XCII.—*Acid Compounds of Natural Yellow Colouring Matters.* Part II.

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IN a previous communication (Perkin and Pate, *Trans.*, 1895, **67**), it was shown that certain yellow colouring matters, when treated with mineral acids in the presence of boiling acetic acid, yield crystalline compounds, the composition of which may be generally represented as an additive product of 1 mol. of the colouring matter with 1 mol. of acid; for instance, the quercetin compounds have the formula, $C_{15}H_{10}O_7, H_2SO_4$, $C_{15}H_{10}O_7, HBr$, and $C_{15}H_{10}O_7, HCl$. These substances in the presence of water are decomposed quantitatively into the colouring matter and free acid. It was there pointed out that the natural *yellow* mordant dye-stuffs, which contain carbon, hydrogen, and oxygen only, belong as far as their constitution is known principally to three classes, namely, the ketones, xanthenes, and phenylated pheno- γ -pyrones. Closely allied also to these is the anthraquinone series, which, however, contains no yellow dye-stuff coming under this head.

Ketone.

Xanthone.

Phenylated pheno-γ-pyrone.

Anthraquinone.

Of the substances which gave this reaction with acids, quercetin and fisetin were known from the work of Herzig to belong to the third group, whilst it has since been shown that there is little doubt that morin (Bablich and Perkin, this vol., 792) also belongs to this class. Previously, no member of the second or xanthone group could be obtained for examination, and but one member of the ketones was available, and it was, therefore, pointed out that before attempting to assign a constitution for these compounds with acids, it was advisable to study the behaviour of members of all these groups in this respect. With this object, the investigation has been continued from time to time, the isolation or purification of many of the substances employed being necessarily slow. Though some of the results are of a negative character, not only are they interesting theoretically, but they tend to show that the property of reacting with acids is peculiar to and distinguishes the quercetin group from those other classes of yellow mordant dye-stuffs at present known.

Ketone Group.—Of this class, “alizarin yellow A” (trihydroxybenzophenone), $C_6H_5 \cdot CO \cdot C_6H_2(OH)_3$ [$(OH)_3 = 1:2:3$], and “alizarin yellow C” (gallacetophenone), $C_6H_2(OH)_3 \cdot CO \cdot CH_3$, were examined, but no compounds with an acid could be obtained from them. In the previous paper (*loc. cit.*), it was shown that maclurin (pentahydroxybenzophenone) does not combine with acids, and as these three substances may be considered as typical dye-stuffs of this group, it appears evident that the ketone colouring matters do not yield acid compounds. It is of interest to mention here that catechin from *Catechu*, kinoïn from Malabar Kino, and cyanomaclurin from *Artocarpus integrifolia*, also do not yield these compounds with acids. The constitution of these substances is not known, but in some respects their properties are similar to those of the ketone group.

Xanthone Group.—Those selected for examination were gentisin, the colouring matter of gentian root (Kostanecki and Tambor, *Monatsh.*, 1895, **15**, 1); datiscetin obtained from the glucoside datiscin which exists in *Datisca cannabina* (Schunck and Marchlewski, *Annalen*, 1894, **277**, 261), and euxanthone. The constitution of these is given in the former paper. As a result it was found that they yielded no compounds with mineral acids.

Various members of the *Anthraquinone* group also gave negative results. The compound of purpuroxanthin with acetic acid

$3C_{11}H_8O_4, 2C_2H_4O_2$, (Plath, *Ber.*, 1877, **10**, 615), is interesting, but this is rather a case of acetic acid of crystallisation, than of an acid compound such as those described in this paper. A somewhat similar product is that from rhamnazin (*Trans.*, 1895, **67**, 498), $C_{17}H_{14}O_7, C_2H_4O_2$, which I obtained in a similar way by crystallising this substance from acetic acid.

Quercetin Group.—The colours of this class previously examined were quercetin, rhamnetin, rhamnazin, fisetin, and morin. Since then, however, the acid compounds of luteolin (this vol., 208), and myricetin (*ibid.*, 1287), have been described, and at the same time it was shown that these colouring matters bear a close relationship to quercetin and fisetin. The various compounds of these colouring matters with acids which have been obtained are given in the following table.

