LXX.—*Acid Compounds of some Natural Yellow Colouring Matters.*

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IN a previous communication by one of us, in conjunction with J. J. Hummel (*Ber.*, 1882, **15**, 2337), it was shown that hæmatein and brazilein, the colouring matters of logwood and brazilwood, yielded peculiar compounds with mineral acids. Thus, from hæmatein, $C_{16}H_{12}O_6$, there was obtained isohæmatein sulphate, $C_{16}H_{11}O_5 \cdot SO_4H$, and isohæmatein chlor- and brom-hydrins, $C_{16}H_{11}O_5Cl$ and $C_{16}H_{11}O_5Br$. These substances, on treatment with water, are decomposed with elimination of acid, the first product formed in the case of the sulphuric acid compound being a basic sulphate,

Further, by treating the chlor- or brom-hydrin with silver oxide, a substance, isohæmatein, $C_{16}H_{12}O_6$, was obtained, which, though isomeric with hæmatein, differed considerably from it in dyeing and

other properties. Brazilein behaved similarly. It was therefore evident that, by the action of mineral acids on these colouring matters, some change other than the mere formation of an acid compound had taken place.

In continuation of this work, it appeared desirable to study in a similar manner the action of acids on the natural yellow dyes. Although it seems to have been already known that some of these substances give colour reactions with some of the mineral acids, no attempt has been made to study this action. The only statements bearing on this subject which we have found appear in Gmelin's *Handbook of Chemistry*. "Warm concentrated hydrochloric acid colours quercetin orange to brown-yellow" (Regaud, 10, 492). "When a solution of quercetin in acetic acid is saturated with hydrochloric acid gas only a trace is decomposed, the rest acquiring an orange-yellow colour" (Hlasiwetz). "According to Chevreul, luteolin unites with acids" (9, 29). "Morin dissolves in oil of vitriol with a dark brown-yellow colour, the solution deposits a red body when warmed or left at rest."

According to the recent researches of Kostanecki (Kostanecki and Tambor, *Monatsh.*, 1895, 15, 1) on gentisin, the colouring matter of gentian root, of Schunck and Marchlewski on datiscetin from *Datisca cannabina* (*Annalen*, 1894, 277, 261), and of Herzig (*loc. cit.*), certain of the natural yellow colouring matters can be divided into two classes, in that they are either derivatives of diphenyl- γ -pyrone or of a phenylated pheno- γ -pyrone,

To the former class belong gentisin, prepared artificially by Kostanecki and Tambor (*loc. cit.*),

and datiscetin, which, according to Schunck and Marchlewski (*loc. cit.*), is thus represented

Fisetin, quercetin, rhamnetin, and rhamnazin (quercetin mono- and di-methyl ethers), and chrysin (Kostanecki, *Ber.*, 1893, **26**, 2901) belong to the second class, in which also most probably should be included morin and luteolin, the colouring matters respectively of old fustic and weld. From a study of its decomposition products, Herzig (*Ber.*, 1895, **28**, 293) considers fisetin to have the following constitution.

There also exists a third class of allied substances, of which maclurin, the second colouring matter of old fustic, and catechin, the chief constituent of catechu, are typical.

The former is usually regarded as a benzophenone derivative.

In the present communication, we have confined ourselves to the study of the action of acids on the members of the second and third classes, and all that are above enumerated have been examined, with the exception of chrysin.

Preliminary experiments were carried out, with the following result. When boiled with hydrochloric or hydrobromic acids, quercetin, fisetin, and morin yielded orange-red to scarlet crystalline compounds, very readily decomposed by water; they were, however, not acted on when similarly treated with dilute sulphuric acid. On the other hand, rhamnetin and rhamnazin were practically not altered by this treatment. By treating with acids solutions of these colouring matters in glacial acetic acid, more satisfactory results were obtained, the presence of water in quantity being thus avoided.

Quercetin.

