XLIV. THE FLOWER PIGMENTS OF *ANTIR- RHINUM MAJUS*. 2. THE PALE YELLOW OR IVORY PIGMENT.

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In a previous communication [Wheldale, 1913], the method of preparation of the crude pigment has been described. The varieties of *A. Majus* originally used for Mendelian experiments were the following:

White
Yellow
Ivory
Yellow tinged with bronze
Ivory tinged with rose doré
Bronze
Rose doré
Yellow tinged with crimson
Ivory tinged with magenta
Crimson
Magenta.

Ivory is dominant to yellow and since white may carry any factor but the one producing yellow, the result of crossing any variety with white depends on the gametic constitution of the white individual used. Of the varieties forming anthocyanin, the Mendelian relationship may be represented in the scheme on p. 442. Dominance is denoted by the direction of the arrows; thus rose doré is dominant to bronze, magenta to rose doré, etc.

It has been previously suggested that ivory contains a chromogen of the nature of a flavone, from which the red and purple anthocyanins are formed by stages of oxidation or polymerisation or both. Also that the pigment

of the yellow variety and of the yellow patch on the palate of all varieties (except white) is due to a second, more deeply coloured flavone. Microscopic examination and microchemical tests show that anthocyanin and yellow pigments are mostly limited to the epidermis of the corolla, while the inner tissues contain the ivory chromogen. It is obvious therefore that all crude extracts of entire flowers will contain two or more pigments.

Although no analyses have yet been made of the anthocyanins from crimson and bronze, yet purification of the crude pigment indicates that these colours are merely due to mixture of magenta with yellow, and red with yellow respectively and not to specifically different pigments.

The constituent pigments of the varieties may be thus expressed :

Yellow (ivory, yellow).

Ivory, lower lip (ivory, yellow).

„ upper lip (ivory).

Yellow tinged bronze, bronze, ivory tinged rose doré, rose doré (yellow, ivory and red).

Yellow tinged crimson, crimson, ivory tinged magenta (yellow, ivory, magenta).

Magenta, lower lip (yellow, ivory, magenta).

„ upper lip (ivory, magenta).

The crude pigment from yellow, ivory (upper lip), ivory tinged magenta, bronze, rose doré, crimson and magenta (both upper and lower lips separately) was extracted with ether for several months.

The yellow ether extracts were in each case crystallised from alcohol, the first deposits, consisting mainly of the ivory pigment, separated off and the

melting points determined. All the products melted between 336° and 340°. In five cases the acetyl derivative was prepared by boiling with acetic anhydride as described in the previous paper and crystallising several times from ethyl acetate. The final products were white substances crystallising in needles and all melting at 181–182°.

The five acetyl derivatives were submitted to combustion, giving the following results:

Acetyl derivations of ivory pigment from

	C.	H.
(1) yellow.....	63·10 %	3·94 %
(2) ivory, upper lip	62·84 %	3·99 %
(3) red.....	63·61 %	4·14 %
(4) bronze	63·10 %	3·92 %
(5) ivory, tinged magenta.....	63·23 %	3·88 %

which agree closely with combustion results of the acetyl derivative previously obtained from ivory extracted from magneta [Wheldale, 1913]:

Acetyl derivative of ivory pigment from magneta:

	C.	H.
(i)	63·19 %	4·30
(ii).....	63·21 %	4·22
(iii).....	62·95 %	4·31

It was there suggested that the ivory pigment might be apigenin, of which the acetyl derivative should theoretically give:

C.	H.
63·64 %	4·04 %

An acetyl derivative of apigenin was obtained by Kostanecki [Rupe, 1909]. Perkin [1897], on the other hand, was unable to acetylate apigenin but prepared a benzoyl derivative by the Schotten-Baumann process. The derivative thus prepared was slightly soluble in alcohol, more readily in benzene, from which it crystallised in colourless needles melting at 210–212°.

A benzoyl derivative having the same properties and melting point as the above was prepared from the ivory pigment by the following method. The pigment was dissolved in about five times its weight of pyridine, cooled in ice and benzoyl chloride added. On addition of dilute sulphuric acid, a yellow oil separated out which was collected and spread on a porous plate. It solidified after a time and was extracted with ether which removed benzoic acid and some yellow products leaving a white wax-like substance. The latter was crystallised from benzene. Melting point 210–212°.

Analysis results:

Benzoyl derivative of ivory pigment:

C.	H.
73.82%	4.02%.

Theoretical result for benzoyl derivative of apigenin:

C.	H.
74.23%	3.78%.

The properties of apigenin given by Aberhalden [1911] are as follows:

Formula, $C_{15}H_{10}O_5$.

M. Pt. 347°. Crystallises in yellowish-white platelets, readily soluble in alcohol, slightly in ether and hot water. Becomes bright yellow in alkali solution. The yellow solution in concentrated sulphuric acid has at first a greenish, later a bluish fluorescence. The alcoholic solution gives a blackish-brown coloration with ferric chloride and brown-red with ferrous sulphate.

The ivory pigment corresponds entirely with this description. From the acetyl derivative, the pure pigment was obtained by hydrolysis with alcoholic soda. On neutralisation with acid, the pigment came down as a yellowish-white precipitate and after crystallisation from dilute alcohol, melted at 347°.

We therefore conclude that the ivory pigment is apigenin, and that it is present in each of the main classes of varieties of *Antirrhinum* with the exception of the white. In the plant, apigenin exists undoubtedly as a glucoside, though the kind of sugar and the number of molecules attached still remain to be ascertained.

It appears possible that the deeper yellow pigment may prove to be a flavone, similar in constitution to apigenin, but deeper in colour owing to the presence of an additional hydroxyl group.

REFERENCES.

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 Perkin, A. G. (1897), *J. Chem. Soc.*, 71, 801.
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