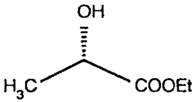
20 R^1 = OH, R^2 = H



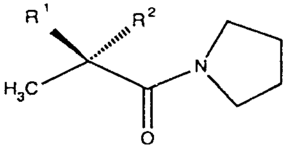
21



22

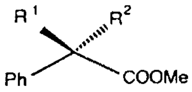


23



24 R^1 = OH, R^2 = H

25 R^1 = H, R^2 = OH



26 R^1 = OH, R^2 = H

27 R^1 = H, R^2 = OH

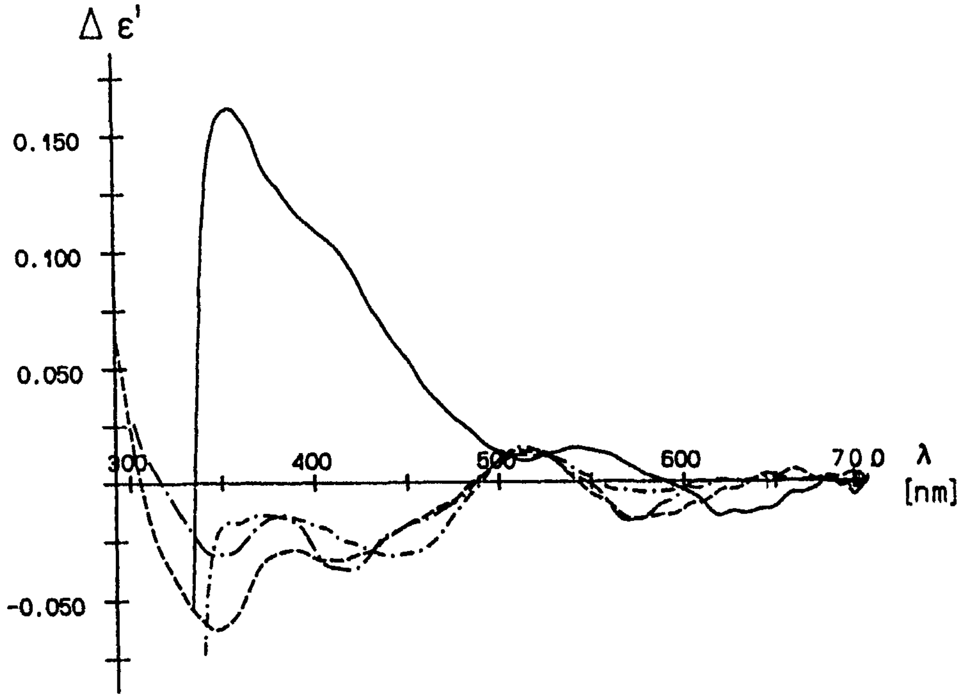


Figure 5. CD spectra of methyl (methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-*manno*-heptofuranosid)uronate (**15**) ————————, methyl (methyl 6-deoxy-2,3-*O*-isopropylidene-β-L-*gulo*-heptofuranosid)uronate (**16**) ----------------, methyl 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-heptofuranos)uronate (**17**) -.-.-.-.-.-, and methyl (methyl 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranos)uronate (**18**) __.__.__.__.__ with $Rh_2(CF_3COO)_4$.

CF_3 groups leads to an increased tendency to accept nucleophiles at the axial position, thus promoting easier formation of adducts as compared with, *e.g.*, $Rh_2(OAc)_4$.

It has been shown earlier,[8] that chiral secondary alcohols can also form chiral complexes with $Rh_2(CF_3COO)_4$. Their CD spectra contain up to five Cotton effects within 700 - 300 nm. Band A occurs at approx. 600 nm, band B at approx. 500 nm, and bands C, D, and E at approx. 450, 400, and 350 nm, respectively. The sign of band E is correlated with the geometry of the molecule. Positive CD at 350 nm is associated with the "bS" configuration and, conversely, negative CD at this wavelenght - with the "bR" configuration. It must be mentioned that substituents at the secondary alcohol center are differentiated according to their bulkiness (**Figure 4**).[8]

Table 3. Δε' - values for the *in situ* complexes of "monoalcohols" **22-27** with $Rh_2(CF_3COO)_4$ in hexane.

Comp. No.		Band E λ [nm] (Δε')	Band D λ [nm] (Δε')	Band C λ [nm] (Δε')	Band B λ [nm] (Δε')	Band A λ [nm] (Δε')
22	267 (-0.150)	348 (+0.283)	406 (+0.142)		512 (-0.024)	578 (+0.020)
23	290 (+0.155)	349 (-0.029)	382 (+0.011)	418 (-0.015)	545 (+0.017)	
24	269 (-0.186)	354 (+0.085)	401 (+0.056)		548 (+0.018)	
25	271 (+0.124)	353 (-0.022)		424 (-0.019)	524 (-0.008)	
26		348 (+0.088)			491 (-0.014)	
27		352 (-0.016)	384 (+0.003)	418 (-0.010)	487 (-0.008)	