In order to prepare this substance from quercitron bark (*Quercus tinctoria*), advantage was taken of a method devised by Dr. W. H. Perkin (private communication), and used by him some years ago for its manufacture. Quercitron bark dust is washed with salt solution to remove impurities, and then extracted with cold dilute ammonia. The extract, when neutralised with dilute sulphuric acid, deposits a brown amorphous precipitate containing little or no colouring matter; this is filtered off, and the clear lemon-yellow solution which contains the glucoside, quercitrin, is acidified and boiled, when crystals of quercetin soon begin to separate; these are collected while the mixture is still warm, in order to prevent their contamination with a brown flocculent matter which usually separates out on further cool-

ing. The product consists of almost chemically pure quercetin, and this can be further purified by recrystallisation from dilute alcohol, or more rapidly by extracting with a mixture of ether and chloroform; on evaporating this extract, crystals of pure quercetin separate, as it is practically insoluble in chloroform.

Quercetin Sulphate.—To a boiling saturated solution of quercetin in acetic acid, a few drops of sulphuric acid were added, which turned the liquid orange coloured, and on cooling it deposited a glistening mass of hair-like needles of the same tint; these were collected, washed with acetic acid, and dried at 100° . If quercetin be made into a thin paste with boiling acetic acid, and sulphuric acid be then added, a similar result is obtained without apparent solution of the quercetin. On analysis, the following numbers were obtained.

0.1558 gave 0.2578 CO_2 and 0.0425 H_2O . C = 45.12; H = 3.03.

$\text{C}_{15}\text{H}_{10}\text{O}_7, \text{H}_2\text{SO}_4$ requires C = 45.00; H = 3.00 per cent.

This substance, when treated with water, is quantitatively decomposed into quercetin and sulphuric acid, as the following results show.

0.4097 gram, standing in water, gave a yellow product, which was collected, washed, and dried at 160° . It weighed 0.3088 = 75.37 per cent. The filtrate yielded 0.2427 BaSO_4 ; S = 8.13 per cent. $\text{C}_{15}\text{H}_{10}\text{O}_7, \text{H}_2\text{SO}_4$ requires $\text{C}_{15}\text{H}_{10}\text{O}_7$ = 75.5; S = 8 per cent.

The yellow product, dried at 160° , was analysed.

0.1145 gave 0.2511 CO_2 and 0.0372 H_2O . C = 59.80; H = 3.61.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires C = 59.60; H = 3.31 per cent.

Quercetin sulphate is slowly decomposed on exposure to moist air, with formation of quercetin and sulphuric acid. It is sparingly soluble in boiling acetic acid, but cannot be recrystallised from this solvent without undergoing decomposition. Boiling acetic anhydride dissolves it readily, forming a colourless solution, which apparently contains an acetyl derivative of quercetin. When strongly heated, it is carbonised, with evolution of sulphurous acid, a small quantity of a crystalline sublimate being simultaneously formed.

Quercetin hydrobromide can be readily prepared by the addition of fuming hydrobromic acid to a boiling solution of quercetin in acetic acid, or to quercetin suspended in the same liquid. The product is washed with acetic acid and dried at 100° . Analysis gave the following result.

0.1173 gave 0.2033 CO_2 and 0.0300 H_2O . C = 47.26; H = 2.84.

$\text{C}_{15}\text{H}_{10}\text{O}_7, \text{HBr}$ requires C = 47.00; H = 2.87 per cent.

It consists of a glistening mass of orange-yellow needles readily decomposed by contact with water.

0.3680 thus treated gave 0.2925 quercetin and 0.1814 AgBr, corresponding with $C_{15}H_{10}O_7 = 79.48$. Br = 20.97.

$C_{15}H_{10}O_7.HBr$ requires $C_{15}H_{10}O_7 = 78.85$; Br = 20.63 per cent.

It is sparingly soluble in acetic acid, but cannot be recrystallised without decomposition.

Quercetin hydrochloride, prepared in a similar manner, closely resembles the hydrobromic acid compound. A sample dried at 100° yielded on analysis C = 57.6; theory requires C = 53.17, and this result was accounted for by the fact that when heated to this temperature it is gradually decomposed, with evolution of hydrogen chloride and formation of quercetin.

Quercetin hydriodide, $C_{15}H_{10}O_7.HI$, forms a glistening mass of orange needles having similar properties to the above compounds.

These results corroborate those of Herzig (*Monatsh.*, 1891, 12, 172), in that they show quercetin to have the formula $C_{15}H_{10}O_7$, and not $C_{24}H_{16}O_{11}$, as previously supposed.

