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The Optical Rotatory Dispersion and Circular Dichroism of Levoglucosenone

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Synopsis. The ORD and CD of levoglucosenone were measured in order to elucidate its abnormally large $[\alpha]_D$ value of $-524°$.[1] The complicated pattern observed was considered to contain three Cotton effects—at 357, 231 and 207 nm; the first one at 357 nm seems to be responsible for the large $[\alpha]_D$ value.

In our previous paper,[1] anhydro sugar homologues, such as levoglucosan (1,6-anhydro-β-D-glucopyranose) (II), 1,6-anhydro-3-deoxy-β-D-glucopyranosen (III),[1,2] and levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glucopyranosen-2-one) (IV),[1,3] were determined to be the primary pyrolysis products of cellulose using Curie-point pyrolysis-gas liquid chromatography. Compound IV was first identified by Halpern *et al.*[3] in 1973; its abnormally large $[\alpha]_D$ value has been reported to be $-460°$ ($CHCl_3$, *c* 1.0)[3] and $-524°$ (C_2H_5OH, *c* 1.0),[1] while those of D-glucose (I), II and III are of the usual magnitude, as Table 1 shows. To elucidate this abnormality, the optical rotatory dispersions (ORDs) and circular dichroisms (CDs) of IV and its related compounds were measured in the wavelength region of 600—190 nm using a JASCO model J-20 spectropolarimeter. The results are shown in Figs. 1 and 2.

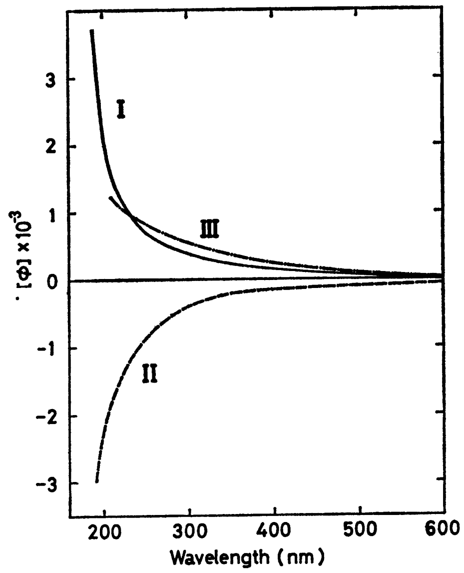


Fig. 1. The ORD curves of D-glucose (I), levoglucosan (II) and 1,6-anhydro-3-deoxy-β-D-glucopyranosen (III) measured in H_2O (I, II) or in C_2H_5OH (III) at 20 °C.
The ordinate is expressed in terms of molar rotation, $[\phi]$.

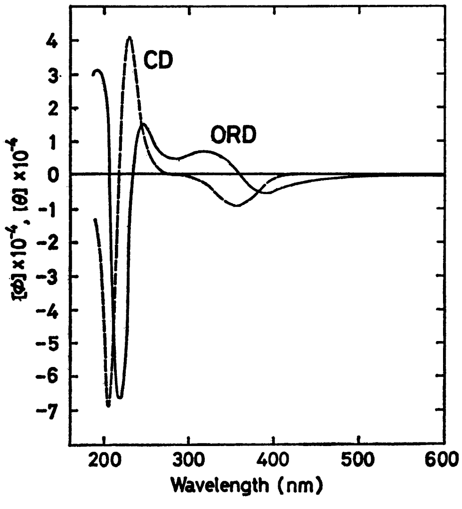
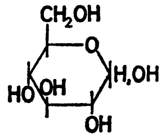
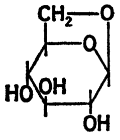
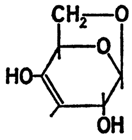
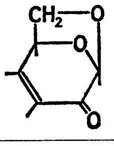


Fig. 2. The ORD and CD curves of levoglucosenone measured in C_2H_5OH at 20 °C.
The ordinate is expressed in terms of molar rotation, $[\phi]$, or molar ellipticity, $[\theta]$.

Table 1. The optical rotation at 589 nm

Compound	Formula	$[\alpha]_D$	Solvent	Reference
I		+52.7°	H_2O	4)
II		−66.5°	H_2O	5)
III		+86°	C_2H_5OH	2)
IV		−460° −524°	$CHCl_3$ C_2H_5OH	3) 1)

Compounds I and III showed a simple positive dispersion of the ORD curves, whereas Compound II showed a simple negative dispersion, as may be seen in Fig. 1. On the contrary, IV showed a complicated ORD curve with peaks at 328 ($[\phi]=+6500°$), 246 (+15000°), and 195 (+31500°) nm and troughs at 390 (−6000°), 293 (+4500°), and 217 (−66500°) nm, as may be seen in Fig. 2. From the CD curves of IV, the first negative Cotton effect, involving the 390 nm trough and the 328 nm peak of the ORD curve, was observed at 357 nm. The second positive Cotton effect, involving the 246 nm peak and the 217 nm trough of the ORD curve, was observed at 231 nm. The third negative Cotton effect, involving the 217 nm trough and the 195 nm peak of the ORD curve, was observed at 207 nm. The negative Cotton effect at 357 nm seems to correspond to the absorption band at 355 nm (ε 85, n-π^*)¹⁾ of the carbonyl group while the other two Cotton effects may correspond to the absorption band at 217 nm (ε 6000, π-π^*).¹⁾

The abnormally large $[\alpha]_D$ value of IV seems to be due to the negative Cotton effect at 357 nm.

References

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