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The Rotatory Dispersion and Stereochemistry of Organic Compounds. XIII.[1] Alkylxanthates of Glucose

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The rotatory dispersions and ultraviolet absorption spectra of six homologs of 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranosyl alkylxanthates have been measured, and the effects of the alkyl groups on the rotatory dispersion have been discussed by comparison with the case of the sugar xanthates already studied by Tsuzuki *et al.* (*Bull. Chem. Soc. Japan*, **37**, 162, 730 (1964)). All show positive Cotton effects, the molecular amplitude of which diminishes with an increase in the number of carbon atoms of the alkyl group, while the molecular extinction coefficient decreases as the carbon number of the alkyl group increases from 1 to 4. These facts agree with the earlier findings and can be interpreted in terms of the relation, $R=\mu\cos\theta\sqrt{D}$, between the electron transition, the rotational strength, and the dipole strength given by S. F. Mason (*Quart. Rev.*, **17**, 20 (1963)).

In previous papers,[2,3] the rotatory dispersion (RD) of sugar ethylxanthates has been reported and discussed with relationship to the configuration. One of the present authors has long ago shown, with a number of derivatives of tartaric

1) Part XII: Y. Tsuzuki, K. Tanabe, K. Okamoto and N. Yamada, This Bulletin, **39**, 2269 (1966).

2) Y. Tsuzuki, K. Tanabe, M. Akagi and S. Tejima, *ibid.*, **37**, 162 (1964).

3) Y. Tsuzuki, K. Tanaka, K. Tanabe, M. Akagi and S. Tejima, *ibid.*, **37**, 730 (1964).

acid,[4] that the rotational strength decreases with an increase in the bulk of the alkyl group attached to the asymmetric carbon atom in the same configurational series, and that the ultraviolet absorption spectrum shows a greater blue shift. Besides, it has been reported by Mason,[5] both theoretically and experimentally, that the amplitude of the anomalous rotatory dispersion is related to the extinction coefficient in the compounds with optically active absorption bands. This paper will present similar studies made with the following C_1-β-alkylxanthates of D-glucose:

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Methylxanthate (compound I),

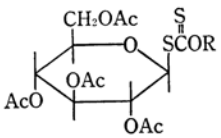
2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Ethylxanthate (compound II),[2]

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Propylxanthate (compound III),

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Butylxanthate (compound IV),

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Cyclohexylxanthate (compound V), and

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Benzylxanthate (compound VI).



I R=$-CH_3$
II R=$-CH_2CH_3$
III R=$-CH_2CH_2CH_3$
IV R=$-CH_2CH_2CH_2CH_3$
V R=$-C_6H_{11}$ (cyclo)
VI R=$-CH_2C_6H_5$

Results and Discussion

As is evident from Figs. 1 and 2, all the compounds exhibit positive Cotton effects. In proportion to the enlargement of the bulk of the alkyl group of β-alkylxanthates of glucose, the RD curve increases in the region from 420 to 700 mμ and the amplitude of the Cotton effect decreases, while the position and the direction of the Cotton effect remain invariable. That is, increasing the carbon number of the alkyl group makes its molecular amplitude, $[A]$ (the difference of $[M]$ between the peak and the trough), smaller. The values of the peak and the trough and the molecular amplitudes are shown in Table 1. It is evident from Table 2 that the values of the molecular extinction coefficients, ε, of the optically active, weak

band due to the group diminishes as the carbon number of the alkyl group increases from 1 to 4.

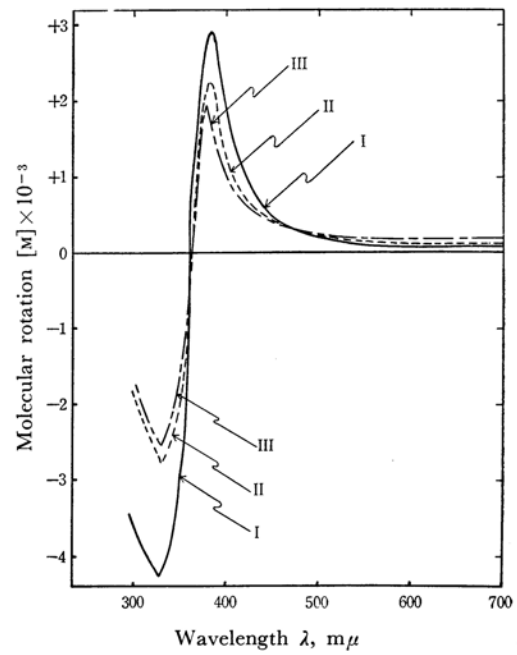


Fig. 1. Rotatory dispersion of alkylxanthates of glucose.

