

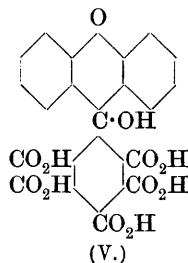
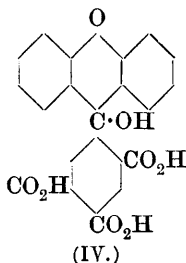
CLXXIII.—*The Relationship of Colour and Fluorescence to Constitution. Part I. The Condensation Products of Mellitic and Pyromellitic Acids with Resorcinol.*

By OSWALD SILBERRAD, Ph.D.

WHEN mellitic or pyromellitic acid is heated with phenols or meta-derivatives of phenols, condensation occurs, with the formation of colouring matters analogous to the phthaleins.*

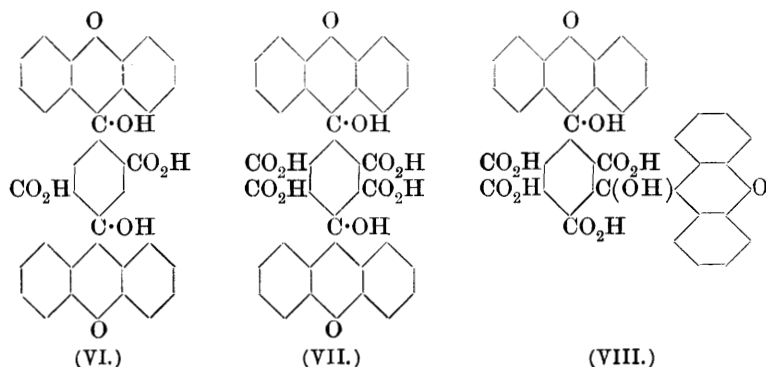
Mellitic acid is capable of forming three series of "melliteins," and similarly, pyromellitic acid can give rise to two series of derivatives. The general structure of the compounds follows from their method of preparation and their analogy to the phthaleins. It is convenient to classify them as mono-, di-, and tri-xanthyl derivatives.

The monoxanthyl derivatives obtained from pyromellitic acid may be regarded as being derived from 9-hydroxyxanthylbenzene-2:4:5-tricarboxylic acid (IV), and those obtained from mellitic acid as derived from 9-hydroxyxanthylbenzene-2:3:4:5:6-pentacarboxylic acid (V).

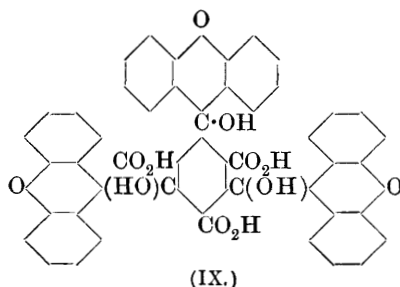


The dixanthyl compounds are similarly derived from 9:9'-di-hydroxy-p-dixanthylbenzene-2:5-dicarboxylic acid (VI), and 9:9'-di-hydroxydixanthylbenzenetetra-carboxylic acid respectively. Of these, the former is derived from pyromellitic acid, and admits of only one isomeride, whilst the latter, derived from mellitic acid, occurs in two modifications, according as the xanthyl groups are para (VII) or meta (VIII) to one another.

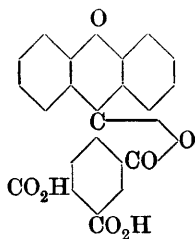
* The application of these compounds as dyestuffs has already been patented (Silberrad, Eng. Pat., No. 28638 of 1902).



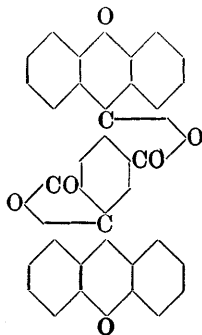
Derivatives of both the meta- and the para-compound have been prepared. They differ from one another in that the meta-compounds (VIII) are capable of condensing with a further pair of phenol molecules to form trianthyl derivatives. The parent compound of the trianthyl group is 9 : 9' : 9''-trihydroxytrianthylbenzenetricarboxylic acid (IX).



Anhydro-derivatives.—It is seen that the above carbinol derivatives are capable of losing water to form lactones. In the phthalic series, the carbinol derivatives are assumed to change spontaneously to lactones on passing from the ionised to the non-ionised condition. In the present study of the melliteins and pyromelliteins, it has been found that all the mellitic derivatives are hydrated and behave as though they contain the full complement of carboxylic acid groups as shown in formulæ (V), (VII), (VIII), and (IX). The pyromellitic derivatives, on the other hand, are anhydrides—presumably lactones—as represented in the formulæ (X) and (XI) :



(X.)

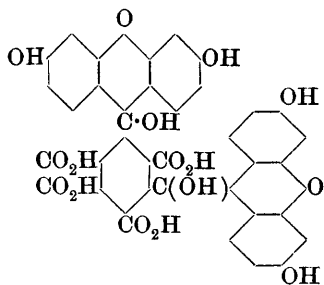


(XI.)

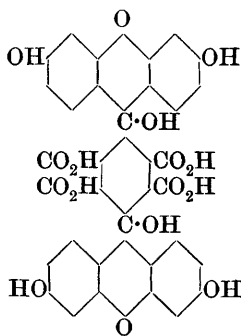
(X) *9-Hydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylic acid*,
and (XI) *9:9'-dihydroxydixanthylbenzene-2:5-dicarboxylactone*.

Orientation of the Xanthyl Groups in Dixanthyl Derivatives of Mellitic Acid.

In the mono- and tri-xanthyl derivatives the orientation of the xanthyl groups is not open to doubt; the dixanthyl compounds, however, are capable of existing in two modifications, according as the xanthyl groups are meta or para to each other, as shown in formulæ (XII) and (XIII). The ortho-position is excluded, as each xanthyl group requires the presence of two carboxylic groups, even although one of these is left intact.



(XII.)



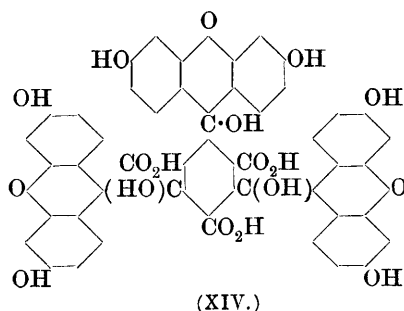
(XIII.)

(XII) *Hexahydroxy-m-dixanthylbenzene-2:4:5:6-tetracarboxylic acid*.

(XIII) *Hexahydroxy-p-dixanthylbenzene-2:3:5:6-tetracarboxylic acid*.

It is seen that only the meta-derivative is capable of combining with a further pair of resorcinol molecules to form nonahydroxy-*sym*-

trixanthylbenzenetricarboxylic acid, since two neighbouring carboxylic groups are necessary for the condensation with resorcinol. This property has been made use of for the orientation of these compounds. It is found that the ordinary hexahydroxydixanthylbenzenetetracarboxylic acid, obtained by direct condensation of resorcinol with mellitic acid, readily unites with a further pair of resorcinol molecules to form a trixanthyl derivative, namely:



(XIV) *Nonahydroxy-sym-trixanthylbenzene-2:4:6-tricarboxylic acid.*

The original compound must therefore have been the metadixanthyl derivative shown in formula (XII).

