 shorts communications

Reduction of the lactone with hydrogen iodide. The lactone C₅H₄O₂ (7.25 g), 25 ml hydrogen iodide (1.7) and 2.9 g of yellow phosphorus were refluxed for 10 h. A yellow layer which formed on top of the solution was isolated, washed with water saturated with sulphur dioxide and dried in a desiccator. After distilling at 49—52°C at 0.15 mm Hg the liquid weighed 6.6 g.

367.0 and 313.7 mg subst. gave 382.1 and 308.7 mg AgI, respectively.
(Found I 53.33, 53.29 %, Calc. for C₅H₄I₂
1 53.30 %). d₂₀ 1.5300, d₄₁ 1.462, [MR]found 50.09,
[MR]calc 49.76.

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Determination of the Configuration of β-Amino and β-Hydroxy Acids by Means of Optical Rotatory Dispersion

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It has recently been shown by Sjöberg, Fredga and Lijeras, 1 that the absolute configuration of α-amino and α-hydroxy acids can be readily derived from the sign of the Cotton effect in the anomalous rotatory dispersion curves of the dithio-
carbamate and xanthate derivatives, respectively. Other thiono derivatives have also been employed for similar purposes \(^\ast\). Some \(\beta\)-amino and \(\beta\)-hydroxy acids have recently been isolated from various natural sources. Although the configuration of a number of \(\beta\)-amino and \(\beta\)-hydroxy acids have been determined by chemical means, no well established simple method for the intercorrelation of \(\beta\)-amino and \(\beta\)-hydroxy acids or for the determination of their absolute configuration seems to exist. In fact, even in recent studies \(^\ast\ast\) there have been put forward contradictory interpretations of the steric course of the deamination of \(\beta\)-amino acids. It was therefore interesting to see if dithiocarbamates and xanthates of \(\beta\)-amino and \(\beta\)-hydroxy acids, respectively, would give anomalous rotatory dispersion curves, and if the sign of the Cotton effects could be used in stereochemical work in the same way as has been done in the alpha-series \(^1\).

As model substances in the present study we chose \(\beta\)-aminobutyric acid and \(\beta\)-aminobutyric acid and the corresponding \(\beta\)-hydroxy acids. The absolute configuration of the optically active forms of these acids seems to be well established \(^\ast\ast\). We used the most readily available enantiomers of the four acids; the methyl dithiocarbamates of \(\text{D}-(\)-\(\beta\)-amino-\(\beta\)-phenylpropionic acid (I) and of \(\text{L}-(\)+\(\beta\)-amino-\(\beta\)-phenylpropionic acid (III) as well as the methyl dithiocarbamates (xanthates) of \(\text{D}-(\)-\(\beta\)-hydroxybutyric acid (II) and of \(\text{L}-(\)+\(\beta\)-hydroxy- \(\beta\)-phenylpropionic acid (IV) were prepared in the usual way by the action of carbon disulphide and methyl iodide on the appropriate carboxylic acids. The thiono derivatives of the two substituted butyric acids (I and II) were isolated as the cyclohexylammonium salts.

\[
\begin{align*}
\text{COO}^+\text{H}_2\text{N}-\text{C}_\text{H}_{11} & \quad \text{COOH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H} & \quad \text{R} \\
\text{CH}_3 & \quad \text{C}_\text{H}_4 \\
\text{S} & \quad \text{S} \\
\text{I.} & \quad -\text{NHC}S\text{C}_\text{H}_3 \quad \text{III.} & \quad -\text{NHC}SC\text{H}_2 \\
\text{II.} & \quad -\text{OCS}\text{C}_\text{H}_3 \quad \text{IV.} & \quad -\text{OCS}\text{C}_\text{H}_2
\end{align*}
\]

Dithiocarbamates of \(\alpha\)-amino and xanthates of \(\alpha\)-hydroxy acids have long wave length absorption bands near 330 and 350 \(\text{m}_{\mu}\), respectively, which are strongly anisotrophic, and it has been found that the absolute configuration of the \(\alpha\)-asymmetric center can be established from the sign of the Cotton effect: members of the \(\text{L}\)-series show a positive Cotton effect and members of the \(\text{D}\)-series exhibit a negative effect \(^1\).

