CXVI.—*Notes on Luteolin and Apigenin.*

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KILIANI AND MAYER (*Ber.*, 1901, **34**, 3577) have recently shown that Fleischer's digitoflavone (*Ber.*, 1899, **32**, 1184) is identical with luteolin, the yellow colouring matter of weld. As the latter author only obtained a tribenzoyl derivative and a tribenzenesulphonate from his substance, it appeared to contain but three hydroxyl groups, whereas luteolin had been previously shown to contain four (Trans., 1896, **69**, 209). Had Fleischer, however, critically examined his acetyl derivative, he would have found that four acetyl groups were present. In their paper, Kiliani and Mayer make the somewhat sweeping statement, "Durch Benzoylirung des Digitoflavons nach der Vorschrift Fleischer's und nach der von Perkin wurde nur ein Tribenzoat erhalten"; thus, employing the Schotten-Baumann method, they obtain a substance melting at 200—201° (my melting point for tetrabenzoyl-luteolin), which on analysis they find to be a tribenzoyl derivative. On further treatment by Deninger's method (*Ber.*, 1895, **28**, 1322), they converted this into tetrabenzoyl-luteolin (m. p. 200·5°). Now as tri- and tetra-benzoyl-luteolin respectively require C = 72·24, and C = 73·50 per cent., and I previously obtained C = 73·33 per cent., a portion of my original substance, which had been placed in the museum of this department, was analysed again :

0·1068 gave 0·2868 CO_2 and 0·0370 H_2O. C = 73·24 ; H = 3·84.

Again, some luteolin was prepared from weld and benzoylated by the Schotten-Baumann method. It melted at 200—201° :

0·1098 gave 0·2962 CO_2 and 0·0380 H_2O. C = 73·57 ; H = 3·84.

It was therefore a *tetrabenzoyl* compound.

To leave no doubt as to the accuracy of this result, a sample of tetrabenzoyl-luteolin, prepared according to the directions of Kiliani and Mayer, was crystallised from benzene in which an equal weight of the substance obtained by the Schotten-Baumann method had been dissolved. As a result, its melting point was unaltered, and there could be no doubt that the *two substances were identical.*

In the first experiments with the object of preparing tetrabenzoyl-luteolin by Deninger's method, an unexpected result was obtained, due, as was subsequently discovered, to the use of an old sample of benzoyl chloride of poor quality. Thus the product was very sparingly soluble in benzene, melted at 217—218°, and, as analysis showed, was evidently Fleischer's *tribenzoyl-luteolin* (m. p. 219°):

0·1134 gave 0·2990 CO_2 and 0·0383 H_2O. C = 71·90 ; H = 3·75.

On heating with benzoic anhydride, this yielded the above tetrabenzoyl derivative.

It is well known that by the Schotten-Baumann method higher or lower benzoyl derivatives result according to the concentration, and the quantity of the alkaline liquid which is employed, probably also the rapidity or otherwise with which the benzoyl chloride is added, may affect the result. Thus Schunck and Marchlewski (Trans., 1894, **65**, 187), employing one part of caustic soda with eight parts of water, obtained heptabenzoylruberythric acid, but with a 10 per cent. solution only a hexabenzoyl derivative was formed. I have usually experimented with a solution of 1 gram of the substance in 30 c.c. of the 10 per cent. alkaline liquid.

As both Fleischer and I obtained the tribenzoyl-luteolin by distinct methods, it seems likely that in the reaction the formation of this compound precedes that of the tetrabenzoyl-luteolin. Should this be the case, the existence of Kiliani and Mayer's tribenzoyl-luteolin (m.p. 200—201°) is difficult to understand.

In his paper on luteolin (*Ber.*, 1900, **33**, 3416), Kostanecki does not notice that the correct melting point for acetyl-luteolin is given in one of my recent papers (Trans., 1899, **75**, 831). The earlier melting point, 213—215°, was too low, and led to the suspicion that a trace of a second colouring matter was present; this was subsequently shown to be apigenin (Trans., 1900, **77**, 1314).

