The Rotatory Dispersion and Stereochemistry of Organic Compounds. VI.[1] Some Observations on the Sign of Partial Rotations in the Derivatives of Xylofuranose and Mannopyranose

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In previous papers[1,2] the rotatory dispersion (RD) of some derivatives of glucose as well as of several anomeric pyranoses has been reported and discussed with relationship to the configuration. In the present paper similar studies will be made on some other monosaccharides, particularly with respect to the sign of the Cotton effect and to the configuration of the functional group, and the results will be compared with the derivatives of glucose. The following compounds will be investigated:

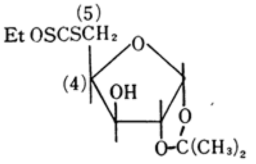
1, 2-*O*-isopropylidene-D-xylofuranose 5-ethylxanthate (compound I),

1, 2-5, 6-*O*-diisopropylidene-D-glucofuranose (compound II),[2]

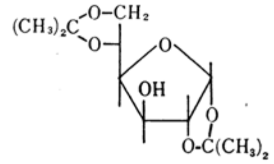
1, 2-5, 6-*O*-diisopropylidene-D-glucofuranose-3-(*S*-methyl)-xanthate (compound III),[2]

2, 3, 4, 6-tetra-*O*-acetyl-*β*-D-glucofuranosyl ethylxanthate (compound IV),[1]

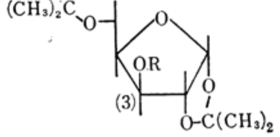
2, 3, 4, 6-tetra-*O*-acetyl-*β*-D-mannopyranosylethylxanthate (compound V).

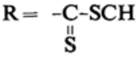


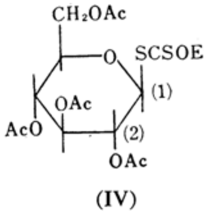
(I)



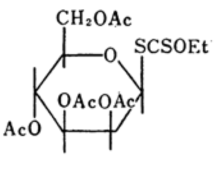
(II)



(III) R=

$R = -\underset{\overset{\|}{S}}{C}-SCH$



(IV)



(V)

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[1] Part V: Y. Tsuzuki, K. Tanabe, M. Akagi and S. Tejima, This Bulletin, 37, 162 (1964).

[2] Y. Tsuzuki, K. Tanaka and K. Tanabe, ibid., 35, 1614 (1962).

Results and Discussion

The RD curve of compound I shows a positive Cotton effect in the region from 300 to 380 mμ (Fig. 1-I). It is interesting to compare this anomalous curve with those of diisopropylidene-D-glucofuranose (compound II) and its 3-methylxanthate (compound III) of a similar configuration.

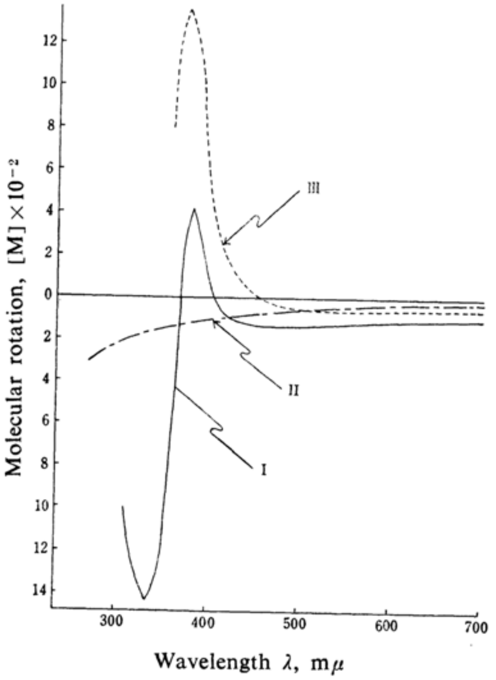

Fig. 1. RD of D-xylofuranose 5-ethylxanthate (I) compared with those of glucofuranose of derivatives (II and III) of similar configuration.

The positive Cotton effect of compound I is due to the $-S-\underset{\underset{S}{\|}}{C}-OC_2H_5$ group attached to the C_4-asymmetric center through the C_5-methylene group. This fact may easily be understood by considering that the compound II, carrying no chromophore, does not show any Cotton effect. In compound III a stronger, positive Cotton effect is observed; this is undoubtedly to be attributed to the $C_3-O-\underset{\underset{S}{\|}}{C}-S-CH_3$ group.[2] In these three compounds the background rotation is always negative, for which the C_3-OH group with an L-configuration may be responsible,[3] although this statement requires further investigation before it can be definitely established.

