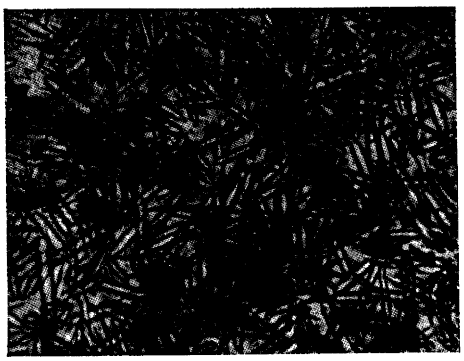

Figur 1. Crystalline horse liver esterase (× 450).

Recrystallization. The crystalline precipitate is separated and taken up in 1/40 of the original volume of extract. Enough ammonium sulfate is added to make it 60—65 % saturated, and the mixture is left standing at room temperature. Crystallization starts slowly but a good crop of crystals is obtained in 24 hours. The crystals (Fig. 1) have needle shape. 1 ml of crystalline enzyme containing 0.1 mg nitrogen when allowed to act on 1.75 g of ethyl butyrate will produce anough acid to neutralize 35.0 ml of 0.01 *N* sodium hydroxide in one half hour.

Work is in progress to study the purity of the preparation electrophoretically and by solubility methods. Investigations on the kinetics, specificity and activation inhibition reactions are also being carried out and will be communicated in more detail in a later publication.

The author desires to express his appreciation and gratitude to Prof. K. Myrbäck for inviting him to work in his laboratories and for his continued zeal and interest.

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Sulphanilylderivatives of Heterocyclic Amines. XI.* Derivatives of Quinoxaline

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In connection with researches on the bacteriostatic effect of isomeric N^1-heterocyclic derivatives of sulphanilamide [1] it was desired to prepare the three isomeric sulphaquinoxalines. It was attempted to prepare 2-amino-quinoxaline from *o*-phenylenediamine plus glyoxylic nitrile or dichloroacetonitrile or from quinoxaline and sodium amide, but with negative results. While these experiments were still in progress, Weijlard, Tishler and Erickson published a paper [2] in which the synthesis of 2-sulphaquinoxaline and 2-aminoquinoxaline, starting from alloxazine, was announced. 2-Sulphaquinoxaline was found to be as effective as sulphadiazine in experimental pneumococcus infections in mice.

The two remaining isomers, 5- and 6-sulphaquinoxaline, have now been prepared by treating the appropriate aminoquinoxalines with acetylsulphanilyl chloride in the presence of pyridine and hydrolyzing the resulting acetyl derivatives. The two aminoquinoxalines required were prepared from 1,2,4- and 1,2,3-triaminobenzene and glyoxal. The 6-aminoquinoxaline

* No. X in this series appeared in *Dansk Tids. Farm.* 17 (1943) 189.

has been described previously [3] while 5-aminoquinoxaline is a new compound.

The two new sulphaquinoxalines form beautiful pale yellow crystals and are more soluble in water than most other sulphonamides. Their bacteriostatic activity against pneumococci (type I) is of the same order as that of sulphathiazole. Thus, analogous to what was found for the sulphaquinolines [4] the bacteriostatic activity is practically independent of the position of the sulphanilamido group.

6-Aminoquinoxaline was prepared from 1,2,4-triaminobenzene and glyoxal-sodium-hydrogensulfite [3]. Recrystallized from ether. M. p. 158—159°.

5-Aminoquinoxaline. The required 1,2,3-triaminobenzene was prepared by decarboxylation of 3,4,5-triaminobenzoic acid [5]. To an aqueous solution of 1,2,3-triaminobenzene (0.60 g) was added glyoxal-sodium-hydrogensulfite (1.40 g), and the mixture was heated for one hour at 50°. After cooling the solution was made strongly alkaline and extracted several times with chloroform. The chloroform solution was evaporated to dryness and the residue recrystallized from water. Yield 0.40 g or 55 % of the theoretical. From water 5-aminoquinoxaline crystallizes in chrome-yellow needles containing one mole of water.

$C_8H_7N_3,H_2O$ (163.2) Calc. N 25.74
Found » 25 87

The compound melts at 90.5°, loosing its water. By sublimation *in vacuo* over P_2O_5 the anhydrous compound is obtained as yellow-orange crystals, melting at 91°.

$C_8H_7N_3$ (145.2) Calc. N 28.94
Found » 28.71

The anhydrous compound is hygroscopic and exposed to air it is soon transformed in the hydrate. It is easily soluble in water and in most organic solvents.