Fisetin.

To prepare this substance, young fustic (*Rhus cotinus*, L.) was extracted with boiling water, and the extract treated with lead acetate solution. The lead compound of the colouring matter thus formed was collected, made into a thin paste with water, and in a fine stream run into boiling dilute sulphuric acid. After removal of the lead sulphate, the dark coloured filtrate on cooling deposited a semi-crystalline, brownish mass, which was collected and purified by crystallisation from dilute alcohol.

Fisetin Sulphate, $C_{15}H_{10}O_6.H_2SO_4$.—To a pasty mass of fisetin and boiling acetic acid, sulphuric acid was added, and the scarlet, crystalline product thus obtained collected and washed with acetic acid. Owing to the somewhat ready solubility of this substance in acetic acid, considerable loss occurs during the washing. This may be avoided to some extent by alternately washing, and draining the mass upon a porous tile. On analysis, the following numbers were obtained

0.1326 dried at 110° gave 0.2282 CO_2 and 0.0385 H_2O . C = 46.93; H = 3.22.

$C_{15}H_{10}O_6.H_2SO_4$ requires C = 46.87; H = 3.12 per cent.

It forms a scarlet glistening mass of fine needles, considerably more soluble in acetic acid than the corresponding quercetin compound. Water converts it into fisetin and sulphuric acid.

0.3909 gave 0.2915 fisetin and 0.2536 $BaSO_4$. $C_{15}H_{10}O_6 = 74.57$; S = 8.88.

$C_{15}H_{10}O_6.H_2SO_4$ requires $C_{15}H_{10}O_7 = 74.48$; S = 8.33 per cent.

Fisetin hydrobromide, $C_{15}H_{10}O_6 \cdot HBr$, and *hydrochloride*, $C_{15}H_{10}O_6 \cdot HCl$, are obtained as fine orange-coloured needles. On heating to 100° they are decomposed, leaving fisetin. *Fisetin hydriodide*, $C_{15}H_{10}O_6 \cdot HI$, closely resembles the above compounds.

Herzig (*Ber.*, 1895, **28**, 293) has assigned to fisetin the formula $C_{15}H_{10}O_6$, with which the above results agree.

Morin.

Morin, which, together with maclurin, is contained in old fustic (*Morus tinctoria*), is best obtained by extracting this dyestuff with boiling water, the extract thus obtained depositing, on cooling, impure morin. For some quantity of this product, we are indebted to the kindness of Messrs. Wood and Bedford of Leeds. It was purified by several crystallisations from alcohol and dilute acetic acid.

Anhydromorin sulphate, $C_{15}H_8O_6 \cdot H_2SO_4$, is readily formed by the addition of sulphuric acid to a boiling solution of morin in acetic acid; the orange-red crystalline mass deposited on cooling was collected, washed with acetic acid, and dried at 110° .

0.1636 gave 0.281 CO_2 and 0.0450 H_2O . $C = 46.84$; $H = 3.05$.

0.1457 gave 0.2507 CO_2 and 0.0402 H_2O . $C = 46.99$; $H = 3.07$; $S = 8.38$.

$C_{15}H_8O_6 \cdot H_2SO_4$ requires $C = 47.11$; $H = 2.62$; $S = 8.32$ per cent.

$C_{15}H_{10}O_7 \cdot H_2SO_4$ requires $C = 45.00$; $H = 3.00$ per cent.

That morin has the formula, $C_{15}H_{10}O_7$, and not $C_{15}H_8O_6$ is evident from the analysis of its compounds with hydrogen bromide and chloride described below. The sulphuric acid compound of morin, therefore, differs from those of quercetin and fisetin previously described, in that one molecule of water is removed during its formation. When treated with water, however, it is reconverted into morin, sulphuric acid being formed. The morin so produced was analysed.

0.1077 gave 0.2335 CO_2 and 0.0345 H_2O . $C = 59.13$; $H = 3.55$.

$C_{15}H_{10}O_7$ requires $C = 59.60$ and $H = 3.31$ per cent.

The crystals of anhydromorin sulphate are considerably larger and of much greater beauty than the corresponding derivatives of fisetin and quercetin. It is almost insoluble in acetic acid.