Myricetin,	$C_{15}H_{10}O_8$	$C_{15}H_{10}O_8, H_2SO_4$	$C_{15}H_{10}O_8, HBr$	$C_{15}H_{10}O_8, HCl^*$	$C_{15}H_{10}O_8, HI^*$
Quercetin,	$C_{15}H_{10}O_7$	$C_{15}H_{10}O_7, H_2SO_4$	$C_{15}H_{10}O_7, HBr$	$C_{15}H_{10}O_7, HCl^*$	$C_{15}H_{10}O_7, HI^*$
Rhamnetin,	$C_{16}H_{12}O_7$	$C_{16}H_{12}O_7, H_2SO_4$	no compound	no compound	no compound
Rhamnazin,	$C_{17}H_{14}O_7$	$C_{17}H_{14}O_7, H_2SO_4$			
Morin,	$C_{15}H_{10}O_7$	$C_{15}H_{10}O_7, H_2SO_4$	$C_{15}H_{10}O_7, HBr$	$C_{15}H_{10}O_7, HCl$	$C_{15}H_{10}O_7, HI^*$
Luteolin,	$C_{15}H_{10}O_6$	$C_{15}H_{10}O_6, H_2SO_4$	$C_{15}H_{10}O_6, HBr, H_2O$	$C_{15}H_{10}O_6, HCl, H_2O$	$C_{15}H_{10}O_6, HI^*$
Fisetin,	$C_{15}H_{10}O_6$	$C_{15}H_{10}O_6, H_2SO_4$	$C_{15}H_{10}O_6, HBr$	$C_{15}H_{10}O_6, HCl^*$	$C_{15}H_{10}O_6, HI^*$

Those marked with an asterisk have not previously been analysed, and this was due to the fact that with few exceptions these substances when heated to 100° are decomposed with evolution of acid. As previously shown (*loc. cit.*), this difficulty was avoided in the case of a hydrochloric acid compound (morin hydrochloride) by using a special method of analysis, and it now appeared desirable to examine, if possible, another of these unstable compounds in a similar way.

Quercetin hydrochloride, freshly prepared, was strongly pressed in order to remove as much adhering acetic acid as possible, suspended in water, and after standing 12 hours, the regenerated quercetin was collected; it weighed 0.5552 gram; the chlorine in the filtrate corresponding to 10.72 per cent. $C_{15}H_{10}O_7, HCl$ requires $Cl = 10.48$ per cent.

Attempts were now made to analyse the hydriodic acid compound of quercetin, but with such unsatisfactory results that this was abandoned. This compound is rapidly decomposed on exposure to the air, evolving hydriodic acid even at 40° , and is probably very slowly attacked even when washed with acetic acid.

Morin Hydriodide.—The hydrobromic and hydrochloric acid compounds of this colouring matter resemble those of quercetin, but the sulphuric acid compound differs from those of the other colouring

matters of this group in that during its formation 1 mol. of water is eliminated; thus its formula is $C_{15}H_8O_6 \cdot H_2SO_4$, and not

as one would be lead to expect. It was interesting, therefore, to examine its hydriodic acid compound, and here again a further distinction between the behaviour of morin and quercetin was observed, the compound being perfectly stable at 100° .

0.1243 dried at 100° gave 0.1915 CO_2 and 0.0295 H_2O . $C = 42.01$; $H = 2.63$.

$C_{15}H_{10}O_7 \cdot HI$ requires $C = 41.86$; $H = 2.55$ per cent.

Luteolin Hydriodide.—In contradistinction to the principal haloïd acid compounds of the colouring matters shown in the above table, those of luteolin have been previously found (*loc. cit.*) to be exceedingly stable, undergoing no alteration even at the temperature of boiling aniline, and appearing to crystallise with $1H_2O$. It appeared probable, therefore, that its hydriodic acid compound would also be stable, and this was found to be the case.

0.1273 gave 0.2043 CO_2 and 0.0292 H_2O . $C = 43.59$; $H = 2.53$.

0.1125 „ 0.1790 CO_2 „ 0.0285 H_2O . $C = 43.39$; $H = 2.79$.

