The Rotatory Dispersion and Stereochemistry of Organic Compounds. VIII.[1] Mono- and Dinitrates of Glucopyranose (Preliminary Report)

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In previous papers it has been reported that the chromophores containing sulfur atoms exercise predominant roles in the rotatory dispersion (RD) of sugar xanthates[2-4] and sugar sulfides[1]. This paper will report on similar studies of the rotatory contribution of a nitrogen-containing chromophore $-O-NO_2$ (nitrate).

Although the nitrate chromophore has never been studied with respect to the RD, it has been reported by Mitchell et al.[5] that dinitrocamphane exhibits an intense negative Cotton effect, and some interesting information has been obtained with several nitro-compounds with regard to the RD.[6,7] Recently Djerassi et al.[8] have studied the circular dichroism and RD of compounds containing a nitro chromophore.

On the other hand, it has been shown with aliphatic nitro-compounds[9,10] that the nitro group exhibits an intense absorption band around 210 mμ and a weak band around 270 mμ due to the $n \rightarrow \pi^*$ transition. Similarly, some alkyl nitrates have also been shown to have a feeble absorption band due to the $n \rightarrow \pi^*$ transition.[9] Thus, it can be expected that with sugar nitrates also the nitrate chromophore will exhibit an optically active absorption. In this paper the following compounds will be investigated with the object of studying how the C_2- and C_3-ONO_2 groups affect the RD of glucose:

Methyl 4:6-*O*-benzylidene-α-D-glucopyranoside 3-nitrate (compound I),

Methyl 4:6-*O*-benzylidene-α-D-glucopyranoside 2,3-dinitrate (compound II),

Methyl 4:6-*O*-benzylidene-α-D-glucopyranoside (compound III),

3,4,6-Tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride (compound IV),

1,3,4,6-Tetra-*O*-acetyl-2-*O*-nitro-α-D-glucopyranoside (compound V),

3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyl chloride (compound VI),

Pentaacetyl-α-D-glucose (compound VII).

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

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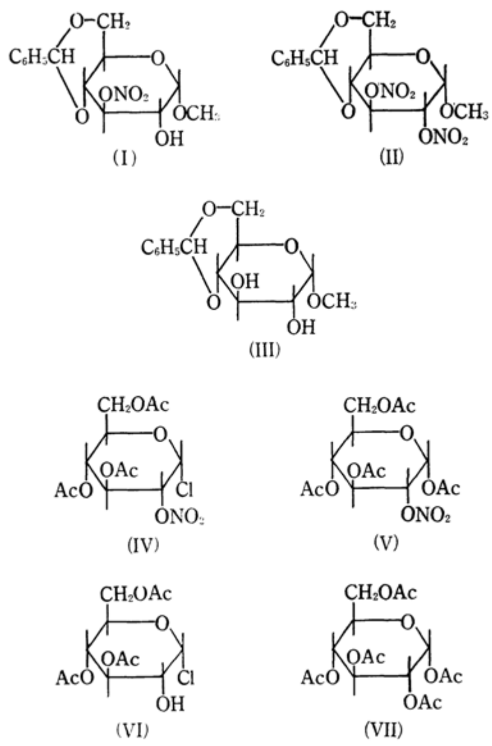

Fig. 1. Structural formulas of investigated glucopyranosides.

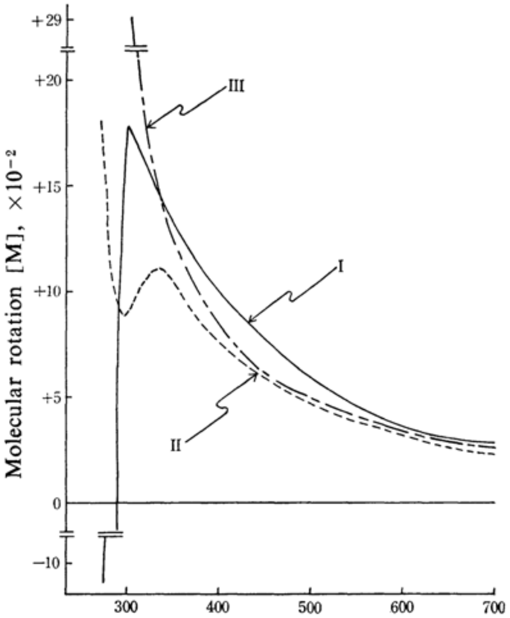

Fig. 2. RD of I—III.

