

XI.—*A Reaction of some Phenolic Colouring Matters.* *Part II.*

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CERTAIN phenolic dye-stuffs are known to decompose potassium acetate in the presence of alcohol with the formation of mono-substituted salts (Trans., 1899, '75, 433). The present work was undertaken with the object of determining whether all dye-stuffs of the mordant class react in this manner, and with the hope of gaining a clearer insight into the nature of this reaction. As a result, numerous typical compounds of this class have now been examined, all of which possess this property, or yield additive products with the acetate. Of the colouring matters studied, the majority have been isolated from natural sources or from such commercial preparations as were available.

Gallacetophenone.

It was previously stated (*loc. cit.*) that with potassium acetate this 1:2:3-trihydroxyacetophenone gave a colourless salt, but the analysis of distinct preparations were not concordant. Analyses of products obtained in subsequent experiments gave percentages of potassium ranging from 14·79 to 13·09, numbers which are not in harmony with those required for a pure salt. It was eventually found that two distinct salts are produced together in this manner unless special precautions are taken.

Monopotassium Gallacetophenone.—Two grams of gallacetophenone dissolved in 20 c.c. of absolute alcohol were rapidly treated at the boiling point with 20 c.c. of a saturated solution of potassium acetate in absolute alcohol, and the fine, yellow, crystalline precipitate which formed was collected while hot, washed with absolute alcohol, and dried at 100°. The air-dried substance does not lose water of crystallisation at 100°:

0.5194, heated at 160°, lost 0.0435 H₂O. H₂O = 8.37.

0.5187 „ „ 0.0415 H₂O. H₂O = 8.00.

0.4772, dried at 160°, gave 0.2012 K₂SO₄. K = 18.89.

0.4759 „ „ 0.1979 K₂SO₄. K = 18.64.

C₈H₇O₄K, H₂O requires H₂O = 8.03 per cent.

C₈H₇O₄K „ K = 18.92 „

It forms pale yellow, glistening needles, and is sparingly soluble in boiling alcohol, but dissolves somewhat readily in boiling water. From the aqueous solution, it crystallises out unchanged on cooling, and in this respect resembles the corresponding alizarin salt, but differs from those of morin, quercetin, &c., which are decomposed by boiling water.

Nencki and Sieber (*J. pr. Chem.*, 1881, [ii], 23, 546) obtained from gallacetophenone, by means of alcoholic potash, a salt, C₈H₈O₄.KHO. An examination of this compound showed it to be identical with that produced by potassium acetate:

Found, H₂O = 7.97, 7.74, and in salt dried at 160°, K = 18.79, 18.74 per cent.

Barium Salt.—This is readily prepared by adding barium chloride to a hot aqueous solution of the potassium compound. It consists of pale yellow needles, sparingly soluble in water:

Found (salt dried at 160°), H₂O = 6.58. Ba = 28.90.

C₁₆H₁₄O₈Ba requires Ba = 29.16 per cent.

Monosodium gallacetophenone can be prepared in a similar way to the potassium salt by employing either (a) alcoholic sodium acetate, or (b) alcoholic soda. When dried at 160°, it loses 1 mol. of water of crystallisation:

(a) Found, H₂O = 8.67, 8.53. Na, in salt dried at 160° = 12.03, 12.15.

C₈H₇O₄Na, H₂O requires H₂O = 8.65 per cent.

C₈H₇O₄Na „ Na = 12.10 „

It forms a pale yellow, crystalline powder consisting of minute leaflets, and is not decomposed by boiling water. From its aqueous solution, on slow cooling, it is deposited in the form of cubes resembling the crystals of cane sugar.

Potassium Trigallacetophenone.—If alcoholic potassium acetate is added drop by drop to a boiling saturated solution of gallacetophenone in the same solvent, the mixture becomes semi-solid owing to the separation of colourless needles; these were collected on the pump and washed with alcohol. The air-dried product does not lose water of crystallisation at 100° :

Found, K = 7.46, 7.29, and 7.40.

$C_{24}H_{23}O_{12}K$ requires K = 7.19 per cent.

It forms a glistening mass of flat needles or leaflets which can be crystallised from water unchanged, and is not a mixture, as continued washing with alcohol does not affect its composition.

The same compound (K = 7.09 per cent.) is readily prepared by dissolving gallacetophenone in a boiling aqueous potassium acetate solution. Aqueous sodium acetate solution, however, does not react with gallacetophenone, the unaltered colouring matter being redeposited on cooling.

By adding barium chloride to a boiling aqueous solution of the compound and cooling, a barium salt separated in colourless needles which were washed with water. When air-dried, it does not lose water of crystallisation at 100° :

Found, Ba = 12.87 and 13.06.

