Carbohydrate Research, 206 (1990) 41–53
Elsevier Science Publishers B.V., Amsterdam

Application of the exciton chirality method to acyclic systems: circular dichroism of acyclic sugar poly-*p*-chlorobenzoates

Jacek Gawronski* and Krystyna Gawronska
Faculty of Chemistry, Adam Mickiewicz University, 60780 Poznan (Poland)

(Received September 1st, 1989; accepted for publication, February 1st, 1990)

ABSTRACT

Exciton Cotton effects for the transition at 250–230 nm of polyol *p*-chlorobenzoates with different configurations and conformations have been determined by adding contributions due to pairs of secondary *p*-chlorobenzoates (core) to the contributions due to terminal (primary) *p*-chlorobenzoate groups. The Cotton effects of a series of acyclic sugar poly-*p*-chlorobenzoates have been compared.

INTRODUCTION

The exciton chirality method[1] has been applied to study the absolute configuration of cyclic sugar di-[2] and poly-(*p*-substituted) benzoates[3]. We have analyzed[4] exciton Cotton effects (e.C.e.) displayed by acyclic diol and triol *p*-chlorobenzoates in order to test their usefulness for establishing the absolute configuration or conformation. Because of the conformational equilibria involved, it was necessary to introduce a set of contributions characteristic of the Cotton effects of 1,2-, 1,3-, and 1,4-acyclic di-*p*-chlorobenzoate conformers (Fig. 1)[4]. The contributions to the e.C.e. at 250–230 nm, given in Fig. 1, were determined, where applicable, from rigid cyclic model compounds[4].

We now report an extension of the analysis of the e.C.e. to *p*-chlorobenzoate derivatives of polyols that have different configurations and conformations.

RESULTS AND DISCUSSION

For a given conformer of a polyol *p*-chlorobenzoate, the net Cotton effect of the transition at 250–230 nm is the sum of the e.C.e. of all participating pairs of *p*-chlorobenzoate chromophores. For a tetra-*p*-chlorobenzoate system, there are six contributing e.C.e. with amplitudes A:

$$A_{1,2,3,4} = A_{1,2} + A_{1,3} + A_{1,4} + A_{2,3} + A_{2,4} + A_{3,4}.$$

The values of the e.C.e. of the *p*-chlorobenzoate pairs in Fig. 1 are used as the contributions of the core *p*-chlorobenzoates, *i.e.*, *p*-chlorobenzoates of the secondary

* Author for correspondence.

0008-6215/90/$ 03.50

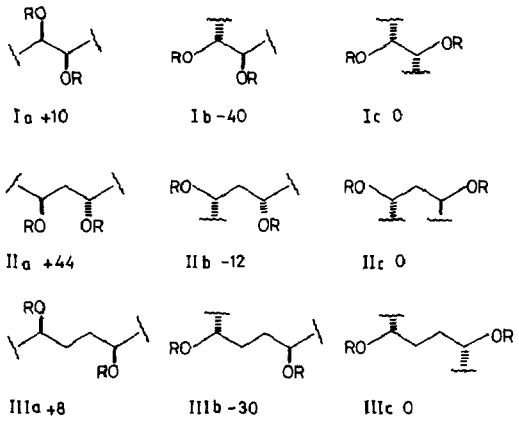
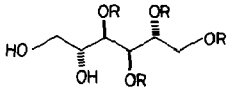


Fig. 1. Contributions of the core di-*p*-chlorobenzoate groups (R) in various conformations.

alcohols. For example, for D-mannitol 1,2,3,4-tetra-*p*-chlorobenzoate (**1**), A = −14, the contributions of the core *p*-chlorobenzoates include the pairs 2,3 (A = 0), 3,4 (A = +10), and 2,4 (A = −44). In D-mannitol derivatives, the conformation of the carbon chain is taken as planar and no other conformers are taken into account. In order to determine the remaining contributions of the 1,2-, 1,3-, and 1,4-*p*-chlorobenzoate pairs in **1**, the distribution of the rotamers of the *p*-chlorobenzoate chromophore at C-1 requires consideration.



1

Of the three rotamers of the terminal –OR group in the extended conformation of the D-*erythro* C_3 chain, that (T) in which the C-1–O and C-2–C-3 bonds are *trans* preponderates. Based on n.m.r. studies of alditols and their derivatives[5], a 50% population is attributed to T, and 40% to the *gauche* (G^+) rotamer. The remaining rotamer (G^-) is disfavoured (10% population) owing to the 1,3-syn OR/OR interaction. In order to calculate the contributions of rotamers to the e.C.e. due to the terminal –OR group, $\Delta\varepsilon$ for **Ia, Ib, IIa,** and **IIb** (Fig. 1) are taken (neglecting for the sake of simplicity the contributions of **IIIa** and **IIIb**) and their magnitudes are adjusted to account for changes in conformation of the terminal *p*-chlorobenzoate chromophore. Thus, the $\Delta\varepsilon$ values for **Ib** and **IIa** are decreased when terminal *p*-chlorobenzoate is present (increased distance between the *p*-chlorobenzoate chromophores) to give **Id** and **IIe**, respectively (Fig. 2). Likewise, the $\Delta\varepsilon$ values for **Ia** and **IIb** are increased due to the presence of terminal *p*-chlorobenzoate (decreased distance between the *p*-chlorobenzoate chromophores), to give **Ie** and **IId**, respectively.

Figure 3 gives the approximate contributions of the primary *p*-chlorobenzoate

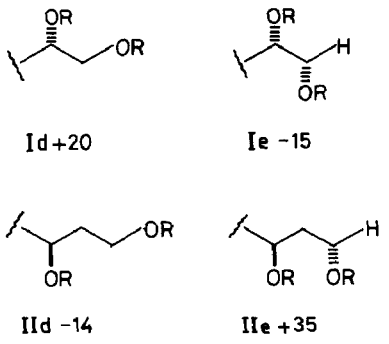


Fig. 2. Contributions of the terminal di-*p*-chlorobenzoate groups (R) in various conformations.

rotamers in the D-*erythro* configuration and extended chain conformation (+11). Thus, the calculated amplitude of the e.C.e. for **1** is 0 + 10 − 44 + 11 = − 23.