In order to prepare the para-isomeride, it is necessary to protect the 1:4-positions. This was accomplished by condensing 1:4-diethyl mellitate with resorcinol and subsequently saponifying the resulting ester. In this way, the para-compound (formula XIII) was obtained. This compound shows no tendency under any conditions to condense further with resorcinol. It will be observed that these derivatives of mellitic acid are hydrated, that is, the carboxylic acid groups adjacent to the xanthyl groups are unaffected, and it should therefore be possible to produce a hexaxanthyl derivative. This, however, has not been realised; it has been suggested that a pair of carboxylic acid groups adjacent, or in the ortho-position to one another, is necessary for the formation of a xanthyl ring. This, however, fails to account for the fact that the para-derivative, which still contains two pairs of ortho-carboxyl groups, does not form tri- and tetra-derivatives. The most logical explanation appears to be that the introduction of two xanthyl groups in adjacent positions is prevented by steric hindrance.

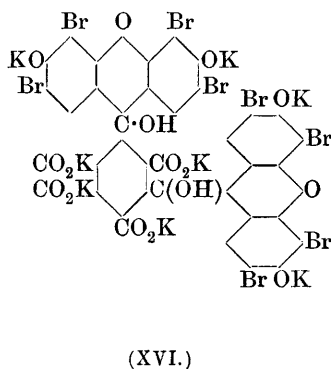
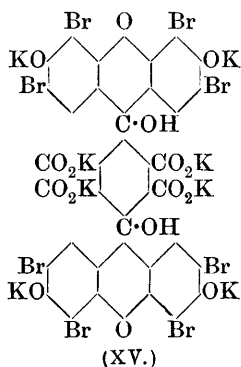
It is of interest to note that the two isomeric series of compounds show a distinct difference of colour. Thus 3:3':6:6':9:9'-hexahydroxy-*p*-dixanthylbenzene-2:3:5:6-tetracarboxylic acid dyes silk and wool a yellow ochre tint, whilst the meta-isomeride gives a brownish-yellow. The octabromo-derivatives of these two compounds show an equally marked difference of colour. The para-compounds

also show a much more intense fluorescence than the corresponding meta-derivatives.

Relationship of Constitution to Colour and Fluorescence.—Much of the interest of the present work lies in its bearing on the influence of constitution on colour and fluorescence. According to the ideas currently accepted, the colour and fluorescence of the phthaleins is attributed to a quinonoid structure of the molecule and to its oscillatory tautomeric relationship with the corresponding lactone. It is therefore a matter of surprise to find, as is shown in the present work, that many compounds of this class, although intensely coloured and strongly fluorescent, cannot reasonably be formulated as quinone derivatives and admit of no possibility of tautomerism. They should, indeed, according to the generally accepted theories, be colourless and non-fluorescent. Thus, the following are examples of compounds prepared in the present work which are saturated and contain neither lactone rings nor quinone groups and are incapable of tautomeric oscillation, yet they exhibit intense colour and fluorescence.

I. Haloid Derivatives of Di- and Tri-xanthyl Compounds.

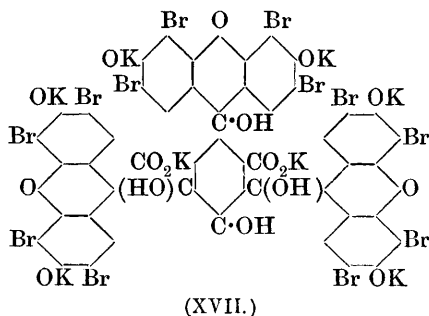
Examples of these are *octabrom-(or iodo)-3:3':6:6':9:9'-hexahydroxy-dixanthylbenzene-2:4:5:6-(or 2:3:4:5)-tetracarboxylic acids*. These compounds act as octabasic acids, forming well-defined and characteristic salts. The *potassium* salts, for example (formulae XV and XVI), are red powders possessing a metallic green reflex; they are very soluble in water, giving intense blood-red solutions which show a brown fluorescence, and dye silk and wool an intense pinkish-red.



(XV) *Potassium octabromohexahydroxy-p-dixanthylbenzene-2:3:5:6-tetracarboxylate.*

(XVI) *Potassium octabromohexahydroxy-m-dixanthylbenzene-2:4:5:6-tetracarboxylate.*

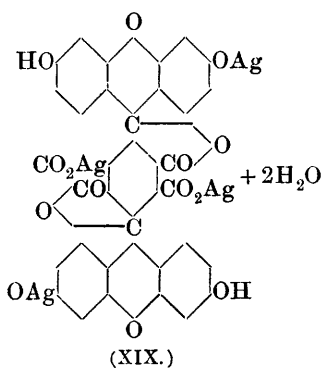
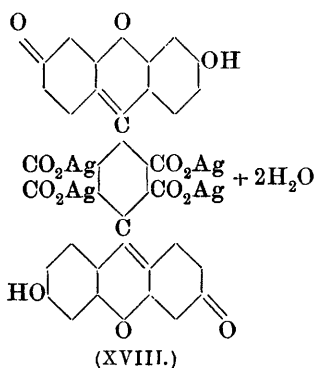
Dodecabromo- (and iodo)- nonahydroxytrixanthylbenzenetricarboxylic acids also belong to this class. They behave as nonabasic acids and yield well-defined salts, for example :



(XVII) *Potassium dodecabromononahydroxy-sym-trixanthylbenzene-2:4:6-tricarboxylate.*

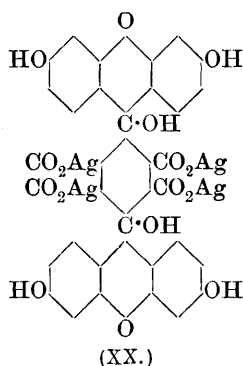
II. The Parent Hydroxy-compounds.

These possess precisely analogous structure, but in their case the basicity of the acid is restricted to the number of carboxylic groups present. This admits of the possibility of two methods of formulation apart from the above. Thus the silver salt, for example, of hexahydroxy-*p*-dixanthylbenzene-2:3:5:6-tetracarboxylic acid, that is, the parent compound corresponding to formula (XV), might be formulated either as (XVIII), or (XIX).



Since, however, the structure of the halogen derivatives has been placed beyond all doubt, and there are no grounds for assuming a difference of structure between these and the parent compounds, it appears that the latter also are saturated, as shown in the formula of *silver hexa-*

hydroxy-p-dixanthylbenzene-2 : 3 : 5 : 6-tetracarboxylate (XX), and contain neither lactonic nor quinonoid linkings.