$C_{48}H_{46}O_{24}Ba$ requires Ba = 12.02 per cent.

This is slowly decomposed at 160° , some gallacetophenone subliming.

Methylation of Monopotassium Gallacetophenone.—When suspended in boiling methyl alcohol, this salt was slowly attacked by methyl iodide, a clear solution usually resulting after digestion for 6 hours. The excess of iodide and alcohol was now removed, the residue extracted with ether, and the ethereal liquid evaporated. The crystalline product consisted of the required ether contaminated with colouring matter, and the latter was removed, in the form of an insoluble lead salt, by adding lead acetate to a boiling aqueous solution of the mixture. By decomposing the pale yellow precipitate with sulphuric acid, removing the lead sulphate by decantation, and extracting the clear liquid with ether, this colouring matter was recognised as gallacetophenone by means of its melting point, $166-168^{\circ}$, and other tests. The filtrate from the lead precipitate deposited, on cooling, long needles of the methyl ether, which, after recrystallisation from benzene, melted at $132-133^{\circ}$:

0.1003 gave 0.2177 CO_2 and 0.0475 H_2O . C = 59.19; H = 5.26.

0.1008 „ 0.1313 AgI. CH_3 = 8.31.

$C_9H_{10}O_4$ requires C = 59.34; H = 5.49; CH_3 = 8.24 per cent.

Gallacetophenone monomethyl ether, $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_3$, is readily soluble in boiling water, and soluble in alkaline solutions with a pale yellow coloration. When crystallised from water, it is colourless, and contains 1 mol. of water of crystallisation (found $\text{H}_2\text{O} = 8.95$); this is removed at 100° , and the substance has then a pale yellow colour.

It does not dye mordanted calico, gives no precipitate with aqueous lead acetate, and no coloration with ferric chloride; with alcoholic lead acetate, however, a gelatinous precipitate is formed which is readily soluble in water. When prepared in the above manner, the yield is exceedingly poor, and is never more than 10 per cent. of the calculated quantity.

The *acetyl* derivative, $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_2 \cdot \text{CO} \cdot \text{CH}_3$, prepared in the usual manner, crystallised from alcohol in colourless, prismatic needles melting at $146-148^\circ$:

0.1125 gave 0.2415 CO_2 and 0.0555 H_2O . $\text{C} = 58.54$; $\text{H} = 5.48$.

$\text{C}_{13}\text{H}_{14}\text{O}_6$ requires $\text{C} = 58.64$; $\text{H} = 5.26$ per cent.

To be certain that this was the diacetyl derivative, it was decomposed with boiling sodium carbonate solution, and the product of the reaction identified as the gallacetophenone monomethyl ether. This was necessary owing to the behaviour of resacetophenone on acetylation, which forms acetoxyacetyl- β -methylchromone in this manner, although more prolonged digestion is required (Kostanecki and Rózycki, *Ber.*, 1901, 34, 102).

By similar methods, a gallacetophenone monoethyl ether was prepared from the monopotassium salt; it crystallised in pale yellow needles melting at 102° .

Gallacetophenone Dimethyl Ether, $\text{C}_8\text{H}_6\text{O}_2(\text{O} \cdot \text{CH}_3)_2$.—An earlier experiment showed (*Trans.*, 1895, 67, 997) that on methylation gallacetophenone gave a dimethyl ether exclusively, and consequently contained only one hydroxyl group in the ortho-position relatively to the carbonyl group. Further investigation showed that this was the case,

and doubtless this substance has the constitution $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_2(\text{O} \cdot \text{CH}_3)(\text{CO} \cdot \text{CH}_3)$.

It formed colourless prisms melting at $77-78^\circ$:

0.1026 gave 0.2292 CO_2 and 0.0584 H_2O . $\text{C} = 60.92$; $\text{H} = 6.32$.

0.1320 „ 0.3104 AgI . $\text{CH}_3 = 15.00$.

$\text{C}_{10}\text{H}_{12}\text{O}_4$ requires $\text{C} = 61.22$; $\text{H} = 6.12$; $\text{CH}_3 = 15.30$ per cent.

To determine if gallacetophenone monomethyl ether gave the same dimethyl ether on further methylation, 0.8 gram, dissolved in a solution of 0.4 gram of potassium hydroxide, was heated in methyl

alcohol with excess of methyl iodide at 100° in a sealed tube for 5 hours. The main product of the reaction crystallised in colourless prisms melting at $77-78^{\circ}$, and was identical with gallacetophenone dimethyl ether.