Other data in Fig. 3 are for the C-2–C-3 skewed conformation with free or restricted rotation of the terminal –OR group, for both D-*erythro* and D-*threo* configurations. From these data, it is apparent that the contribution of the terminal –OR group to the e.C.e. is >0 in *p*-chlorobenzoates of D-polyols, being higher in the *erythro* series compared to the *threo* series[6].

It is now possible to calculate the e.C.e. of *p*-chlorobenzoylated polyols with various configurations, by adding core (Fig. 1) and terminal contributions (Fig. 3).

Different conformations of the polyols need to be considered when the extended chain conformation is destabilized owing to the 1,3-syn interactions[7]. The conformations of polyols have been studied by ^{1}H-n.m.r.[5,8,9] and X-ray diffraction[10–12] techniques. The calculated amplitudes of the e.C.e. of *p*-chlorobenzoylated D-polyols* with various configurations and conformations are shown in Table I.

The sign of the e.C.e. in Table I depends on the configuration or conformation. For numerous compounds, the conformers show e.C.e. of opposite sign, and for the *ido* conformers **XVIIb** and **XVIIc** the amplitudes differ by ~200. This feature could be helpful in distinguishing the conformers of *p*-chlorobenzoylated polyols by their c.d. spectra.

In general, there seems to be reasonably good correlation between the preferred conformation of polyols, deduced from ^{1}H-n.m.r. data, and the conformation of their *p*-chlorobenzoates as indicated by the c.d. data. Thus, for the D-*erythro* triol derivative **2**, the measured amplitude (+35.1) of the e.C.e. indicates the presence of both the extended T conformer (+11) and the G^+ conformer (+75) with the possible participation of the G^- conformer (−27). The presence of the three conformers in solution has been postulated[8] for erythritol tetra-acetate from n.m.r. studies. Similar reasoning applies to the D-threitol derivative **3** which can exist in the conformations T, G^+, and G^-. The D-*arabino* compounds **4** and **5** exhibit negative e.C.e., as has been calculated for the strain-free extended-chain conformer TT. This situation also applies to the ho-

* The data for some compounds were obtained from the L forms (see Experimental).

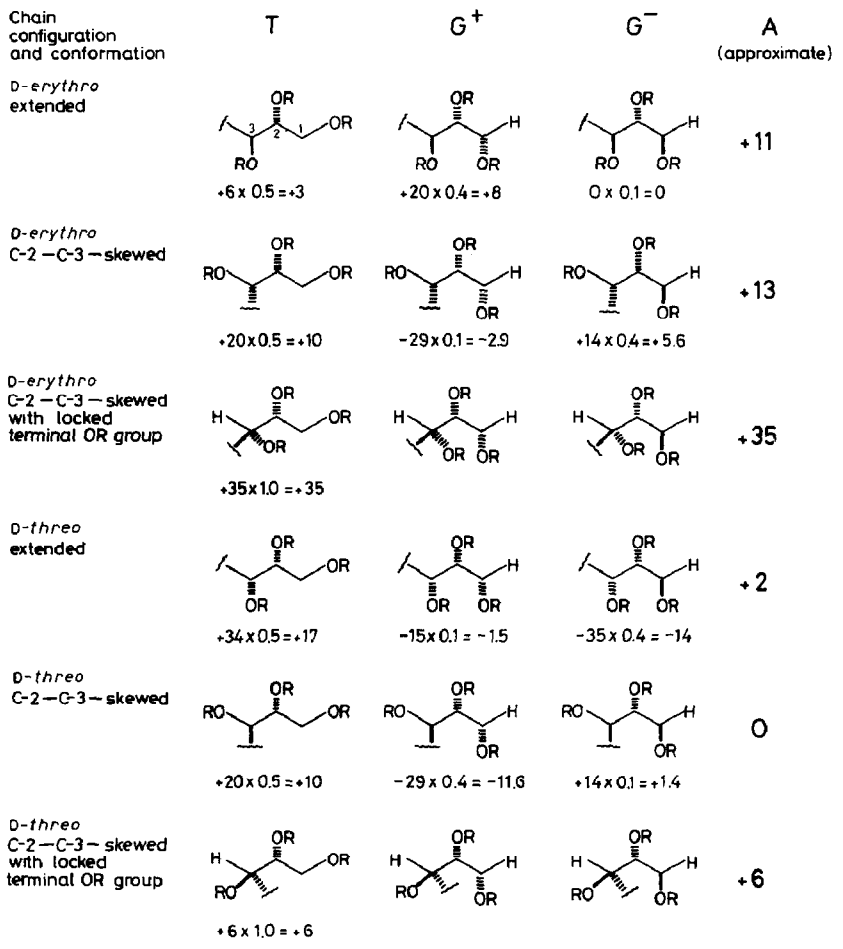


Fig. 3. Contributions of the RO–C-1–C-2–C-3 rotamers to the exciton Cotton effect of the C-1 *p*-chlorobenzoate (R) chromophore.

mochiral D-*lyxo*-compound **6** that has an extended-chain TT conformation. For the D-*ribo* (**7**) and D-*xylo* (**8**) compounds, the extended-chain conformers TT show 1,3-syn OR/OR interactions. From the amplitudes of the e.C.e., it follows that strain-free conformers TG^+ and G^-T/TG^+ are preferred for **7** and **8**, respectively. A similar conclusion was reached for the acetylated analogs of **7** and **8** from ^{1}H-n.m.r. studies[9]. For **8**, the ratio of the G^-T and TG^+ conformers can be estimated as 2:1 from the calculated amplitudes, +64 and −62, respectively.

