

japonicus and $2n = 20 + \alpha + \beta_1 + \beta_2$ in *Protohermes grandis*.

The opinion put forward by Tillyard in 1936 on palaeontological grounds therefore seems to be supported by the cytological evidence. Raphidioidea may be even closer to Planipennia than to Sialoidea, and the distinction between Megaloptera and true Neuroptera therefore unsound.

Note added in proof. Since writing the present note, I have received an article by Naville and Beaumont *Arch. d'Anat. micr.*, 32, 1936), which shows the same behaviour as I have found in another species of Raphidia.

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Jan. 29.

¹ Tillyard, *Proc. Linn. Soc. N.S. Wales*, 41 (1916).

² Withycombe, *Trans. Entom. Soc. London* (1924).

³ Killington, "A Monograph of the British Neuroptera", 1 (1936).

⁴ Handlirsch, in Schröder's "Handbuch der Entomologie", 3 (1925).

⁵ Handlirsch (& Beier), in Kükenthal's "Handbuch der Zoologie", 4 (1936).

⁶ Tillyard, *Proc. Linn. Soc. N.S. Wales*, 51 (1926).

⁷ Martynov, *Trav. Mus. geol. Acad. Sci. U.S.S.R.*, 4 (1928).

⁸ Tillyard, *Amer. J. Sci.*, (5), 23 (1932).

⁹ Naville and Beaumont, *Arch. d'Anat. micr.*, 29 (1933).

¹⁰ Ito, *Dobutsugakuzasshi*, 45 (1933).

Duality of the Reversibly Oxidized Forms of Vitamin C and the Polarization of its Dienol Group

OUR recent work¹ on oxygen absorption of acid vitamin C solutions suggested the existence of the oxidized form: vitamin + $\frac{1}{2}$ O, or vitamin - H. This form corresponds to the first step of the reversible oxidation of the vitamin, deshydroascorbic acid being the second. New evidence corroborates the duality of the reversibly oxidized forms of vitamin C. Phosphomolybdic acid ($P_2O_5(MoO_3)_{24} + 16 H_2O$) mixed with an acid solution of vitamin C develops a blue or a green colour. The blue colour reaches its maximum intensity when the ratio

$\frac{\text{ascorbic acid}}{\text{phosphomolybdic acid}}$ approaches $\frac{176}{3000}$. This colour

fades when the quantity of the oxidizer, the phosphomolybdic acid, is diminished, and turns green when it increases.


The blue colour may be obtained not only by the consequent increase of the concentration of vitamin, but also by adding to the weak ascorbic acid solution a substance such as cysteine. This last substance is not capable by itself of giving any colour reaction with phosphomolybdic acid, but acts by lowering considerably the potential of the solution. The changes from the blue to the green reaction and vice versa evidently depend upon the potential. Therefore these reactions must be evidence of the existence of two reversibly oxidized forms of the vitamin. To make this clearer, we have produced the maximum blue and green reactions and treated the solutions with hydrogen sulphide. Testing the liquids (after removal of hydrogen sulphide) with the Bezssonoff reagent [$3(MoO_3 \cdot 17(WO_3) \cdot P_2O_5 + 24H_2O)$] and iodine, we find about 94 per cent of the vitamin which was present before the colour reactions.

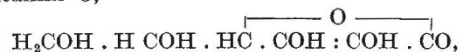
We also ascertained that after precipitation of the green colour by means of neutral lead acetate, and lead with sulphuric acid, the liquid no longer gives

the reactions of ascorbic acid. Later treatment with hydrogen sulphide restores the vitamin reactions.

Phosphomolybdic acid gives similar blue and green reactions with hydroquinol but not with pyrogallol, nor with various other polyphenols. Catechol gives a completely distinct yellow colour reaction; however, it possesses like vitamin C the common group COH : COH. The presence of such a group in the vitamin C molecule² is shown by the well-established formula of Hirst and confirmed by means of a titanium sulphate colour reaction (Ettori³).

Thus, phosphomolybdic acid gives identical colour reactions with hydroquinol and vitamin C, but not with catechol, in spite of the presence in these last two substances of the same dienol group (COH : COH). It is therefore evident that the dienol groups of vitamin C and hydroquinol are subject to a common influence which does not occur in the case of catechol.

The structure of hydroquinol, HO  OH, and of vitamin C,



indicates that in both substances the dienol group is polarized. This peculiarity does not distinguish the enol groups of catechol and of pyrogallol.

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¹ Bezssonoff, N., et Woloszyn, Mme. M., *C.R. Soc. Biol.*, 122, 941 (1936); *C.R. Acad. Sci.*, 203, 275 (1936).

² Pointed out first by Bezssonoff, *C.R. Acad. Sci.*, 180, 970 (1925).

³ Ettori, *C.R. Acad. Sci.*, 202, 852 (1936).

Tyrosine in Diseased Pedipalps

THE value of X-ray methods in the identification of minute quantities of crystalline substances is well demonstrated in the following example. Dr. E. Warren has been studying part of the collection of Pedipalps (arachnids related to the scorpions) in the British Museum (Natural History), and in two series of *Hypoctonus formosus* Butler, from Further India, he has found evidence of a fungus disease (actinomycosis), which had affected at least 70 per cent of the specimens. Associated with the fungus centres, which are scattered throughout the tissues of the host, there are yellowish-white spherules measuring up to $\frac{1}{2}$ mm. in diameter. These spherules are made up of radiating, birefringent needles which are probably pseudomorphous after the radiating fibres and hyphal tubes of an Actinomyces.

An X-ray photograph (using copper radiation) of one of the spherules yields a well-marked 'powder pattern' identical with a photograph of powdered artificial *l*-tyrosine, thus confirming Dr. Warren's preliminary determination based on solubility tests. Possible alternatives such as uric acid, the two hydrates of calcium oxalate, leucine, etc., are also excluded by their X-ray patterns. Moreover, two samples of *dl*-tyrosine, prepared by different methods, which were kindly sent to me by Prof. H. S. Raper, give patterns similar to, but not identical with, those of *l*-tyrosine. This distinction between *l*- and *dl*-tyrosine is enhanced in powder photographs of the hydrochloride derivatives. Hence tyrosine is present