Apigenin.

Since the previous communication (Trans., 1900, **77**, 416), Czajkowski, Kostanecki, and Tambor (*Ber.*, 1900, **33**, 1988) have synthesised apigenin,* and the constitution assigned to this substance (Trans., 1897, **71**, 806) is thus completely established. To this substance, and also to chrysin, I have assigned feeble tinctorial properties, which these authors appear to doubt, for the following statements occur in their paper. "Das 1:3:4′-Trioxyflavon färbt ebenso wie das Chrysin, gebeizte Baumwolle nicht an." "Das Vitexin soll nämlich nach Perkin gebeizten Kattun anfärben und soll . . . . ein Glykosid des Apigenins . . . . sein. Als Begründung für diese Ansicht führt Perkin unter Anderem an, dass das Puriri-Holz ähnlich dem Apigenin färbt. Lindenborn halt aber . . . . dass das Apigenin kein beizenzeihender gelber Farbstoff ist." This statement is full of inaccuracies, as I do not once refer to "gebeizten Kattun," I have not said that "Puriri-Holz" dyes like apigenin, and finally I have considered

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* A misprint occurs in Trans., 1897, **71**, 815. The melting point of acetylapigenin diethyl ether, I find on referring to my notebook, should be written as 151—152°, and obviously not as 181—182°.

vitexin to be apigenin with a side chain attached, and *possibly* a stable glucoside of this substance. Other references to the tinctorial properties of these substances are as follows: "Gebeizte Baumwolle wird durch Chrysin nur sehr wenig gefärbt, man erhält auf Thonerde ein ganz blasses Schwefelgelb; auf Eisen ein schwaches Kastanienbraun (Rupe 'Die Chemie der naturlichen Farbstoffe,' p. 69)." "Apigenin und Methyl-luteolin differiren wenig in der Intensität der Färbung. Bei ersterem kann kaum von einer solchen gesprochen werden, Methyl-luteolin färbt etwas besser. . . . . Beide sind keine Farbstoffe; man kann mit keinem von beiden Körpern nur annähernd einer Färbung erzielen . . . ." (Vongerichten, *Ber.*, 1900, **33**, 2337). As I have previously shown, mordanted wool is far preferable as a test of the dyeing properties of these and allied colouring matters than mordanted calico; thus, whereas rhamnazin yields well-defined shades with the former, towards the latter it hardly behaves as a dyestuff. In the case also of wool mordanted with aluminium and iron, it is beneficial to add a trace of chalk to the dye-bath.

Now, although I was the first to prepare chemically pure apigenin (by means of the ethyl ether), the material I principally employed, as Vongerichten has shown, was contaminated with a trace (not more than half a per cent.) of luteolin methyl ether, which, from its close resemblance to apigenin, I did not at first suspect to be present. Vongerichten was able to obtain a very crude specimen of the substance (*loc. cit.*, p. 2335), containing about 50 per cent. of the glucoside of luteolin methyl ether. Such being the case, fresh specimens of apigenin and chrysin were prepared and submitted to most exhaustive purification. Dyeing experiments with these corroborated in all respects the results previously given, and there can be no doubt that these substances possess a distinct, though feeble, dyeing property. In other words, it is impossible to prepare specimens of chrysin or apigenin which do not behave in this manner, and although the shades are weak, and for practical purposes useless, the matter is scientifically interesting, and can be used for purposes of identification. It was the chocolate shade given by the iron mordant which first pointed to a similarity in constitution between apigenin and vitexin, and later work has considerably enhanced this view. It has been previously pointed out (Trans., 1896, **69**, 1290) that both gentisin and euxanthone behave as feeble dyestuffs towards mordanted wool, but according to Rupe (*loc. cit.*, p. 9) "Euxanthon hat keine färbenden Eigenschaften."

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