As expected, the D-*manno* compounds **9–12** showed strong negative e.C.e., typical for the strain-free extended-chain conformer TTT. The amplitudes of the e.C.e. of **9** (−42.8) and **10** (−35.6) seem to be less negative than those calculated (−70 and −59, respectively). Although the origin of the difference is not clear, the participation of the conformer $G^+G^+G^+$ in the equilibrium cannot be ruled out. The presence of this

conformer has been postulated from the ^{1}H-n.m.r. study[8] of D-mannitol hexa-acetate.

The weak positive e.C.e. of the D-*galacto* compounds **13** and **14** is consistent with the amplitude calculated for the extended-chain conformer TTT.

For the D-*gluco* compounds **15** and **16**, the extended-chain conformer TTT is disfavoured owing to the syn-1,3 OR/OR interaction. For **15**, the conformer TG^+G^+ appears to be favoured (calculated amplitude +13), although ^{1}H-n.m.r. studies[9] indicated the preference of conformer G^-TT for the acetylated analogue. The conformer G^-TT (calculated amplitude −1) is clearly preferred for **16**, in agreement with the ^{1}H-n.m.r. data[8] for D-glucitol hexa-acetate, although the participation of the TTT conformer cannot be ruled out. Similar conclusions can be reached for the D-*gulo* conformations TTT and TTG^+, which are enantiomeric with D-*gluco* derivatives when X = Y.

The D-*talo* and D-*altro* compounds have identical structures when X = Y. As it is evident from the data in Table I, the difference between e.C.e. of extended-chain and *gauche* conformers (TTT and G^+TT in the D-*talo* series, TTT and TTG^+ in the D-*altro* series) is relatively small and hence of less significance for conformational analysis. Chiral D-*allo* compounds are possible only when X ≠ Y. However, even where Y = CH_2OR, the differences between the calculated e.C.e. of the extended-chain TTT and *gauche* TG^-T/TG^+T and G^-TG^+ conformers of the D-*allo* compounds are not large enough to allow the conformers to be distinguished.

The extended-chain conformation TTT of the D-*ido* compound is destabilized by the two syn-1,3 OR/OR interactions. Therefore, both of the unstrained conformers TG^-T and G^+TG^+ contribute to the equilibrium, each of which gives a strong e.C.e. but of opposite sign. The observed e.C.e. is either positive (as in **17**) or negative (as in **18**), depending on the conformational equilibrium. For **17** and **18**, the ratio of TG^-T to G^+TG^+ can be estimated as 3:2 and 1:1, respectively.

It appears that the amplitudes of the e.C.e. of *p*-chlorobenzoylated polyols show diversity that is large enough to justify their use in stereochemical analysis of acyclic systems. Furthermore, the present study shows that, even within the simplifications involved in the analysis of the e.C.e., reliable conclusions with regard to the polyol conformation or configuration can be drawn.

EXPERIMENTAL

General. — I.r. spectra were recorded with a Perkin–Elmer 180 instrument (KBr or neat), and u.v. and c.d. spectra were recorded with a Shimadzu UV 160 spectrophotometer and a Jobin–Yvon III dichrograph, respectively, for solutions in 1,4-dioxane. The ^{1}H-n.m.r. spectra were recorded with a JEOL FX 90Q spectrometer for solutions in $CDCl_3$, with Me_4Si as internal standard. Elemental analyses were performed on a Perkin–Elmer 240 CHN analyzer.

p-Chlorobenzoylation. — A 0.5M solution of the polyol in dry pyridine was stirred overnight at room temperature with 1.5 equiv. of *p*-chlorobenzoyl chloride, then heated with acetone–water at 70° for 1–3 h. The products were extracted with ether–dichloro-

TABLE I

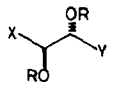
Calculated and measured amplitudes (A) of the exciton Cotton effects of *p*-chlorobenzoylated D-polyols in various conformations (see Fig. 4)

Conformer	*Calculated A*			*Compound*			*Found*
	X, Y ≠ CH_2OR	*X ≠ CH_2OR Y = CH_2OR*	*X, Y = CH_2OR*		*X*	*Y*	*A*
D-*erythro*							
T	0	+11	0	**2**	Et	CH_2OR	+35.1
G^+	+40	+75	+62				
G^-	−40	−27	−62				
D-*threo*							
T	+10	+12	+14	**3**	CH_2OR	CH_2OR	+3.8
G^+	−40	−40	−40				
G^-	0	+6	+12				
D-*arabino*							
TT	−34	−23	−21	**4**	$CH(SEt)_2$	CH_2OR	−14.0
				5	CH_2OR	CH_2OR	− 6.5
D-*lyxo*							
TT	−34	−32	−21	**6**	$CH(SEt)_2$	CH_2OR	−33.2
D-*ribo*							
TT	0	+11	0	**7**	$CH(SEt)_2$	CH_2OR	+53
G^-T	−28	−17	−52				
TG^+	+28	+63	+52				
D-*xylo*							
TT	0	+2	0	**8**	$CH(SEt)_2$	CH_2OR	+19.6
G^-T	+62	+64	+64				
TG^+	−62	−62	−64				
D-*manno*							
TTT	−70	−59	−48	**9**	Et	Et	−42.8

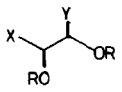
$G^+G^+G^+$	+40	+75	+110	**10**	Me	CH_2OR	−35.6
				11	$CH(SEt)_2$	CH_2OR	−56.0
				12	CH_2OR	CH_2OR	−42.3
D-*galacto*							
TTT	0	+2	+0	**13**	Me	CH_2OR	+5.0
				14	$CH(SEt)_2$	CH_2OR	+8.4
D-*gluco*							
TTT	−44	−33	−35	**15**	$CH(SEt)_2$	CH_2OR	+13.2
G^-TT	−12	−1	−1	**16**	CH_2OR	CH_2OR	−6.7
TG^+G^+	−22	+13	+11				
D-*gulo*							
TTT	+44	+46	+35				
TTG^+	+12	+12	+1				
D-*talo*							
TTT	−26	−24	−13				
TG^+G^+	−36	−34	+1				
D-*altro*							
TTT	−26	−15	−13				
TTG^+	−36	−1	+1				
D-*allo*							
TTT	0	+11	0				
$TG^-T + TG^+T$	0	(+?)[a]	0				
G^-TG^+	0	+35	0				
D-*ido*							
TTT	+18	+20	+22	**17**	Et	Et	+13.2
TG^-T	+84	+86	+88	**18**	CH_2OR	CH_2OR	−7.1
G^+TG^+	−114	−114	−114				

[a]Amplitude depends on the ratio of conformers TG^-T and TG^+T.