The structural difference between compounds IV and V lies in the configuration of the C_2-group, which is reflected in the RD curves seen in Fig. 2. The weaker, positive Cotton effect naturally originates in the $\beta-C_1-S-\underset{\underset{S}{\|}}{C}-OC_2H_5$ group, the amplitude of which is strikingly smaller than that of its epimer (IV).[1]

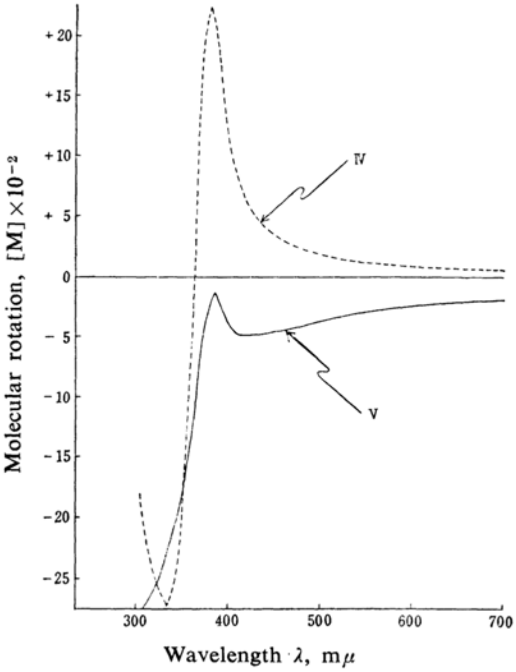

Fig. 2. RD of tetraacetyl β-D-mannopyranosyl 1-ethylxanthate (compound V) compared with its epimer (compound IV).

That the mannofuranose (V) is generally less levo-rotatory than its epimer (IV) is because the C_2-acetoxy group of the former has a configuration of the L-type, suggesting that its partial rotation due to this group is negative in sign. This statement becomes more evident upon analysis of the dispersion data obtained by means of the Drude equation, which will be described later.

The rotatory dispersion constants and the ultraviolet absorption maxima of compounds I and V are tabulated in Table I. The optically-active absorption maximum, λ_0, of compound I lies near 360 mμ, in good agreement with the λ_{max} of its R-band (357 mμ). Although no trough could be observed, the value of λ_0 is presumably not far from the λ_{max} of its R-band (360 mμ), as the amplitude is small.

The data of the RD measurements were calculated according to an abbreviated two-term expression of the Drude equation:

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[3] See Y. Tsuzuki, K. Tanaka and K. Tanabe, ibid., 35, 1615 (1962).

TABLE I. RD CONSTANTS AND UV ABSORPTION MAXIMA

Compound	Rotatory dispersion				Ultraviolet absorption			
	Peak		Trough		R-band		K-band	
	λ, mμ	[M]	λ, mμ	[M]	λ_{max}, mμ	ε	λ_{max}, mμ	ε
I	382	+411°	335	−1420°	357	34.0	280	11800
V	385	−147°	—	—	360	36.7	274	8510

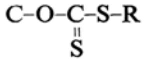
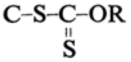
$$[\mathrm{M}]=\frac{A}{\lambda^2}+\frac{B}{\lambda^2-\lambda_c{}^2}$$

The results are shown in Table II, together with some previous data (III,[2] IV[1]) for the sake of comparison.

TABLE II. DISPERSION CONSTANTS FOR SUGAR DERIVATIVES

Compound	A	B	$\lambda_c{}^2$
I	−61.12	11.79	$(0.361)^2$
III	−37.82	4.54	$(0.380)^2$
IV	−13.68	27.33	$(0.369)^2$
V	−97.29	2.14	$(0.369)^2$

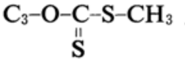
The agreement of the observed and the calculated values of rotation is tolerable over the range from 310 to 700 mμ, the difference between them being mostly only a few percent outside the absorption region.

The values of λ_c are from 361 to 380 mμ, in good accord with the corresponding absorption maxima of the R-band shown in Table I and in previous papers. Among these the λ_c value (0.380 μ) of compound III is particularly high. Here it should be pointed out that the chromophore of III is of the  $\mathrm{C{-}O{-}\underset{\underset{\displaystyle S}{\Vert}}{C}{-}S{-}R}$ type, unlike those of the others, which are all of the  $\mathrm{C{-}S{-}\underset{\underset{\displaystyle S}{\Vert}}{C}{-}OR}$ type.