It was thus evident that the methoxy-group in this monomethyl ether must exist in the meta- or para-position relatively to the carbonyl group, but, unfortunately, all attempts to solve this point have been unsuccessful at present. It seemed possible, for instance, that a monoether of pyrogallol could be converted into a gallacetophenone ether, which might be identical or otherwise with that prepared from gallacetophenone itself; and, on the other hand, could the pyrogallol ether be converted by means of phthalic anhydride into an anthragallol compound, the position of the methoxy-group would probably be ascertained by the absence of dyeing property or otherwise. Such experiments as were carried out resulted in the elimination of the methyl or ethyl group as part of the reaction and were thus abortive. It has been shown, however, that the monopotassium salts of alizarin and anthragallol on methylation give products containing the methoxy-group in the para-position relatively to one carbonyl group, and it is therefore likely that the gallacetophenone ether is similarly constituted.

During this work, some quantity of a pyrogallol monoethyl ether, $C_6H_3(OH)_2 \cdot O \cdot C_2H_5$, was prepared by digesting a mixture of 30 parts of pyrogallol, 15 parts of potassium hydroxide, 60 parts of ethyl iodide, and 300 parts of alcohol at the boiling point. The product soluble in alkali was distilled, the distillate dissolved in benzene, and the crystals which separated on standing purified by recrystallisation from the same solvent. This substance melted at $102-104^{\circ}$ and is most probably identical with that described by Benedikt (*Ber.*, 1876, 9, 125), which was prepared by digesting pyrogallol with alcoholic potash and potassium ethylsulphate, and melted at 95° :

0.1286 gave 0.2924 CO_2 and 0.0670 H_2O . $C = 62.00$; $H = 5.79$.

0.1890 „ 0.2844 AgI. $Et = 18.57$.

$C_8H_{10}O_3$ requires $C = 62.33$; $H = 6.49$; $Et = 18.83$ per cent.

Ellagic Acid.

This yellow colouring matter is obtained from numerous tannin matters, as valonia, myrabolans, agarobilla, &c., being derived from the ellagitannic acid which is present in these substances. It can be prepared artificially by the action of alkalis on ethyl gallate (Ernst and Zwenger, *Annalen*, 1871, 159, 32), and is most probably a fluorene derivative. Owing to its sparing solubility in boiling alcohol,

it is not readily attacked by potassium acetate, and recourse was therefore had to its acetyl compound, which, although also sparingly soluble, is more suitable for the purpose. This substance,* on digestion with boiling alcoholic potassium acetate, slowly becomes pale yellow without apparent solution, and to ensure complete conversion into the potassium salt it is necessary to heat for about four hours. The product was collected, washed with alcohol, and dried at 160° :

Found, $K = 11.48, 10.98$. $C_{14}H_5O_8K$ requires $K = 11.47$ per cent.

This compound consisted of minute, lemon-yellow needles, insoluble in cold alcohol. When submitted to the further action of boiling alcoholic potassium acetate for about two days, it is gradually transformed into a second salt without any appreciable change in its appearance:

Found, $K = 20.19$. $C_{14}H_4O_8K_2$ requires $K = 20.63$ per cent.

Thus obtained, the *dipotassium* salt of ellagic acid forms pale yellow, microscopic needles insoluble in alcohol.

By dissolving ellagic acid in sodium hydroxide solution and passing carbon dioxide through the liquid, Wöhler and Merklein (*Annalen*, 1845, 55, 129) obtained a salt, $C_{14}H_4O_8Na_2, H_2O$, and Ernst and Zwenger (*Annalen*, 1871, 159, 32) prepared the salt $C_{14}H_5O_8Na, H_2O$ by the action of sodium carbonate on ethyl gallate.

Daphnetin.

Daphnetin, a dihydroxycoumarin contained in the form of its glucoside, daphnin, in the bark of *Daphne alpina* and prepared synthetically (Pechmann, *Ber.*, 1884, 17, 1934) by the action of sulphuric acid on a mixture of pyrogallol and malic acid, is a moderately strong colouring matter, and gives the following shades with mordanted woollen cloth:

Chromium.	Aluminium.	Tin.	Iron.
Olive-yellow.	Pale olive-yellow.	Very pale yellow.	Olive-black.

Addition of potassium acetate to a boiling alcoholic solution of daphnetin caused the separation of a crystalline precipitate, which was collected, washed with alcohol, and dried at 160° :

Found, $K = 14.03, 14.13, 14.10, 14.36$.

$C_9H_6O_4, C_2H_3O_2K$ requires $K = 14.13$ per cent.

* According to Schiff (*Annalen*, 1873, 107, 79), acetyllellagic acid is a yellow, crystalline powder, whereas the compound we obtained by means of acetic anhydride and sodium acetate crystallised in small, colourless needles. This point is consequently undergoing further investigation.

