# *The Rotatory Dispersion and Stereochemistry of Organic Compounds. V.*[1]
# *On Anomeric Pyranoses with a Xanthate Group*

By Yojiro TSUZUKI, Koko TANABE, Masuo AKAGI and Setsuzo TEJIMA

(Received July 27, 1963)

In a previous paper[1] it was shown that some of the rotatory contribution of the hydroxyl groups in glucose can be studied by means of rotatory dispersion with its derivatives which contain a xanthate group. The present paper will report on similar, comparative studies made of a variety of newly-synthesized xanthates with a pyranose configuration, namely:

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

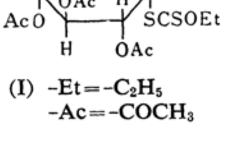
2, 3, 4, 6-Tetra-*O*-acetyl-β-D-glucopyranosyl ethylxanthate (compound II),

2, 3, 4-Tri-*O*-acetyl-β-D-xylopyranosyl ethylxanthate (compound III),

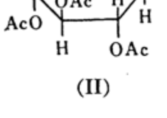
Methyl 2, 3, 4-tri-*O*-acetyl-β-D-glucopyranuronate 1-ethylxanthate (compound IV),

2-Acetamido-2-desoxy-3, 4, 6-tri-*O*-acetyl-β-D-glucopyranosyl ethylxanthate (compound V),

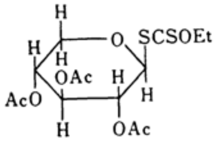
6-Desoxy-6-ethylxanthogen-α-D-glucopyranose tetraacetate (compound VI),



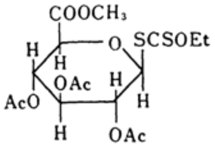
(I) $-Et=-C_2H_5$
$-Ac=-COCH_3$



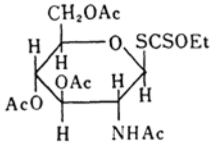
(II)



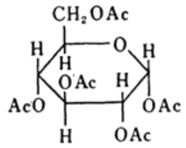
(III)



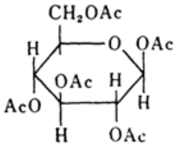
(IV)



(V)



(VI)



(VII)

6-Desoxy-6-ethylxanthogen-β-D-glucopyranose tetraacetate (compound VII).

---

[1] Y. Tsuzuki, K. Tanaka and K. Tanabe, This Bulletin, 35, 1614 (1962).

## Results and Discussion

The RD curves of these compounds are shown in Figs. 1, 2 and 3. Figure 1 shows distinctly the difference between $\alpha$- and $\beta$-anomers. The rotatory background of the $\alpha$-form I is, as expected, more positive, but its Cotton effect is negative in sign, the peak being 380 m$\mu$, whereas the $\beta$-form II shows a stronger, positive Cotton effect (the peak being 381 m$\mu$, the trough, 334 m$\mu$).

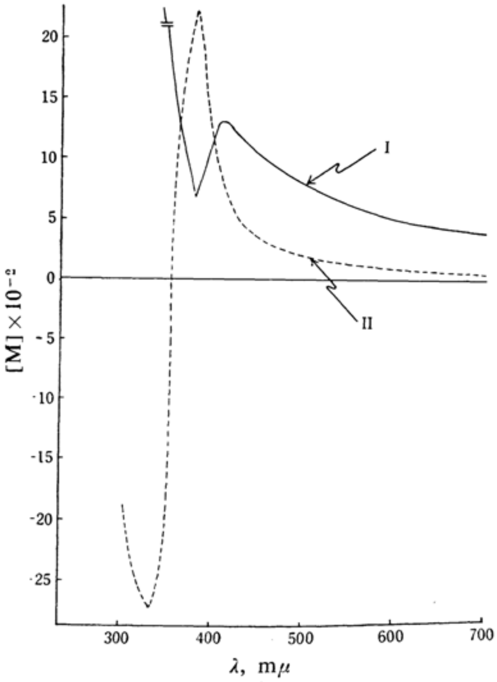


Fig. 1. RD of $\alpha$- and $\beta$-1-xanthogen glucose.