The rotational strength B due to the chromophore (the xanthyl group) is in all cases positive in sign, but the configuration of the functional group is always of the L-type. This fact is in harmony with the information that the xanthates of L-hydroxylic acids show positive Cotton effects[4] even through the functional group (OH) is expected to contribute to the levo partial rotation, as was pointed out in a previous paper.[2]

The value of B is the largest in β-glucopyranosyl xanthate (IV), but incomparably smaller in the corresponding derivative of mannose (V). Here the chromophore is cis to the adjacent acetoxy group, C_2-OAc (1L-*e*, 2L-*a*), while in the glucose derivative (IV) the conformation (1L-*e*, 2D-*e*) is trans. As there might be some steric disturbance between these two groups, especially in the cis configuration, giving rise to this remarkable difference in B between the epimers (IV and V), the authors have observed the influence of the temperature on RD with V; they expected some change in optical rotation due to thermal agitation, but in reality the RD curve was almost independent of the temperature below 60°C.

The residual rotational strength of A is in all cases negative in sign, and it is greater than that of the main partial rotational strength B except in glucopyranosyl xanthate (IV).

As the RD curve II typically shows, the background rotation of these compounds is negative in sign (Fig. 1). The strong positive rotation near the absorption region of III is, as has already been pointed out, due to the  $\mathrm{C_3{-}O{-}\underset{\underset{\displaystyle S}{\Vert}}{C}{-}S{-}CH_3}$ group.

It is noteworthy that A is negative in compound IV, although the rotation is positive. (Fig. 2-IV) This fact can be interpreted thus: the β-form of the C_1-ligand should contribute potentially to a negative rotation, which is embodied in the negative rotational strength of A, but this negative partial rotation is now canceled by the positive, rotational contribution due to both the C_2 group of D-configuration and the C_1-xanthyl group. That the value of A is unusually large in the mannopyranosyl xanthate (V) may be due to the L-type C_2-acetoxy group, which is evidenced in another expression of RD by the two-term equation of Drude. The RD of compound V is rather better expressed by the following equation, where the calculated values of the molecular rotation are in good agreement with the observed values, with an accuracy of more than 95% over the spectral region from 305 to 700 mμ except in the absorption region:

$$[\mathrm{M}]=\frac{-99.35}{\lambda^2-(0.233)^2}+\frac{13.02}{\lambda^2-(0.363)^2}$$

In the above equation the first negative term is inferred as expressing mainly the partial rotation due to the C_2-acetoxy group of the L-type; in reality the value of λ_1 (0.233 mμ) nearly coincides with the ultraviolet absorption of the acetoxy group.

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[4] B. Sjöberg, A. Fredga and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 5002 (1959).

Experimental

The rotatory dispersion was measured in tetrahydrofuran at room temperature over the wavelength region from 300 to 700 mμ with a Rudolph photometric spectropolarimeter. The ultraviolet absorption was measured in the same solvent with a self-recording spectrophotmeter of the Hitachi type. The calculation from the data of RD was made by means of the least-squares method with an electronic computer of the Fuji FACOM 201 type.

The method of preparation and the other properties of the following compounds will be described elsewhere by Akagi and his collaborators.

1, 2-*O*-Isopropylidene-D-xylofuranose 5-Ethylxanthate. (Compound I).—Was prepared from its corresponding iodo compound.[5] Colorless crystals. M. p. 126°C. $[\alpha]_{700}^{16.5}=-33.0°$, $[\alpha]_{589}=-39.9°$, $[\alpha]_{382}=+140°$ (peak), $[\alpha]_{335}=-483°$ (trough), $[\alpha]_{310}=-341°$ (*c* 0.2936, tetrahydrofuran).

2,3,4,6-Tetra-*O*-acetyl-*β*-D-mannopyranosyl 1-Ethylxanthate (Compound V).—Colorless crystals. M. p. 127～128°C. $[\alpha]_{700}^{17}=-43.4°$, $[\alpha]_{589}=-58.1°$, $[\alpha]_{420}=-110°$ (broad extreme), $[\alpha]_{385}=-32.4°$ (peak), $[\alpha]_{305}=-602°$, (*c*, 0.4362, tetrahydrofuran).

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[5] P. A. Levene and J. Compton, *J. Biol. Chem.*, **111**, 325 (1935).