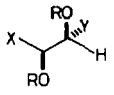
D-*erythro*



T

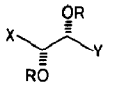


G^+

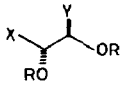


G^-

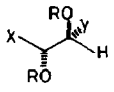
D-*threo*



T

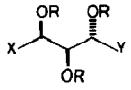


G^+



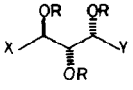
G^-

D-*arabino*



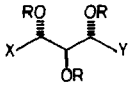
TT

D-*lyxo*

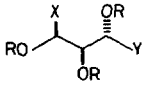


TT

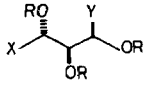
D-*ribo*



TT

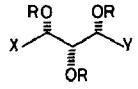


G^-T

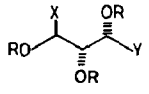


TG^+

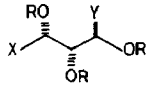
D-*xylo*



TT

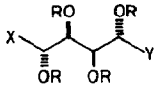


G^-T

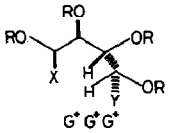


TG^+

D-*manno*

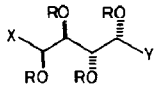


TTT



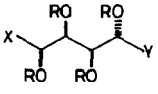
$G^+G^+G^+$

D-*galacto*

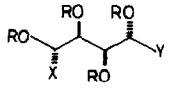


TTT

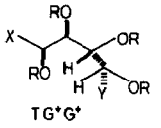
D-*gluco*



TTT

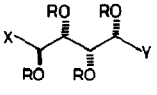


G^-TT

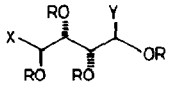


TG^+G^+

D-*gulo*

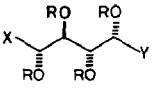


TTT

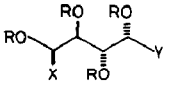


TTG^+

D-*talo*



TTT



G^+TT

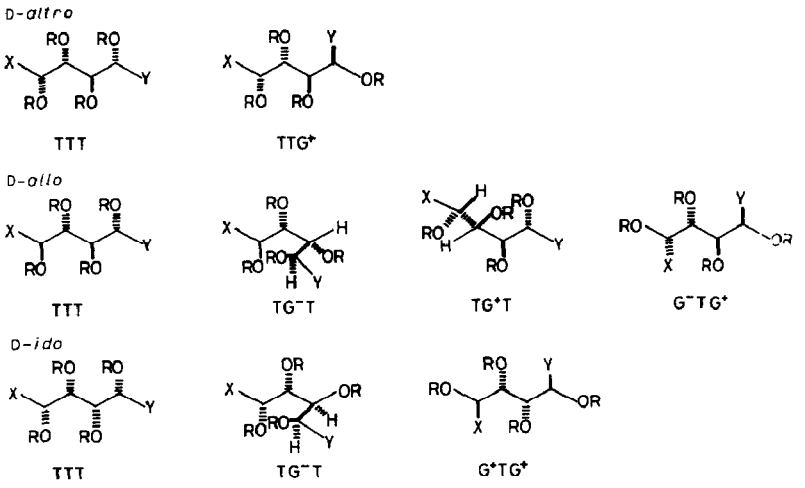


Fig. 4. Conformations referred to in Table I.

methane, and the extracts were washed with 2M HCl, water, aqueous 10% Na_2CO_3, and water, dried ($MgSO_4$), and concentrated. The product was purified by centrifugal chromatography on Silica Gel 60 PF_{254}, using dichloromethane.

1,2,3,4-Tetra-O-p-*chlorobenzoyl*-D-*mannitol* (**1**). — Prepared from 1,2-*O*-isopropylidene-D-mannitol[13] by *p*-chlorobenzoylation followed by hydrolysis (3 h, room temperature) with 6M HCl in tetrahydrofuran, **1** was an oil, $[\alpha]_D^{20}$ +20° (*c* 1.4, chloroform); ν_{max} 3480, 1725, 1590, 1262, 1100, 1012, 845, and 755 cm^{-1}; λ_{max} 242.5 nm (64 700): c.d. −4.5 (256 nm) and +9.5 (239 nm). ^{1}H-N.m.r. data: δ 2.47 (s, 2 H, 2 OH), 3.62 (m, 4 H), 4.51 (dd, 1 H, *J* 5.4 and 13.0 Hz), 4.83 (dd, 1 H, *J* 13.0 and 3.0 Hz), 5.51 (d, 1 H, *J* 8.6 Hz), 5.80 (m, 1 H), 6.14 (d, 1 H, *J* 8.3 Hz), 7.2–7.5 (m, 8 H), and 7.8–8.1 (m, 8 H).

Anal. Calc. for $C_{34}H_{26}Cl_4O_{10}$: C, 55.40; H, 3.56. Found: C, 55.36; H, 3.45.