Figure 2 shows the effects of the $C_2$ and $C_5$ groups on the rotatory contribution in the $\beta$-xanthate series, which exhibit, without exception, obviously positive Cotton effects. Since, in D-glucose and D-xylose and their derivatives, the $C_2$ group is expected to contribute to the positive rotation, it is possible that the glucosamine derivative V, being a $\beta$-configuration, is distinguished from others in high rotation. Its molecular amplitude (the difference of [M] between peak and trough) is also far greater. It is observed that the $C_5$ effect is insignificantly small when it carries no chromophoric group. The [M] values of these compounds are almost identical above the absorption region, irrespective of the $C_5$ groups (H, $COOCH_3$, $CH_2OCOCH_3$) ; however in molecular amplitude there are little grades of difference which might be of some significance as to the configuration and the group of optically-active absorption, but at present the authors can not consider this point since the sign of the rotatory contribution of the $C_5$ group has not yet been elucidated. It should, however, be pointed out that all the peaks are situated near 380 m$\mu$, the troughs at 334 m$\mu$, and $\lambda_0$, the optically-active absorption maximum, at 360 m$\mu$.

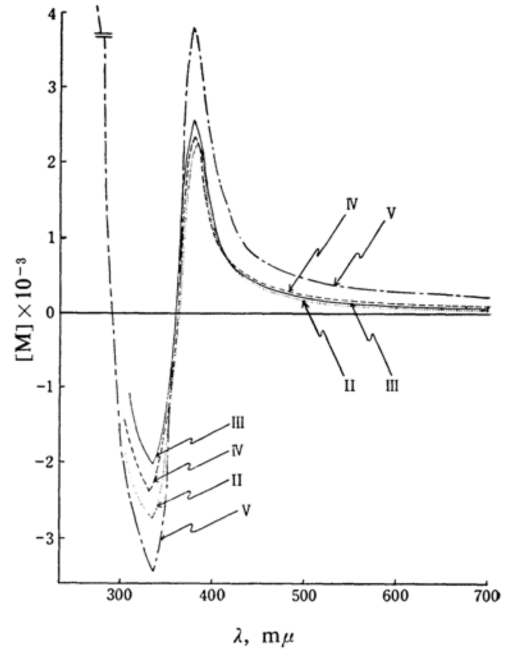


Fig. 2. RD of $\beta$-1-xanthates.

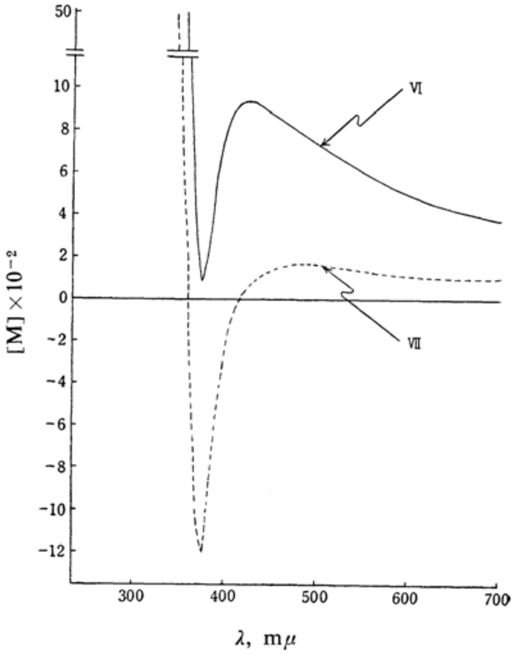


Fig. 3. RD of 6-xanthogen $\alpha$- and $\beta$-acetylglucose.