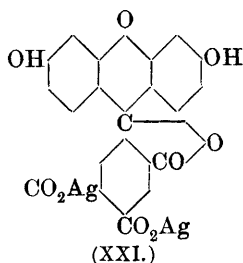
Notwithstanding the absence of all groups usually recognised as chromophores, these compounds are intensely coloured and show strong fluorescence. Further, it is seen that they are closely allied to the phthaleins themselves, thus the formation of derivatives which cannot be formulated so as to contain a quinonoid structure casts grave doubts on the presence of a quinone group in any of these compounds. Undoubtedly, in the instances cited above, another chromophore must be sought. The observations made in the present work appear to lend weight to Baeyer's theory of the constitution of phthaleins and other dyes (*Ber.*, 1905, 38, 569), according to which the colour is not due to a quinonoid structure but to a peculiar form of carbon linking. It certainly appears from the examples given that the 9-carbon atom of these xanthyl derivatives, which corresponds to the carbinol carbon atom of triphenylcarbinol compounds, possesses latent chromophoric properties, the development of which depends on the substituents in the xanthyl or other groups attached thereto.

Stability of the Lactone Ring in Phthaleins.—It is generally assumed that phenolphthalein and many of its derivatives exist in the form of lactones in the free state, but undergo a desmotropic change into quinone derivatives containing a carboxylic group in presence of alkali. According to this assumption, the lactone ring is supposed to be very labile, breaking open at once in presence of dilute alkali, whilst in fluorescent compounds the two formulæ are assumed to represent tautomeric compounds capable of constantly oscillating between the two configurations.

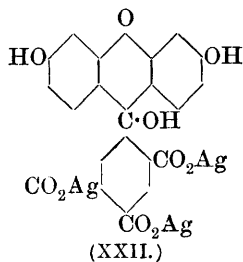
The present work gives indications that the change from the lactonic to the quinonoid structure frequently does not take place with the ease which has been generally assumed. In other cases, again, the com-

pounds show no tendency to pass into the lactonic form when liberated from their salts, but remain as carboxylic acids. Thus, in many instances the salt-formation occurs without any molecular rearrangement. The analogy between these compounds and the phthaleins is so close that a modification of the theory of these compounds may become necessary.

When trihydroxyxanthylbenzene-2-carboxylactonedicarboxylic acid is warmed with a quantity of caustic potash less than sufficient to dissolve it completely, and the excess of xanthyl compound separated, the solution yields on precipitation *silver trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylate* (XXI). Thus the compound acts as a

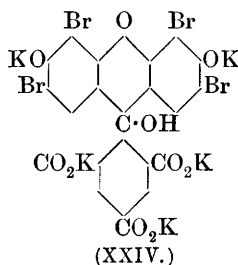
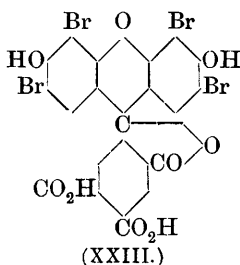


dibasic acid in these circumstances, indicating that the lactone ring does not break open so easily as is generally believed. If, however, the dipotassium salt is dissolved in water, and treated with a drop of caustic potash, a marked change of colour occurs. The solution, which was originally a bright orange, becomes much darker, more intensely coloured, and the fluorescence increases considerably. This evidently indicates that the lactone ring is broken open in presence of caustic alkali. Indeed it was found possible to precipitate *silver trihydroxyxanthylbenzene-2:4:5-tricarboxylate* (XXII) from a solution prepared by



treating one molecule of the xanthyl compound with three molecules of caustic potash. It will be observed that the salts corresponding to formula XXII are fully saturated compounds and cannot be formulated as quinone derivatives, unless a molecule of water is considered

as water of crystallisation. It is noteworthy that the tri-metallic salts show a much more brilliant metallic reflex and possess a much more intense colour and fluorescence in solution than the di-metallic salts, that is to say, the colour and fluorescence are strongest in the compounds which, according to the ideas hitherto accepted, contain no chromophore and do not admit of tautomerism, and should therefore be colourless and devoid of fluorescence. The haloid derivatives of the above compound are also lactonic (XXIII), but in this case the lactone ring readily opens on treatment with alkalis as above, and the compound acts as a pentabasic acid.



(XXIII) *Tetrabromotrihydroxyxanthylbenzenecarboxylactonedicarboxylic acid.*

(XXIV) *Potassium tetrabromotrihydroxyxanthylbenzenetricarboxylate.*

The results recorded in the present paper may be summarised as follows :

(1) Mellitic and pyromellitic acids condense with resorcinol to form a series of coloured compounds analogous to the phthaleins.

(2) Neither the colour nor the fluorescence of these compounds is dependent on the presence of quinone linkings, for in many instances a quinonoid structure is impossible.

(3) The change from a lactonic to a quinonoid structure, and *vice versa*, does not appear to take place with the ease which is generally assumed.

EXPERIMENTAL.

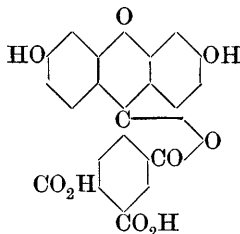
[With CHARLES SMART ROY.]—For the conversion of mellitic into pyromellitic acid the following conditions were found, after a series of experiments, to give the most favourable results. Fifty grams of mellitic acid are mixed with 80 grams of potassium hydrogen sulphate and made up into a thick paste with sulphuric acid. The mixture is heated to 200° for six hours and then distilled in a retort fitted with a long air condenser dipping into a receiver, so that when a little sulphuric acid has distilled over the vapours must bubble through it.

1796 SILBERRAD: THE RELATIONSHIP OF COLOUR AND

The decomposition gases carry over a considerable quantity of pyromellitic acid; this is collected by passing the vapour through cold water. White fumes are evolved at first, and after a time sulphuric acid passes over. Toward the end of the distillation the pyromellitic acid distils over in considerable quantity, and care must be taken to avoid choking of the condenser. The distillation is continued until no more acid passes over. The water and sulphuric acid, in which a portion of the pyromellitic acid has collected, are mixed and cooled to allow the dissolved acid to crystallise out. The acid is purified by recrystallisation from water. The yield amounts to 54 per cent.

I. *Monoxanthyl Derivatives.*

3 : 6 : 9-Trihydroxyxanthylbenzene-2-carboxylactone-4 : 5-dicarboxylic Acid (*Diresorcinolpyromellitein*), $C_{22}H_{12}O_9$.—This is prepared by heat-



ing a finely ground mixture of equal parts of pyromellitic acid and resorcinol to 160° for six hours. The mixture, which at first melts, gradually loses water and solidifies. When cold, the dark brown mass is powdered, extracted with boiling water, and the residue dissolved in a small quantity of alcohol. By this treatment a small quantity of a red organic compound insoluble in cold alcohol is removed. It is suggested that this may be the corresponding anthraquinone derivative. The anhydroxanthyl product is isolated and purified by fractional precipitation of its alcoholic solution by the addition of water. On analysis:

- I.* 0.2230 gave 0.5154 CO_2 and 0.0521 H_2O . C = 63.03; H = 2.59.
 II. 0.2157 „ 0.4974 CO_2 „ 0.0528 H_2O . C = 62.89; H = 2.72.
 II. 0.1898 „ 0.4375 CO_2 „ 0.0469 H_2O . C = 62.86; H = 2.74.
 III. 0.2091 „ 0.4800 CO_2 „ 0.0555 H_2O . C = 62.60; H = 2.94.
 Mean C = 62.85; H = 2.77.