1,2,3-Tri-O-p-*chlorobenzoyl-(2R,3S)-1,2,3-pentanetriol* (**2**). — Prepared from (2*R*,3*S*)-1,2,3-pentanetriol[14], **2** had m.p. 61–65°, $[\alpha]_D^{20}$ −99° (*c* 1.1, chloroform); ν_{max} 1729, 1717, 1592, 1260, 1112, 1087, 1012, 845, and 755 cm^{-1}; λ_{max} 241.5 nm (51 000); c.d. +24.6 (248 nm) and −10.5 (231 nm). ^{1}H-N.m.r. data: δ 1.04 (t, 3 H, *J* 7.5 Hz), 1.90 (m, 2 H), 4.57 (dd, 1 H, *J* 12.1 and 7.1 Hz), 4.76 (dd, 1 H, *J* 12.1 and 3.3 Hz), 5.51 (dt, 1 H, *J* 4.9, 5.1 and 7.5 Hz), 5.70 (ddd, 1 H, *J* 3.3, 4.9, and 7.1 Hz), 7.4–7.45 (m, 6 H), and 7.9–8.0 (m, 6 H).

Anal. Calc. for $C_{26}H_{21}Cl_3O_6$: C, 58.23; H, 3.95. Found: C, 58.37; H, 3.99.

Tetra-O-p-*chlorobenzoyl*-L-*threitol* (**3**). — Compound **3** (ref. 15) had m.p. 112–114°, $[\alpha]_D^{21}$ +1.2° (*c* 3.0, chloroform); ν_{max} 1720, 1590, 1265, 1085, 1010, 840, and 752 cm^{-1}; λ_{max} 241.5 nm (68 600); c.d. −2.2 (251 nm) and +1.6 (231 nm). ^{1}H-N.m.r. data: δ 4.64 (dd, 2 H, *J* 6.0 and 12.1 Hz), 4.74 (dd, 2 H, *J* 3.9 and 12.1 Hz), 5.92 (m, 2 H), 7.38, 7.41, 7.89, and 7.95 (4 d, 8 H, *J* 8.7 Hz).

Anal. Calc. for $C_{32}H_{22}Cl_4O_8$: C, 56.78; H, 3.28. Found: C, 56.83; H, 3.36.

2,3,4,5-Tetra-O-p-*chlorobenzoyl*-D-*arabinose diethyl dithioacetal* (**4**). — Prepared

from D-arabinose diethyl dithioacetal, **4** was an oil, $[\alpha]_D^{21}$ +43° (*c* 1.5, chloroform); ν_{max} 1727, 1590, 1252, 1092, 845, and 752 cm^{-1}; λ_{max} 242 nm (67 700); c.d. −4.0 (257 nm) and +10.0 (239 nm). ^{1}H-N.m.r. data: δ 1.17 and 1.18 (2 t, 6 H, *J* 7.4 Hz), 2.65 (m, 4 H), 4.18 (d, 1 H, *J* 6.9 Hz), 4.52 (dd, 1 H, *J* 6.6 and 12.2 Hz), 4.80 (dd, 1 H, *J* 3.5 and 12.2 Hz), 5.77 (m, 1 H), 5.78 (dd, 1 H, *J* 3.7 and 6.9 Hz), 6.31 (dd, 1 H, *J* 3.7 and 6.1 Hz), 7.3–7.5 (m, 8 H), 7.8–8.1 (m, 8 H).

Anal. Calc. for $C_{37}H_{32}Cl_4O_8S_2$: C, 54.77; H, 3.98. Found: C, 54.90; H, 3.70.

Penta-O-p-*chlorobenzoyl*-D-*arabinitol* (**5**). — Compound **5** had m.p. 128–130°, $[\alpha]_D^{20}$ +23° (*c* 2.1, chloroform); ν_{max} 1715, 1590, 1255, 1085, 1010, 840, and 748 cm^{-1}; λ_{max} 242 nm (87 100); c.d. −3.8 (256 nm) and +2.7 (242 nm). ^{1}H-N.m.r. data δ 4.53 (dd, 1 H, *J* 5.6 and 12.4 Hz), 4.57 (dd, 1 H, *J* 7.0 and 11.9 Hz), 4.71 (dd, 1 H, *J* 4.4 and 11.9 Hz), 4.82 (dd, 1 H, *J* 3.2 and 12.4 Hz), 5.83 (m, 1 H), 5.96 (m, 1 H), 6.06 (dd, 1 H, *J* 3.6 and 7.3 Hz), 7.3–7.5 (m, 10 H), 7.8–8.1 (m, 10 H).

Anal. Calc. for $C_{40}H_{27}Cl_5O_{10}$: C, 56.81; H, 3.22. Found: C, 56.61; H, 3.37.

2,3,4,5-Tetra-O-p-*chlorobenzoyl*-D-*lyxose diethyl dithioacetal* (**6**). — Prepared from D-lyxose diethyl dithioacetal, **6** was an oil, $[\alpha]_D^{21}$ −0.9° (*c* 3.3, chloroform); ν_{max} 1728, 1590, 1257, 1090, 845, and 755 cm^{-1}; λ_{max} 242.5 nm (65 600); c.d. −20.7 (253 nm) and +12.5 (234 nm). ^{1}H-N.m.r. data: δ 1.20 and 1.23 (2 t, 6 H, *J* 7.4 Hz), 2.68 (m, 4 H), 4.23 (d, 1 H, *J* 5.8 Hz), 4.52 (dd, 1 H, *J* 7.2 and 11.6 Hz), 4.58 (dd, 1 H, *J* 5.0 and 11.6 Hz), 5.83 (dd, 1 H, *J* 5.8 and 6.0 Hz), 6.02 (m, 1 H), 6.18 (dd, 1 H, *J* 2.0 and 6.0 Hz), 7.2–7.4 (m, 6 H), 7.45, 7.72, 7.83, 7.84, and 7.97 (5 d, 10 H, *J* 8.7 Hz).

Anal. Calc. for $C_{37}H_{32}Cl_4O_8S_2$: C, 54.77; H, 3.98. Found: C, 55.12; H, 3.77.