TABLE I. RD COSTANTS AND UV ABSORPTION MAXIMA

| Compound | Rotatory dispersion | | | | Molecular amplitude | Ultraviolet absorption | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Peak | | Trough | | | R-band | | K-band | |
| | mμ | [M] | mμ | [M] | ×$10^{-1}$ | mμ | ε | mμ | ε |
| I | 380<br>(negative) | +686° | — | — | — | 363 | 32.0 | 276 | 4280 |
| II | 381 | +2220° | 334 | −2720° | 494° | 363 | 36.4 | 275 | 10400 |
| III | 378 | +2510° | 335 | −2010° | 452° | 364 | 42.5 | 275 | 9750 |
| IV | 378 | +2270° | 330 | −2320° | 459° | 360 | 40.0 | 274 | 3330 |
| V | 378 | +3780° | 335 | −3340° | 712° | 360 | 42.3 | 276 | 11400 |
| VI | 375<br>(negative) | +98.7° | — | — | — | 356 | 49.7 | 279 | 13100 |
| VII | 376<br>(nagative) | −1190° | — | — | — | 356 | 40.4 | 279 | 12900 |

It can readily be seen from Fig. 3 that the negative Cotton effects are both due to the $C_6$-xanthate groups, the $\alpha$-anomer VI showing the RD curve of the greater positive rotation, as expected. The negative peaks are in both cases situated at 375 mμ.

Some characteristic constants of the Cotton effects are collected in Table I, together with those of the ultraviolet absorption, which were measured with a self-recording spectrophotometer of the Hitachi EPU-II type.

The values of $\lambda_0$ practically coincide with those of the absorption maximum of the weak band due to the $-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{S}$ group. The absorption maxima of the strong K-band due to the $>\mathrm{C}{=}\mathrm{S}$ moiety are also inserted in the table, although the latter may have no direct relation with the optical activity in these cases.

### Expression by the Two-term Drude Equation and the Physical Meaning of the Dispersion Constants

In the expectation that the dispersion data would conform, at least approximately, to the two-term Drude equation:

$$[\mathrm{M}] = \frac{A_1}{\lambda^2 - \lambda_1{}^2} + \frac{A_2}{\lambda^2 - \lambda_2{}^2}$$

the authors carried out very complicated calculations by means of the least square method using an electronic computer of the Fuji FACOM 201 type. The results are shown in Table II. The agreement between the observed and the calculated values of rotation is tolerably good, the difference between them being mostly only a few per cent outside the absorption region, although in the neighborhood of the absorption center it sometimes rises to even fifty per cent.

TABLE II. DISPERSION CONSTANTS FOR D-GLUCOSE DERIVATIVES (BY THE TWO-TERM DRUDE EQUATION)

| Compound | $A_1$ | $A_2$ | $\lambda_1{}^2$ | $\lambda_2{}^2$ |
|---|---|---|---|---|
| I | 167.77 | −6.544 | $0.211^2$ | $0.370^2$ |
| VI | 204.39 | −29.83 | $0.202^2$ | $0.353^2$ |
| VII | 67.13 | −19.90 | $0.209^2$ | $0.366^2$ |

As may be seen in Table II, the values of $\lambda_2$ thus calculated from the dispersion data are in the neighborhood of 360 mμ and practically coincide with the corresponding absorption maxima of the R-band shown in Table I; therefore, their physical meaning is self-evident. The strength and sign of the rotatory contribution of the chromophor is embodied in the term of $A_2$, which is, in these compounds, negative in sign and relatively small as compared to $A_1$, an important factor in the residual rotation. The negative sign of $A_2$ is natural, since the negative Cotton effects of compounds VI and VII are obviously to be attributed to their xanthate groups attached to the $C_5$ conformation of the L-type.[2]

The cotton effect is especially feeble in compound I, the value of $A_2$ being particularly small, probably because it is overwhelmed by the strong background of the dextrorotatory $\alpha$-configuration.

On the contrary, all the $\beta$-ethylxanthates (compounds II, III, IV, and V) show distinctly positive Cotton effects, although the optically-active xanthate group is situated in the $\beta$-configuration. This apparent anomaly may also be accounted for by the idea of the inversion of the sign of rotation, as has been suggested in a previous paper.[1]

With these $\beta$-ethylxanthates the dispersion

---

[2] In a previous, preliminary paper (This Bulletin, 35, 1617) the authors (Y. T. and K. T.) provisionally interpreted the apparently positive, feeble Cotton effect of a derivative of D-glucose 6-benzylxanthate in terms of the inversion of the sign of rotation, but it is now realized that the Cotton effect should be judged as negative, considering the position of the negative peak. Reinvestigation of this point, together with recalculation, is being made; the results will be published in due time.

data conform more suitably to the following abbreviated two-term expression of the Drude equation :

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

The results of calculations are shown in Table III. The agreement with the experimental results is not yet satisfactory, the difference between them often exceeding several percentage points, even outside the absorption region. It may be advisable to study them more fully, but at present the authors think they can preliminarily offer some interesting stereochemical information.