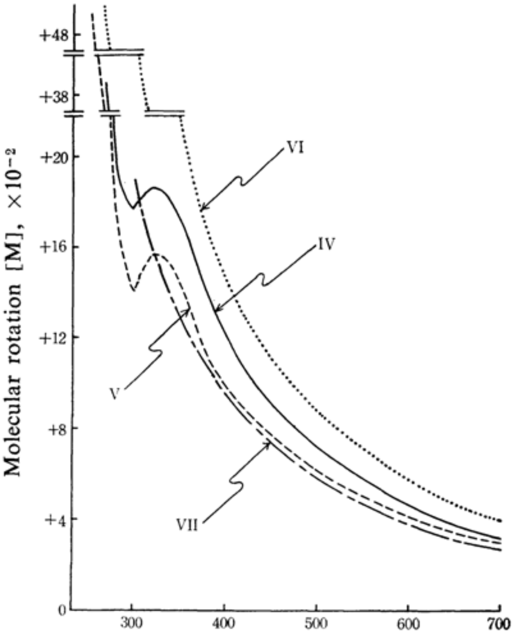

Fig. 3. RD of IV—VII.

Results and Discussion

The RD curves of compounds I, II and III are shown in Fig. 2. Curve III is considered to represent the background rotation of curves I and II. As is shown in Fig. 4, the ultraviolet absorption spectra of compounds I and II are found to have the λ_{max} at 250—270 mμ, and their absorption is optically active.

As is evident from Fig. 2, compound I (C_3-nitrate) exhibits a positive Cotton effect (the peak at 300 mμ), while compound II (2, 3-dinitrate) shows a very feeble negative Cotton effect. The broad peak around 335 mμ of curve II is produced from the positive background RD of curve III superposed by a slight negative Cotton effect, the peak of which appears at 295 mμ, nearly identical with the peak (300 mμ) of the Cotton effect of curve I.

Thus, the C_3-ONO_2 group may be supposed to give rise to a positive Cotton effect, as the C_3-xanthate group does in glucose,[2,4] even though the C_3-group of glucose is usually believed to make a levo-rotatory contribution because of the β-type of C_3-configuration (i. e., the inversion of the sign of rotation).

In comparing the C_2-ONO_2 group with the 3-nitrate in rotatory contribution, the value of the $[\alpha]_D$ of the 2, 3-dinitrate (compound II) is lower than that of the 3-nitrate (compound I), and Honeyman et al.[11] have given a value of 104° to the specific rotation of methyl 4 : 6-*O*-benzylidene-α-D-glucopyranoside 2-nitrate, which is also lower than that of the corresponding 3-nitrate. These facts suggest that the

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[11] J. Honeyman and J. W. W. Morgan, *J. Chem. Soc.*, **1955**, 3669.

C_2-ONO_2 group contributes somewhat to the negative rotation.

In order to make a further study of the rotatory contribution of the C_2-ONO_2 group, compounds IV and V have also been studied.

The RD curves of compounds IV and V are shown in Fig. 3, together with those of VI and VII as illustrations of the background curves. As may be seen in Fig. 2, the absorption maxima appear at the region of 295—300 mμ in the RD due to the nitrate chromophore. The peaks around 325 mμ on the curves of IV and V are properly to be attributed to a small Cotton effect (negative peak around 300 mμ) overlapped on the positive background RD curves. Thus, the Cotton effects of compounds IV and V are to be judged negative in sign, the negative peaks being located respectively at 295 and 300 mμ, quite in coincidence with those of compounds I and II (Fig. 2).