2,3,4,5-Tetra-O-p-*chlorobenzoyl*-D-*ribose diethyl dithioacetal* (**7**). — Prepared from D-ribose diethyl dithioacetal, **7** was an oil, $[\alpha]_D^{20}$ +60° (*c* 0.9, chloroform); ν_{max} 1727, 1590, 1257, 1090, 845, and 755 cm^{-1}; λ_{max} 242.5 nm (68 600); c.d. +37.4 (250 nm) and −16.4 (232 nm). ^{1}H-N.m.r. data: δ 1.12 and 1.22 (2 t, 6 H, *J* 7.4 Hz), 2.65 (m, 4 H), 4.14 (d, 1 H, *J* 5.8 Hz), 4.53 (dd, 1 H, *J* 7.0 and 12.2 Hz), 4.86 (dd, 1 H, *J* 3.1 and 12.2 Hz), 5.88 (dd, 1 H, *J* 5.8 and 5.9 Hz), 5.98 (m, 1 H), 6.28 (dd, 1 H, *J* 4.7 and 5.9 Hz), 7.3–7.5 (m, 8 H), 7.86, 7.93, 7.94, and 8.02 (4 d, 8 H, *J* 8.6 Hz).

Anal. Calc. for $C_{37}H_{32}Cl_4O_8S_2$: C, 54.77; H, 3.98. Found: C, 54.77; H, 3.94.

2,3,4,5-Tetra-O-p-*chlorobenzoyl*-D-*xylose diethyl dithioacetal* (**8**). — Prepared from D-xylose diethyl dithioacetal, **8** was an oil, $[\alpha]_D^{21}$ +28° (*c* 1.4, chloroform); ν_{max} 1727, 1590, 1257, 1090, 845, and 755 cm^{-1}; λ_{max} 242 nm (68 000); c.d. +10.2 (252 nm) and −9.4 (235 nm). ^{1}H-N.m.r. data: δ 1.24 and 1.28 (2t, 6 H, *J* 7.4 Hz), 2.54 and 2.76 (2 m, 4 H), 4.21 (d, 1 H, *J* 5.0 Hz), 4.57 (dd, 1 H, *J* 6.3 and 12.0 Hz), 4.66 (dd, 1 H, *J* 4.6 and 12.0 Hz), 5.82 (dd, 1 H, *J* 5.0 and 6.2 Hz), 5.88 (m, 1 H), 6.35 (dd, 1 H, *J* 4.0 and 6.2 Hz), 7.3–7.5 (m, 8 H), 7.8–8.0 (m, 8 H).

Anal. Calc. for $C_{37}H_{32}Cl_4O_8S_2$: C, 54.77; H, 3.98. Found: C, 54.90; H, 3.90.

3,4,5,6-Tetra-O-p-*chlorobenzoyl-(3R,4R,5R,6R)-octanetetraol* (**9**). — Prepared from 4,5-*O*-isopropylidene-(3*R*,4*R*,5*R*,6*R*)-octanetetraol[16] by hydrolysis (2 h, reflux) with M trifluoracetic acid and *p*-chlorobenzoylation, **9** had m.p. 190–193°, $[\alpha]_D^{21}$ +13° (*c* 1.9, chloroform); ν_{max} 1720, 1592, 1260, 1095, 842, and 750 cm^{-1}; λ_{max} 242 nm (66 400); c.d. −24.4 (252 nm) and +18.4 (234 nm). ^{1}H-N.m.r. data: δ 1.00 (t, 6 H, *J* 7.3 Hz), 1.93

(quintet, 4 H, *J* 7.3 Hz), 5.37 (m, 2 H), 5.81 (m, 2 H), 7.29 (d, 2 H, *J* 8.7 Hz), 7.35 (d, 2 H, *J* 8.7 Hz), 7.80 (d, 2 H, *J* 8.7 Hz), 7.83 (d, 2 H, *J* 8.7 Hz).

Anal. Calc. for $C_{36}H_{30}Cl_4O_8$: C, 58.98; H, 4.12. Found: C, 58.81; H, 4.11.

Penta-O-p-*chlorobenzoyl*-L-*rhamnitol* (**10**). — Compound **10** had m.p. 74–76°, $[\alpha]_D^{20}$ −27° (*c* 1.5, chloroform); ν_{max} 1725, 1590, 1255, 1090, 1010, 840, and 755 cm^{-1}; λ_{max} 242.5 nm (86 200); c.d. +18.0 (253 nm) and −17.6 (235 nm). ^{1}H-N.m.r. data: δ 1.47 (d, 3 H, *J* 6.5 Hz), 4.54 (dd, 1 H, *J* 6.1 and 12.3 Hz), 4.84 (dd, 1 H, *J* 3.5 and 12.3 Hz), 5.49 (dd, 1 H, *J* 6.1 and 6.5 Hz), 5.73 (m, 1 H), 5.86 (dd, 1 H, *J* 4.0 and 6.1 Hz), 6.07 (dd, 1 H, *J* 4.0 and 6.3 Hz), 7.3–7.5 (m, 10 H), 7.8–8.0 (m, 10 H).

Anal. Calc. for $C_{41}H_{29}Cl_5O_{10}$: C, 57.28; H, 3.40. Found: C, 57.06; H, 3.31.

2,3,4,5,6-Penta-O-p-*chlorobenzoyl*-D-*mannose diethyl dithioacetal* (**11**). — Prepared from D-mannose diethyl dithioacetal, **11** had m.p. 134–135°, $[\alpha]_D^{21}$ −8.7° (*c* 1.9, chloroform); ν_{max} 1725, 1590, 1253, 1085, 1075, 845, and 752 cm^{-1}; λ_{max} 242.5 nm (79 400): c.d. −34.0 (253 nm) and +22.0 (236 nm). ^{1}H-N.m.r. data: δ 1.24 and 1.26 (2 t, 6 H, *J* 7.4 hz), 2.7 (m, 4 H), 4.37 (d, 1 H, *J* 7.8 Hz), 4.45 (dd, 1 H, *J* 5.2 and 12.4 Hz), 4.79 (dd, 1 H, *J* 3.2 and 12.4 Hz), 5.68 (m, 1 H), 5.75 (dd, 1 H, *J* 4.6 and 7.8 Hz), 6.22 (m, 2 H), 7.10 (d, 2 H, *J* 8.6 Hz), 7.3–7.45 (m, 8 H), 7.56 (d, 2 H, *J* 8.6 Hz), 7.8–8.0 (m, 8 H).