The dithiocarbamates and xanthates (I—IV) of the \(\beta\)-amino and \(\beta\)-hydroxy acids absorb around 330 and 350 \(\mu\). From the optical rotatory dispersion curves of these compounds (Fig. 1) it can be seen that they exhibit strong Cotton effects. The dispersion curves of the cyclohexylammonium salts of N-dithiocarbamothioxy-\(\text{D}-(\)-\(\beta\)-

\[\text{Fig. 1. Optical rotatory dispersion curves of N-dithiocarbamothioxy-\(\text{D}-(\)-\(\beta\)-aminobutyric acid cyclohexylammonium salt (I), N-dithiocarbamothioxy-\(\text{L}-(\)-\(\beta\)-aminobutyric acid cyclohexylammonium salt (II), N-dithiocarbamothioxy-\(\text{L}-(\)-\(\beta\)-aminobutyric acid cyclohexylammonium salt (IV).}]

\[\text{Acta Chem. Scand. 16 (1962) No. 4}\]
aminobutyric acid (I) and of O-dithiocarbomethoxy-D-(−)-β-hydroxybutyric acid (II) have positive Cotton effects centered around the 330 and 350 nm absorption bands, and the dispersion curves of N-dithiocarbomethoxy-L-(+)-β-amino-β-phenylpropionic acid (III) and of O-dithiocarbomethoxy-L-(+)-β-hydroxy-β-phenylpropionic acid (IV) have negative Cotton effects. Although the study of this problem has so far been limited to the investigation of only four structurally varied compounds, it seems as though the sign of the Cotton effect would indicate the absolute configuration of the β-asymmetric center in β-amino and β-hydroxy acids. Since, however, the derivatives of the α- and β-substituted acids of the same configuration have opposite sign of the Cotton effect, the following extension of the previously established relationship is suggested: If a dithiocarbamate of an amino acid, or a xanthate of a hydroxy acid, has an optical rotatory dispersion curve with a positive Cotton effect, then in the case of an α-amino or an α-hydroxy acid we have the L-configuration and in the case of a β-amino or a β-hydroxy acid the D-configuration.

A full report of this work will be published later.

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Separation of α- and β-Glucosetasaccharinic Acids by Means of Anion Exchange Chromatography

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In previous papers it has been shown that hydroxy acids which are formed during the alkaline degradation of cellulose can be separated chromatographically by means of anion exchange resins. Several hydroxy acids containing 4–6 carbon atoms can be effectively separated by elution with borate solution, whereas with acids such as glyceric and lactic acid the separation is simpler and more efficient in acetate medium. In connection with further work on the separation and identification of hydroxy acids which are formed in various technical processes, it has been found desirable to investigate the possibility of separating the stereoisomeric forms of glucosetasaccharinic acids by means of anion exchange chromatography.

As shown by Kenner and Richards, β-glucosetasaccharinic acid can easily be obtained in a pure form by alkaline degradation of 3-O-methylglucose. Large amounts of α-glucosetasaccharinic acid are also formed in this reaction. In the present work (Figs. 1 and 3) it is shown that these stereoisomers can be effectively separated by chromatographic elution with 0.07 M sodium tetraborate solution under conditions which have been described in earlier papers for the separation of other saccharinic acids. The fractions were analyzed using the Technicon Auto-Analyzer which means a considerable saving in time compared with the manual dichromate titration used earlier. The elution bands corresponding to β-glucosetasaccharinic acid appears before that of α-glucosetasaccharinic acid and a quantitative separation can be obtained on a fairly short column.

Alkaline degradation of 3-O-methylglucose. The alkaline degradation of 3-O-methylglucose and the isolation of β-glucosetasaccharinic acid from the reaction mixture has, with small changes, been performed according to the procedure given by Kenner and Richards. A solution of 5.13 g of 3-O-methylglucose in