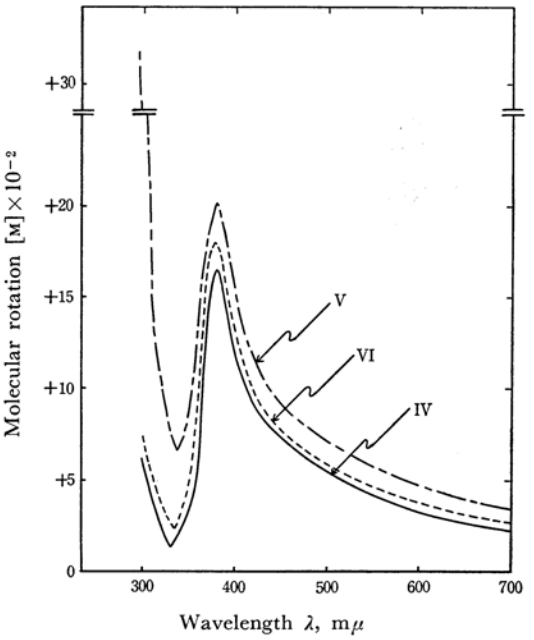


Fig. 2. Rotatory dispersion of glucose xanthates.

Now let us consider the relation of the amplitude, $[A]$, of the Cotton effect to the molecular extinction coefficient, ε. It has been demonstrated by Mason[5] that electric transitions may be characterized by the relations between the rotational

4) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **36**, 31 (1939).
5) S. F. Mason, *Quat. Rev.*, **17**, 20 (1963).

Table 1. Rotatory dispersion of alkylxanthates of glucose

Compound	Peak		Trough		Molecular amplitude [A]
	λ, mμ	[M]	λ, mμ	[M]	
I	383	+2950°	330	−4240°	7210°
II	381	+2220°	334	−2720°	4940°
III	378	+2010°	335	−2530°	4540°
IV	380	+1660°	330	+131°	1530°
V	380	+2030°	340	+659°	1370°
VI	378	+1800°	335	+232°	1570°

Table 2. Ultraviolet absorption and dispersion constants of alkylxanthates of glucose

Alkyl group of xanthate	[A]	Ultraviolet absorption			Dispersion constant		
		λ_{max}, mμ	ε	$\Delta\nu$,* $cm^{-1} \times 10^7$	R_1	R_2	λ_0
CH_3	7210°	361	38.9	65	+38.5	−23.7	0.368
C_2H_5	4940°	363	36.4	66	+27.3	−13.7	0.369
n-C_3H_7	4540°	362	37.4	66	+25.9	−0.67	0.365
n-C_4H_9	1530°	360	15.1	64	+13.1	+99.9	0.361
C_6H_{11} (cyclo)	1370°	363	18.4	66	+13.8	+176	0.368
CH_2- 	1570°	360	14.0	60	+13.6	+114	0.366

* $\Delta\nu$ is half-band width.

strength (R) and the dipole strength (D) of a given transition in a related series of compounds. The relation was given by the following equation:[5]

$$R = \mu \cos\theta \sqrt{D} \qquad (1)$$

where μ is the magnetic transition moment and θ is the angle between the directions of the electric and magnetic transition moments.

Since D is proportional to ε, as may be seen from Fig. 3, as well as from the constant values, $\Delta\nu$, shown in Table 2, the log ε and log R terms make a linear function. Formula (1) shows that the $\mu \cos\theta$ term is a constant characteristic of the molecule. When we assume $\mu \cos\theta$ to be constant in the alkylxanthates, the log [A] and log ε terms eventually form a linear equation, because R is proportional to the molecular amplitude, [A]. Mason[5] presented some examples which show that a linear relationship exists between log ε and log [A].

