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DETECTION BY CIRCULAR DICHROISM OF INVERSIONS IN SUGAR OSAZONE DERIVATIVES

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Sugar osazones (1,2) and their acetates have circular dichroism spectra with multiple Cotton effects, showing three typical bands. Band I is located between 340 and 420 nm, with a negative Cotton effect, when the C-3 hydroxyl is to the right in the Fischer-formula. Band II is located between 240 and 340 nm, and shows two maxima with inverse Cotton effect compared to the Cotton effect of Band I. Band III is located between 240 and 230 nm, and shows a reversed Cotton effect with regard to band II. If the C-3 hydroxyls are located to the left in the Fischer-formula, the circular dichroism spectra are symmetrically reversed. Symmetry centers other than those of C-3 affect only the intensity of band I.

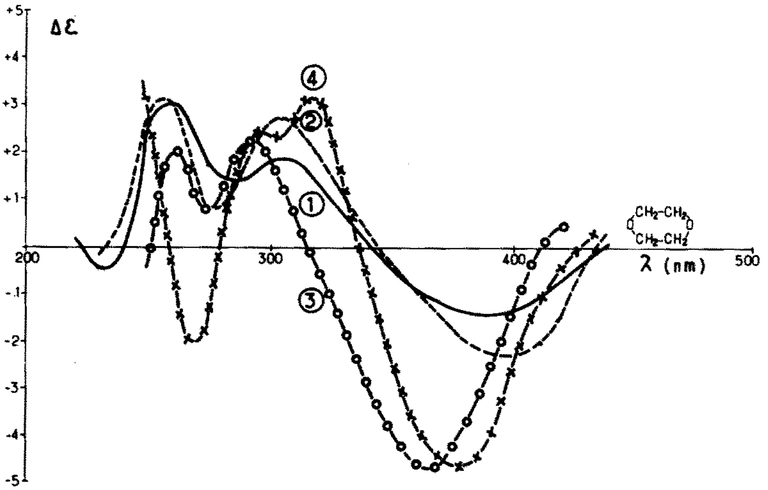
Sugar osazone derivatives, like Diels anhydro-osazones (3), dehydro-osazones (4) and Percival dianhydro-osazones (5), have essentially similar circular dichroism spectra; the derivatives which have at C-3 a free or substituted hydroxyl to the right in the Fischer-formula, show multiple Cotton effects similar in sign to those of sugar osazones having the C-3 hydroxyl to the right, and vice versa. In all cases, the configuration of C-3 determines the signs of the multiple Cotton effects in the same manner.

In the circular dichroism spectra of Diels anhydro-osazones the intensity of the two maxima of band II are nearly equal. In dehydro-osazones the two nearly equal maxima of band II are compressed into an area between 250 to 315 nm, and they show very important bands I and III. In Percival's dianhydro-osazones band II is compressed into the area between 280 to 340 nm, forming a slightly accentuated double maxima followed by an important band III, which is located between 260 and 280 nm (figure 1.).

During the preparation of Diels anhydro-osazones (6,7), dehydro-osazones (8) and Percival's dianhydro-osazones (9,10,11) inversions at C-3 are often observed. However, no general rule was formulated to predict in which case such an inversion would be expected. The inversion at C-3 was often established by comparison with the corresponding isomer (enantiomer or diastereomer). However, it was not easy to determine which of the two isomers suffered inversion.

A systematic comparison of the circular dichroism spectra of the above mentioned compounds permitted the establishment of a general empirical rule regarding the inversion at C-3 :

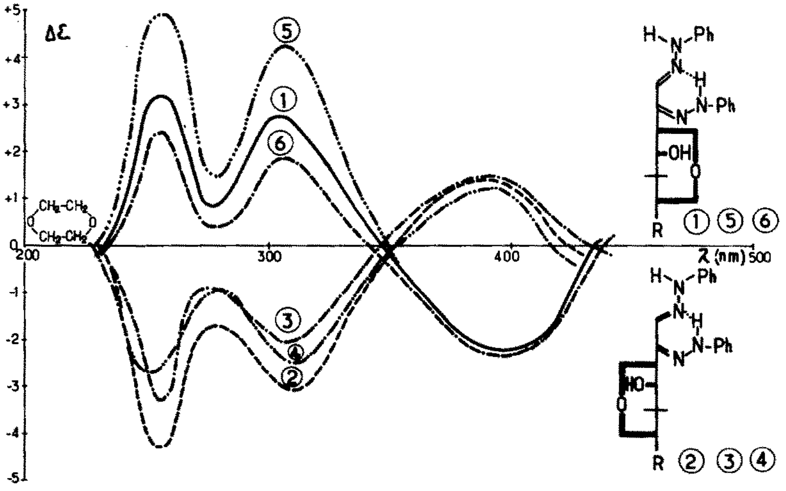
Fig. 1



CIRCULAR DICHROISM OF SUGAR OSAZONE DERIVATIVES

① ——— Phenylosazones
② ------- Diels anhydro-osazones
③ o–o–o– Dehydro-osazones
④ x–x–x– Percival's dianhydro-osazones