In a previous paper⁴⁾ it has been shown that the C_2-$OCOCH_3$ group in D-mannose exhibits a negative rotatory contribution; accordingly, the C_2 group of D-glucose (of α-configuration) may be presumed to contribute to the positive rotation. However, the Cotton effects of IV and V due to the nitrate group in the C_2 position are to be considered negative in sign, as has already been stated and as may be seen in Fig. 3, so the nitrate group may also be assumed to exhibit an inversion effect in the sign of rotation, as has already been observed and pointed out with several xanthates.²,³⁾

The ultraviolet absorption spectra of compounds I and II are given in Fig. 4, and those of IV and V, in Fig. 5. The first two curves are distinguished in that both exhibit fine structures in the region of 250—270 mμ, the forms of which structure are almost entirely identical in chloroform as well as in tetrahydrofuran. It is worthy of note that the ultraviolet absorption curves of I and II rather resemble those of alkyl nitrates,⁹⁾ although the nitrites exhibit weak absorption bands (ε ~80) of fine structures in the longer wavelength region around 370 mμ.

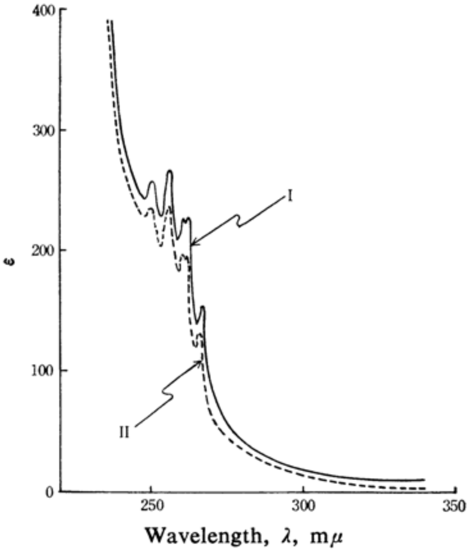

Fig. 4. UV absorption spectra of I and II.

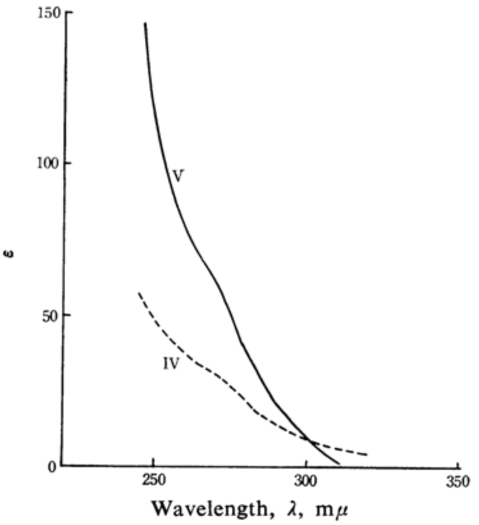

Fig. 5. UV absorption spectra of IV and V.

Compounds IV and V do not exhibit any noticeable ultraviolet absorption in tetrahydrofuran; although in chloroform their curves do show slight anomalies, they do not exhibit so distinct inflections as are observed in alkyl nitrates,⁹⁾ which occur around 270 mμ (ε ~20.¹²⁾

Apparently the ultraviolet absorption curves of these compounds (IV and V) have no relation to the behaviors of RD, but it is worthy of attention that the RD curves exhibit optically active absorptions at longer wavelengths of 295—300 mμ, and that also in some nitrites the first peaks of the Cotton effects are situated at longer wavelengths than are the ultraviolet absorption maxima⁸⁾ by 10—20 mμ.

With the nitro-chromophore such red shifts have also been observed as with the first peaks of RD, which are displaced toward longer wavelengths from the ultraviolet absorption maxima.

It is thus reasonable, in view of the above-stated facts, to assume that the peaks of the Cotton effects due to the nitrate chromophore are observed at wavelengths about 20 mμ

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12) It is likely that distinct absorption maxima will result if the spectra are taken in less polar solvents. See C. N. R. Rao, "Ultra-violet and Visible Spectroscopy," Butterworths, London (1961), p. 22.

longer than the ultraviolet absorption maxima.

Finally, it should be noted that the authors, as usual, have tried to express the RD by means of the equations of Drude, but the complex RD curves could not successfully be expressed. This is probably because the shapes of the curves are peculiar, and because the falls between the peaks of the feeble Cotton effects are too small. The values of the dispersion constants obtained by the usual calculation method often fail to give proper physical significance. Further detailed studies will be necessary for a quantitative analysis and for more comprehensive treatment of the dispersion data.

