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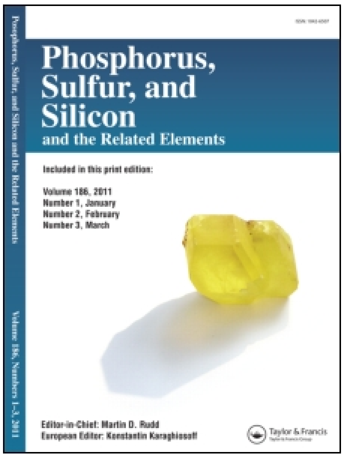

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# CHIROPTICAL PROPERTIES OF 1-DEOXY-1-THIOGALACTOPYRANOSIDES

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# CHIROPTICAL PROPERTIES OF 1-DEOXY-1-THIOGALACTOPYRANOSIDES

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Continuing our studies of optically active sulfides we have investigated flexible systems incorporating the 1.3-O,S-chromophore, e.g., alkyl α- and β-D-thiogalactopyranosides and their tetraacetates. Although most substances were known from the literature, constitutional, configurational, and conformational assignments had hardly ever been proved rigorously; we therefore had to provide a firm basis by a systematic analysis of the $^{1}H$ and $^{13}C$ NMR spectra of thioglycosides, the complexity of the carbohydrate signals necessitating high field studies. The compounds were thus, in the end, correlated with the natural thiogalactoside lincomycin, whose structure including its absolute configuration is known from X-ray investigations. CD curves have been measured at various temperatures in the range of 185-300 nm on a commercial spectropolarimeter equipped with a data processor and connected to a table calculator and plotter, directly furnishing data suitable for, e.g., Kronig-Kramers type transformations or curve analysis and displaying the results. These CD data were correlated with the UV spectra and the ORD curves of the substrates. Typically, the UV curves are devoid of detail except in the case of the acetates, where a shoulder in the region of the $n \longrightarrow \pi^{*}$ transition is discernible. In the ORD, the Cotton effects (CE) are largely suppressed by the background contribution of the "invisible giant" in the far UV. In the thiogalactopyranosides all accessible Cotton effects are associated with electron transitions within the sulfur or possibly the coupled O-C-S chromophore, whereas a relatively small negative, composite CE is contributed by the acetate carbonyl groups in the acetates. The spectroscopic results include (approximate wavelength range of the CE maxima at room temperature and typical $\Delta\varepsilon$ values, in parentheses, given):

1) α-Thiogalactopyranosides
   CE at 220 nm ( +2) and 195 nm ( -2), end absorption (EA) (below approximately 190 nm) strongly negative; $\Delta\varepsilon$ at 250 nm $\leqslant 10^{-3}$

2) ß-Thiogalactopyranosides
CE at 220 nm ( +1) and 195 nm ( +1), EA strongly negative; $\Delta\varepsilon$ at 250 nm $\leqslant 10^{-3}$

3) α-Thiogalactopyranoside tetraacetates
CE at 250 nm ( -0.02), 220 nm ( +0.4), and 195 nm ( -3), EA strongly positive

4) ß-Thiogalactopyranoside tetraacetates
CE at 250 nm ( -0.02) and 220 nm ( +0.4), EA strongly positive.

The significance of these spectral properties will be discussed. Attention will be drawn to the "abnormal" positive D-line rotation of the ß-methyl compounds and its relevance for the application of Hudson's isorotation rule; it is remarkable that only these "exceptional" compounds thus reflect the sign of the Cotton effects above 190 nm. Comparison with the chiroptical properties of simple aliphatic sulfides will point to the stereoelectronic requirements of the $-O-\overset{|}{\underset{|}{C}}-S-$ -chromophore. The waning and waxing of the 250 nm CE in the various sulfides is particularly noteworthy.

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