$C_{22}H_{12}O_9$ requires C = 62.72; H = 2.87 per cent.

The substance is a bright yellow, amorphous powder melting at above 300° . It dyes silk and wool a brilliant yellow. It is insoluble

* These numerals refer to the different preparations.

in benzene, ether, or chloroform, and very slightly soluble in concentrated hydrochloric acid or water, giving in the latter solvent a very faint pink coloured solution having a most intense green fluorescence. It is fairly soluble in aniline, phenol, ethyl acetate, glacial acetic acid, or concentrated sulphuric acid, readily so in acetone or alcohol, in which solvents it gives a reddish-orange coloured solution having an intense green fluorescence; it is precipitated from these solvents on addition of water.

The compound dissolves readily in dilute aqueous caustic potash and ammonia, giving deep orange solutions having an intense green fluorescence; on acidifying these solutions, the acid is precipitated.

The alkali salts were prepared by warming a solution of caustic alkali with excess of the xanthyl compound, and after separating the excess of the latter, evaporating the filtrate. The salts of the heavy metals were obtained from the potassium salts by double decomposition.

The *lithium* and *potassium* salts are dark orange-red powders having a green metallic reflex.

The *silver* salt, $C_{22}H_{10}O_9Ag_2$, is a bright orange-red powder which is fairly stable to heat. It is readily soluble in ammonia; dilute nitric and glacial acetic acids dissolve the salt, precipitating out the free acid. On analysis:

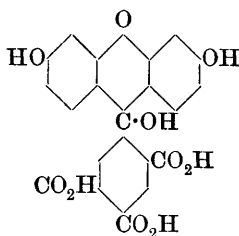
Preparation	I.	0.2176	gave	0.0744	Ag.	Ag = 34.19.
„	II.	0.2757	„	0.0942	Ag.	Ag = 34.16.
„	II.	0.2327	„	0.0795	Ag.	Ag = 34.16.
„	III.	0.5219	„	0.1771	Ag.	Ag = 33.93.
						Mean Ag = 34.11.

$C_{22}H_{10}O_9Ag_2$ requires Ag = 34.05 per cent.

The *copper*, *cobalt*, *lead*, *ferrous*, and *chromium* salts are formed as orange precipitates.

The *ferric* salt is a dark brownish-red powder.

3 : 6 : 9-*Trihydroxyxanthylbenzene*-2 : 4 : 5-*tricarboxylic Acid*, $C_{22}H_{14}O_{10}$.



This acid does not exist in the free state; on liberation from its salts it at once loses water, yielding 3 : 6 : 9-*trihydroxyxanthylbenzene*-2-

1798 SILBERRAD: THE RELATIONSHIP OF COLOUR AND

carboxylactone-4:5-dicarboxylic acid. The *potassium* salt is obtained by suspending 2.1 parts of 3:6:9-trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylic acid in water and adding 0.838 parts of potassium hydroxide. After about 0.6 part has been run in, additional alkali causes a marked increase in colour and fluorescence. On evaporating the solution, the salt separates as a dark red powder having a bright olive-green, metallic reflex. It is very soluble in water, giving a brownish-red solution having a very intense green fluorescence. The *lithium* and *sodium* salts closely resemble the potassium salt.

The *silver* salt, $C_{22}H_{11}O_{10}Ag_3$, is a dark crimson powder having an olive-green, metallic reflex. It dissolves instantly in ammonia: dilute nitric and glacial acetic acids dissolve the salt, precipitating the lactonedicarboxylic acid. It is fairly stable to heat and light. On analysis:

I.*	from sodium salt	0.2371	gave	0.1001	Ag.	Ag = 42.22.
II.	„	sodium salt	0.1285	„	0.0546	Ag. Ag = 42.49.
II.	„	sodium salt	0.1918	„	0.0814	Ag. Ag = 42.44.
III.	„	lithium salt	0.1278	„	0.0544	Ag. Ag = 42.56.
III.	„	lithium salt	0.1142	„	0.0485	Ag. Ag = 42.46.
						Mean Ag = 42.43.

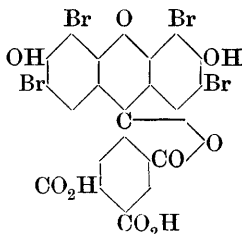
$C_{22}H_{11}O_{11}Ag_3$ requires Ag = 42.66 per cent.

The *copper* salt is a reddish-brown powder which turns dark brown on addition of ammonia.

The *cobalt* and *mercuric* salts are orange-red powders.

The *lead*, *chromium*, *ferrous*, and *ferric* salts are bright reddish-orange, dark yellowish-orange, brown, and dark brownish-red powders respectively.

2:4:5:7-Tetrabromo-3:6:9-trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylic Acid (*Tetrabromodiresorcinolpyromellitein*), $C_{22}H_8O_9Br_4$.



The foregoing compound is dissolved in alcohol, cooled, and a slight excess of bromine slowly added. After twenty-four hours the mixture

* See footnote on p. 1796.

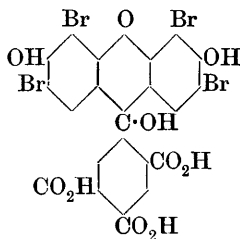
is thrown into water, the precipitate of the bromo-compound separated, and purified by exhaustive fractional precipitation of its alcoholic solution by the addition of water. On analysis :

Preparation	I.	0.5359	gave	0.5498	AgBr.	Br = 43.66.
	II.	0.3124	„	0.3199	AgBr.	Br = 43.57.
	III.	0.2209	„	0.2268	AgBr.	Br = 43.69.
	IV.	0.2098	„	0.2134	AgBr.	Br = 43.28.
						Mean Br = 43.55.

$C_{22}H_8O_9Br_4$ requires Br = 43.46 per cent.

The substance is a bright orange-red, amorphous powder melting at $186-189^\circ$, and dyes silk and wool a brilliant crimson. It is insoluble in water, benzene, ether, chloroform, or concentrated hydrochloric acid, but slightly soluble in concentrated sulphuric and acetic acids, from which it is precipitated on dilution. It is fairly soluble in ethyl acetate and readily so in warm aniline, giving a fine deep red solution having a brown fluorescence; on cooling, the colouring matter separates. It is also soluble in phenol, acetone, or alcohol, giving deep red solutions from which the compound is precipitated on dilution with water. It dissolves in dilute potassium hydroxide or ammonia, with rupture of the lactone ring. The solutions have a fine deep red colour and a brown fluorescence.

2 : 4 : 5 : 7-Tetrabromo-3 : 6 : 9-trihydroxyxanthylbenzene-2 : 4 : 5-tri-



carboxylic Acid, $C_{22}H_{10}O_{10}Br_4$.—This acid is known only in the form of its metallic salts. When liberated it at once loses water, and is converted into *tetrabromotrihydroxyxanthylbenzenecarboxylactonedicarboxylic acid*.

The salts are prepared from the preceding lactone by the addition of alkali, which breaks open the lactone ring. The *sodium* and *lithium* salts are dark red powders having a very brilliant green metallic reflex, and are very readily soluble in water.