TABLE III. DISPERSION DATA FOR $\beta$-ETHYLXANTHATES
(BY AN ABBREVIATED TWO-TERM DRUDE EQUATION)

| Compound | $A$ | $B$ | $\lambda_c{}^2$ |
|---|---|---|---|
| II | −13.68 | 27.33 | $0.369^2$ |
| III | −2.38 | 23.28 | $0.361^2$ |
| IV | −3.88 | 33.43 | $0.357^2$ |
| V | 46.23 | 39.62 | $0.362^2$ |

As may be seen in Table III, the values of $\lambda_c$ are again nearly 360 m$\mu$, practically in good accord with the corresponding absorption maxima of the R-band shown in Table I. In contrast to the former cases (Table II), the values of $B$ are positive, showing that the sign of the Cotton effects is definitely positive. The first term, $A/\lambda^2$, of the equation is the sum of the rotational contributions from the other optically-active centers. In the first three compounds (II, III, IV), the sign $A$ is negative, presumably because the basically strong levorotation of the $\beta$-configuration predominates, while in the last compound V, the acetamino group of the D-configuration is, as has already been mentioned, likely to overwhelm the other, partial rotations.

## Experimental

The rotatory dispersion was measured with a Rudolph spectropolarimeter, mostly at 22.5~22.6°C over the wavelength region of 270 to 700 m$\mu$. Under each compound several values of the specific rotation will be described so as to indicate the main features of the RD curve.

As the light source a xenon lamp was used. The length of the layer was 1 dm., but below 380 m$\mu$ 0.1 dm.

**2, 3, 4, 6-Tetra-*O*-acetyl-$\alpha$-D-glucopyranosyl Ethylxanthate[3] (Compound I).**—Syrup. $[\alpha]_D=+133.2°$ ($c$ 1.1, chloroform).[3] The RD was measured at 22.6°C in tetrahydrofuran (T.H.F.) ($c$ 1.1934). $[\alpha]_{700}$ 86.06°, $[\alpha]_{600}$ 114.8°, $[\alpha]_{589}$ 119.7°, $[\alpha]_{500}$ 173.5°, $[\alpha]_{412}$ 291.3° (broad extreme), $[\alpha]_{400}$ 256.5°, $[\alpha]_{380}$ 152° (negative peak), $[\alpha]_{315}$ 838°.

**2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl Ethylxanthate (Compound II).[4,5]** — M. p. 75~76°C. $[\alpha]_D=+30.0°$ ($c$ 1.2, chloroform).[5] The RD was measured at 22.5°C in T.H.F. ($c$ 1.0176). $[\alpha]_{700}$ 11.3°, $[\alpha]_{600}$ 17.8°, $[\alpha]_{589}$ 19.5°, $[\alpha]_{500}$ 39.2°, $[\alpha]_{400}$ 247.6°, $[\alpha]_{381}$ 491° (peak), $[\alpha]_{334}$ −601° (trough), $[\alpha]_{305}$ −416°.

**2,3,4-Tri-*O*-acetyl-$\beta$-D-xylopyranosyl Ethylxanthate (Compound III).[6]**—M. p. 105~105.5°C, $[\alpha]^{25}_D$ 17.30° (chloroform). The RD was measured at 22.6°C in T.H.F. ($c$ 1.0391). $[\alpha]_{700}$ 15.69°, $[\alpha]_{600}$ 21.80°, $[\alpha]_{589}$ 23.53°, $[\alpha]_{500}$ 62.75°, $[\alpha]_{400}$ 305.1°, $[\alpha]_{378}$ 660° (peak), $[\alpha]_{335}$ −529° (trough), $[\alpha]_{310}$ −292°.