The values of the molecular extinction coefficient, ε, and the molecular amplitude [A] are collected in Table 2, together with the dispersion constants calculated from the dispersion data according to the Drude equation (2):

$$[M] = \frac{R_1}{\lambda^2 - \lambda_0^2} + \frac{R_2}{\lambda^2} \qquad (2)$$

As may be seen in Table 2, the sign of the R_1 value agrees with that of the Cotton effect in every case, and the magnitude of the R_1 value well expresses the molecular amplitude, [A], in harmony with the RD curve. The R_2 value in general represents the background rotation, the sign of which corresponds to the β-C_1 configuration. Apparently this regularity does not hold

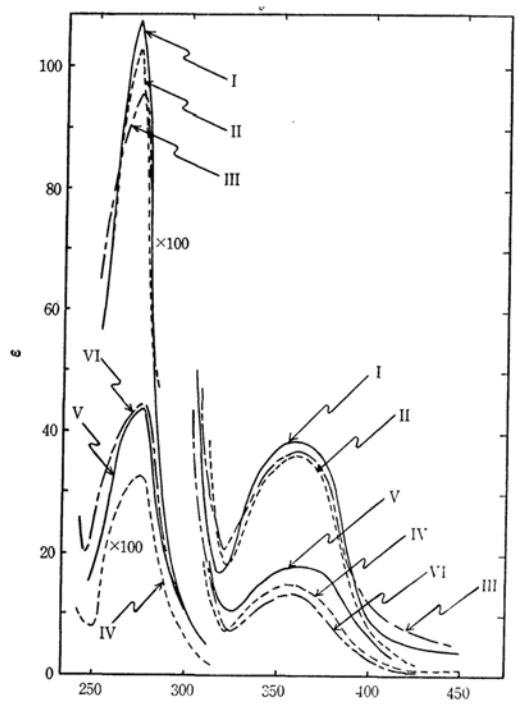
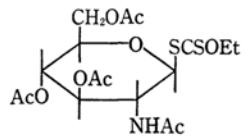
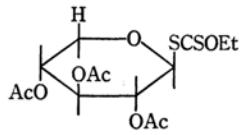
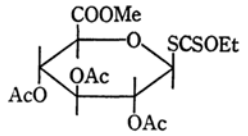
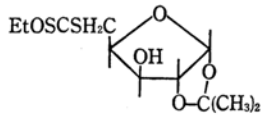


Fig. 3. The UV spectra of alkylxanthates of glucose in tetrahydrofuran.
The absorptions of shorter wavelengths on the scale of one to a hundred.

TABLE 3. ULTRAVIOLET ABSORPTION AND MOLECULAR AMPLITUDE OF SUGAR XANTHATES

	Sugar xanthate		UV Absorption λ_{max}, mμ	UV Absorption ε	[A]
VII	2-Acetamido-2-desoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl ethylxanthate[2]		360	42.3	7120°
VIII	2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl ethylxanthate[2]		364	45.5	4530°
IX	Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranuronate 1-ethylxanthate[2]		360	40.0	4590°
X	1,2-*O*-Isopropylidene-D-xylofuranose 5-ethylxanthate[3]		357	34.1	1840°

when the size of the alkyl group increases, but it may be assumed that some steric effect due to the alkyl group affects the C_2 group of the D configuration.

The values of λ_0 (Table 2) lie in a narrow range, from 361 to 369 mμ, quite in accord with the corresponding absorption maxima.

As can be seen from Table 2, the molecular extinction coefficient varies with the bulkiness of the alkyl group. The intensity of the absorption decreases in consequence of a slight steric hindrance, which arises upon the introduction of a large group into the xanthyl group, and although the position of the absorption maximum shows almost no shift, the intensity is diminished. Similar phenomena due to steric hindrance have already been observed in some compounds of conjugated systems.[6] It is interesting to observe that the diminution in the intensity of the ultraviolet absorption maximum is accompanied by a decrease in the molecular amplitude of the Cotton effect. This relation between ε and [A] is valid in the C_1-β-alkylxanthates only when the alkyl groups are different, but it is likely that some other factors must also be taken into consideration when the compounds to be compared are different in configuration outside the chromophore (Table 3). The factors expected to be dominant are the optical contributions of the non-chromophoric asymmetric centers. These contributions find expression, for example, in Hudson's rule of optical superposition. This shows that the factors not appearing in the observed ultraviolet absorption can contribute to the rotatory dispersion.

