and eluted separately in a minimum amount of 0.01 *M* phosphate buffer pH 7.4. The eluates from several chromatographic strips were combined to obtain sufficient amounts of labelled compounds.

A 10^{-3} *M* solution of pure thiotaurine[3] was added with labelled thiotaurine: 0.5 ml of this solution were chromatographed in phenol, and the strip was scanned for radioactivity by passing it under the mica window of a Geiger counter, protected by a lead shield with a 1.5 cm long window: 1.5 cm long portions of the strip were counted for 1 min each (Figure a).

The same solution was then made 10^{-3} or $3 \cdot 10^{-3}$ *M* in respect to hypotaurine, and, after 15 min standing, 0.5 ml were chromatographed, and scanned quantitatively for radioactivity (Figure b, c).

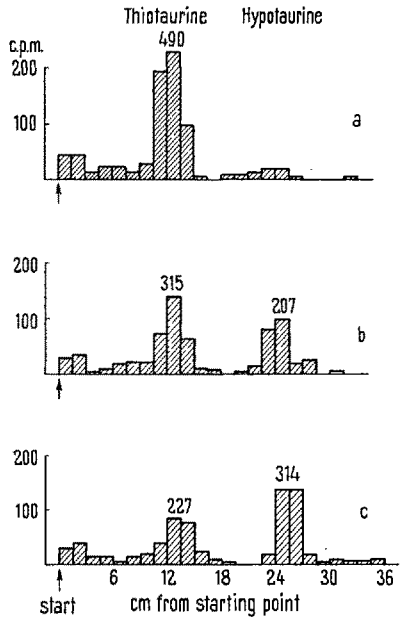
The procedure was repeated with a 10^{-3} *M* solution of pure hypotaurine[4] labelled by the addition of ^{35}S hypotaurine and then added with thiotaurine.

These experiments show that radioactivity passed from labelled thiotaurine to hypotaurine and *vice versa*, and demonstrate the occurrence of a readily spontaneous transulfuration reaction.

This reaction, like those described previously, is of some interest also from a technical point of view. Transulfuration could in fact be responsible for the appearance in radiochromatograms of unexpected radioactive spots upon addition of unlabelled compounds.

Finally, the above results clearly demonstrate that spontaneous transulfuration between compounds of the *R*-SO_2-SH and *R*-SO_2H type is a general reaction for compounds in which *R* is either a HOOC-$CHNH_2CH_2$- or a H_2N-CH_2-CH_2-residue.

Résumé. Les auteurs ont préparé avec une enzyme de la thiotaurine et de l'hypotaurine marquées par le et S^{35} ont démontré que ces deux composés peuvent échanger spontanément un atome de soufre en se transformant l'un dans l'autre.



Unidimensional chromato-radiograms developed in phenol of: (a) labelled thiotaurine; (b) labelled thiotaurine (final concentration $10^{-3}M$) added with unlabelled hypotaurine (final concentration 10^{-3} *M*); (c) labelled thiotaurine (final concentration 10^{-3} *M*) added with unlabelled hypotaurine (final concentration $3 \cdot 10^{-3}$ *M*).

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'Cystine Monosulfoxide' and Related Compounds

The oxidation states which are intermediate between cystine (I) and cysteic acid (VII) are of considerable interest in studies of the metabolism of cystine[1] and the oxidation of cystine residues in proteins[2,3]. Until recently only two of the possible intermediate oxidation products had been synthesized; the thiolsulfonate (III)[4–6] and the sulfinic acid (VI)[7]. Syntheses have been reported of the corresponding thiolsulfinate (II)[4,8,9], disulfone (IV)[10] and sulfenic acid (V)[11], some of which were unstable, but as these products had variable compositions, they were probably mixtures. Last year in this journal[12] a new synthesis of the 'monosulfoxide' (II) was described, whereby III was reduced with HI to give a stable product.

I Cys–S–S–Cys
II Cys–S–SO–Cys
III Cys–S–SO_2–Cys
IV Cys–SO_2–SO_2–Cys
V Cys–SOH
VI Cys–SO_2H
VII Cys–SO_3H

Cys = *L*–CH_2–CH(NH_2)(CO_2H)

This preparation[12] has been repeated. However, when the product is examined by paper electrophoresis in 10% acetic acid, or better paper electrophoresis followed by paper chromatography in the transverse direction[13], it is found to be a mixture of (I) and (III). On polarographic reduction in 0.1 *N* HCl solution at the dropping mercury cathode, the 'monosulfoxide' gives a complex wave with inflections at -0.18 *V* and -0.45 *V* (versus the saturated calomel electrode). Under the same conditions and in the same voltage range III and I give simple waves with half-wave potentials at -0.18 *V* and -0.45 *V* respectively, again suggesting that the 'monosulfoxide' product is a