Morin hydrobromide forms a glistening mass of long orange-coloured needles, almost insoluble in acetic acid. On analysis

0.157 gave 0.272 CO_2 and 0.0410 H_2O . $C = 47.24$; $H = 2.90$.

0.149 „ 0.2568 CO_2 and 0.0386 H_2O . $C = 47.00$; $H = 2.87$.

0.5168 „ 0.2592 $AgBr$. $Br = 21.34$.

$C_{15}H_{10}O_7 \cdot HBr$ requires $C = 47$; $H = 2.84$; $Br = 20.63$ per cent.

It is readily decomposed by water into morin and hydrobromic acid.

Morin hydrochloride closely resembles the preceding compound, but is somewhat less stable at 100°. In order to submit this compound to analysis, the freshly prepared substance, after washing with acetic acid, was well pressed, treated with water, and the morin produced dried at 160°. It weighed 0.2285 gram. The filtrate was neutralised, evaporated to dryness, ignited, and the amount of chlorine present in the residue determined. It yielded 0.105 AgCl.

Morin = 89.21 per cent. Cl = 10.14 per cent.

$C_{15}H_{10}O_7 \cdot HCl$ requires $C_{15}H_{10}O_7$ = 89.21. Cl = 10.49 per cent.

Morin hydriodide, $C_{15}H_{10}O_7 \cdot HI$, closely resembles the above compound.

The ready production of these compounds, together with their sparing solubility in glacial acetic acid, and also the fact that maclurin yields no compounds with acid, provides a method for greatly facilitating the purification of morin. The crude morin is crystallised twice from alcohol, the product suspended in acetic acid and converted into the hydrogen bromide compound; this is collected, washed with acetic acid until the filtrate is nearly colourless, suspended in a little boiling acetic acid and the mixture treated with its own volume of boiling water. A clear solution is thus obtained which, on cooling, deposits long, colourless, glistening needles of pure morin.

The study of morin has received but little attention, and consequently there has been some uncertainty as to its molecular weight. Two formulæ have been assigned to it, namely, $C_{13}H_8O_6$ (Hlasiwetz and Pfaundler, *Annalen*, 1863, **127**, 252) and $C_{15}H_{10}O_7$ (Löwe, *Zeit. anal. Chem.*, **14**, 119), both having a similar percentage composition. The above results show that Löwe's formulæ, $C_{15}H_{10}O_7$, must be regarded as correct.

Rhamnetin.

This substance was prepared from Persian berries in the manner described in a previous communication (Perkin and Geldard, this vol. p. 496). If a pasty mass of rhamnetin in boiling acetic acid be treated with a few drops of sulphuric acid, the liquid becomes somewhat yellower, but the suspended rhamnetin remains unaltered. It was at first supposed that it did not form a compound with sulphuric acid, but it was subsequently found that a large excess of sulphuric acid is required. To rhamnetin suspended in boiling acetic acid, sulphuric acid was added drop by drop until it dissolved; the clear solution, on standing, quickly deposited a mass of beautiful, orange-coloured, prismatic needles, sometimes interspersed with unaltered

rhamnetin. If this was the case, fresh acid was then added and the mixture again boiled. The product was collected upon glass wool with the aid of the pump, and washed twice with acetic acid; it could not, however, be thoroughly washed with acetic acid, as it was gradually decomposed into sulphuric acid and rhamnetin, this, however, could be avoided by the use of acetic acid containing 25 per cent. of acetic anhydride. The product, drained upon a porous tile which had been previously heated and allowed to cool over sulphuric acid, was left in a dessicator for three or four days before being analysed.

0.1283 dried at 160° gave 0.2195 CO_2 , 0.0400 H_2O . $\text{C} = 46.65$; $\text{H} = 3.46$.

$\text{C}_{16}\text{H}_{12}\text{O}_7 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 46.37$; $\text{H} = 3.38$ per cent.

By treatment with water, it is decomposed quantitatively into rhamnetin and sulphuric acid.

0.2985 gave 0.2275 rhamnetin, and 0.1792 BaSO_4 . $\text{C}_{16}\text{H}_{12}\text{O}_7 = 76.21$; $\text{S} = 8.17$ per cent.

