

XCVI.—*The Occurrence of Flavone as the Farina of the Primula.*

By HUGO MÜLLER.

MANY species of primula exhibit a characteristic dusty or mealy secretion on their leaves, flower stalks, and seed capsules, known to gardeners as meal or farina, and this peculiarity is specially pronounced in the case of certain specimens introduced in recent times from China and Japan. Similar cuticular exudations are of frequent occurrence in plants, and often give a characteristic appearance to leaves, fruits, and other parts, and it therefore

appeared of considerable interest to endeavour to ascertain the chemical nature of the secretion, especially as a preliminary examination had shown that it was not, as was at first supposed, of a wax-like nature. It was found possible to collect some of the powder with the aid of a brush from a considerable number of plants of *P. pulverulenta*, and also by sifting the seeds and seed capsules, and this formed part of the material for the present investigation, but some was also obtained from *P. japonica* and other specimens. The substance collected from the plant in this way is a soft, mealy powder, and is either quite white or has a faint yellow tinge. With the exception of a minute quantity of accidental impurity, the powder is readily soluble in the usual organic solvents, and it was found that light petroleum was the most suitable for its purification, because it is fairly readily soluble in the boiling solvent, and separates almost completely on cooling in bulky, crystalline tufts, which cause the solution, if concentrated, to appear nearly solid. By this means, a product was obtained which, after recrystallisation, had the appearance of being homogeneous and pure. The final mother liquors yielded a small quantity of wax-like substances, and it is clear that the material under examination consisted almost entirely of the substance obtained in the form of the silky, crystalline tufts.

As only a portion of the powder could be removed from the plant by the brush and by sifting, the remainder was obtained by extracting with benzene, in which the powder is readily soluble. In this case, the process of purification is more troublesome, because the benzene extract contains a considerable quantity of wax and other substances which hinder crystallisation; but the difficulty was finally surmounted by a preliminary treatment of the benzene extract with a weak solution of sodium hydroxide in the cold, which dissolves a considerable portion of the impurities. The residue was then digested with 40 per cent. alcohol, in which the wax is sparingly soluble, and, after repeated alternate recrystallisation from this solvent and light petroleum, the substance was obtained in a pure state:

0.0892 gave 0.2647 CO_2 and 0.0372 H_2O . $\text{C}=80.9$; $\text{H}=4.6$.

0.1507 „ 0.4475 CO_2 „ 0.0614 H_2O . $\text{C}=81.0$; $\text{H}=4.5$.

$\text{C}_{15}\text{H}_{10}\text{O}_2$ requires $\text{C}=81.1$; $\text{H}=4.5$ per cent.

This formula was also confirmed by molecular-weight determinations made by the cryoscopic method. The substance melts at $99-100^\circ$, and, when heated in a charcoal vacuum, distils without change. It is readily soluble in alcohol, acetone, benzene, and the usual organic solvents; in concentrated sulphuric acid and nitric acid it dissolves, and on addition of water separates appar-

ently unchanged. In cold water it is almost insoluble, but when boiled with water it dissolves to a slight extent, and, on cooling, the solution first becomes milky, and later on deposits silky tufts. It is insoluble in cold dilute sodium hydroxide, but on boiling dissolves gradually, yielding a yellow solution, and at the same time the characteristic odour of acetophenone becomes perceptible. Decomposition takes place still more readily when the substance is digested with methyl alcoholic sodium hydroxide, but the most satisfactory result was obtained by the use of methyl alcoholic barium hydroxide. When the substance is mixed with this reagent in the cold, it rapidly changes to a bright orange, crystalline mass, the solution becomes deep yellow, and, on warming, the odour of acetophenone becomes very perceptible. After remaining overnight, water was added, the whole saturated with carbon dioxide, and submitted to distillation in steam, when, so soon as the methyl alcohol had been removed, a milky distillate passed over, from which a heavy oil separated. This crystallised on cooling with ice, and melted again when the temperature was raised to about 20° ; the addition of phenylhydrazine acetate caused the separation of acicular crystals of a phenylhydrazone, which melted at 105° , and there can, therefore, be no doubt that the oil was acetophenone. The yellow solution left in the steam distillation flask was diluted considerably with water, acidified with a slight excess of hydrochloric acid, and the yellow precipitate collected, washed with water, dried, and recrystallised from methyl alcohol with the aid of animal charcoal. This new substance separates from methyl alcohol, in which it is sparingly soluble in the cold, in beautiful yellow prisms,* and melts at 120° :

0.1086 gave 0.2988 CO_2 and 0.0502 H_2O . $\text{C}=75.0$; $\text{H}=5.3$.

$\text{C}_{15}\text{H}_{12}\text{O}_3$ requires $\text{C}=75.0$; $\text{H}=5.0$ per cent.