The *silver* salt, $C_{22}H_5O_{10}Br_4Ag_5$, is precipitated as a bright crimson precipitate which is fairly stable to heat and light, and is readily soluble in ammonia. Dilute nitric and glacial acetic acids dissolve the salt and precipitate the acid. On analysis :

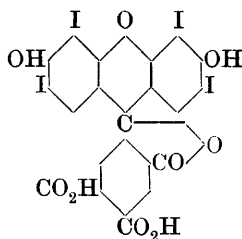
1800 SILBERRAD: THE RELATIONSHIP OF COLOUR AND

Preparation	I.	0.5819	gave	0.4204	AgBr.	Ag = 41.50.
"	II.	0.3451	"	0.2522	AgBr.	Ag = 41.98.
"	II.	0.1998	"	0.1461	AgBr.	Ag = 42.00.
"	III.	0.2189	"	0.1600	AgBr.	Ag = 41.98.
"	IV.	0.1859	"	0.1349	AgBr.	Ag = 41.68.
						Mean Ag = 41.83.

$C_{22}H_5O_{10}Br_4Ag_5$ requires Ag = 41.88 per cent.

The *copper, barium, cobalt, lead, ferrous, and chromium* salts are formed as blood-red powders, the barium and copper salts being unaltered by ammonia; the *ferric* salt is a dull brownish-red powder.

2 : 4 : 5 : 7-Tetraiodo-3 : 6 : 9-trihydroxyxanthylbenzene-2-carboxylactone-4 : 5-dicarboxylic Acid (Tetraiododiresorcinolpyromellitein),
 $C_{22}H_8O_9I_4$.



Eight grams of trihydroxyxanthylbenzenecarboxylactonedicarboxylic acid are dissolved in 30 c.c. of a 20 per cent. caustic potash solution. This solution is boiled, and to it a boiling solution of 50 grams of iodine in 100 c.c. of 10 per cent. caustic potash is slowly added. The whole is then boiled for ten minutes and allowed to cool, when the iodo-compound separates out and is filtered off, washed thoroughly with hot water, dissolved in dilute caustic potash, and fractionally precipitated by addition of hydrochloric acid. On analysis:

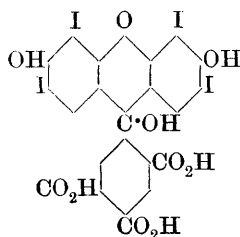
Preparation	I.	0.3855	gave	0.3918	AgI.	I = 54.93.
"	II.	0.2554	"	0.2608	AgI.	I = 55.20.
"	III.	0.2459	"	0.2520	AgI.	I = 55.39.
						Mean I = 55.17.

$C_{22}H_8O_9I_4$ requires I = 54.96 per cent.

This substance is a dark red, amorphous powder, which decomposes without melting at 187° with evolution of vapours of iodine. It is insoluble in water, concentrated hydrochloric acid, and nearly all organic solvents, but slightly soluble in concentrated sulphuric acid, giving a light brown solution; on dilution with water, the red colour appears, and the iodo-compound is precipitated. It is fairly soluble in alcohol, giving a bright red solution, and readily so in dilute alkalis

or ammonia, the lactone ring being thereby broken, and salts of the acid described below being formed. The solutions have a fine deep red colour, and on addition of hydrochloric acid the above lactonic acid is obtained.

2 : 4 : 5 : 7-*Tetraiodo-3 : 6 : 9-trihydroxyxanthylbenzene-2 : 4 : 5-tricarboxylic Acid*, $C_{22}H_{10}O_{10}I_4$.



This acid, like the corresponding bromo-derivative, exists only in the form of its salts. When liberated from these, it loses water and forms the preceding lactone.

The salts are prepared from the lactone described above by the addition of alkali, which breaks open the lactone ring.

The *lithium* and *potassium* salts are dark red powders having a brilliant green, metallic reflex.

The *silver* salt, $C_{22}H_5O_{10}I_4Ag_5$, is a blood-red powder soluble in ammonia. Glacial acetic and dilute nitric acids dissolve it and precipitate the lactone. On analysis :

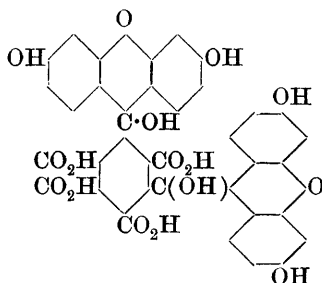
Preparation	I.	0.2020	gave	0.1617 Ag.	Ag = 36.78.
„	II.	0.2151	„	0.1718 Ag.	Ag = 36.69.
„	II.	0.1891	„	0.1509 Ag.	Ag = 36.66.
„	III.	0.1910	„	0.1526 Ag.	Ag = 36.70.
					Mean Ag = 36.71.

$C_{22}H_5O_{10}I_4Ag_5$ requires Ag = 36.54 per cent.

The *copper*, *barium*, *cobalt*, *lead*, *ferrous*, and *chromium* salts are blood-red powders, the copper and barium salts being unaltered by ammonia. The ferrous salt is dark orange-red.

II. *Dixanthyl Derivatives.*

3 : 3' : 6 : 6' : 9 : 9' - *Hexahydroxy-m-dixanthylbenzene-2 : 4 : 5 : 6-tetracarboxylic Acid (Tetraresorcinol-mellitein)*, $C_{36}H_{22}O_{16}$,



is prepared by heating a finely-powdered mixture of 12.5 parts of mellitic acid and 8 parts of resorcinol to 160° for eight hours. After cooling, the mass is boiled with water and filtered, the residue being dissolved in alcohol, filtered, and the condensation product precipitated from the alcoholic solution by dilution with water. The precipitate is separated and purified by repeated fractional precipitation from its alcoholic solution by addition of water, the purified product being dried at 100° . On analysis :

- I.* 0.1112 gave 0.2488 CO_2 and 0.0319 H_2O . C = 61.02 ; H = 3.19.
 II. 0.2887 „ 0.6421 CO_2 „ 0.0855 H_2O . C = 60.65 ; H = 3.29.
 III. 0.1190 „ 0.2660 CO_2 „ 0.0353 H_2O . C = 60.96 ; H = 3.29.
 Mean C = 60.88 ; H = 3.26.

$C_{36}H_{22}O_{16}$ requires C = 60.83 ; H = 3.12 per cent.

The substance is a dark yellow, amorphous powder which decomposes above 300° without melting and dyes silk and wool a brownish-yellow. It is insoluble in cold water, ether, benzene, or chloroform, slightly soluble in boiling water, ethyl acetate, phenol, or concentrated hydrochloric acid, and fairly so in glacial acetic acid, from which solution it is precipitated on dilution with water. It is very soluble in acetone, giving a red solution, from which the acid is not readily precipitated on dilution with water. The substance is readily soluble in aniline or alcohol, giving reddish-brown solutions having an intense green fluorescence. On diluting the alcoholic solution with water, the acid is precipitated. It is also readily soluble in concentrated sulphuric acid, and is precipitated unchanged on dilution.