Anal. Calc. for $C_{45}H_{37}Cl_5O_{10}S_2$: C, 55.15; H, 3.81. Found C, 55.51; H, 4.31.

Hexa-O-p-*chlorobenzoyl*-D-*mannitol* (**12**). — Compound **12** had m.p. 78–82°, $[\alpha]_D^{20}$ +35° (*c* 1.1, chloroform); ν_{max} 1725, 1590, 1255, 1088, 845, and 755 cm^{-1}; λ_{max} 242 nm (101 000); c.d. −23.7 (254 nm) and +18.6 (238 nm). ^{1}H-N.m.r. data: δ 4.39 (dd, 2 H, *J* 5.5 and 12.4 Hz), 4.77 (dd, 2 H, *J* 3.3 and 12.4 Hz), 5.68 (m, 2 H), 6.04 (d, 2 H, *J* 6.2 Hz), 7.3–7.5 (m, 12 H), 7.8–8.0 (m, 12 H).

Anal. Calc. for $C_{48}H_{32}Cl_6O_{12}$: C, 56.83; H, 3.18. Found: C, 56.54; H, 3.30.

Penta-O-p-*chlorobenzoyl*-L-*fucitol* (**13**). — Compound **13** had m.p. 173–174°, $[\alpha]_D^{20}$ −3.5° (*c* 1.8, chloroform): ν_{max} 1725, 1590, 1257, 1087, 1010, 840, and 752 cm^{-1}; λ_{max} 242 nm (85 500); c.d. −5.0 (256 nm). ^{1}H-N.m.r. data: δ 1.34 (d, 3 H, *J* 6.5 Hz), 4.44 (dd, 1 H, *J* 7.3 and 11.8 Hz), 4.58 (dd, 1 H, *J* 4.5 and 11.8 Hz), 5.51 (dd, 1 H, *J* 2.9 and 6.5 Hz), 5.75 (dd, 1 H, *J* 2.9 and 8.1 Hz), 5.89 (m, 1 H), 5.96 (dd, 1 H, *J* 2.4 and 8.1 Hz), 7.2–7.5 (m, 10 H), 7.7–8.0 (m, 10 H).

Anal. Calc. for $C_{41}H_{29}Cl_5O_{10}$: C, 57.28; H, 3.40. Found: C, 57.11; H, 3.39.

2,3,4,5,6-Penta-O-p-*chlorobenzoyl*-D-*galactose diethyl dithioacetal* (**14**). — Prepared from D-galactose diethyl dithioacetal, **14** had m.p. 130–132°, $[\alpha]_D^{21}$ −14° (*c* 1.7, chloroform); 1728, 1590, 1255, 1085, 845, and 752 cm^{-1}; λ_{max} 242 nm (85 300); c.d. +2.4 (255 nm) and −6.0 (238 nm). ^{1}H-N.m.r. data: δ 1.11 and 1.12 (2 t, 6 H, *J* 7.4 Hz), 2.60 (m, 4 H), 4.09 (d, 1 H, *J* 7.2 Hz), 4.51 (dd, 1 H, *J* 6.6 and 12.1 Hz), 4.64 (dd, 1 H, *J* 4.2 and 12.1 Hz), 5.77 (dd, 1 H, *J* 2.8 and 7.2 Hz), 5.90 (m, 2 H), 6.28 (dd, 1 H, *J* 2.8 and 5.2 Hz), 7.3–7.5 (m, 10 H), 7.8–8.0 (m, 10 H).

Anal. Calc. for $C_{45}H_{37}Cl_5O_{10}S_2$: C, 55.15; H, 3.81. Found: C, 55.10; H, 3.99.

2,3,4,5,6-Penta-O-p-*chlorobenzoyl*-D-*glucose diethyl dithioacetal* (**15**). — Prepared from D-glucose diethyl dithioacetal, **15** was an oil, $[\alpha]_D^{21}$ +56° (*c* 1.0, chloroform); ν_{max} 1727, 1590, 1255, 1090, 845, and 755 cm^{-1}; λ_{max} 242.5 nm (88 300); c.d. +7.5 (254 nm) and −5.7 (240 nm). ^{1}H-N.m.r. data: δ 1.10 and 1.30 (2 t, 6 H, *J* 7.4 Hz), 2.46, 2.54,

2.76, and 2.84 (4 dq, 4 H, *J* 7.4 and 12.5 Hz), 4.39 (d, 1 H, *J* 4.0 Hz), 4.42 (dd, 1 H, *J* 4.6 and 12.0 Hz), 4.81 (dd, 1 H, *J* 2.9 and 12.0 Hz), 5.62 (ddd, 1 H, *J* 2.9, 4.6, and 8.3 Hz), 5.77 (dd, 1 H, *J* 4.0 and 7.8 Hz), 6.05 (dd, 1 H, *J* 2.2 and 8.3 Hz), 6.37 (dd, 1 H, *J* 2.2 and 7.8 Hz), 7.2–7.5 (m, 10 H), 7.7–8.0 (m, 10 H).

Anal. Calc. for $C_{45}H_{37}Cl_5O_{10}S_2$: C, 55.15; H, 3.81. Found: C, 55.13; H, 3.87.