I am indebted to Mr. T. V. Barker for the following crystallographical examination of this substance.

This substance crystallises in the monoclinic system. Complex-symbol: †

$$\begin{array}{r} 4h; + 12\frac{3}{4} \\ 64\frac{1}{2} \\ 1 \end{array}$$

* In some of the experiments the yellow colour of the crystals was very faint and it is possible that the substance is, in reality colourless.

† In the following description the indices are allotted in accordance with the principles adopted by Fedorov in his work on the correct setting of crystals. The "complex-symbol" unambiguously epitomises the crystallographic characters which distinguish the compound from every other substance, and will facilitate any future identification by the method of crystallochemical analysis.

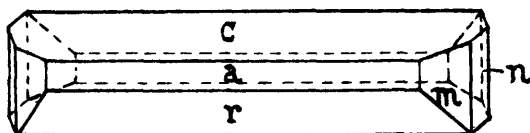
The habit of the original crystals (from alcohol) was prismatic (see Fig.), owing to an elongation along the symmetry axis, the forms being $c\{001\}$, $r\{\bar{1}01\}$, $a\{100\}$, $m\{110\}$, and $n\{130\}$. Since the crystals afforded very poor reflexions on the goniometer, the substance was recrystallised from acetone. The crystals thus obtained differed from the original specimen in the following particulars: although the habit was again prismatic, the elongation was parallel to the edge mm , the predominant prismatic form being n ; moreover, the form $s\{101\}$ was occasionally observed. Following are the results of the goniometrical measurement.

Ratios of the axes $a : b : c = 1.06 : 1 : 1.50$; $\beta = 102\frac{3}{4}^\circ$:

	Mean measured.	Calculated.
$ar = \bar{1}00 : \bar{1}01$	$39\frac{1}{2}^{\circ*}$	—
$rc = \bar{1}01 : 001$	$63\frac{1}{2}^{\circ*}$	—
$cs = 001 : 101$	47	$46\frac{1}{2}^{\circ}$
$sa = 101 : 100$	$30\frac{1}{2}$	$30\frac{3}{4}$
$nn = 130 : \bar{1}30$	36°	—
$am = 100 : 110$	$46\frac{1}{2}$	46

An optical determination carried out on the Fedorov universal stage gave the following results: Axial plane (010); positive acute

o-Hydroxydibenzoylmethane.



disectrix exactly parallel to the vertical edge mm . Observed (uncorr.) axial angle 75° . Pleochroism strong: γ =deep yellow, β =light yellow, α =colourless. Double refraction, strong.

The yellow substance, melting at 120° , gives a deep violet coloration when ferric chloride is added to its alcoholic solution.

It is readily soluble in sodium hydroxide, and, if the deep yellow solution is boiled, it is decolorised; drops of acetophenone separate, and the filtered liquid gives with hydrochloric acid a colourless, crystalline precipitate, which consists mainly of salicylic acid, but contains a small quantity of another acid, which is doubtless benzoic acid.

When the yellow substance is digested with acetic anhydride and a little anhydrous sodium acetate for half an hour, it yields a colourless *acetyl* derivative, which crystallises from alcohol in needles, and melts at 118° :

0.1018 gave 0.2883 CO_2 and 0.0432 H_2O . $\text{C} = 77.2$; $\text{H} = 4.7$.

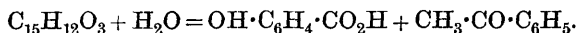
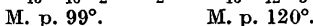
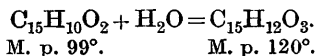
$\text{C}_{17}\text{H}_{12}\text{O}_3$ requires $\text{C} = 77.3$; $\text{H} = 4.5$ per cent.

The dilute aqueous filtrate from which the yellow substance

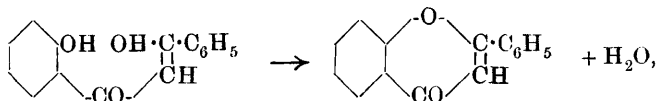
(m. p. 120°) had been precipitated by hydrochloric acid, as explained on p. 874, and which contained barium chloride, was exactly freed from barium by sulphuric acid and concentrated on the water-bath. As the concentration proceeded, slender crystals gradually formed, and these, after collecting, washing, and drying, exhibited all the reactions of salicylic acid; thus, for example, the solution in water gave a violet coloration with ferric chloride, and, on distillation with lime, the odour of phenol was recognised. The melting point was, however, much too low, namely, about 130—135°, and this was apparently due to slight admixture with benzoic acid, which was difficult to remove. However, by fractional distillation in steam and subsequent fractional crystallisation from light petroleum, glistening needles were ultimately obtained, which softened at 150°, melted at 153—154°, and consisted of almost pure salicylic acid. (Found, C=61·5; H=4·6. Calc., C=60·9; H=4·4 per cent.)