By decomposition with acid, it yielded 63.59 per cent. of daphnetin, whereas theory requires 64.49 per cent. It was obtained in the form of pale yellow needles, decomposed by boiling water with separation of daphnetin.

Monopotassium Daphnetin.—When alcoholic potash is added drop by drop to a boiling alcoholic solution of daphnetin, the orange-red coloration thus produced is not at first permanent, but quickly disappears. The pale yellow, crystalline precipitate formed at this stage was collected, washed with alcohol, and dried at 160°:

Found, $K = 9.93$. $C_{18}H_{11}O_8K$ requires $K = 9.90$ per cent.

It consisted of pale yellow, prismatic needles, soluble, with decomposition, in boiling water, from which crystals of daphnetin were deposited on cooling.

If the addition of alcoholic potash is continued until the orange-red coloration is permanent, a precipitate of minute, garnet-red, prismatic needles then separated:

Found, $K = 18.07$. $C_9H_5O_4K$ requires $K = 18.05$ per cent.

Monopotassium daphnetin is soluble in cold water, forming an orange-yellow liquid, which is not decomposed at the boiling point. The barium salt is obtained as a dull orange precipitate when barium chloride is added to this solution.

Flavone Group.

In the previous communication (*loc. cit.*), it was pointed out that with the exception of morin those colouring matters of the flavone group which reacted with potassium acetate to form sparingly soluble monopotassium salts possessed two hydroxyl radicles in the ortho-position relatively to one another. The description in subsequent papers of the salts of gossypetin, $C_{15}H_9O_8K$, myricetin, $C_{15}H_9O_8K$, quercetagenin, $C_{15}H_9O_8K$, and luteolin, $C_{15}H_9O_6K$, was in harmony with this deduction, but on the other hand, kampherol, which gives the salt $C_{15}H_9O_6K$, proved a second exception to the rule. It was therefore desirable to examine in this respect the colouring matters kampheride (kampherol monomethyl ether) and galangin, and although the work has been hampered by the small amounts of these rare colouring matters available, the results have been sufficiently good for the present purpose.

Monopotassium galangin is usually obtained as a bright yellow, amorphous precipitate, but by employing a somewhat dilute solution and cautiously adding, the acetate is then deposited in minute needles:

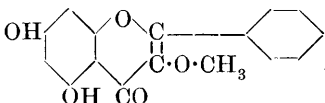
Found, K = 11·67, 11·67, 11·24 per cent.

$C_{15}H_9O_5K, H_2O$ requires K = 11·96 per cent.

Monopotassium kampheride is a bright yellow salt :

Found, K = 10·87. $C_{16}H_{11}O_6K, H_2O$ requires K = 10·95 per cent.

In both cases, these salts are decomposed by boiling water with regeneration of the colouring matter.

Galangin monomethyl ether, , it will be

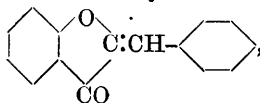
observed, is constituted, as regards the free hydroxyl groups which it contains, in an analogous manner to chrysin (*loc. cit.*). As was to be anticipated, therefore, it gave no sparingly soluble salt by this method.

It is worthy of mention that the above three colouring matters in the presence of acetic acid yield crystalline, yellow compounds with mineral acids which are readily decomposed by water. Galangin monomethyl ether, however, resembles rhamnetin (Trans., 1895, 67, 650) in this respect, for the sulphuric acid compound only could be produced, and this with difficulty.

In the former communication, the salt $C_{32}H_{23}O_{14}K$ was prepared from rhamnetin* by treating an alcoholic solution of this substance with potassium acetate. It has now been found that on decomposing acetylramnetin in alcoholic solution with potassium acetate, the salt $C_{16}H_{11}O_7K$ is produced in the form of orange-yellow needles, which are readily decomposed by boiling water :

Found, K = 11·07. $C_{16}H_{11}O_7K$ requires K = 11·01 per cent.

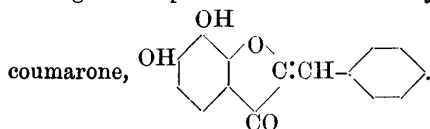
With the flavone derivatives at present examined containing contiguous hydroxyl groups, it may be noticed that in no case have these radicals been situated in the pheno- γ -pyrone nucleus. Such compounds have not as yet been isolated from natural sources, and their preparation synthetically is somewhat difficult. A closely allied class of colouring matters derived from benzylidenecoumarone,



has been synthetically prepared by Friedländer and Rüdts (*Ber.*, 1896, 29, 878) by the interaction of *o*-hydroxyaromatic ketones which have been chlorinated in the side chain and aromatic aldehydes. Thus