In dilute potassium hydroxide or ammonia it is exceedingly soluble,

* See footnote on p. 1796.

giving reddish-brown solutions having a most intense green fluorescence even when extremely dilute. From these solutions the acid is precipitated on acidifying.

The *ammonium* salt, prepared by adding excess of ammonia to the acid suspended in water, boiling, filtering, and evaporating the solution to dryness, first on the water-bath and finally in a vacuum desiccator over concentrated sulphuric acid, is a brownish-yellow powder readily soluble in water.

The *lithium* and *potassium* salts were prepared by boiling an excess of the acid with dilute aqueous solutions of the alkalis, separating the unchanged acid, and evaporating the solutions to dryness on the water-bath. These salts are dark reddish-brown powders having a green, metallic reflex. They are readily soluble in water, and the solutions have an intense green fluorescence.

The *silver* salt, $C_{36}H_{18}O_{16}Ag_4$, is a yellowish-orange precipitate which is fairly stable to heat and light. It is soluble in ammonia; dilute nitric acid and glacial acetic acid dissolve the salt with separation of the acid. On analysis:

Preparation I. 0.2137 gave 0.0814 Ag. Ag = 38.09.

„ II. 0.2579 „ 0.0983 Ag. Ag = 38.11.

Mean Ag = 38.10.

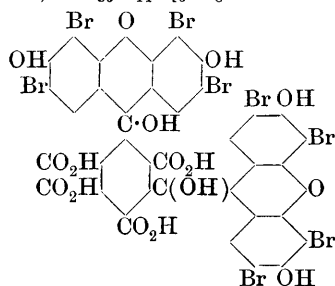
$C_{36}H_{18}O_{16}Ag_4$ requires Ag = 37.94 per cent.

The *copper*, *lead*, and *mercuric* salts are precipitated as yellowish-orange powders.

The *barium* salt is a light yellow powder slightly soluble in water; on addition of ammonia the colour becomes darker.

The *cobalt*, *ferric*, and *ferrous* salts are dark reddish-orange powders.

2:2':4:4':5:5':7:7'-Octabromo-3:3':6:6':9:9'-hexahydroxy-m-dixanthylbenzene-2:4:5:6-tetracarboxylic Acid (Octabromotetraresorcinol-mellitein), $C_{36}H_{14}O_{16}Br_8$.



The foregoing compound is suspended in glacial acetic acid and an excess of bromine gradually added. After allowing the mixture to

stand for 24 hours, it is heated on a water-bath for an hour, allowed to cool, and poured into a large quantity of water. The light red bromo-compound is separated and washed thoroughly with boiling water, dissolved in as small a quantity of alcohol as possible, filtered, and the alcoholic solution poured into water. The octabromo-derivative is precipitated from alcohol as a deep red, amorphous precipitate which is purified by fractional precipitation. On analysis:

Preparation I. 0.2065 gave 0.2307 AgBr. Br = 47.54.

„ II. 0.2173 „ 0.2432 AgBr. Br = 47.61.

Mean Br = 47.58.

$C_{36}H_{14}O_{16}Br_8$ requires Br = 47.68 per cent.

It is a dark orange-red, amorphous powder, which on rapid heating commences to decompose at 205°. It dyes silk and wool pink. It is insoluble in water, benzene, chloroform, or hydrochloric acid, but slightly soluble in ether or ethyl acetate, and easily so in acetone, phenol, aniline, or alcohol. The alcoholic solution is deep red, and shows an intense brown fluorescence; on dilution with water the acid is precipitated. The substance is fairly soluble in glacial acetic acid or concentrated sulphuric acid, from which solutions it is precipitated on dilution. It dissolves readily in dilute potassium hydroxide or ammonia, giving a deep blood-red solution having a brown fluorescence; from these solutions the compound is precipitated on acidification.

The *potassium* salt is a bright red powder having a bronzy-green, metallic reflex. The *lithium* salt is a deep red powder having a bronze reflex. The *silver* salt, $C_{36}H_6O_{16}Br_8Ag_8$, is a deep red powder which is fairly stable to heat and light. It is insoluble in water, but dissolves instantly in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the acid. On analysis:

Preparation I. 0.3661 gave 0.2518 AgBr. Ag = 39.50.

„ II. 0.3390 „ 0.2328 AgBr. Ag = 39.44.

„ III. 0.2131 „ 0.1467 AgBr. Ag = 39.54.

„ IV. 0.1812 „ 0.1236 AgBr. Ag = 39.18.

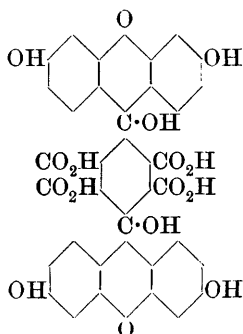
Mean Ag = 39.42.

$C_{36}H_6O_{16}Br_8Ag_8$ requires Ag = 39.30 per cent.

The *barium*, *lead*, *cobalt*, *copper*, *ferrous*, and *chromium* salts are precipitated as bright red powders, the barium and copper salts being unaltered by ammonia.

The *ferric* salt is obtained as a brownish-red, gelatinous precipitate.

3 : 3' : 6 : 6' : 9 : 9' - *Hexahydroxy - p - dixanthylbenzene-2 : 3 : 5 : 6-tetra-carboxylic Acid (Tetraresorcinol-mellitein)*, $C_{36}H_{22}O_{16}$.



This is prepared by heating 16 parts of *p*-diethyl mellitate with 17.6 parts of resorcinol to 150° for 8 hours. The hard mass is powdered, dissolved in concentrated aqueous caustic potash, and heated on the steam-bath for 3 hours to saponify the ester.

The solution is neutralised with hydrochloric acid, evaporated to dryness, and the residue extracted with alcohol. The condensation product is precipitated from its alcoholic solution by water and purified by repeated fractional precipitation. On analysis :

- I.* 0.1698 gave 0.3790 CO_2 and 0.0500 H_2O . C = 60.87 ; H = 3.30.
 II. 0.2153 „ 0.4816 CO_2 „ 0.0628 H_2O . C = 61.00 ; H = 3.24.
 Mean C = 60.94 ; H = 3.27.

$C_{36}H_{22}O_{16}$ requires C = 60.83 ; H = 3.12 per cent.

The substance is a dark yellowish-orange, amorphous powder, decomposing without melting above 300° , and dyes silk and wool yellow. It is insoluble in ether, benzene, or chloroform, slightly soluble in phenol, ethyl acetate, or concentrated hydrochloric acid, giving light reddish-brown solutions, and in water giving a light yellow solution having a most intense green fluorescence. It is fairly soluble in aniline or glacial acetic acid, giving deep red solutions, and exceedingly so in acetone or alcohol, giving with the latter a reddish-brown solution having an intense green fluorescence ; on addition of water to a concentrated solution the acid is precipitated. The compound is also soluble in dilute caustic alkali or ammonia, the solutions having an intense green fluorescence. On acidifying these solutions the acid is precipitated.

The *ammonium* salt is a dark brown powder having a dark green metallic reflex.

* See footnote on p. 1796.