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mixture. When allowed to react with sulphite ion 1 Mol of the 'monosulfoxide' produced 0.5 Mol of thiol as measured by amperometric titration with mercuric chloride[14]. This is difficult to explain on the basis of structure (II) but can be reconciled with the assumption that the product is an equimolar mixture of (I) and (III), since (III) does not yield thiol under these conditions[3]. The hypothesis that the 'monosulfoxide' is an equimolar mixture of (I) and (III) agrees with the figures[12] for elementary analyses and equivalent weight; and the specific rotation ($[\alpha]_D^{24} = -111°$)[12] is approximately the mean of the rotations of I (– 213°) and III (– 22°). Contrary to the previous report[12] it is now found that in the region 7–10 μ the infra-red spectra[15] of the 'monosulfoxide' and of an equimolar mixture of I and III are indistinguishable. Simple aliphatic and aromatic thiolsulfinates are unstable and readily disproportionate into a mixture of the corresponding disulfide and thiolsulfonate[16,17] and it is possible that 'cystine monosulfoxide' decomposes in this way as soon as it is formed in the acidic solution (HCl + KI).

To further investigate possible intermediate oxidation products of cystine, the performic acid oxidation method[5] has been studied using varying amounts of oxidant (1–5 Mol). The products of these oxidations were analysed quantitatively using the iodometric reduction method of TOENNIES and LAVINE[4] and also qualitatively by the combination of paper electrophoresis and paper chromatography[13]. The reaction course is found to be markedly affected by the presence of HCl, presumably because the effective oxidant in this case is chlorine, formed *in situ*. In the presence of HCl large amounts of the two intermediate oxidation products III and VI are formed[18] whereas in the absence of HCl the final oxidation stage cysteic acid (VII), is reached with only minor amounts of III and VI; and VII is the ultimate product when excess of performic acid is used either in the presence or absence of HCl. It is noteworthy that there is no evidence for intermediates other than III and VI whereas the whole range of products from R–S–SO–R to R–SO_2–SO_2–R can be prepared in the simple aliphatic and aromatic series[19,20]. Recent work has shown that although apparently simple, the oxidation of thiols to disulfides[21] and of thiolsulfinates to thiolsulfonates[22] may involve complex reaction mechanisms[23].

Zusammenfassung. Die früher als «Cystinmonosulfoxyd» beschriebene Verbindung (Thiosulfinat II) verhält sich wie eine äquimolekulare Mischung von Cystin (I) und dem entsprechenden Thiosulfonat (III). Oxydation von Cystin mit Perameisensäure führt, besonders in Gegenwart von HCl, über die Zwischenprodukte Thiosulfonat (III) und Sulfinsäure (VI) zu Cysteinsäure (VII).

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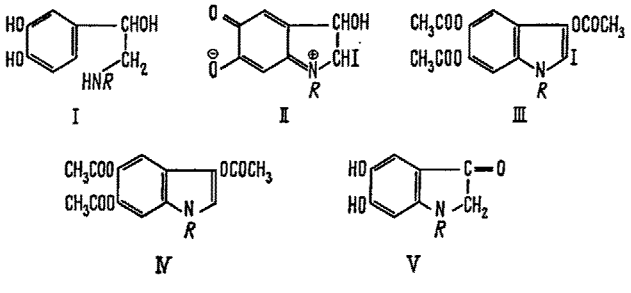
Noradrenolutin

It has been known for many years that fluorescent substances can be obtained from the oxidation products of adrenaline (I: $R = CH_3$) and noradrenaline (I: $R = H$) by treatment with alkali and this phenomenon has been widely used in the fluorometric estimation of these catecholamines in body fluids (for references see HEACOCK[1], VON EULER[2], and PERSKEY[3]). The fluorescent derivative of adrenaline, known as adrenolutin (5,6-dihydroxy-N-methylindoxyl (V: $R = CH_3$))[4] was isolated and characterized several years ago[6]; however isolation of the fluorescent oxidation product of noradrenaline in the solid state has not yet been reported. BU'LOCK and HARLEY-MASON failed to obtain any crystalline material from the alkaline rearrangement products of solutions of noradrenaline, which had been oxidized with potassium ferricyanide[7]. An alternative unsuccessful route attempted by these authors[7] has been reexamined and crystalline noradrenolutin (i.e. 5,6-dihydroxyindoxyl (V: $R = H$)) has now been obtained.

2-Iodonoradrenochrome (II: $R = H$) can be obtained from the oxidation of noradrenaline hydrochloride with potassium iodate[7,8]. (The procedure described by BU'LOCK and HARLEY-MASON gives a poor yield of crystalline product and only after removal of much tarry material[7].) However, a moderate yield of crystalline 2-iodonoradrenochrome with minimal formation of tarry



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