

Paper Chromatographic Analysis of Urine from a Few Cases of Porphyrinuria

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Totter *et al.* have reported a connexion between the amount of glycine in the diet and the porphyrin excretion¹. Dent and Rimington recently discussed the possibility that a peptide containing methionine sulphone may be the porphyrinurogenic agent². During investigations of the amino acid and peptide excretion in some diseases³, urines from three cases of porphyrinuria were analyzed by two-dimensional paper partition chromatography. For technical details see references 3, 4. In two cases an orange-yellow-coloured spot was seen on the papers directly under the alaninethreonine spot (see Fig. 1).

It was thought that the spot corresponded to porphobilinogen, a substance earlier described by Waldenström and Wahlquist⁵ as present in such urines. To verify this hypothesis three parallel runs were made for each sample of urine. One paper was developed with ninhydrin, the other two papers were treated with Ehrlich reagent⁶, or with diazotized sulfanilic acid⁴. On positions corresponding to the yellow ninhydrin spot, positive reactions were obtained in both cases. Therefore, it seems likely, that the yellow spot corresponds to porphobilinogen. This would then appear to be another example of the large variety of substances which react with ninhydrin. The orange-yellow colour resembles the proline and hydroxyproline colours, and supports the conclusion of Waldenström and Wahlquist that porphobilinogen also is a pyrrole derivate.

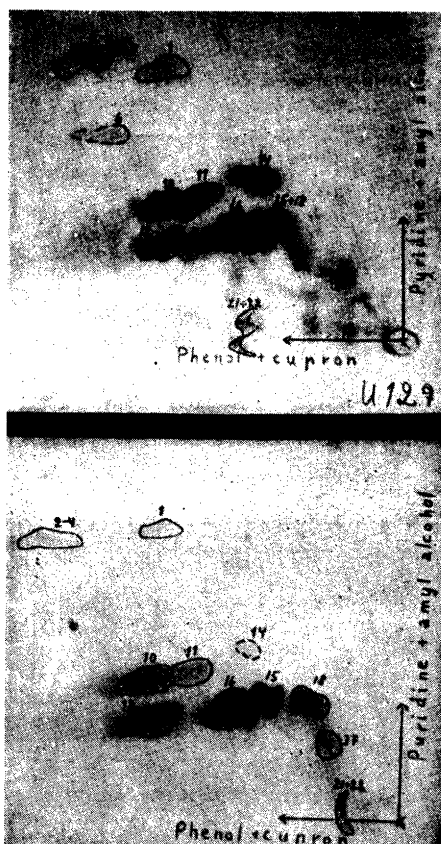


Fig. 1. Photograph of a two-dimensional chromatogram of urine from a case of porphyrinuria, above, and normal urine, below. In both cases an amount of urine containing 1.2 mg creatinine was used.

- | | |
|-------------------|----------------------|
| 1 = Tyrosine | 14 = Taurine |
| 2 = Phenylalanine | 15 = Serine |
| 3 = Isoleucine | 16 = Glycine |
| 4 = Leucine | 18 = Histidine |
| 6 = Valine | 21 = Arginine |
| 10 = Alanine | 22 = Lysine |
| 11 = Threonine | 37 = An orange spot, |
| 12 = Glutamine | which did not |
| | give any nin- |
| | hydrin-reacting |
| | substances after |
| | hydrolysis |

The yellow spot is not numbered, but is encircled directly under the threonine spot.

There was no pronounced difference in the amino acid pattern of urines from normals and cases of porphyrinuria.

1. Totter, J. R., Amos, E. S., and Keith, C. K. *J. Biol. Chem.* **178** (1949) 847.
2. Dent, C. E., and Rimington, C. *Biochem. J.* **41** (1947) 253.
3. de Verdier, C.-H. *Acta Med. Scand.* **138** (1950) 344.
4. Ågren, G., and Nilsson, T. *Acta Chem. Scand.* **3** (1949) 525.
5. Waldenström, J., and Wahlquist, B. Z. *Physiol. Chem.* **260** (1939) 189.
6. Syngé, R. L. M. *Biochem. J.* **38** (1944) 285.

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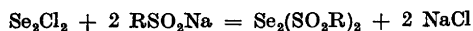
Reactions of Diselenium Dichloride with Sodium Sulphinates

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This note is a preliminary report on the synthesis of two new types of selenium sulphur compounds, *viz.*, diselenium and triselenium disulphinates.

The diselenium disulphinates, $\text{Se}_2(\text{SO}_2\text{R})_2$, are formed when diselenium dichloride reacts, under cooling in ice, with an excess of finely powdered, anhydrous sodium benzene- or *p*-toluenesulphinate, suspended in benzene:



The following proportions of reagents have been used: 10 g of sodium benzenesulphinate in 20 ml of benzene, or 12 g of sodium *p*-toluenesulphinate in 40 ml of benzene; 2 ml of diselenium dichloride. The contents of the flask are stirred with a glass rod for a few minutes, until the diselenium dichloride colour disappears. The mixture is subsequently heated rapidly, the sodium chloride and the excess of so-

dium sulphinate are filtered off, and ligroin is added to the filtrate.

The benzene compound melts at 79–80° C, the *p*-toluene compound at 104–106° C (dec.).

0.1801 g substance: 33.34 ml of 0.09754 *N* iodine (Norris & Fay).

$\text{Se}_2(\text{SO}_2\text{C}_6\text{H}_5)_2$ (440.3)

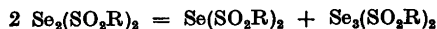
Calc. Se 35.86 Found Se 35.63

0.1408 g substance: 23.61 ml of 0.1022 *N* iodine.

$\text{Se}_2(\text{SO}_2\text{C}_7\text{H}_7\text{-}p)_2$ (468.3)

Calc. Se 33.72 Found Se 33.83

The triselenium disulphinates, $\text{Se}_3(\text{SO}_2\text{R})_2$, result if, for the above process, the sodium sulphinates are suspended in dry ether instead of in benzene. Probably a rearrangement of primarily formed diselenium disulphinate takes place:



The last change is in accordance with the behaviour of the corresponding sulphur compounds, $\text{S}_2(\text{SO}_2\text{R})_2$, which undergo rearrangement to give trithionic and pentathionic compounds ^{1, 2}.

Triselenium di(benzenesulphinate) melts and decomposes rapidly at 101–102° C, while the triselenium di(*p*-toluenesulphinate) crystals liberate selenium at 130–140° C (preheated bath).

0.1069 g substance: 25.33 ml of 0.09754 *N* iodine.

$\text{Se}_3(\text{SO}_2\text{C}_6\text{H}_5)_2$ (519.2)

Calc. Se 45.61 Found Se 45.62

0.1073 g substance: 24.21 ml of 0.09754 *N* iodine.

$\text{Se}_3(\text{SO}_2\text{C}_7\text{H}_7\text{-}p)_2$ (547.3)

Calc. Se 43.28 Found Se 43.44

The diselenium and triselenium disulphinates form greenish yellow crystals, which appear to be relatively stable at room temperature; thus, some samples have so far been kept unchanged for several weeks.