**Methyl 2, 3, 4-Tri-*O*-acetyl-$\beta$-D-glucopyranuronate 1-Ethylxanthate (Compound IV).[7]**—M. p. 114~115°C, $[\alpha]^{16}_D=42.0°$ ($c$ 1, chloroform).[7] The RD was measured at 23.8°C in T.H.F. ($c$ 0.4404). $[\alpha]_{700}$ 20.4°, $[\alpha]_{600}$ 29.1°, $[\alpha]_{589}$ 32.5°, $[\alpha]_{500}$ 56.5°, $[\alpha]_{400}$ 234°, $[\alpha]_{378}$ 518° (peak), $[\alpha]_{330}$ −529° (trough), $[\alpha]_{305}$ −341°.

**2-Acetamido-2-desoxy-3, 4, 6-tri-*O*-acetyl-$\beta$-D-glucopyranosyl Ethylxanthate (Compound V).[8]**— M. p. 142~143°C, $[\alpha]^{15}_D=+36.1°$ ($c$ 1.2, chloroform).[8] The RD was measured at 22.0°C in T.H.F. ($c$ 0.1997). $[\alpha]_{700}$ 46.1°, $[\alpha]_{600}$ 60.1°, $[\alpha]_{589}$ 64.6°, $[\alpha]_{500}$ 104.7°, $[\alpha]_{400}$ 461.7°, $[\alpha]_{378}$ 838.8° (peak), $[\alpha]_{335}$ −740° (trough), $[\alpha]_{300}$ −531°, $[\alpha]_{270}$ +3830°.

**6-Desoxy-6-ethylxanthogen-$\alpha$-D-glucopyranose Tetraacetate (Compound VI).[9]** — M. p. 129~130.0°C, $[\alpha]_D=+98.9°$ ($c$ 0.8, chloroform).[9] The RD was measured at 22.6°C in T.H.F. ($c$ 0.8714). $[\alpha]_{700}$ 85.84°, $[\alpha]_{600}$ 110.5°, $[\alpha]_{589}$ 114.3°, $[\alpha]_{500}$ 161.5°, $[\alpha]_{424}$ 206.7° (broad extreme), $[\alpha]_{400}$ 178.0°, $[\alpha]_{375}$ 21.8° (negative peak), $[\alpha]_{320}$ 1230°.

**6-Desoxy-6-ethylxanthogen-$\beta$-D-glucopyranose Tetraacetate (Compound VII).[9]** — M. p. 121~123°C, $[\alpha]^{24}_D=+23.2°$ ($c$ 1.1, chloroform).[9] The RD was measured at 22.5°C in T.H.F. ($c$ 0.9656). $[\alpha]_{700}$ 21.75°, $[\alpha]_{600}$ 26.20°, $[\alpha]_{589}$ 27.34°, $[\alpha]_{500}$ 34.07°, $[\alpha]_{490}$ 34.9° (broad extreme), $[\alpha]_{400}$ −51.9°, $[\alpha]_{376}$ −263° (negative peak), $[\alpha]_{310}$ +1088°.

*Department of Chemistry*
*Tokyo College of Science*
*Kagurazaka, Tokyo (Y. T. & K. T.)*

*Faculty of Pharmaceutical Sciences*
*School of Medicine*
*Hokkaido University*
*Sapporo (M. A. & S. T.)*

---

[3] M. Akagi et al., unpublished.

[4] W. Schneider, R. Gille and K. Eisfeld, *Ber.*, **61**, 1244 (1928).

[5] M. Akagi, S. Tejima and M. Haga, to be published.

[6] M. Gehrke and W. Kohler, *Ber.*, **64**, 2696 (1931).

[7] M. Akagi, S. Tejima and M. Haga, *Chem. & Pharm. Bull.*, **8**, 1114 (1960).

[8] M. Akagi, S. Tejima and M. Haga., ibid., **9**, 360 (1961).

[9] M. Akagi et al., ibid., **10**, 562 (1962).