When the disodium salt of 6-nitroprotocatechuic aldehyde was treated with two molecules of chloromethyl ether in benzene, 3 : 4-bis-(methoxymethoxy)-6-nitrobenzaldehyde was obtained, and this compound on treatment with acetone and alkali gave 5 : 6 : 5′ : 6′-tetra(methoxymethoxy) indigo in good yield. Hydrolysis with dilute mineral acid then yielded the required tetrahydroxyindigo. The product was a greenish-black powder, slightly soluble in pyridine and nitrobenzene with a greenish-blue colour. It was readily soluble in aqueous sodium hydroxide giving an intense permanganate-violet solution, and was reprecipitated unchanged by addition of acid. Acetylation with acetic anhydride and pyridine gave the tetra-acetyl derivative which crystallized well from nitrobenzene. On reduction with sodium hydrosulphite and alkali a yellow vat was obtained, re-oxidizing readily in air to give a violet solution.

The tetrahydroxyindigo is thus quite different from melanin, which is slightly soluble in alkali with a greenish-brown colour. Furthermore, it is scarcely possible that melanin can be a quinone or semi-quinone derived from tetrahydroxyindigo, since such a compound would undoubtedly be reduced by sodium hydrosulphite and alkali to the same leuco-compound as that formed from the tetrahydroxy-indigo itself: this latter is certainly not obtained from melanin, as the hydrosulphite vat from this substance does not re-oxidize to give the characteristic violet colour shown by alkaline solutions of the tetrahydroxyindigo.

Full details of this work will be published elsewhere in due course.

J. Harley-Mason

University Chemical Laboratory,
Cambridge.

[1] Clemo and Weiss, *J. Chem. Soc.*, 702 (1945).
[2] Raper, *Biochem. J.*, **21**, 89 (1927); **31**, 2162 (1937).
[3] *Ber.*, **36**, 1528 (1903).
[4] *Ber.*, **36**, 2930 (1903).
[5] *Rec. Trav. Chim.*, **49**, 18 (1930).

The interesting method used successfully by Harley-Mason for demethylenation is similar to that worked out in Germany[1] during the War using pyridine hydrochloride for the demethylation of phenol ethers, which was unknown to us at the time of our work.

The conclusions reached in our paper were largely based on the determination of the oxidation equivalents by H. S. Raper. Accepting Raper's figures, the indigoid formulation suggests itself as the most likely one on the basis of our experiments and on the known behaviour of dihydroxyindole. As implied in our paper, and bearing in mind the marked instability of catechol compounds under biological *p*H conditions, it is very unlikely that the hydroxyl groups are present in the free state.

If, on the other hand, one admits higher oxidation figures than those given by Raper, then clearly there is the possibility of polymerization products of indigoid type, for example, with a dehydrotype as polymerizing unit.

G. R. Clemo
J. Weiss

Chemistry Department,
King's College,
Newcastle-upon-Tyne.

[1] Prey, V., *Ber.*, **75B**, 350 (1943).

Existence of Cupric Hexammino Sulphate

While the hexammino compounds of the halides, nitrates and other salts of copper are well known, nothing seems to be on record regarding the existence of cupric hexammino sulphate. In recent communications, Dey and Bhattacharya[1] have described a new method for the isolation of cupric pentammino sulphate, from ammoniacal solutions of cupric sulphate. In other publications from this laboratory, Dey has recorded the results of the conductometric measurements of mixtures of cupric nitrate[2] or chloride[3], with ammonium hydroxide solutions, of various compositions. The conductometric curves gave breaks corresponding to three, four, five and six molecules of ammonia for one molecule of the copper salt, thus affording the evidence for the existence of tri-, tetra-, penta- and hexa-ammino cupric compounds. In the case of cupric ammino sulphates, however, the triammino compound is not found, whereas the three other compounds are formed. The changes in the extinction coefficients of mixtures have also been studied by means of a Nutting's spectrophotometer, and the results confirm those obtained by the electrical conductivity method. We thus find that these results indicate the definite existence of cupric hexammino sulphate, as well, in an ammoniacal solution of cupric sulphate.

I am indebted to Dr. A. K. Bhattacharya, head of the Department of Chemistry, University of Saugor, for his interest in this work.

Arun K. Dey

Department of Chemistry,
University of Allahabad.
Dec. 3.

[1] Dey and Bhattacharya, *Curr. Sci.*, **14**, 201 (1945); *Proc. Ind. Acad. Sci.*, A, **23**, 259 (1946).
[2] Dey, *Nature*, **158**, 95 (1946).
[3] Dey, *Curr. Sci.*, **15**, 317 (1946).

Statistical Methods in Chemical Analyses

It is well established that many of the distributions met in biological work approximate to the normal, and the modern developments of statistics are associated with this fact. Most of the techniques are dependent for their validity, to a greater or less extent, on the goodness of the normal equation as a description of the experimental distributions. Since there cannot be any *a priori* reasons for expecting distributions in chemical work to be normal, and there seems to have been very little investigation of the natures of the distributions actually occurring, application of methods which presume normality may be highly dangerous.

With the view of ascertaining whether such methods can be applied, I have carried out an investigation of a number of distributions arising in the course of analysing chemically a wide variety of the products of industry in the Chemical Inspection Department of the Ministry of Supply. The products included metals, alloys, 'pure' and 'commercial' chemicals, mixtures, etc., from thirty or forty different firms. Some 250 distributions, involving about 50,000 chemical analyses, have been examined. The analyses were of various kinds, such as determinations of impurities present as traces or in larger amounts, assays of substances both pure and crude, and measurements of characteristics, by chemical and physical methods, such as are ordinarily carried out in the control laboratories of chemical industry.

© 1947 Nature Publishing Group