* Since the previous communication, the position of the methoxy-group in rhamnetin has been determined (Trans., 1902, 81, 469), and consequently the influence this was suggested to bear upon its salt-forming property requires modification.

chlorogallacetophenone and benzaldehyde yield dihydroxybenzylidene-

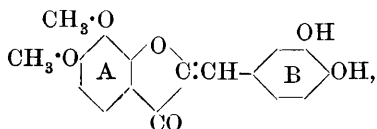


A concentrated alcoholic solution of this colouring matter, on treatment with alcoholic potassium acetate at the boiling point, at once deposited a salt crystallising in orange-yellow needles which were collected and washed with alcohol. Thus prepared, it appeared to contain alcohol of crystallisation, for on heating at 100° for two days it became orange-red and lost 11.54 per cent. in weight.

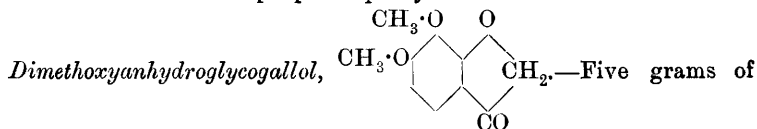
Found, K = 11.60. $C_{15}H_{10}O_4 \cdot C_2H_3O_2K$ requires K = 11.08 per cent.

It thus appeared to be a compound of the colouring matter with potassium acetate analogous to those given by daphnetin and hesperitin (*loc. cit.*). A monopotassium salt would require K = 13.37 per cent., but even after drying at 160° for three days, which caused the substance to become dark coloured and probably partially decomposed, it then contained no more than 12.24 per cent. of potassium.

For the sake of comparison, it was now of interest to study a colouring matter of this group containing only two free hydrogen groups in the benzylidene nucleus, and in the ortho-position relatively to one another. Such a compound has already been prepared, but from the materials which were available it was more convenient to construct a colouring matter having the constitution



which would answer the purpose equally well.



chlorogallacetophenone dissolved in methyl alcohol were treated with excess of methyl iodide and the mixture digested at the boiling point during two days with a solution of 6 grams of potassium hydroxide in methyl alcohol added drop by drop. It is necessary that the alkali be added very gradually, otherwise the result is not satisfactory. That portion of the product insoluble in aqueous potassium hydroxide was purified by crystallisation from alcohol, from which it separated in long, glistening, pale yellow needles melting at 122° :

0.1101 gave 0.2495 CO_2 and 0.0518 H_2O . $\text{C} = 61.80$; $\text{H} = 5.21$.

$\text{C}_{10}\text{H}_{10}\text{O}_4$ requires $\text{C} = 61.85$; $\text{H} = 5.15$ per cent.

Molecular proportions of this substance and protocatechuic aldehyde were dissolved in boiling alcohol, a small quantity of aqueous hydrochloric acid was added, and the digestion continued for about half-an-hour. On addition of hot water and cooling, orange-red needles separated which were collected, washed with a little ether, and purified by crystallisation from dilute alcohol:

0.1138 gave 0.2712 CO_2 and 0.0463 H_2O . $\text{C} = 64.99$; $\text{H} = 4.52$.

$\text{C}_{17}\text{H}_{14}\text{O}_6$ requires $\text{C} = 64.96$; $\text{H} = 4.46$ per cent.

This colouring matter evidently has the constitution given above. When pure, it has an orange colour, and resembles in its reactions the colouring matters of this group, previously described by Friedländer (*loc. cit.*).

Addition of potassium acetate to its solution in boiling alcohol causes the production of a deep orange-red coloration, and, on cooling, the monopotassium salt separates in the form of a granular precipitate. This was collected and washed with cold alcohol, in which it is somewhat soluble:

Found, $\text{K} = 11.16$. $\text{C}_{17}\text{H}_{13}\text{O}_6\text{K}$ requires $\text{K} = 11.08$ per cent.

It is thus evident, as regards these colouring matters, that from the presence of contiguous hydroxyl groups in the nuclei A or B, the formation of a monopotassium salt in this manner can be anticipated, and it is reasonable to suppose that analogous compounds of the closely allied flavone group will possess a similar property. It is probable, however, that the position of these contiguous hydroxyl groups in the various nuclei may have an important bearing upon this reaction. Unfortunately, however, this point could not be elucidated, for no colouring matters of this description have hitherto been synthetically prepared.

Carminic Acid.

According to the latest researches, carminic acid, the colouring matter of cochineal, is probably a hydrindene derivative (Liebermann, *Ber.*, 1898, 31, 2079). Various salts of this substance have been described, and those obtained by Hlasiwetz and Grabowski (*Annalen*, 1867, 141, 335) are most worthy of mention. By means of alcoholic potash, these chemists obtained the salt $\text{C}_{11}\text{H}_{10}\text{O}_7\text{K}$, and from this the barium and calcium compounds were prepared by double decomposition.