1806 SILBERRAD: THE RELATIONSHIP OF COLOUR AND

The *potassium* and *lithium* salts are very dark reddish-brown powders having a dark green, metallic reflex. They are very soluble in water, giving reddish-brown solutions.

The *silver* salt, $C_{36}H_{18}O_{16}Ag_4$, is a reddish-orange powder, having a nearly black, metallic reflex. It is fairly stable to heat and light, and dissolves instantly in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the free acid. On analysis :

Preparation	I.	0.1859	gave	0.0699	silver.	Ag = 37.50.
	„	I.	0.2128	„	0.0800	„ Ag = 37.59.
	„	II.	0.1316	„	0.0496	„ Ag = 37.68.
						Mean Ag = 37.59.

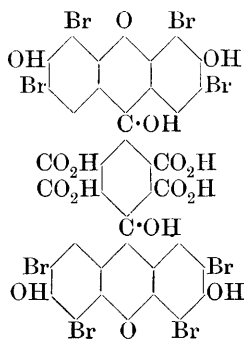
$C_{36}H_{18}O_{16}Ag_4$ requires Ag = 37.94 per cent.

The *copper* salt is a greenish-yellow precipitate, turning darker in colour on addition of ammonia.

The *barium* salt is a yellowish-orange powder.

The *cobalt*, *lead*, *ferrous*, *chromium*, and *mercuric* salts are heavy brown powders, the *ferrie* salt being dark yellowish-orange.

2 : 2' : 4 : 4' : 5 : 5' : 7 : 7' - Octabromo - 3 : 3' : 6 : 6' : 9 : 9' - hexahydroxy - p-dixanthylbenzenetetracarboxylic Acid (Octabromotetraresorcinol-mellitein), $C_{36}H_{14}O_{16}Br_8$.



This is prepared by suspending the foregoing acid in glacial acetic acid and adding excess of bromine. After allowing to stand 24 hours, the mixture is heated on the water-bath for one hour, allowed to stand overnight, and poured into water. The precipitate of the bromo-compound is separated and thoroughly washed with boiling water, dissolved in a small quantity of alcohol, filtered, and the compound precipitated from its alcoholic solution by the addition of water. It is further purified by fractional precipitation. On analysis :

Preparation	I.	0.3216	gave	0.3621	AgBr.	Br = 47.91.
	„	II.	0.2070	„	0.2310	AgBr. Br = 47.48.
	„	III.	0.4951	„	0.5528	AgBr. Br = 47.51.
Mean Br = 47.63.						

$C_{36}H_{14}O_{16}Br_8$ requires Br = 47.68 per cent.

The compound is a dark reddish-brown, amorphous powder, which on rapid heating commences to decompose at 260° . It dyes silk and wool a brownish-pink. It is insoluble in water, chloroform, benzene, or concentrated hydrochloric acid, and readily soluble in ethyl acetate, phenol, acetone, aniline, or alcohol, which latter gives a blood-red solution having a brown fluorescence, the compound being precipitated on addition of water. It is also soluble in concentrated sulphuric acid, being precipitated on dilution with water, and very soluble in dilute caustic alkalis or ammonia, giving deep blood-red solutions having a brownish-green fluorescence; on acidifying, the compound is precipitated. When obtained in this way from acetic acid, it is dark orange-red, whilst from alcohol it is dark reddish-brown.

The *potassium* and *lithium* salts are dark red powders having a dark red, metallic reflex, and are very soluble in water, giving a blood-red solution.

The *silver* salt, $C_{36}H_6O_{16}Br_8Ag_8$, is a dark red powder with a brownish-violet reflex. It is readily soluble in ammonia: dilute nitric or glacial acetic acids dissolve the salt with separation of the free acid. It is very stable to heat and light. On analysis:

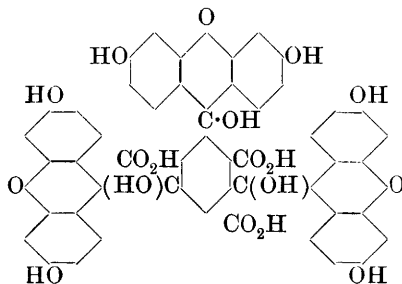
Preparation	I.	0.1767	gave	0.1203	AgBr.	Ag = 39.10.
	„	II.	0.1987	„	0.1350	AgBr. Ag = 39.02.
	„	III.	0.1358	„	0.0926	AgBr. Ag = 39.17.
Mean Ag = 39.10.						

$C_{36}H_6O_{16}Br_8Ag_8$ requires Ag = 39.30 per cent.

The *copper*, *barium*, *cobalt*, *lead*, and *ferrous* salts are precipitated as bright red powders, the copper and barium salts being unaltered by ammonia. The *ferric* and *chromium* salts are deep brownish-red powders.

III. *Trixanthyl Derivatives*. [With WALTER HAMIS GLOVER, Ph.D.]

3 : 3' : 3'' : 6 : 6' : 6'' : 9 : 9' : 9''-Nonahydroxy - sym - trixanthylbenzene-2 : 4 : 6-tricarboxylic Acid (*Hexaresorcinol-mellitein*), $C_{48}H_{30}O_{18}$.



This compound is obtained by heating a mixture of 17 parts of mellitic acid and 33 parts of resorcinol to 160° for eight hours. Condensation rapidly occurs, the fused mass gradually thickening, and becoming solid and almost black in colour. The fusion is extracted with dilute aqueous caustic potash, and the condensation product precipitated with acid and purified by repeated fractional precipitation from its alcoholic solution by the addition of water. On analysis :

- I.* 0.1783 gave 0.4219 CO_2 and 0.0550 H_2O . C = 64.53 ; H = 3.42.
 II. 0.2103 „ 0.4981 CO_2 „ 0.0658 H_2O . C = 64.60 ; H = 3.47.
 III. 0.2100 „ 0.4991 CO_2 „ 0.0657 H_2O . C = 64.81 ; H = 3.47.
 Mean C = 64.65 ; H = 3.45.

$C_{48}H_{30}O_{18}$ requires C = 64.42 ; H = 3.35 per cent.

The acid is a yellowish-orange, slightly hygroscopic, amorphous powder, which decomposes, without melting, above 300° . It dyes silk and wool brownish-yellow. It is insoluble in cold water, ether, benzene, chloroform, or ethyl acetate, slightly soluble in phenol or concentrated hydrochloric acid, and readily so in aniline, acetone, or alcohol, giving with the latter a yellow solution having a most intense green fluorescence. It is fairly soluble in glacial acetic acid, from which solution it is precipitated on dilution. With concentrated sulphuric acid it gives a dark red solution, from which the acid is precipitated unaltered on dilution with water.

In dilute caustic alkalis or ammonia it is very soluble, giving a green fluorescence even in extremely dilute solutions. On acidifying these solutions, the compound is precipitated.

The *ammonium* salt is a reddish-yellow powder having a green,

* See footnote on p. 1796.

metallic reflex. The *potassium* and *lithium* salts are dark orange-red powders having a green reflex.