6-Sulphanilamidoquinoxaline. 6-Aminoquinoxaline (1 g) was dissolved in dry pyridine (5 ml) and pure acetylsulphanilyl chloride (1.6 g) was added with stirring. When all had dissolved the solution was heated to boiling point and then left cooling. By addition of 50 ml of water an oily product separated, which by addition of hydrochloric acid and rubbing soon became crystalline. The crude acetyl compound was filtered, washed with water, suspended in 20 ml of 2 N-hydrochloric acid and refluxed one hour; the product gradually dissolved. The hot solution was treated with activated carbon, filtered, neutralized with sodium hydroxide and chilled. The pale yellow crystals were filtred, washed with water and recrystallized from water containing 10—20 % ethanol. The purified product form very pale yellow needles with m. p. 231.5—232° (corr.). Yield 0.60 g~30 %. The compound contains half a mole of water of crystallization, which is given off at 198—200° or at room temperature over P_2O_5.

$C_{14}H_{12}O_2N_4S, \frac{1}{2}H_2O$ (309.3) Calc. N 18.10
Found » 18.18
$C_{14}H_{12}O_2N_4S$ (300.3) Calc. N 18.65
Found » 18.71

The compound is slightly soluble in hot water, very soluble in ethanol.

5-Sulphanilamidoquinoxaline. This compound was prepared from 5-aminoquinoxaline in exactly the same way as the 6-derivative. It crystallizes, however, from the aqueous solution without water of crystallization:

$C_{14}H_{12}I_2N_4S$ (300.3) Calc. N 18.65
Found » 18.69

The compound form pale yellow plates with m. p. 168.5—169.5° (corr.).

The author is indebted to Mr. M. Solstad for preparing 1,2,3-triaminobenzene and 5-aminoquinoxaline and to Dr. Kai Schmith for carrying out the bacteriological tests.

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Über die Ursache der Farbreaktionen des Holzes

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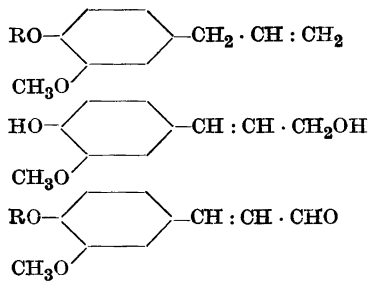
Seit der Entdeckung der Farbreaktionen verholzter Gewebe mit Anilin oder Phenol-Salzsäure (Runge 1834) sind zahlreiche Versuche unternommen worden, den Träger dieser Reaktionen zu charakterisieren, ohne dass eine klare Entscheidung erzielt worden ist [1]. Unsere Ergebnisse stützten zunächst die auch von manchen anderen Autoren früher vertretene Auffassung, wonach die Reaktionen auf das Lignin selbst und nicht etwa (ausschliesslich) auf accessorische Bestandteile des Holzes zurückzuführen sind. Eine Identifizierung der dabei in Reaktion tretenden Gruppen könnte daher von Bedeutung für die Kenntnis der Konstitution des Lignins sein.

Bisher schien es aber, als ob die »Holzreaktionen» weitgehend unspezifisch seien. So wurde z. B. behauptet, dass sowohl Eugenol (I) und dessen Methyläther (II) [2] wie Coniferylalkohol (III) [3] und Coniferylaldehyd (IV) [4] die für Holz typischen Farbreaktionen mit Phenolen und aromatischen Aminen liefern. Eine nähere Untersuchung von Präparaten von I und II zeigte aber, dass die Farbreaktionen nicht von den reinen Substanzen gegeben werden, sondern durch aldehydische Verunreinigungen verursacht sind. Die Reaktionen waren nämlich nach Behandeln der Präparate mit Hydroxylamin oder Dimedon oder nach sehr sorgfältiger Destillation negativ. Aus einem Handelspräparat von Eugenolmethyläther (II) wurden Veratrumaldehyd sowie ein weiterer, vorher unbekannter Aldehyd in Form ihrer 2,4-Dinitrophenylhydrazone isoliert. Der letztere erwies sich als identisch mit Coniferylaldehyd-methyläther (V), den wir aus Veratrumaldehyd und Acetaldehyd synthetisierten (Schmp. 86—87°). Es zeigte sich, dass dieser Aldehyd ebenso wie der freie Coniferylaldehyd (IV) die »Holzreaktionen» in typischer Weise gibt.

Wir überzeugten uns ferner davon, dass durch Emulsinspaltung von Coniferin * frisch dargestellter Coniferylalkohol (III) die Holzreaktionen nicht liefert. Auch zahlreiche andere Substanzen, die irgendwie in Beziehung zu Lignin bzw. den untersuchten Modellsubstanzen stehen, wurden geprüft, mit negativem Ergebnis. Die »Holzreaktionen» sind somit spezifisch für die Coniferylaldehydstruktur.

Extrahierbares, sog. »natives» Lignin nach Brauns [5] wurde in alkoholischer Lö-

* Für die freundliche Überlassung dieser Substanz sind wir Herrn Prof. B. Holmberg zu grossem Dank verpflichtet.



I. R = H II. R = CH_3

III.

IV. R = H V. R = CH_3