LXXVII.—*Occurrence of Quercetin in the Outer Skins of the Bulb of the Onion* (Allium cepa).

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It has long been the custom to use the outer dry skins of the bulb of the onion for dyeing Easter eggs; for this purpose the eggs are wrapped in the skins, the latter being kept in position by tying with thread or otherwise, after which the eggs are boiled in the usual manner. By this means a marbled or mottled pattern is obtained in various shades of brown, orange, and yellow.

The effect thus produced seemed to indicate that onion skins probably contain a yellow adjective colouring matter towards which, in the custom alluded to, the lime of the egg shell acts as a mordant. To test this point, a piece of ordinary striped mordanted calico was dyed for about ten minutes at a boiling heat with onion skins, when the aluminium mordant became a full bright yellow, the iron mordant a dark greenish-olive. Samples of wool mordanted with chromium, aluminium, tin, and iron, were also dyed with onion skins, the colours obtained being respectively brownish-olive, yellow, bright orange, and greenish-olive.

These results proved that this supposition was correct, and finding by further comparative dyeing experiments that the colouring power of onion skins was quite equal to that of such well known dye-stuffs as old fustic and quercetin bark, it seemed desirable to ascertain, if possible, the nature of the colouring matter, and so determine whether or not it is identical with any existing mordant colouring matter.

At the time of making these preliminary experiments, we were not aware that onion skins had ever been used for the purpose of dyeing textile materials, but the following passage, translated from Leuch's *Farben und Färbekunde*, **1**, 434, (1825), shows that they were formerly so employed, probably, however, only to a limited extent, and in districts where the art of dyeing was still practised as a home industry:—"The outer skins of onion bulbs which are of a brownish-orange colour, have long been used in German households for dyeing Easter eggs yellow, and in conjunction with alum, for dyeing woollen, linen, and cotton materials. The colour yielded is fast and particularly brilliant. According to Kurrer's observations, onion skins are very suitable for dyeing cotton, on which they give a cinnamon-brown with acetate of alumina, a fawn with alumina and iron, a grey with iron salts, and a variety of shades with other additions."

The colouring matter was extracted by boiling the onion skins (500 grams) for one hour with distilled water (9 litres). The yellow liquor thus obtained was strained through calico and allowed to cool over-night, when the impure colouring matter was deposited in the form of a pale olive precipitate. Several kilos. of skins were treated in this manner, and by extracting three times with water instead of once only, the yield of crude colouring matter was increased, the average yield of dry precipitate being about 1·3 per cent. on the weight of onion skins. The filtered orange-brown liquors when concentrated did not deposit any further precipitate on cooling, they were, therefore, evaporated to dryness, and yielded a considerable quantity of a brown, friable, resinous, dry extract.

The finely ground, impure colouring matter was digested with boiling alcohol, filtered to remove a brown, insoluble product, and the filtrate evaporated to a small bulk. On cooling this solution, crystals were deposited, but as they were contaminated with a wax-like substance, and could not be readily purified by recrystallisation, the hot alcoholic liquid was poured into a large bulk of ether, and the mixture washed with water until colourless washings were obtained, and a sticky, black product no longer separated. On extracting the ethereal solution with dilute alkali, the whole of the colouring matter was removed, the wax remaining dissolved in the ether; on neutralising the alkaline liquid, a yellow precipitate was thrown down, which was collected and purified by crystallisation from dilute alcohol.

0·1088 dried at 160° gave 0·2368 CO_2 and 0·0355 H_2O. C = 59·36; H = 3·62.

$C_{15}H_{10}O_7$ requires C = 59·60; H = 3·31 per cent.

The substance was obtained as a glistening mass of yellow needles sparingly soluble in boiling water, readily in alcohol. Its alcoholic solution gives with lead acetate, an orange-red precipitate, and with ferric chloride a dark green coloration. When suspended in boiling acetic acid and treated with mineral acids, crystalline compounds were obtained, which by the action of water became decomposed into the colouring matter and free acid. In order to ascertain its molecular weight, the sulphuric acid compound was analysed.

0·1295 gave 0·2158 CO_2 and 0·0345 H_2O. C = 45·44; H = 2·96.

$C_{15}H_{10}O_7 \cdot H_2SO_4$ requires C = 45·00; H = 3·00 per cent.

Its true formula was, therefore, $C_{15}H_{10}O_7$.

It was converted into its acetyl compound by digestion with acetic anhydride and anhydrous sodium acetate in the usual way. The product, when crystallised from alcohol, formed colourless needles melting at 190—191°.

0·1221 gave 0·2622 CO_2 and 0·0437 H_2O. C = 58·56; H = 3·97.
$C_{15}H_5O_7(C_2H_3O)_5$ requires C = 58·59; H = 3·90 per cent.

To determine the number of acetyl groups present in this compound, it was decomposed by sulphuric acid in acetic acid solution, water being then added and the regenerated colouring matter collected and weighed.

1·0236 gave 0·6075 $C_{15}H_{10}O_7$. $C_{15}H_{10}O_7$ = 59·34.
$C_{15}H_5O_7(C_2H_3O)_5$ requires $C_{15}H_{10}O_7$ = 58·98 per cent.

It therefore contained five hydroxyl groups.

Action of Fused Alkali.—The colouring matter was heated at 150—170° for half an hour with a solution of ten times its weight of potassium hydroxide in a little water. The product was dissolved in water, the solution neutralised with acid, extracted with ether, and the crystalline residue remaining after evaporation of the ether, dissolved in water and treated with lead acetate solution. A colourless precipitate was thus formed, which was collected, suspended in water and decomposed in the usual manner. From the aqueous liquid, by extraction with ether, a product was obtained which crystallises from water in colourless needles, melting at 195° and giving with ferric chloride in aqueous solution a green coloration. It was evidently *protocatechuic acid*. The filtrate from the lead salt of the above acid was found to contain *phloroglucinol*.

Dyeing experiments were carried out with the colouring matter, using striped mordanted calico, and wool mordanted with chromium, aluminium, iron, and tin. The shades obtained were identical with those given by quercetin. The above results prove conclusively that the colouring matter of onion skins is *quercetin*. It may be mentioned that though no further confirmation is necessary, a bromine derivative was prepared which had all the properties of dibromoquercetin.

As above shown in the identification of this substance considerable pains have been expended, and this was considered necessary on account of the close similarity in external properties of the various known colouring matters of the quercetin group, and also the slight differences between the melting points of their derivatives. Numerous isomerides of quercetin have yet to be discovered and reasoning by analogy, these will probably possess very similar properties.

It is interesting to note with regard to the quercetin group, that whereas fisetin is only known at present to exist in young fustic (*Rhus cotinus*), luteolin in weld (*Reseda luteola*), morin in old fustic and jackwood (*Morus tinctoria* and *Artocarpus integrifolia*), and rhamnetin and rhamnazin in Persian berries, quercetin itself has a much more widely distributed existence. For instance, it has been found present

in quercitron bark, Persian berries, catechu and in tea leaves; also in the bark of the apple tree and horse chestnut, and in numerous other natural products. That this coincidence is more apparent than real is possible, for there are indications that this is so in further work that is being carried out in this department on the yellow colouring matters of numerous plants.

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