The *silver* salt, $C_{48}H_{27}O_{18}Ag_3$, is a buff-coloured powder, readily soluble in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the acid. It is fairly stable to heat and very stable to light. On analysis :

Preparation I. 0.3127 gave 0.0793 Ag. Ag = 25.36.

„ II. 0.2009 „ 0.0511 Ag. Ag = 25.43.

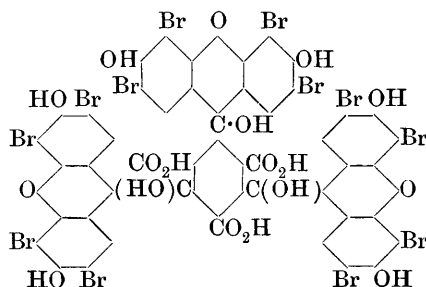
Mean Ag = 25.40.

$C_{48}H_{27}O_{18}Ag_3$ requires Ag = 25.51 per cent.

The *copper*, *cobalt*, *barium*, *lead*, and *mercuric* salts are precipitated as reddish-orange powders.

The *ferric*, *ferrous*, and *chromium* salts are brown.

2 : 2' : 4 : 4' : 5 : 5' : 7 : 7'-Dodecabromo-3 : 3' : 3'' : 6 : 6' : 6'' : 9 : 9' : 9''-nonahydroxy - sym - trixanthylbenzene - 2 : 4 : 6-tricarboxylic Acid (Dodecabromohexaresorcinol-mellitein), $C_{48}H_{18}O_{18}Br_{12}$.



The foregoing acid is dissolved in glacial acetic acid, excess of bromine added, and the mixture boiled for six hours, allowed to stand overnight, then poured into water. The precipitate is thoroughly washed with boiling water and purified by exhaustive fractional precipitation from its alcoholic solution by the addition of water. On analysis :

Preparation I. 0.3161 gave 0.3892 AgBr. Br = 52.39.

„ II. 0.1893 „ 0.2331 AgBr. Br = 52.39.

„ III. 0.2912 „ 0.3590 AgBr. Br = 52.46.

Mean Br = 52.41.

$C_{48}H_{18}O_{18}Br_{12}$ requires Br = 52.08 per cent.

The substance is a dark red, amorphous powder, which on rapid heating froths up at 210° . It dyes silk and wool red, with a tinge of violet. It is insoluble in water, benzene, ether, ethyl acetate, or

1810 SILBERRAD: THE RELATIONSHIP OF COLOUR AND

concentrated hydrochloric acid, slightly soluble in glacial acetic acid or concentrated sulphuric acid; the latter solution is yellow, and on dilution the compound is precipitated unaltered,

It is very soluble in acetone, phenol, or alcohol, giving with the latter a dark red solution having a brown fluorescence; on dilution, the acid is precipitated as a dark red powder. In dilute caustic alkalis or ammonia it is exceedingly soluble, forming dark crimson solutions having a brown fluorescence, and on acidifying the compound is precipitated.

The *potassium* and *lithium* salts are dark red powders, having a dark red, metallic reflex.

The *silver* salt, $C_{48}H_9O_{18}Br_{12}Ag_9$, is a dark violet-red powder, which becomes still darker on heating. It is readily soluble in ammonia: dilute acids dissolve the salt with separation of the acid. On analysis:

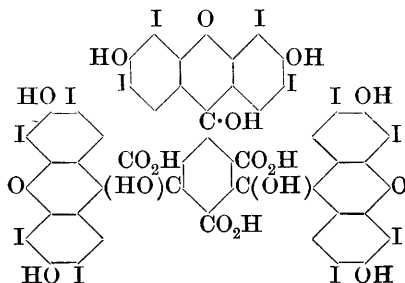
Preparation	I.	0.2568	gave	0.1542	AgBr.	Ag = 34.50.
"	I.	0.2007	"	0.1205	AgBr.	Ag = 34.49.
"	II.	0.1081	"	0.0648	AgBr.	Ag = 34.43.
						Mean Ag = 34.47.

$C_{49}H_9O_{18}Br_{12}Ag_9$ requires Ag = 34.64 per cent.

The *barium*, *chromium*, *cobalt*, *copper*, and *lead* salts are blood-red powders. The barium salt is unaltered by ammonia, but the copper salt becomes reddish-violet.

The *ferric* and *ferrous* salts are brownish-red.

2 : 2' : 2'' : 4 : 4' : 4'' : 5 : 5' : 5'' : 7 : 7' : 7'' - *Dodecaiodo-3 : 3' : 3'' : 6 : 6' : 6'' : 9 : 9' : 9''-nonahydroxy-sym-trixanthylbenzene-2 : 4 : 6-tricarboxylic Acid* (*Dodecaiodohexaresorcinol-mellitein*), $C_{48}H_{18}O_{18}I_{12}$.



8.9 Parts of nonahydroxy-sym-trixanthylbenzenetricarboxylic acid are dissolved in 40 parts of 50 per cent. aqueous caustic potash and heated to boiling; 60 parts of iodine are dissolved in 15 parts of aqueous caustic potash and added slowly to the hot liquid, the temperature being allowed to rise. When all the iodine solution is added, the

mixture is boiled for ten minutes, then allowed to cool, when the iodo-compound separates. The product is filtered off and purified by repeated fractional precipitation from its solution in caustic potash by the addition of acid. On analysis :

Preparation I. 0.2109 gave 0.2455 AgI. I = 62.91.

„ II. 0.1592 „ 0.1859 AgI. I = 63.11.

Mean I = 63.01.

$C_{48}H_{18}O_{18}I_{12}$ requires I = 63.33 per cent.

The compound is a dark orange-red, amorphous powder, which when rapidly heated loses iodine at 255° , and on further heating decomposes completely without melting. It dyes silk and wool pink. It is insoluble in ether, benzene, chloroform, ethyl acetate, or concentrated hydrochloric acid, slightly soluble in glacial acetic acid or alcohol, giving orange solutions, and fairly so in acetone or phenol, giving deep red solutions. It is very soluble in aniline, slightly so in concentrated sulphuric acid, and readily so in dilute aqueous caustic potash, giving a fine deep red coloured solution, from which the acid is precipitated on acidifying.

The *potassium* and *lithium* salts are very dark red powders, readily soluble in water, giving deep red solutions.

The *silver* salt, $C_{48}H_9O_{18}I_{12}Ag_9$, forms a heavy, deep red precipitate, which dries to a dark violet-red powder having a violet reflex. It is soluble in ammonia : dilute acids dissolve the salt with separation of the acid. It is fairly stable to heat and light. On analysis :

Preparation I. 0.1258 gave 0.0797 AgI. Ag = 29.11.

„ II. 0.1551 „ 0.0983 AgI. Ag = 29.13.

„ III. 0.2119 „ 0.1339 AgI. Ag = 29.03.

Mean Ag = 29.09.

$C_{48}H_9O_{18}I_{12}Ag_9$ requires Ag = 28.85 per cent.

The *copper*, *barium*, *lead*, *cobalt*, *ferrous*, and *chromium* salts are precipitated as heavy, bright red powders, the copper and barium salt being unaltered by ammonia. The *ferric* salt is dull reddish-orange.

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