The material employed by us was purchased from Kahlbaum; a portion was recrystallised, but this, it subsequently appeared, was unnecessary.

Hlasiwetz and Grabowski (*loc. cit.*) mention that when alcoholic potash is slowly added to an alcoholic solution of carminic acid a red precipitate is first formed, which changes to violet on the addition of more alkali. It was found that potassium acetate behaves similarly. The violet or purplish-coloured precipitate produced by employing excess of the reagent was collected on filter paper, washed several times with boiling alcohol, drained by means of the pump, and again washed two or three times with alcohol and dried at 160° :

Found, K = 14.26, 14.29. $C_{11}H_{11}O_6K$ requires K = 14.03 per cent.

Monopotassium carminate is soluble in boiling water (with a violet-red coloration) without apparent decomposition, and resembles, in this respect, the corresponding salts of the anthraquinone colouring matters. The barium salt, prepared from this in the usual manner, is a violet-black powder almost insoluble in water:

Found, Ba = 21.50. $C_{22}H_{22}O_{12}Ba$ requires Ba = 22.27 per cent.

Hlasiwetz and Grabowski's violet potassium salt was prepared according to their methods, and was evidently identical with that obtained by means of potassium acetate.

To obtain some insight into the composition of the red salt, a small quantity was prepared by adding the acetate drop by drop to a boiling alcoholic solution of carminic acid so long as the red precipitate thus produced showed no violet tinge. The product was collected, washed with boiling alcohol, and dried at 160° :

Found, K = 7. $C_{22}H_{23}O_{12}K$ requires K = 7.52 per cent.

It formed a scarlet powder, almost indistinguishable from carminic acid itself, but was insoluble in cold alcohol, although dissolving easily in water to a red liquid. It is probably a monopotassium salt of a double molecule of carminic acid, but this is not certain, as the molecular weight of this colouring matter may possibly be represented as $(C_{11}H_{12}O_6)_2$.

A sodium salt, $C_{22}H_{23}O_{12}Na$, may be prepared in a similar manner to the potassium compound, and is a scarlet, amorphous powder:

Found, Na = 4.63. $C_{22}H_{23}O_{12}Na$ requires Na = 4.58 per cent.

Styrogallol.

This colouring matter is a dihydroxyanthracoumarin, and is prepared by heating a mixture of cinnamic and gallic acids with sulphuric acid. Owing to its sparing solubility in alcohol, it was converted into its diacetyl derivative, and this was digested with boiling alcoholic

potassium acetate for about two hours.* The substance, without appearing to dissolve, was gradually converted into a purplish, crystalline mass which was collected, washed with alcohol, and dried at 160° :

Found, $K = 12.56, 12.59$. $C_{16}H_7O_5K$ requires $K = 12.26$ per cent.

Monopotassium styrogallol forms minute, purplish-coloured needles, and is soluble in boiling water with a red coloration.

Naphthazarin.

On adding potassium acetate to a boiling alcoholic solution of pure crystallised naphthazarin, the deep red liquid gradually became of a brownish-yellow tint as if a reduction had ensued. On standing for a short time with access of air, the red colour was restored, and a finely divided, black precipitate was deposited. This was collected while still hot, washed repeatedly with boiling alcohol, then transferred to the filter pump, and again washed two or three times with alcohol and finally dried at 160° :

Found, $K = 8.09, 8.20, 7.99$. $(C_{10}H_6O_4)_2, C_2H_3O_2K$ requires 8.16 per cent.

This substance is a purplish-black, amorphous powder, and is sparingly soluble in cold water, forming a purple solution.

Curcumin.

As stated in the previous communication, curcumin, the colouring matter of turmeric, on solution in alcohol and treatment with potassium acetate, gives a blood-red coloration but no deposit. It has since been found that if this solution be evaporated, a semi-solid, orange-red mass, consisting of fine, hair-like needles, separates. This precipitate, which is somewhat soluble in alcohol, was collected, washed with small quantities of this solvent, and finally two or three times with ether. Numerous preparations of this substance were analysed, but although these gave results sufficiently accurate for the purpose, they did not accord perfectly either among themselves or with the latest molecular weight, $C_{21}H_{20}O_6$, assigned to this substance by Ciamician and Silber (*Ber.*, 1897, 30, 192). Dried at 100° , it gave:

$K = 10.07, 10.90, 9.72, 10.21$.

$C_{21}H_{19}O_6K$ requires $K = 9.60$ per cent.