Hexa-O-p-*chlorobenzoyl*-D-*glucitol* (**16**). — Compound **16** had m.p. 152.5–154°, $[\alpha]_D^{21}$ +44° (*c* 1.2, chloroform); ν_{max} 1722, 1590, 1260, 1090, 1010, 842, and 750 cm^{-1}; λ_{max} 242 nm (100 500): c.d. −3.2 (257 nm) and +3.5 (233 nm). ^{1}H-N.m.r. data: δ 4.44 (dd, 1 H, *J* 5.2 and 12.5 Hz), 4.66 (dd, 1 H, *J* 3.8 and 12.1 Hz), 4.77 (dd, 1 H, *J* 2.8 and 12.1 Hz), 4.81 (dd, 1 H, *J* 3.3 and 12.5 Hz), 5.77 (m, 2 H), 6.14 (m, 2 H), 7.2–7.45 (m, 12 H), 7.7–8.0 (m, 12 H).

Anal. Calc. for $C_{48}H_{32}Cl_6O_{12}$: C, 56.83; H, 3.18. Found: C, 56.87; H, 3.26.

3,4,5,6-Tetra-O-p-*chlorobenzoyl-(3*S,*4*R,*5*R,*6*S)-octanetetraol* (**17**). — Obtained from 4,5-*O*-isopropylidene-(3*S*,4*R*,5*R*,6*S*)-octanetetraol[16] by hydrolysis (6 h, room temperature) with 6M HCl in tetrahydrofuran and *p*-chlorobenzoylation, **17** had m.p. 149–152°, $[\alpha]_D^{20}$ −58° (*c* 1.0, chloroform); ν_{max} 1725, 1592, 1260, 1090, 842, 758, and 753 cm^{-1}; λ_{max} 241 nm (65 900); c.d. −13.2 (247 nm). ^{1}H-N.m.r. data: δ 0.94 (t, 6 H, *J* 7.3 Hz), 1.79 (quintet, 4 H, *J* 7.3 Hz), 5.5 (m, 2 H), 5.76 (m, 2 H), 7.31, 7.37, 7.81, and 7.91 (4 d, 16 H, *J* 8.6 Hz).

Anal. Calc. for $C_{36}H_{30}Cl_4O_8$: C, 58.98; H, 4.12. Found: C, 58.80; H, 3.93.

Hexa-O-p-*chlorobenzoyl*-L-*iditol* (**18**). — Compound **18** had m.p. 130–132°, $[\alpha]_D^{20}$ +11° (*c* 1.3, chloroform); ν_{max} 1727, 1590, 1260, 1085, 1010, 842, and 750 cm^{-1}; λ_{max} 242.5 nm (100 500); c.d. +3.3 (246 nm) and −3.8 (229 nm). ^{1}H-N.m.r. data: δ 4.53 (dd, 2 H, *J* 5.3 and 11.9 Hz), 4.66 (dd, 2 H, *J* 5.5 and 11.9 Hz), 5.96 (m, 2 H), 6.07 (m, 2 H), 7.26, 7.32, 7.36, 7.77, 7.82, and 7.85 (6 d, 24 H, *J* 8.7 Hz).

Anal. Calc. for $C_{48}H_{32}Cl_6O_{12}$: C, 56.83; H, 3.18. Found: C, 56.83; H, 3.22.

ACKNOWLEDGMENTS

This work was supported by the RP II.13.2.10. programme. We thank Professor H. -D. Scharf for the samples of starting materials, (for the preparation of **2**), Professor J.-C. Depezay (for the preparation of **9** and **17**), Dr. J. Kuszmann (for the preparation of **1**), and A. Pieta for technical assistance.

REFERENCES

1 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy–Exciton Coupling in Organic and Bioorganic Chemistry*, University Science Books, Mill Valley, CA, 1983.
2 N. Harada and K. Nakanishi, *J. Am. Chem. Soc.*, 91 (1969) 3989–3991; N. Harada, S. Suzuki, H. Uda, and K. Nakanishi, *ibid.*, 93 (1971) 5577–5579.
3 N. Harada, H. Sato, and K. Nakanishi, *J. Chem. Soc., Chem. Commun.*, (1970) 1691–1693; J. Golik, Huang-Wen Liu, M. Dinovi, J. Furukawa, and K. Nakanishi, *Carbohydr. Res.*, 118 (1983) 135–146.
4 N. Harada, A. Saito, J. Gawronski, K. Gawronska, T. Sugioka, M. Uda and T. Kuriki, unpublished data.

5 G. E. Hawkes and D. Lewis, *J. Chem. Soc., Perkin Trans 2*, (1984) 2073–2078; D. G. Gillies and D. Lewis, *ibid.*, (1985) 1155–1159.
6 K. Gawronska, D.Sc. Thesis, A. Mickiewicz University, Poznan, 1990.
7 J. F. Stoddart, *Stereochemistry of Carbohydrates*, Wiley–Interscience, New York, 1971, ch. 3.3.
8 S. J. Angyal, R. Le Fur, and D. Gagnaire, *Carbohydr. Res.*, 23 (1972) 121–134.
9 D. Horton, *Pure Appl. Chem.*, 42 (1976) 301–325; M. Blanc-Muesser, J. Defaye, and D. Horton, *Carbohydr. Res.*, 87 (1980) 71–86; D. Horton and J. D. Wander, *ibid.*, 10 (1969) 279–288.
10 G. A. Jeffrey and H. S. Kim, *Carbohydr. Res.*, 14 (1970) 207–216, and references therein.
11 Y. J. Park, G. A. Jeffrey, and W. C. Hamilton, *Acta Crystallogr., Sect. B*, 27 (1971) 2393–2401.
12 N. Azarnia, G. A. Jeffrey, and M. S. Shen, *Acta Crystallogr., Sect. B*, 28 (1972) 1007–1013.
13 J. L. Debost, J. Gelas, and D. Horton, *J. Org. Chem.*, 48 (1983) 1381–1382.
14 A. Yusufoglu, S. Antons, and H.-D. Scharf, *Liebig's Ann. Chem.*, (1986) 1119–1123.
15 V. Schurig, B. Koppenhoeffer, and W. Buerkle, *J. Org. Chem.*, 45 (1980) 538–541.
16 Y. Le Merrer, A. Dureault, C. Gravier, D. Languin, and J. C. Depezay, *Tetrahedron Lett.*, 26 (1985) 319–322.