XII. THE PIGMENTS OF BUTTERFLIES' WINGS.

I. *MELANARGIA GALATEA*.

BY DAVID LANDSBOROUGH THOMSON

(1851 *Exhibition Senior Student*).

From the Biochemical Laboratory, University of Cambridge.

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THE wings of the "Marbled White," *Melanargia galatea*, a Satyrine butterfly not uncommon in southern England, bear a pattern of black markings on a ground varying from creamy white to pale yellow. It was observed by Coste [1890] and various others that this ground colour was reversibly changed to a bright yellow by the action of alkalies or ammonia vapour, the colour returning to the normal pale tint when the alkali was washed away or the vapour allowed to diffuse into the air. This suggested to the writer that the pigment might be a flavone or flavonol, and when Sir F. G. Hopkins very kindly presented some 200 specimens of this butterfly from his own collection, an attempt was made to isolate the pigment in the hope of proving this.

The wings, carefully removed from the bodies, were first extracted with ether in a Soxhlet, and the yellow filtrate shaken with dilute aqueous ammonia, into which most of the colour passed. A certain amount of pigment insoluble in ammonia was, however, also present, and was divided between light petroleum and methyl alcohol. The fraction soluble in light petroleum gave the colour reactions with H_2SO_4 and HNO_3 characteristic of lipochromes, and showed the absorption spectrum of carotene. The much smaller amount of pigment dissolving in the methyl alcohol gave no reactions or spectrum to support the assumption that it was xanthophyll. Lipochromes have repeatedly been found in the lymph of larval Lepidoptera, for example by Poulton [1885], and in the wings of the imagines by Wieland and Schöpf [1925] in *Gonepteryx rhamni*. They occur probably in the spaces between the two laminae of the wing, rather than in the chitinous scales.

The wings were then extracted with alcohol, which removed most of the pigment, and the filtrate diluted with water and freed from alcohol by distillation under reduced pressure. They were further extracted with aqueous ammonia, which was filtered and neutralised and then repeatedly shaken up with ether to extract the pigment. The aqueous layer, however, retained a yellow colour, which became deeper in alkaline solution and was probably

mainly due to the presence of decomposition products of a tarry nature. Alkaline solutions of the pigment rapidly turn dark in air, and on neutralising yield a brown amorphous substance, possibly analogous to quercetinamide.

The various lots of pigment were washed several times by extracting with ether from neutral aqueous solutions and removing from the ether with ammoniacal solutions. They were then united in a concentrated alkaline solution, and the pigment precipitated by acidification. The precipitated pigment was dissolved in alcohol and recrystallised from this solvent three times, precipitation being aided by the addition of distilled water to the filtered solution.

In this way about half a milligram of a solid product was obtained, in the form of a yellow crystalline powder, somewhat sandy in appearance. It was readily soluble in acetic acid or hot alcohol, sparingly soluble in ether, and very slightly soluble in water. It dissolved readily in alkalis or in concentrated mineral acids with a bright yellow colour. The alcoholic solution gave a deep yellow precipitate with lead acetate, and with ferric chloride a greenish brown solution, fluorescing green but changing to a uniform deep red on warming. When boiled with magnesium powder and a few drops of HCl it yielded a pink filtrate which became bright yellowish green on making alkaline (formation of an allocyanidin). The melting point obtained was 253° (corrected), liquefaction being accompanied by partial decomposition. The molecular weight was determined by Rast's camphor method, 0.039 mg. pigment in 0.988 mg. camphor of melting point 174° , giving a depression of the melting point of 4.8° : this indicates a molecular weight of 313 ± 30 , the probable error with such small quantities and so slight a depression being not less than 10 %. The writer does not hesitate to say that these properties definitely lead to the conclusion that the pigment is a flavone or flavonol. Whilst no claim of identity can be made, the described properties of quercetin (molecular weight 302, melting point just over 250° with partial decomposition, and colour reactions similar to those described above, except that the lead salt is spoken of as orange or brick-red) agree fairly well with those of the substance discussed.

It is probable that the flavone is obtained by the larva from its food plants (*Dactylis glomerata*, *Phleum pratense* and other grasses), but the writer has been unable to find any reference to the flavones of these plants in the literature. Nor is anything known of the behaviour of such substances in the animal body, except that euxanthone passes partly unchanged through the mammalian body to reappear in the urine ("Indian yellow"). Palmer and Knight [1924] obtained from a Hemipteron, *Leptocoris trivittatus*, aqueous solutions of a yellow colour which was intensified by alkalis, and which they considered to be due to a flavone-like pigment; but they did not show that it was derived from plants. The writer hopes to continue the research in this direction.

SUMMARY.

A yellow pigment having the properties of a flavone or flavonol has been isolated from the wings of the Marbled White Butterfly, *Melanargia galatea*.

My best thanks are due to Prof. Sir F. G. Hopkins for his continued interest in this research, and especially for providing me with the butterflies used.

REFERENCES.

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