This want of agreement may have been due to incomplete washing,

* By the decomposition of the acetyl derivatives in this manner, ethyl acetate is formed, and the reaction appears to be as follows:



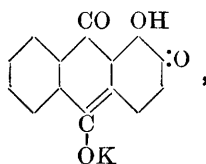
for the operation is somewhat difficult owing to the solubility of the substance in alcohol and its tendency to clot together. When dried at the ordinary temperature, this salt has an orange-brown colour, which at 100° changes to a maroon tint, and at 160° becomes darker and partially resinifies. Jackson and Menke (*Amer. Chem. J.*, 1883, 4, 77) describe a salt, $C_{14}H_{13}O_4K$.

Gallein.—The commercial product was acetylated and the acetyl derivative, after purification, digested with a boiling alcoholic solution of potassium acetate for some hours. A potassium salt is thus obtained in the form of fine, maroon-coloured, prismatic needles possessing a green iridescence, but unfortunately its exact composition has not been determined. After drying at 100°, it slowly but steadily loses weight at 160°, and a further loss is experienced at 180° without apparent decomposition. For example, a specimen at 100° contained 13.8, at 160°, 16.7, and at 180°, 19.7 per cent. of potassium, and similar results were obtained from other preparations. A further study of this substance will be instituted.

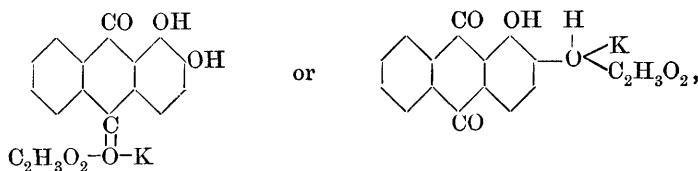
Summary.

The results of this and the preceding investigation indicate that all phenolic colouring matters which possess strong tinctorial properties are capable of decomposing the alkali acetates in the way indicated, with formation of sparingly soluble salts. As a rule, mono-substituted salts are produced; but in some cases additive products of the colouring matter and alkali acetate result. The weaker dyes of this class, such as apigenin, chrysin, and vitexin, give no insoluble precipitate, but as their alcoholic solutions are coloured yellow by addition of the acetate, it appears likely that some unstable compound is thus formed. It was previously suggested that the formation of the mono-substituted salts might be explained according to the quinonoid theory of coloured compounds, and we are at present inclined to retain this view. An interesting point which was referred to in the previous paper, and which has now been accentuated by further work, was the fact that, in the flavone series, the compounds which gave these salts gave also some well-defined additive products with mineral acids. The latter substances, hitherto formulated only according to the quinonoid theory, are now regarded as oxonium derivatives (Collie and Tickle, *Trans.*, 1899, 75, 714; Baeyer and Villiger, *Ber.*, 1901, 34, 2679). The "acid" and "basic" natures of the flavone derivatives as expressed by these two reactions are so markedly similar in each case as to suggest an intimate connection, and a likelihood that both, at least in the first instance, are due to the same cause. Certain compounds have been isolated which are additive

products of the colouring matter with potassium acetate; a compound of morin with potassium oxalate has also been referred to, and no doubt it would be possible to prepare numerous salts of this type. These substances are isolated when the phenol, although forming mono-substituted salts in the presence of alcoholic potassium or sodium hydroxide, is not sufficiently acidic to decompose the potassium acetate or other salt. Accordingly, it is therefore considered probable that in all cases the first step in this reaction is the production of an additive product of the colouring matter and the alkali salt; this, as a rule, is too unstable for isolation, and is rapidly decomposed with formation of the mono-substituted salt. Again, when the alkali hydroxide is employed at first, an additive compound is possibly formed, which changes almost immediately into the salt derived from the acetate. Such additive products can, of course, be readily formulated as oxonium derivatives, $\text{K}-\text{O}-\text{C}_2\text{H}_3\text{O}_2$ or $\text{K}-\text{O}-\text{OH}$, and this at once expresses their relation to the acid compounds, which is so marked in the flavone series. Assuming this to be correct, the question arises as to how the decomposition of these unstable derivatives with subsequent formation of the mono-substituted salt is best explained. It has been pointed out that the potassium salt of alizarin on digestion with methyl iodide at 220° is converted into the monomethyl ether ($\text{OH}:\text{O}\cdot\text{CH}_3=1:2$), and that the salts of other anthraquinone colouring matters behave similarly. Consequently, it was suggested that the constitution of the potassium salt was best represented as:



the marked change of colour between this substance and alizarin itself being due to an alteration in the quinonoid form. In accordance with this, therefore, the unstable additive compound of alizarin with the acetate could be formulated in two ways:




the first of which might be considered preferable, as it more readily expresses the change to the monopotassium salt as represented.

