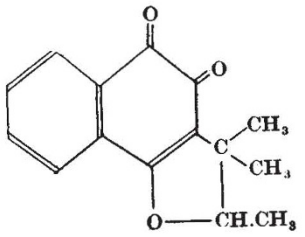
The new pigment, for which we propose the name *dunnione*, crystallizes in orange-red needles, m.p. 98–99°, from light petroleum or water, and has the molecular formula $C_{15}H_{14}O_3$. Its physical and chemical properties and the results of degradative experiments, including the formation of phthalic acid in oxidation processes, show it to be a β-naphthaquinone derivative. The third oxygen atom is neither hydroxylic nor ketonic, and the behaviour of dunnione towards alkalis indicates that the oxygen atom is a member of an easily ruptured chromane or coumarane ring. Acidification of the alkaline solution obtained under certain conditions does not regenerate dunnione but a new substance which is probably an α-naphthaquinone derivative. The formation of acetaldehyde by oxidation with alkaline hydrogen peroxide and the amount of acetic acid (1·6 mol.) produced on oxidation with chromic acid suggest that dunnione is 2 : 3 : 3-trimethyl-6 : 7-benzocoumarane-4 : 5-quinone (I) or the isomeride with the gem-dimethyl group directly attached to oxygen.



(I)

This is supported by the close agreement of the properties of dunnione and 2 : 3-dimethyl-6 : 7-benzocoumarane-4 : 5-quinone, which has been synthesized by Fieser[3].

A more complete account of this investigation will be published elsewhere.

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[1] *J. Indian Chem. Soc.*, **14**, 703 (1937).
[2] *Cf.* Robinson and Robinson, *Biochem. J.*, **28**, 1718 (1934).
[3] *J. Amer. Chem. Soc.*, **49**, 857 (1927).

Hæmocuprein, a Copper-Protein Compound of Red Blood Corpuscles

THAT copper is present in human blood has been known since 1875[1]. Its concentrations in the red blood corpuscles and serum of man and different animals, at different ages, under normal and pathological conditions, have been estimated by several workers[2,3]. Very little has been known, however, as to the state in which the copper is present in the blood.

The object of this investigation was to ascertain whether the copper present in the red blood corpuscles of mammals is free as an inorganic salt, or is combined with an organic substance.

The mere fact that the copper cannot be removed from a solution of plasmolysed red blood corpuscles by a very prolonged dialysis makes the possibility of its presence in the form of an inorganic salt very doubtful. That this copper is bound to a protein we are now able to demonstrate by isolating from the red blood corpuscles of the ox a pure crystalline copper-protein compound.

The main steps of isolation and purification of this compound are as follows: Red blood corpuscles of ox, after a thorough washing with salt solution, are plasmolysed with distilled water and treated with an alcohol chloroform mixture. The hæmoglobin-free solution which is filtered off contains most of the copper present in the corpuscles. This solution is treated with lead acetate, the precipitate being eluted with alkaline phosphate, dialysed, and the impurities removed with tricalcium phosphate. The clear solution is then precipitated with acetone, dissolved in water, fractionated by adsorption on alumina $c\gamma$ and dialysed. The clear and distinctly bluish solution thus obtained, on treating with alcohol, becomes opalescent, and on standing in the cold yields, within a short time, bluish crystals of a copper-protein compound. These crystals easily settle down forming a distinctly blue sediment. The analysis of the crystals shows 14·35 per cent nitrogen, 1·12 per cent sulphur and 0·34 per cent copper.

The copper-protein compound thus obtained, for which we propose the name of *hæmocuprein*, forms a fourth organic copper compound known in living organisms. Of the three other compounds, hæmocyanine and polyphenol oxidase are copper-protein compounds, while turacin is a copper-uroporphyrin compound.

We have found that in serum also the copper is present as a blue copper-protein compound very similar to hæmocuprein. Its identity with the latter will, however, be ascertained when this compound will be isolated in a pure state.

A more detailed account of the purification, properties and relationship of hæmocuprein to the copper of serum and tissues will be published elsewhere.

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[1] Porter, J. A., "Principles of Chemistry" (New York, 1875), 333 (from Sachs, A., *et al.*, 1935).
[2] Elvehjem, C. A., *Physiol. Rev.*, **15**, 471 (1935), contains extensive literature.
[3] Sachs, A., Levine, V. E. and Fabian, A. A., *Arch. Internal Medic.*, **55**, 227 (1935).

A Hæmoglobin from Bile Pigment

WHEN a solution of hæmoglobin and ascorbic acid in alkaline phosphate or in phosphate buffer of *p*H 7·6 is exposed to air at 20° for 48 hours, the solution shows an absorption band in the red (at about 674 mμ). On reduction by hyposulphite, this band is replaced by a strong band at 629 mμ[1]. By denaturation of the globin by alkali or pyridine, a hæmochromogen with an absorption band at 619 mμ is obtained. The latter is identical with the "α-pseudohæmoglobin" of Barkan and Schales[2]; in the preparation of these authors the denaturation is caused by the strong alkalinity of the cyanide solution.

At higher temperatures the conversion of hæmoglobin to these substances is much more rapid, but the oxidation of the prosthetic group is accompanied by a progressive oxidative denaturation of the globin part of the molecule. This causes at first the formation of an alkali-soluble green precipitate and ultimately of alkali-insoluble compounds. In such products[3] the prosthetic group becomes condensed