The Identity of the Substance (m. p. 99—100°) from the Farina of the Primula with Flavone.

The substance (m. p. 99—100°) has the formula $C_{15}H_{10}O_2$, and, on hydrolysis with baryta, is converted into the yellow substance, $C_{15}H_{12}O_3$ (m. p. 120°), which, by the continued action of alkalis, decomposes into acetophenone and salicylic acid:



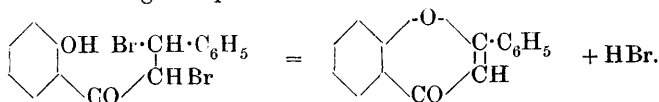
It follows that the substance, $C_{15}H_{12}O_3$, must be *o*-hydroxy-dibenzoylmethane, $OH \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_5$, a substance which does not appear to have been previously described. If water is eliminated from this substance, so as to ascertain the constitution of the substance, $C_{15}H_{10}O_2$, the most natural direction of the change would be for the enolic modification of the diketone to lose water according to the scheme:



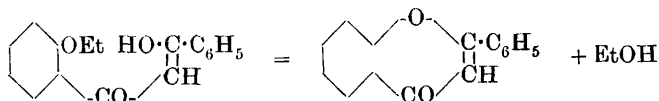
and, if this view is correct, it follows that the substance, $C_{15}H_{10}O_2$, of which the farina of the primula essentially consists, must be flavone.

Flavone was first obtained by Kostanecki and Feuerstein (*Ber.*, 1898, **31**, 1758) from 2-acetoxyphenyl styryl ketone dibromide by

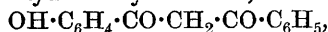
the action of alkalis, the acetyl group and hydrogen bromide being eliminated during the process:



Subsequently (*Ber.*, 1900, **33**, 333), the same investigators showed that flavone is readily produced when *o*-ethoxydibenzoylmethane is boiled with hydriodic acid:



When obtained by either of these reactions, flavone crystallised in colourless needles, melting at 97° , and, when hydrolysed with alkalis, it yielded acetophenone, salicylic acid, benzoic acid, and *o*-hydroxyacetophenone, and although Kostanecki and Feuerstein assume that *o*-hydroxydibenzoylmethane,



is an intermediate stage, they did not succeed in isolating this substance from the product of hydrolysis.

It will be seen that flavone, prepared synthetically by either of the above methods, has properties which are practically identical with those of the substance, $\text{C}_{15}\text{H}_{10}\text{O}_2$ (m. p. 99 – 100°), obtained from the farina of the primula. In order to leave no doubt as to the identity, a small quantity of flavone was prepared by the second of the synthetical methods described above, and a careful examination showed that the pure substance melts at rather a higher temperature than Kostanecki and Feuerstein state, namely, at 99 – 100° , and that, on hydrolysis with alcoholic barium hydroxide, it yields *o*-hydroxydibenzoylmethane (m. p. 120°); furthermore, no alteration in melting point was observed when the substance from the primula was mixed with synthetical flavone.

The observation that the farina of the primula consists of flavone in an almost pure condition is a matter of considerable interest, and it does not appear that this substance had previously been observed in the vegetable kingdom, although it has long been known that many of the yellow colouring matters, for example, quercitrin, chrysin, and luteolin, which are so widely distributed in plants, are hydroxy-derivatives of flavone.

It is difficult to form any idea of the physiological function which flavone exercises in the economy of the plant life of the primula.

The fact that it is excreted so freely on the surface of the plant would seem to imply that it is of no further use in the life process,

although its repellent action towards water may be a useful function.

In this connexion, it may be mentioned that, whilst in some species of primula, as, for example, in *P. auricula*, the leaves are covered all over from an early stage, in others, such as *P. frondosa*, only the underside is covered. Generally speaking, the flavone makes its appearance only with the development of the inflorescence, and its secretion increases with the maturation of the seeds, as, for example, in the case of *P. kewensis*, *P. japonica*, *P. cockburniana*, *P. pulverulenta*, and others.

It is remarkable that the excretion of flavone does not appear to be a necessary result of the life process of the plant. It has, for instance, been observed that, amongst a number of plants of *P. denticulata* raised from seed, there were several the leaves of which did not secrete any flavone, and yet they were perfectly healthy, and the same behaviour has also been noticed in the case of *P. capitata*. The reason for the occurrence of flavone is therefore, in the meantime, as much a puzzle as that of the occurrence of so many other substances, often of much more complicated nature, as normal secretions of plants.

In conclusion, I wish to record my thanks to Prof. Perkin for the interest he has taken in this investigation and the analyses he has kindly made for me in the chemical laboratory, Oxford.

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