CCCCXLV.—*Hydroxyanthraquinones. Part I. A Synthesis of Purpurin.*

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FOR the purposes of some biological work it was found necessary to prepare quinizarin-2-sulphonic acid. The literature contains little mention of this compound apart from some patent references. Von Georgievics (*Centr.*, 1905, i, 1515) reports that a quinizarin monosulphonic acid is obtained by heating quinizarin with 3 parts of 20% oleum for 5 hours at 140°, but the orientation is not certain. On the other hand, Zimmermann (*Z. physiol. Chem.*, 1930, **188**, 180) claims to have obtained an 88% yield of the 2-sulphonic acid by heating 10 g. of quinizarin with 20 c.c. of 20% oleum at 130—150° for 2 hours. Careful attempts were made to repeat this work under the same conditions and a yield of more than 90% of a sulphonic acid was obtained. However, the sodium salt of this acid (or acids) behaved in an entirely different manner from that prepared by other methods, and although the author had not the available time to determine the orientation of the product, it can definitely be stated that Zimmermann's method does not give exclusively the 2-sulphonic acid. According to D.R.-P. 287,867 (Bayer) the sodium 2-sulphonate can be obtained by boiling quinizarin in water with 2 parts of sodium sulphite. A yield of about 30% was thus obtained, a figure which was increased to 70% by the further addition of manganese dioxide. The use of potassium sulphite and manganese dioxide as recommended in another section of the above patent was found to be unsatisfactory.

However, by the use of sodium sulphite and copper oxide, an almost theoretical yield of sulphonic acid was obtained. By autoclaving the sodium salt with milk of lime, a good yield of purpurin was obtained (confirmed by mixed m. p. of the product itself and of its triacetyl derivative), and no other product of the

reaction could be identified, thus proving that the action of sodium sulphite on quinizarin in presence of copper oxide is to produce exclusively the 2-sulphonic acid, and providing at the same time a useful method for the synthesis of purpurin.

Previous syntheses of purpurin have been accomplished by von Baeyer and Caro (*Ber.*, 1875, **8**, 152) from quinizarin by the action of manganese dioxide and sulphuric acid at 140°, and by Wacker (*J. pr. Chem.*, 1896, **54**, 90) by oxidation of alizarin in sulphuric acid solution with ammonium persulphate at 30°, but no yields are stated. De Lalande (*Ber.*, 1874, **7**, 1545) obtained it from alizarin by the use of manganese dioxide or arsenic pentoxide and sulphuric acid, but gives no details or yields. Brasch (*Ber.*, 1891, **24**, 1614) also obtained it by the action of nitrous acid on 4-aminoalizarin, but this method is merely of theoretical interest.

Experimental.

Quinizarin-2-sulphonic Acid (*Sodium Salt*).—10 G. of quinizarin, 25 g. of sodium sulphite, and 5 g. of copper oxide were boiled under reflux with 500 c.c. of water for 24 hours; the solution was then acidified with dilute sulphuric acid and filtered while boiling. The small residue was extracted with a further small quantity of hot water and sodium chloride was added to the combined filtrates. On cooling, the sodium salt was obtained in theoretical yield (14 g.) as a mixture of orange-red needles and orange rectangular plates. It separated from a strong saline solution exclusively in the needle form or from 50 parts of water exclusively as plates.

Purpurin.—5 G. of sodium quinizarinsulphonate, 10 g. of slaked lime, and 70 c.c. of water were autoclaved at 250° (440 lb./sq. inch) for 8 hours. 100 C.c. of water were added and the whole was heated to boiling and acidified with hydrochloric acid. The precipitated purpurin was filtered off, washed twice with hot, very dilute acetic acid, and dried. Yield, 2·9 g. (84%). It sublimed in red needles (m. p. 255°) and on recrystallisation from glacial acetic acid had m. p. 263° (Schunck and Roemer, *Ber.*, 1877, **10**, 550, give 253°), which was unchanged on admixture with an authentic specimen of sublimed natural purpurin also recrystallised from glacial acetic acid.

Triacetylpurpurin, was obtained by boiling 0·05 g. of purpurin with 2 c.c. of acetic anhydride and a fragment of anhydrous sodium acetate for 5 minutes. When the product was poured into 3 volumes of water and partially neutralised with ammonia, the triacetyl derivative crystallised; after recrystallisation from 90% alcohol, it formed yellow needles, m. p. 200—201° (alone or mixed with the triacetyl derivative of natural purpurin).

The author is indebted to Mr. S. Ellingworth for details of some of the patent literature and to Messrs. Scottish Dyes, Ltd. for the gift of the quinizarin used. He also wishes to record his thanks to Dr. Bain of the Department of Chemistry, University of Edinburgh, and to Professor Rowe and Dr. R. B. Forster of the University of Leeds for facilities afforded him in connection with this work.

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[*Received, October 19th*, 1931.]