The fact has been noted that certain mono-substituted salts as, for

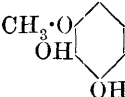
instance, those of alizarin and gallacetophenone, are stable towards boiling water, whereas those of the flavone series are not. This distinction suggested the possibility that the flavone compounds were not true salts, but might be represented as additive compounds of the colouring matter and alkali hydroxide. From the previous work, this did not appear likely, but to set all doubt at rest the potassium derivative of morin was again investigated, with the result that this must be regarded as a true salt, $C_{15}H_9O_7K$, and not an additive compound, $C_{15}H_{10}O_7 \cdot KHO$ (found $K = 11.45, 11.46$; calc. $K = 11.47$).

As an explanation of the instability of the flavone (and other) salts, it is suggested that in the presence of water monopotassium quercetin, for example, tends to pass into the oxonium derivative, $C_{15}H_{10}O_7 \cdot KHO$, which being unstable is decomposed into quercetin and its salt, $C_{15}H_9O_7K$.

In support of the quinonoid structure of the salts, it is interesting to note that all the colouring matters of known constitution at present examined can readily be represented as *p*-quinonoid compounds. Except in the case of flavone derivatives (Trans., 1902, 81, 590), it appears to be generally true that all colouring matters carefully investigated, from this point of view, contain two hydroxyl groups in the ortho-position relatively to one another. As this peculiar salt formation may be taken as an expression of the dyeing property, it would be most interesting to determine whether an

acetyl catechol having the constitution OH  $CO \cdot CH_3$ would be a

dyestuff, as this could evidently not be expressed as a *p*-quinonoid compound. Unfortunately, this and similarly constituted substances do not seem to have been prepared, although it is considered probable that the gallacetophenone monomethyl ether described in this paper

has the constitution $CH_3 \cdot O$  $CO \cdot CH_3$. Definite knowledge of the

behaviour of such phenolic compounds should decide the constitution assigned to these salts.

The tendency of some colouring matters to form what may be termed *semimonosubstituted salts*, as in the case of daphnetin, $C_9H_6O_4 \cdot C_9H_5O_4K$, is interesting and has led us to attempt the formation of such compounds from alizarin and other colouring matters, but as yet without success. It is evident that these substances, as in the case of the product obtained from daphnetin and potassium acetate, &c., could be represented as oxonium derivatives in the manner suggested above, but the peculiar gallacetophenone com-

pound, $(C_8H_5O_4)_2, C_8H_7O_4K$, indicates that such an explanation is hardly feasible. The existence of these semi-monosubstituted salts indicates that the composition of such derivatives must not without further evidence be taken to represent the molecular weight of the compound under consideration; as has been the case with hesperitin and rottlerin (Trans., 1898, 73, 1035; 1895, 67, 230). The former yielded derivatives, $C_{32}H_{28}O_{12}, C_2H_3O_2K$ and $C_{32}H_{27}O_{12}K$, and the latter $C_{33}H_{29}O_9K$ and $C_{33}H_{29}O_9Na$, and other methods of molecular weight determination will be carried out to determine if these substances are semi-salts or otherwise.

It has been observed in the cases of ellagic acid and galloflavin that by means of potassium acetate both colouring matters form dipotassium salts. This apparently abnormal behaviour appears to be due to the fact that both substances are acids, and that to the carboxylic group is due the presence of the second potassium atom in these compounds. The special activity of one hydroxyl group in colouring matters known to possess several such radicles is no doubt of importance in connection with their property of forming lakes with the heavier metals and their basic salts. It would be extremely interesting if the corresponding mono-substituted salts of aluminium and tin could be prepared in order to observe the colour of these products, and to determine how closely they resemble the shades produced in the ordinary manner with mordanted fabrics. Compounds, however, of this simple character are not produced by methods of soluble decomposition, and salts of a basic nature have only at present been isolated when experimenting in this direction.

In connection with oxonium derivatives, it may be here mentioned that during experiments with kampherol, with the object of preparing Testoni's methylkampherol trimethyl ether (*Gazzetta*, 1900, 30, ii, 327), a substance resembling but not identical with this compound resulted. It melted at $182-185^\circ$, and although analyses were carried out, these, as was subsequently discovered, were vitiated by the fact that the product contained a considerable quantity of iodine. Owing to the scarcity of the material and the expense of the methods necessary for isolating kampherol, these experiments have not as yet been repeated, but it is possible that the compound in question may be represented as an oxonium derivative containing the group $Me-\overset{|}{O}-I$, analogous to the substance, $C_7H_8O_2 \cdot EtOH$, which Collie and Steele (Trans., 1900, 77, 971) obtained from dimethylpyrone. The subject will be further investigated.

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