



## University of Groningen

## Eenvoudige disulfocarbonzuren

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## VII. SUMMARY OF RESULTS.

The purpose of this research was to prepare and to study simple aliphatic disulphocarboxylic acids.

The most simple example is disulphoacetic acid. It was prepared by oxidation of formylmethionic acid with hydrogen peroxide in acetic solution:

CHO. 
$$CH(SO_3H)_2 + O \rightarrow CO_2H$$
.  $CH(SO_3H)_2$ .

The disulphoacetic acid crystallizes with  $2\frac{1}{2}$  mol. of water (m.p. 85—86°). By heating at  $130^{\circ}$  it decomposes into carbon dioxide and methionic acid:

$$CO_2H. CH(SO_3H)_2 \rightarrow CO_2 + H_2C(SO_3H)_2.$$

Three disulphobutyric acids are described, viz.  $\beta$ ,  $\gamma$ -,  $\alpha$ ,  $\gamma$ - and  $\alpha$ ,  $\beta$ -disulphobutyric acid.

In order to obtain  $\beta$ ,  $\gamma$ -disulphobutyric acid,  $\gamma$ -sulphocrotonic acid was prepared. This unsaturated acid is not known in chemical literature. It arises by the action of  $\gamma$ -chlorocrotonic acid with sulphite:

$${\rm CO_2NH_4.~CH:CH.~CH_2Cl} + {\rm (NH_4)_2SO_3} \rightarrow {\rm CO_2NH_4.~CH:CH.~CH_2SO_3NH_4.}$$

The free acid, several salts, the dimethyl ester and the dichloride are described. By addition of bisulphite to  $\gamma$ -sulphocrotonic acid,  $\beta$ ,  $\gamma$ -disulphobutyric acid is formed. The velocity of this reaction at 80° was measured.

$$CO_2NH_4$$
. CH : CH.  $CH_2SO_3NH_4 + NH_4HSO_3 \rightarrow CO_2NH_4$ . CH<sub>2</sub>. CH( $SO_3NH_4$ ). CH<sub>2</sub>SO<sub>3</sub>NH<sub>4</sub>.

The same disulpho acid is also formed by the action of two molecules sulphite with one molecule  $\gamma$ -chlorovinyl acetic acid:

$$CO_2NH_4$$
.  $CH_2$ .  $CH: CHCI + (NH_4)_2SO_3 + NH_4HSO_3 \rightarrow CO_2NH_4$ .  $CH_2$ .  $CH(SO_3NH_4)$ .  $CH_2SO_3$ .  $NH_4$ .

The free  $\beta$ ,  $\gamma$ -disulphobutyric acid gives a dihydrate melting at 95°.

 $\alpha$ ,  $\gamma$ -Disulphobutyric acid is formed by sulphonation of  $\gamma$ -sulphobutyric acid, which can be obtained by the action of sulphite with  $\gamma$ -bromobutyric acid:

$$CO_2NH_4$$
·  $CH_2$ ·  $CH_2$ ·  $CH_2Br + (NH_4)_2SO_3 \rightarrow CO_2NH_4$ .  $CH_2$ ·  $CH_2$ ·  $CH_2SO_3NH_4$ .

This monosulphocarboxylic acid contains  $\frac{1}{2}$  mol. of water and melts at 93—93.5°.

Our hope to obtain  $\alpha$ -sulpho- $\gamma$ -bromobutyric acid by sulphonation of  $\gamma$ -bromobutyric acid (for the preparation of  $\alpha$ ,  $\gamma$ -disulphobutyric acid) was not fulfilled, because this reaction gave  $\alpha$ -sulpho- $\gamma$ -oxybutyric acid. Neither could  $\alpha,\gamma$ -disulphobutyric acid be obtained by addition of bisulphite to  $\alpha$ -sulphovinylacetic acid.

The sulphonation of  $\beta$ -sulphobutyric acid gives a mixture of a saturated and a unsaturated disulphocarboxylic acid with four carbon atoms. Catalytic reduction of this mixture yields the  $\alpha$ ,  $\beta$ -disulphobutyric acid.

The three disulphobutyric acids were separated into their enantiomorphs by means of the strychnine salts. The strychnine salt of the dextrorotating component of  $\beta$ ,  $\gamma$ - and  $\alpha$ ,  $\gamma$ -disulphobutyric acid is the least soluble. The salts of  $\alpha$ ,  $\beta$ -disulphobutyric acid show a rotation opposite to that of the free acid.

		[	M] <sub>D</sub> salt	$[M]_{D}$ acid
$a$ , $\beta$ -disulphobutyric		acid	— 6°	$+16^{\circ}$
α, γ-	,,	,,	<b>7</b> °	90
β, γ-	,,	,,	50°	60°

The racemisation was examined; only for the two acids, which have a sulpho group fixed to the  $\alpha$ -carbon atom, a decrease of the rotation is noticed.