$C_{15}H_{10}O_6 \cdot HI$ requires $C = 43.48$. $H = 2.65$ per cent.

This compound contains, therefore, no water of crystallisation, and differs in this respect from the hydrobromic and hydrochloric acid compounds.

Friedländer and Rüdts (*Ber.*, 1896, **29**, 878) have lately obtained a colouring matter which they consider to be the first artificial member of the quercetin series, dihydroxyflavone,

by the interaction of chlorogallacetophenone with benzaldehyde in the presence of alkali. Discussing the constitution of this dihydroxyflavone in a second paper (*ibid.*, 1753), they state that like the natural colouring matters it yields with mineral acids beautifully crystalline salts readily decomposed by water; it, therefore, behaves in this respect like the members of the quercetin group above studied.* The only remaining member of this class which had not

* Kesselkaul and Kostanecki in a later paper (*Ber.*, 1896, **29**, 1886) consider that the reaction proceeds in a different manner, the colouring matter being in reality not dihydroxyflavone but a benzylideneanhydroglycogallol,

To this Friedländer and Rüdts have not yet replied.

yet been examined was chrysin, the colouring matter of poplar buds, to which the following constitution has been assigned

Some of this was prepared according to Piccard's method (*Ber.*, 1873, **6**, 884) but curiously enough was found to be *incapable* of combining with acids in this way.

In concluding these experiments, it appeared of interest to examine the behaviour toward acids of some substitution products of these colouring matters, and for this purpose quercetin tetramethyl ether, dibromoquercetin, and tetrabromomorin were selected. The former yields with sulphuric acid, although with difficulty, an exceedingly unstable compound, crystallising in orange-red needles, but is not acted on by hydrobromic or hydrochloric acid. Its behaviour is, therefore, identical with that of rhamnetin (quercetin monomethyl ether), described in the previous paper (*loc. cit.*).

From dibromoquercetin and tetrabromomorin, *acid compounds could not be obtained.*

In the previous paper (*loc. cit.*), it was stated that these acid compounds on treatment with boiling acetic anhydride are decomposed apparently with production of the acetyl compound of the colouring matter. To be sure of this, quercetin sulphate was digested with boiling acetic anhydride without the addition of sodium acetate. The substance was quickly attacked, a *colourless* solution being almost immediately formed; after heating for one hour, this was poured into water, and allowed to stand several days. As the acetylated product separated from the mixture with difficulty, a little alcohol was added and this greatly facilitated its deposition. The colourless precipitate was collected, and after crystallisation from alcohol, formed colourless needles, melting at 189—191°, and having the properties of acetyl-quercetin.

Theoretical Considerations.

The results of this investigation show that members of the ketone and anthraquinone group do not yield compounds with mineral acids, and that all members of the xanthone class here examined are also devoid of this property. On the other hand, all members of the quercetin or phenylated pheno- γ -pyrone group, with the exception of chrysin, combine with acids, and, further, whereas the methyl ethers of quercetin react only with sulphuric acid, the bromine substitution products of quercetin and morin yield no compounds of this class.

This property of combining with acids is possessed, as previously described, by hæmatein and brazilein (*loc. cit.*); from resacetein also, Nencki and Sieber (*J. pr. Chem.*, [2], **23**, 54) have obtained the compounds $C_{16}H_{12}O_4 \cdot HCl + 2H_2O$ and $(C_{16}H_{12}O_4)_2 \cdot H_2SO_4$, but as the true constitution of the substances themselves is yet unknown, they possess at present but little interest.

More interesting are the acid compounds of the phthaleins, of which fluorescein (Baeyer, *Annalen*, 1876, **183**, 1) yields a sulphate,

and orcinphthalein (E. Fischer, *Annalen*, 1876, **183**, 63) a hydrochloride, $C_{22}H_{16}O_5 \cdot HCl$. In a paper on the constitution of fluorescein, Nietzki and Schröter (*Ber.*, 1895, **28**, 50) describe a hydrochloric acid compound of colourless fluorescein diethyl ether, (I) which salt crystallises in intensely yellow needles, readily decomposed by water. To this they assign the constitution (II), based on the theory that

whereas in the free state fluorescein possesses a lactone group, that in the form of its salts and other coloured compounds it has a quinonoid structure,

A close resemblance in fact can be traced between these compounds and the salts of the triphenylmethane and allied bases.