In the CD spectra of complexes of compounds **13-21** with $Rh_2(CF_3COO)_4$ five bands were observed in the majority of cases. Band E appeared usually as a pronounced maximum (or minimum) (**Table 2**). Only in case of **17** did this band appear as a negative maximum at 358 nm. This was certainly caused by the strong CD band at 304 nm which prevented the development of the normal band at *ca.* 350 nm (**Figure 5**). 1,2:5,6-Di-*O*-isopropylidene-α-**D**-glucofuranose (**20**) does not exhibit any Cotton effect with $Rh_2(CF_3COO)_4$. We assume that this lack is due to the presence of the freely rotating large substituent (dimethyldioxolane group at C4) *cis* to the C3-OH group. Steric hindrance makes the formation of a chiral complex impossible. In the *allo* stereoisomer

(**19**) the same substituent is *trans* to the C3-OH group and does not prevent the formation of a rhodium complex.

Direct application of the above mentioned empirical rule to sugar derivatives **13-21** is not straightforward. Especially difficult is the assignment of substituents to the M or L type. It must be added that the rule was established for terpene and steroidal alcohols which do not contain other functional groups and the differentiation of substituents was not difficult. We found that for compounds of **D** configuration the sign of the CD band at approx. 350 nm is always positive and, conversely, is negative for the **L** series.

In order to confirm this conclusion we recorded CD spectra of model compounds **22-27** of known configuration (**Table 3**). Here again, band E had positive sign for compounds of **D** configuration, and negative for compounds of **L** configuration. Thus, a confirmation of results drawn for sugar derivatives was obtained. This provides an extension of the *in situ* CD method for determination of abs configuration of monoalcohols. We expect that further investigations in this field should provide possibilities for establishment of a more general rule for different classes of alcohols.

EXPERIMENTAL

General procedures. CD spectra were measured between 800 and 250 nm at room temperature with a Jobin-Yvon ISA dichrograph Mark III, using for $Mo_2(OAc)_4$ complexes solutions in DMSO, and for $Rh_2(CF_3COO)_4$ complexes solutions in hexane. Data were collected on-line with a PDS-8/e computer (1 or 2 data points per nm), and curve smoothing making use of the Golay-Savitzky algorithm. Depending on the S/N - ratio the λ-scan speed was 0.2 or 0.5 nm/s.

To a stock solution of $Mo_2(OAc)_4$ in DMSO, solid diol was added so that the molar ratio of the stock complex to the diol was about 1:0.5 to 1:0.7. As the true concentration of the individual optically active complexes are not known, apparent $\Delta\varepsilon'$ values are given, calculated for the total ligand concentration.

To *ca.* 6-8 mg $Rh_2(CF_3COO)_4$ and 3-6 equivalents (4-10 mg) of optically active monoalcohols 10 mL spectrograde hexane was added. If necessary, the solution was shaken vigorously and warmed with a stream of hot air for several minutes. The $\Delta\varepsilon'$ values were calculated on the basis of achiral stock complex.

Compounds **1-8**, **11**, **12**, **15-18** were obtained from suitably blocked pentodialdo-1,4-furanose by two-carbon-atom elongation.[11] Compounds **9** and **10** were obtained from 4-*O*-benzyl-2,3-*O*-isopropylidene-L-threose by similar methods.[11] Compounds **13** and **14**[12], **24** and **25**[13] were prepared according to literature methods.

ACKNOWLEDGMENTS

Authors thank the Polish Science Foundation (Grant PONT '92) and Deutsche Forschungsgemeinschaft for their valuable financial support.

REFERENCES

1. Presented at *XVIth International Carbohydrate Symposium*, 5-10 July, 1992, Paris.
2. G. Snatzke, U. Wagner and H.P. Wolf, *Tetrahedron*, **37**, 349 (1981).
3. J. Frelek, A. Perkowska, G. Snatzke, M. Tima, U. Wagner and H.P. Wolf, *Spectros. Int. J.*, **2**, 274 (1983).
4. J. Frelek and G. Snatzke, *Fresenius Z. Anal. Chem.*, **316**, 261 (1983).
5. A. Liptak, J. Frelek, G. Snatzke and J. Vlahov, *Carbohydr. Res.*, **164**, 149 (1987).
6. G. Snatzke, Z. Raza, I. Habus and V. Sunjic, *Carbohydr. Res.*, **182**, 179 (1988).
7. F.A. Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York (1982).
8. M. Gerards and G. Snatzke, *Tetrahedron: Asymm.*, **1**, 221 (1990).
9. J. Frelek, G. Snatzke and W.J. Szczepek, submitted for publication.

10. J. Frelek, Z. Majer, A. Perkowska, G. Snatzke, J. Vlahov and U. Wagner, *Pure Appl. Chem.*, **57**, 441 (1985).

11. Z. Pakulski, Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Ph. D. Thesis, in preparation.

12. J. Gawronski, D. Radocki, J. Jurczak, Z. Pakulski, J. Raczko, J. Ramza and A. Zamojski, *J. Org. Chem.*, **55**, 1118 (1990).

13. Y. Ito, Y. Kobayashi, T. Kawabata, M. Takase and S. Terashima, *Tetrahedron*, **45**, 5767 (1989).