The compound VII (Table 3) is far greater in molecular amplitude ([A]) and in absorption intensity (ε) than the corresponding 2-acetoxyxanthate (II), since the rotatory contribution of the C_2 group is different from that of the C_1-chromophore; the $\mu \cos\theta$ term may also be different. This remarkable effect of the C_2-NHAc group is likely to justify the assumption that the $\mu \cos\theta$ term is constant in the alkylxanthates.

On the other hand, it may be seen by comparing the compounds VIII and IX (Table 3) that they exhibit almost the same [A] values; this shows that the C_5-asymmetric center has only a small influence on the Cotton effect.

The C_5-xanthate (compound X) exhibits an absorption intensity comparable in magnitude to those of the C_1-xanthates (compounds VII—IX), but its molecular amplitude is far smaller (Table 3). These facts show that the chromophore, irrespective of its position in the molecule, always gives rise to almost the same ultraviolet absorption, but that it contributes differently to the rotatory dispersion as the conformation is changed. The difference is that which appears in the molecular amplitude.

6) E. A. Braude, *Experientia,* **11**, 457 (1955).

Experimental

The rotatory dispersion was measured in tetrahydrofuran at about 20°C over the wavelength region from 300 to 700 mμ with a Rudolph spectropolarimeter. The ultraviolet absorption was measured in the same solvent with a self-recording spectrophotometer of the Hitachi type. The calculation from the RD data was made by means of the least-squares method with an electric computer of the Fuji FACOM 201 type.

2, 3, 4, 6 - Tetra - *O* - acetyl - β - D - glucopyranosyl Methylxanthate (Compound I).[7] Colorless needles; mp 99°C. The RD was measured at 22.5°C (*c* 0.5745). $[\alpha]_{700}$ +14.1°, $[\alpha]_{589}$ +24.7°, $[\alpha]_{383}$ +649° (peak), $[\alpha]_{330}$ −937° (trough), $[\alpha]_{310}$ −818°.

2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl Propylxanthate (Compound III).[8] Colorless crystals; mp 90—91°C. The RD was measured at 20.3°C (*c* 0.7992). $[\alpha]_{700}$ +15.8°, $[\alpha]_{589}$ +26.0°, $[\alpha]_{378}$ +430° (peak), $[\alpha]_{335}$ +543° (trough), $[\alpha]_{310}$ +428°.

2, 3, 4, 6 - Tetra - *O* - acetyl - β - D - glucopyranosyl Butylxanthate (Compound IV).[8] Colorless crystals; mp 114—115°C. The RD was measured at 20.3°C (*c* 0.4026), $[\alpha]_{700}$ +47.4°, $[\alpha]_{589}$ +75.0°, $[\alpha]_{380}$ +345° (peak), $[\alpha]_{330}$ +27.3° (trough), $[\alpha]_{300}$ +132°.

2, 3, 4, 6 - Tetra - *O* - acetyl - β - D - glucopyranosyl Cyclohexylxanthate (Compound V).[8] Colorless crystals; mp 111—112°C. The RD was measured at 20.5°C (*c* 0.3919). $[\alpha]_{700}$ +66.4°, $[\alpha]_{589}$ +97.0°, $[\alpha]_{380}$ +401° (peak), $[\alpha]_{340}$ +130° (trough), $[\alpha]_{300}$ +633°.

2, 3, 4, 6 - Tetra - *O* - acetyl - β - D - glucopyranosyl Benzylxanthate (Compound VI).[7] Colorless crystals; mp 129°C. The RD was measured at 20.3°C (*c* 0.4649). $[\alpha]_{700}$ +53.3°, $[\alpha]_{589}$ +76.6°, $[\alpha]_{378}$ +351° (peak), $[\alpha]_{335}$ +45.2° (trough), $[\alpha]_{300}$ +112°.

7) M. Sakata, M. Haga, S. Tejima and M. Akagi, *Chem. Pharm. Bull.*, **12**, 652 (1964).

8) M. Akagi, S. Tejima and M. Haga, *Chem. Pharm. Bull.*, **11**, 1081 (1963).