In considering the constitution of the acid compounds of the quercetin group,

it appears to me that their formation may be represented in two ways: (1) either similarly to these phthalein compounds, or (2) by the saturation of the ethylene bond in the pyrone ring. Thus, taking fisetin hydrochloride as an example, its constitution would then be

Fisetin (stable modification).

Unstable modification (not known).

Hydrochloride.

Hydrochloride.

In favour of this first formula is the intense orange to orange-red colour of these acid salts, compared with the pale yellow colour of the original substances.* Further, it is possible in this way to account for the non-production of acid salts from the substituted bromine derivatives. The quercetin compound studied by Herzig was found to be peculiar, in that by frequent recrystallisation it was slowly decomposed, and that by reducing agents it could be reconverted into quercetin. This is no doubt due to the fact that the bromine substitution takes place in the phloroglucinol nucleus, for, as is well known, tribromophloroglucinol possesses somewhat similar properties. It is very probable that, on bromination, the hydroxyls adjacent to the bromine in dibromoquercetin assume the ketonic condition, the formula in this case being unsusceptible of change under the influence of acids,

Moreover, by this formula (I) the decomposition of these acid compounds by acetic anhydride can be understood, in that the acetyl compounds of these colouring matters exist only in the stable, colourless, or non-quinonoid form.

The acid compounds of fluorescein and orcinophthalein (*loc. cit.*) are, however, more stable than those of the quercetin group, for the former is not altered by washing with cold water and crystallisation from alcohol, and both require hot water to effect their decom-

* Armstrong, "Theory of Coloured Carbon Compounds" (*Proc. Chem. Soc.*).

position. In general properties, however, they appear to be very similar, and the above distinction appears easy to understand when the difference in constitution of these two groups of colouring matters is considered.

Formula II.—The difficulty with which the ethers of quercetin react with sulphuric acid, and their non-reaction with the haloid acids, distinguishes more markedly this class of colouring matter from that of the phthalein group, in so far as the latter has been examined in this respect. Fluorescein diethyl ether (*loc. cit.*), for instance, readily combines with hydrochloric acid. Taking the constitution at present assigned to luteolin, quercetin, and rhamnetin as correct, the effect on the stability of the haloid acid compounds produced by the substitution of the hydrogen in the α -position in the pyrone ring by hydroxyl or methoxyl is remarkable.

For instance (1) all haloid acid compounds of luteolin are stable when heated to 180° , moreover, the hydrochloride and hydrobromide appear to crystallise with $1\text{H}_2\text{O}$.

(2) Quercetin hydrobromide is stable at 100° , but, when heated to this temperature, the hydrochloride and hydriodide are decomposed with evolution of acid.

(3) Rhamnetin does not combine with the haloid acids.

On this account the second constitution above given for these acid compounds suggested itself, namely, that which depends on the saturation of the ethylene bond in the pyrone ring. Experiments carried out in this way on the behaviour of chelidonic and meconic acids,

towards mineral acids added no support to this theory, for no additive products were thus obtained. It is also noteworthy that neither

these acids nor the members of the quercetin group form additive compounds with bromine.

The strong colour of the acid salts of the quercetin group appears so cogent an argument in favour of the quinonoid formula, that of the two it must be considered by far the more preferable. I am actively engaged in the study of natural yellow dye-stuffs, with the hope of isolating new members of this class. If such be obtained, the study of their behaviour with mineral acids should throw further light on the nature of this interesting reaction.

From the above experiments it appears probable that the colouring matters of the xanthone class do not react with acids; but this cannot be absolutely decided until other members of varied constitution are available for examination. Should this be the case, however, this property of forming compounds with acids will be of value in that *it can be employed as a means of distinguishing the members of the quercetin group from those other natural classes of non-nitrogenous, yellow, mordant dye-stuffs which are at present known to exist.*

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