Fig. 2

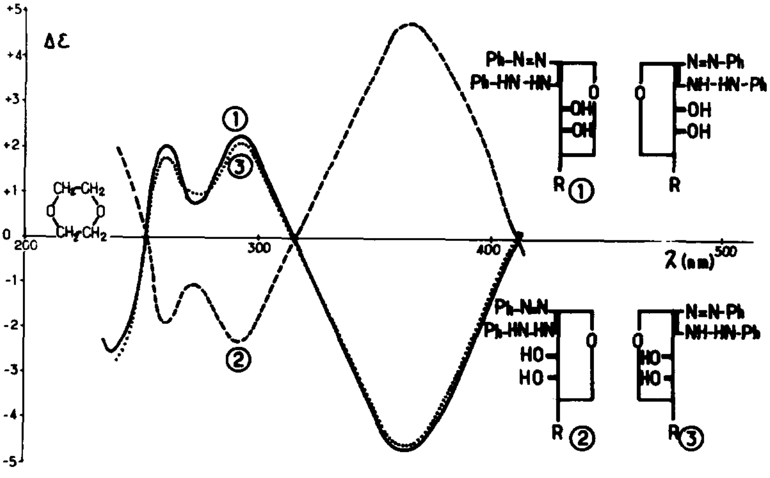


CIRCULAR DICHROISM OF DIELS ANHYDRO SUGAR OSAZONES

PREPARED FROM:

① ——— D-*arabino*-Hexulose phenylosazone
② ---- D-*lyxo*-Hexulose phenylosazone
③ –·–·– D-*gluco*-Heptulose phenylosazone
④ –··– D-*galacto*-Heptulose phenylosazone
⑤ –···– 7-Desoxy-L-*manno*-heptulose phenylosazone
⑥ –·–·– D-*glycero*-D-*gulo*-Octulose phenylosazone

Fig. 3



CIRCULAR DICHROISM OF DEHYDRO SUGAR OSAZONES

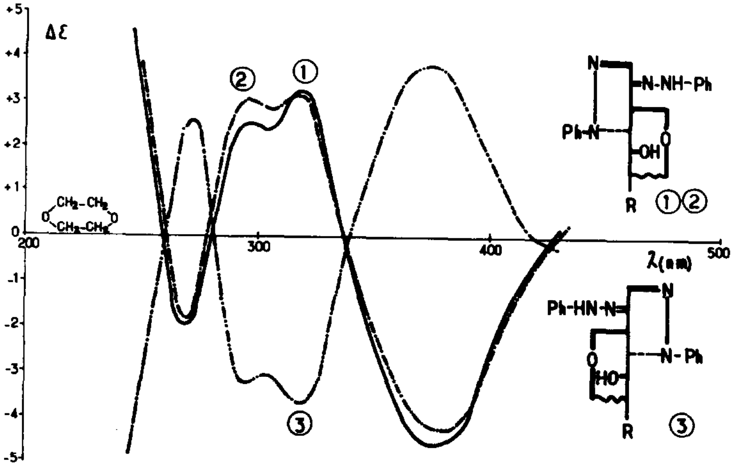
PREPARED FROM:

① ——— D-*arabino*-Hexulose phenylosazone (D-glucosazone)

② - - - - - D-*lyxo* - Hexulose phenylosazone (D-galactosazone)

③ ············ L-*xylo*-Hexulose phenylosazone (L-gulosazone)

Fig. 4



CIRCULAR DICHROISM OF PERCIVAL'S DIANHYDRO SUGAR OSAZONES

PREPARED FROM:

① ——— D-Hexulose phenylosazones

② —·—·— D-*gluco* Heptulose phenylosazone

③ —··—··— D-*galacto*-Heptulose phenylosazone

"In anhydro-and dehydro-osazones the carbon atom in position three always seeks to acquire the configuration of the subsequent carbon atom not involved in ring formation".

Thus, in the case of Diels anhydro-osazones and dehydro-osazones the C-3 atom endeavours to have the same configuration as C-4 (figures 2 and 3). In Percival's dianhydro-osazones the C-4 atom being involved in a diazine ring, the C-3 atom, strives to have the same configuration as C-5 (figure 4). Therefore Diels anhydro-osazones and dehydro-osazones undergo inversion at C-3, if in the starting osazone the C-3 and C-4 hydroxyls are in *trans* positions. In Percival's dianhydro-osazones an inversion occurs at C-3, if in the initial osazones the C-3 and C-5 hydroxyls are in opposite positions.

Consequently, starting with 8 hexose phenylosazones, there are only four Diels anhydro-osazones and four dehydro-osazones available : two in the D-series and two in the L-series. Similarly, there is only one D-type and one L-type dianhydro-osazone.

The study of sugar osazones by circular dichroism permits an easy establishment of the C-3 configuration in the parent sugars. The reported circular dichroism of Diels anhydro-osazones and dehydro-osazones enables an easy recognition of the C-4 configuration, while the circular dichroism spectra of Percival's dianhydro-osazones give the same information concerning the C-5 atom.

C. D. Spectra. - Circular dichroism data were recorded in dioxane (c = 40 mg/lt ; l = 1 cm) on a "Dichrograph-II" Jouan, Paris.

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References

1. L. Mester, *Chimia*, *23*, 133 (1969)
2. L. Mester, G. Vass and J. Parello, unpublished results.
3. O. Diels and R. Meyer, *Annalen*, *519*, 157 (1935)
4. O. Diels, E. Cluss, H.J. Stephen and R. König, *Ber*. *71*, 1189 (1938).
5. E. G. V. Percival, *J. Chem. Soc.* 1770 (1936)
6. E. Hardegger and E. Schreier, *Helv. chim. Acta*, *35*, 232, (1952)
7. H. El Khadem, E. Schreier, G. Stöhr and E. Hardegger, *Helv. chim. Acta*, *35*, 993 (1952).
8. L. Mester and E. Moczar, *J. Org. Chem.*, *29*, 247 (1964)
9. E.G.V. Percival, *J. Chem. Soc*. 1384 (1938)
10. G. Henseke, U. Müller and G. Badicke, *Chem. Ber.*, *91*, 2270 (1958)
11. H. El Khadem and M.M.A. Abdel Rahman, *J. Org. Chem.*, *31*, 1178 (1966)