$\text{C}_{16}\text{H}_{12}\text{O}_7 \cdot \text{H}_2\text{SO}_4$ requires $\text{C}_{16}\text{H}_{12}\text{O}_7 = 76.32$; $\text{S} = 7.73$ per cent.

Rhamnetin sulphate is exceedingly unstable, becoming pasty on exposure to the air, with formation of sulphuric acid and rhamnetin. As is well known, rhamnetin is a quercetin monomethyl ether and has the formula, $\text{C}_{16}\text{H}_{12}\text{O}_7$, with which the above results agree.

No compounds of rhamnetin with hydrogen bromide or chloride could be obtained.

Rhamnazin.

As previously shown, this substance is a quercetin dimethyl ether (this vol., 496), and is contained, together with rhamnetin and quercetin, in Persian berries. Its behaviour towards sulphuric acid closely resembles that of rhamnetin, except that an even larger quantity of sulphuric acid is necessary for the formation of this derivative. On analysis, the following numbers were obtained.

0.1269 gave 0.2244 CO_2 and 0.0435 H_2O . $\text{C} = 48.24$; $\text{H} = 3.81$.

$\text{C}_{17}\text{H}_{14}\text{O}_7 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 47.66$; $\text{H} = 3.74$ per cent.

Rhamnazin sulphate is exceedingly unstable, being readily decomposed by contact with glacial acetic acid, and appears also to undergo slow decomposition even when standing over sulphuric acid. It forms a mass of beautiful, scarlet, glistening needles, moderately soluble in cold acetic anhydride. No compounds of rhamnazin with hydrogen chloride or bromide could be obtained.

Maclurin was prepared from old fustic in the usual manner. When acted on with acids by the methods above described, its nearly colourless solution in acetic acid became of an orange tint. No crystalline

compounds, however, could be isolated, and we are of opinion that the change of colour, above referred to, is due rather to a decomposition than to any combination of the acid and colouring matter. This appears to be corroborated by the fact that Wagner (*Jahrsber.*, 1851, 420) obtained a substance, rufimoric acid, $C_{16}H_{14}O_9$, (?) by the action of cold sulphuric, or boiling hydrochloric, acid on maclurin.

Catechin.—No acid compounds could be obtained from this substance, its solution in acetic acid being unaffected by the addition of acid. By prolonged action of acid, catechin is converted into a dark red-brown powder (Kraut, Delden, *Annalen*, 1863, 128, 291), termed catechuretin, $C_{42}H_{30}O_{13}$, in this respect somewhat resembling maclurin.

Curcumin.—While examining the action of acids on the above colouring matters, it appeared of interest to test the behaviour of curcumin when similarly treated, and, for this purpose, a small quantity of it was prepared from turmeric in the usual manner. An acetic acid solution, when treated with sulphuric or hydrochloric acids, acquires a blood-red colour, but no crystalline matter separated on standing. That this coloration, however, was due to the formation of acid compounds appeared probable, for, by treatment with water, a yellow precipitate was formed, which seemed to consist of unchanged curcumin. When boiled with strong aqueous hydrochloric or hydrobromic acids, curcumin is decomposed, with formation of a resinous product.

Summary of Results.

It is shown by this investigation that quercetin and fisetin react readily with sulphuric, hydrochloric, hydrobromic, and hydriodic acids, forming well-defined, crystalline compounds, the composition of which is represented as the addition of 1 mol. of acid to the colouring matter. With hydrobromic, hydrochloric, and hydriodic acids, morin behaves similarly, but differs in that, during the formation of its sulphuric acid derivative, 1 mol. of water is eliminated. No action takes place between rhamnetin or rhamnazin (quercetin mono- and dimethyl-ethers) and the haloïd acids, but with sulphuric acid, compounds are produced, though far from readily. This difference in behaviour must be accounted for by the methoxy-groups they contain.

The acid derivatives of all these colouring matters are almost instantaneously decomposed by water into acid and the original colouring matter, thus showing considerable difference from those produced from hæmatein and brazileïn, which are referred to in the introduction to this paper. Maclurin and catechin do not yield compounds with acids.

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Before entering into a discussion of the constitution of these substances, we feel it preferable to study the behaviour of acids towards that class of dyes and allied substances to which gentisein and datiscetin belong.

This investigation will be proceeded with when the necessary raw material is to hand.

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