Experimental

The derivatives of glucose were prepared according to the methods of the literature. The rotatory dispersion was measured with a Rudolph spectropolarimeter over a wavelength region from about 265 mμ to 700 mμ. The ultraviolet absorption was measured with a self-recording spectrophotometer of Hitachi EPU-II type.

Methyl 4 : 6-O-Benzylidene-α-D-glucopyranoside 3-Nitrate (Compound I).[11] — Colorless crystals, m. p. 168—169°C. The RD was measured at 22.5°C in tetrahydrofuran (c 0.0939). $[\alpha]^{22.5}_{700}$ +87.3°, $[\alpha]_{589}$ +118°, $[\alpha]_{500}$ +179°, $[\alpha]_{400}$ +305°, $[\alpha]_{300}$ +544° (peak), $[\alpha]_{275}$ −330°.

Methyl 4 : 6-O-Benzylidene-α-D-glucopyranoside 2 : 3-Dinitrate (Compound II).[11] — Needles, m. p. 122—123°C. The RD was measured at 22°C in tetrahydrofuran (c 0.9623). $[\alpha]^{22}_{700}$ +66.1°, $[\alpha]_{589}$ +90.5°, $[\alpha]_{500}$ +127°, $[\alpha]_{400}$ +202°, $[\alpha]_{335}$ +297° (broad extreme), $[\alpha]_{295}$ +241° (negative peak), $[\alpha]_{270}$ +483°.

Methyl 4 : 6 - O - Benzylidene - α - D - glucopyranoside (Compound III).[13]—Needles, m. p. 163—164°C. The RD was measured at 20°C in chloroform (c 0.1). $[\alpha]_{650}$ +95.0°, $[\alpha]_{589}$ +123°, $[\alpha]_{400}$ +320°, $[\alpha]_{305}$ +1101°.

3,4,6-Tri-O-acetyl - 2 - O - nitro - α - D - glucopyranosyl Chloride (Compound IV).[14] — Syrup. The RD was measured at 21°C in chloroform (c 0.5935). $[\alpha]^{21}_{700}$ +85.1°, $[\alpha]_{589}$ +132°, $[\alpha]_{500}$ +192°, $[\alpha]_{400}$ +333°, $[\alpha]_{325}$ +505° (broad extreme), $[\alpha]_{295}$ +492° (negative peak), $[\alpha]_{265}$ +1054°.

1,3,4,6-Tetra-O-acetyl-2-O-nitro-α-D-glucopyranose (Compound V).[14] — Needles, m. p. 91°C. The RD was measured at 21°C in chloroform (c 1.2886). $[\alpha]^{21}_{700}$ +77.5°, $[\alpha]_{589}$ +108°, $[\alpha]_{500}$ +154°, $[\alpha]_{400}$ +252°, $[\alpha]_{320}$ +403° (broad extreme), $[\alpha]_{300}$ +358° (negative peak), $[\alpha]_{255}$ +1242°.

3,4,6 -Tri - O - acetyl - α - D - glucopyranosyl Chloride (Compound VI).[15] — Needles, m. p. 93—94°C. The RD was measured at 21°C in chloroform (c 0.9374). $[\alpha]^{21}_{700}$ +126°, $[\alpha]_{589}$ +184°, $[\alpha]_{500}$ +268°, $[\alpha]_{400}$ +465°, $[\alpha]_{300}$ +1038°, $[\alpha]_{250}$ +1900°.

Pentaacetyl-α-D-glucopyranoside (Compound VII).[16] —Colorless crystals, m. p. 112—113°C. The RD was measured at 21°C in chloroform (c 1.0820). $[\alpha]^{21}_{700}$ +68.6°, $[\alpha]_{589}$ +102°, $[\alpha]_{500}$ +146°, $[\alpha]_{400}$ +245°, $[\alpha]_{300}$ +486°.

Summary

The RD and ultraviolet absorption have been observed with some derivatives of glucose carrying a nitrate group in the C_2 and C_3 positions in order to study the optical contributions of the C_2- and C_3-ligands with respect to their configurations.

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