

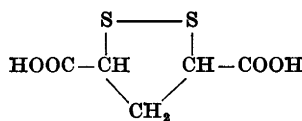
Polarographic Studies on Cyclic Disulphides

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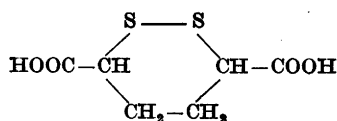
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In the course of recent work by one of the authors (L.S.) on cyclic disulphides related mainly to glutaric^{1,2} and pimelic^{3,4} acid it seemed to be of interest to examine the polarographic behaviour of analogous compounds, especially as very little attention has hitherto been devoted to this subject in polarography. It has recently been shown that the disulphide linkage in 6,8-thioctic acid (α -lipoic acid) is reducible at the dropping mercury electrode⁵. However, no conclusions were drawn about the ring system.

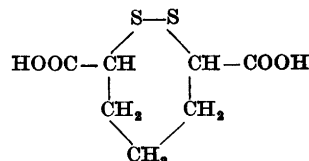
The α,α' -disubstituted dicarboxylic acids, *racem*-1,2-dithiolane-3,5-dicarboxylic acid (I), 1,2-dithiane-3,6-dicarboxylic acid (II) and 1,2-dithiepane-3,7-dicarboxylic acid (III) have been investigated together with the related dimercaptans. For (II) and (III) both the diastereomers were examined. The substances have all been studied in standard buffer solutions and at a concentration of 1.00×10^{-3} M.



(I)



(II)



(III)

Racem-(I) gives in acid solution a very good wave, reversible in character, with a half-wave potential of -0.330 V vs. the sat. calomel electrode (S.C.E.) at pH = 2.2. In neutral medium, on the other hand, the wave is quite deformed and at higher pH no waves are found.

Racem- and *meso*-(II) give polarographic waves only in acid solution. The waves are rather drawn out indicating irreversible electroreduction. The half-wave potential value is -0.75 V.

Analogous behaviour, as compared with (II) exists for *racem*- and *meso*-(III). The corresponding value for the half-wave potentials is -0.92 V.

The wave height and the relation $\log [i/(i_d - i)]$ vs. the applied potential E for *racem*-(I) suggest a two electron reduction. Analogous to the polarographic behaviour of a number of aliphatic disulphides (cysteine, glutathione) the wave obtained seems to be due to the reduction of Hg-complexes, which are formed on the drop at the rupture of the S—S linkage. The pronounced irreversible appearance of (II) and (III) in acid solution indicates that the primary reaction — the cleavage of the S—S group — in these cases does not proceed so readily as with *racem*-(I). A greater ring stability for the six- and seven-membered cyclic disulphides as compared with the 1,2-dithiolane derivative is apparent. This is in agreement with data from spectrochemical studies⁶⁻⁸ and from the characteristics of the unsubstituted heterocycles⁹.

An interesting analogy supporting our interpretation can be found *i. a.* in the behaviour of dithio- and diseleno-diglycolic acid. Leussing and Kolthoff¹⁰ have shown that dithio-diglycolic acid gives only irreversible polarographic waves. On the other hand, one of us (B.N.)¹¹ has found that the corresponding diselenide is characterized by reversible effects over the whole pH range. Thus the radical cleavage necessary for the formation of electroreducible Hg-complexes on the mercury drop is more easily realized for the selenium compound.

Fredga¹² has already established a striking difference between the aliphatic S—S and Se—Se groups in reactivity against Hg.

The α,α' -dimercapto dicarboxylic acids related to (I), (II) and (III) have been found to give polarographic effects, the qualitative nature of which resemble each other. Thus a double wave is obtained in acid and neutral media; the smaller one remains in basic solution. Its half-wave potentials vary with pH.

It is obvious from the foregoing that the polarographic effects of the 1,2-dithiolane derivatives may be of special interest. For a closer investigation of this disulphide system a number of 4-substituted com-

pounds⁷ (originally prepared by Backer and co-workers) were also examined. They all gave good polarographic waves over the whole pH range indicating a two electron reduction. Especially in acid solution the agreement between their half-wave potentials and that of *racem*-(I) is excellent. — In this connection the polarographic method has been used to further emphasize the improbability of coordinated sulphur-sulphur bonds⁸.

This general polarographic character of the five-membered cyclic disulphide has also been found to include that of 6,8-thioctic acid.

Experimental. The investigation was performed at 25° C with a Leybold Polarograph model 54. In order to minimize the influence of the cathodic mercury on the solution a special type of polarographic cell according to Schwabe and Berg was used.

In connection with a current polarographic investigation of a number of aliphatic diseleno dicarboxylic acids a closer examination of the above subject will be undertaken.

The authors are indebted to Professor Mark von Stackelberg for valuable discussions and for making it possible for one of us (B.N.) to carry out this preliminary study at the Institute of Physical Chemistry, University of Bonn, Germany. — Thanks are also due to Professor Arne Fredga for kind interest in our work and for placing certain materials at our disposal. The sample of 6,8-thioctic acid was kindly supplied by Docent Stig Sunner.

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Carotene Isomers in some Red Algae

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According to previous investigations, β -carotene is the only carotene isomer present in most red algae (Table 1). An investigation of the unsaponifiable matter of *Rhodymenia palmata*, carried out at the Institute of Organic Chemistry at the Norwegian Technical University in Trondheim, seemed to indicate the presence of both α - and β -carotene in this alga. As this was contrary to previous observations of Heilbron *et al.*¹ (Table 1), it was decided to carry out a further investigation of the carotene isomers in red algae.

Samples of the more common red algae were collected in the Trondheimsfjord during the months of May to August 1955. The samples were blanched with steam at 100° C as soon as possible after harvesting and dried at approximately 35° C overnight. This proved to be the best procedure, since quantitative extraction of the carotene from fresh material was difficult to accomplish and no carotene breakdown was observed during the steam-treatment and drying². After having been ground to pass a 60 mesh sieve, 1 g of the sample was moistened with 5 ml of water, and extracted overnight with 25 ml of acetone. The extraction was repeated until the extract was colourless. The carotene was extracted from the acetone solution, after addition of more water, with light petroleum, and the light petroleum extract concentrated to a small volume on a water bath. The carotenes were separated from chlorophylls and other carotenoids by chromatography on magnesium oxide — Hyflo Super-Cel (1:3). The carotene zones were washed through the column with light petroleum containing 0.5 % acetone, the eluate made up to 50 ml and the carotene concentration determined by reading the optical density at 436 μ in a Beckman spectrophotometer.

In the case of *Rhodymenia palmata*, two zones were observed on the column, apart from the stationary chlorophyll and carotenoid zones: A fast moving yellow zone, and a slower moving brick-red zone. Complete separation of the two pigments was