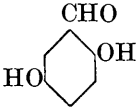
CCXCIV.—*Mercuration of Some Polyhydroxybenzaldehydes and their Monomethyl Ethers.*

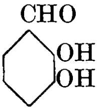
By Thomas Anderson Henry and Thomas Marvel Sharp.

Mercuration takes place with remarkable rapidity when alcoholic solutions of 2 : 3-, 2 : 4-, 2 : 5-, or 3 : 4-dihydroxybenzaldehyde are mixed at room temperature with mercuric acetate, as is shown by the fact that, within a few minutes of mixing, a test portion dissolves completely in aqueous alkali. This result is doubtless due to the well-known activating effect on mercuration of phenolic hydroxyl groups, an effect which would naturally be enhanced by multiplying these groups.

With the aldehydes which have their two hydroxyl groups in the ortho- or para-position to each other it has not been possible to isolate the mercury compounds in a pure state owing to the ease with which they undergo intramolecular oxidation with the separation of mercury as metal or in the mercurous condition. In the case of gentisinaldehyde (I) mercuration is quickly followed by oxidation, with the separation of mercurous acetate.



(I.)



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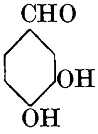
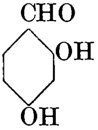


(III.)

With 2 : 3-dihydroxybenzaldehyde (II) and protocatechualdehyde (III), sparingly soluble, dark-coloured mercury compounds, mixed with mercurous acetate or oxide, are obtained. The mercurated aldehydes are soluble in sodium hydroxide solution, but the liquids so formed rapidly deposit metallic mercury and become dark in colour. It has not been found possible to isolate the oxidation product, which is possibly quinonoid in character.

Resorcylaldehyde (IV), in which the hydroxyl groups are in the meta-position to each other, is mercurated normally and readily with the formation of 3 : 5-*diacetoxymercuri*-2 : 4-*dihydroxybenzaldehyde,* the constitution of which is proved by its conversion into a dibromo-2 : 4-dihydroxybenzaldehyde, which on methylation yields the known 3 : 5-dibromo-2-hydroxy-4-methoxy- and 3 : 5-dibromo-4-hydroxy-2-methoxy-benzaldehydes (Rao, Srikantia, and Iyengar, J., 1929, 1579; Lindemann and Forth, *Annalen*, 1923, **435**, 219), with some 3 : 5-*dibromo*-2 : 4-*dimethoxybenzaldehyde.*



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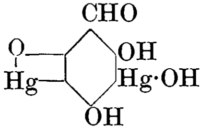

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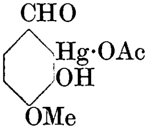
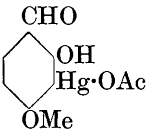


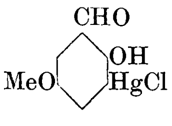
(VI.)

In view of the above results it was thought that the only trihydroxybenzaldehyde likely to furnish a stable mercury compound would be phloroglucinaldehyde. This aldehyde is mercurated as easily and rapidly as the dihydroxyaldehydes, but no doubt owing to the large number of groups attached to the nucleus, internal condensation takes place with the formation of an anhydride of the probable constitution (V).

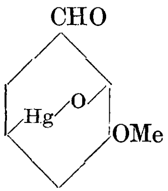
Of the monomethyl ethers of the dihydroxybenzaldehydes, vanillin (4-hydroxy-3-methoxybenzaldehyde) has already been shown by Paolini to form a monomercuri-compound, the mercury in which was replaced by iodine with the formation of an iodovanillin of undetermined constitution (*Gazzetta*, 1921, **51**, ii, 188). The mercury is now shown to be in the 5-position by conversion into the known 5-bromovanillin (Dakin, *Amer. Chem. J.*, 1909, **42**, 493). The monomethyl ethers are not mercurated so readily as the dihydroxybenzaldehydes themselves and have in all cases yielded monomercuri-compounds. The mercuri-group enters the ortho-position to the hydroxyl group when that position is free, as in vanillin, *iso*vanillin, 2-hydroxy-4-methoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde, and the para-position when the ortho-position is occupied, as in *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde), earlier observations on the directing influence of the hydroxyl group in mercuration (compare Henry and Sharp, J., 1922, **121**, 1055; 1924, **125**, 1049; 1926, 2432) thus being confirmed. For instance, *iso*vanillin forms 2-*acetoxymercuri*-3-*hydroxy*-4-*methoxybenzaldehyde* (VI), 2-hydroxy-4-methoxybenzaldehyde yields 3-*acetoxymercuri*-2-*hydroxy*-4-*methoxybenzaldehyde* (VII), and 2-hydroxy-5-methoxybenzaldehyde gives rise to 3-*chloromercuri*-2-*hydroxy*-5-*methoxybenzaldehyde* (VIII).



(VII.)



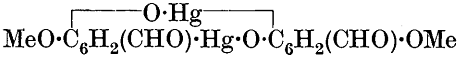
(VIII.)



(IX.)

In the case of *o*-vanillin the acetoxymercuri-compound is no doubt first formed, but this on drying loses acetic acid with the formation of 2 : 5-*anhydro*-5-*hydroxymercuri*-2-*hydroxy*-3-*methoxybenzaldehyde* (IX). This formula accounts for all the properties of the substance, but a structure such as (X) is not excluded. The product is soluble only in acetic acid, which converts it into 5-acetoxymercuri-2-hydroxy-3-methoxybenzaldehyde, and consequently the molecular weight, which would decide between these two formulæ, could not be determined.

(X.)



$$\mathrm{MeO{\cdot}\overset{\ulcorner\text{———O·Hg———}\urcorner}{C_6H_2(CHO){\cdot}Hg{\cdot}O{\cdot}C_6}H_2(CHO){\cdot}OMe}$$

Although anhydride formation between a hydroxyl group and a hydroxymercuri-group in the ortho-position is quite common, a similar condensation between groups in the para-position (IX) does not seem to have been recorded previously.

The constitution of the mercuri-compound from *iso*vanillin (VI) follows from its conversion into a bromo*iso*vanillin, m. p. 211—212°, which is shown to be the 2-bromo-derivative by the formation from it of methyl 2-bromoveratrate, of known constitution (Zincke and Francke, *Annalen*, 1896, **293**, 185). The bromo-aldehyde is identical with a compound prepared by Pauly (*Ber.*, 1915, **48**, 2010) which he wrongly assumed to be 6-bromo*iso*vanillin. In preparing Pauly's bromo*iso*vanillin, the authors obtained a second monobromo-derivative, m. p. 112—114°. This is shown to be 6-bromo*iso*vanillin by (*a*) methylation to the known 6-bromo-3 : 4-dimethoxybenzaldehyde (Pschorr, *Annalen*, 1912, **391**, 23), and (*b*) oxidation to the corresponding acid and preparation of the methyl ester, m. p. 81—82° (corr.), for which Zincke and Francke (*loc. cit.*) record a melting point of 88—89°, but since the melting points of the methyl esters of 2-bromo- and 5-bromo-veratric acids are respectively 46° and 71—72° there can be no doubt that the ester formed here is the 6-bromo-derivative.

Replacement of the mercury in the compound from 2-hydroxy-4-methoxybenzaldehyde (VII) by bromine gives a bromo-derivative, m. p. 119—121°, which is not identical with 5-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 120—121°, prepared by Rao, Srikantia, and Iyengar (*loc. cit.*) since the melting point of a mixture of the two substances is depressed by about 30°. It is shown to be 3-*bromo*-2-*hydroxy*-4-*methoxybenzaldehyde* by bromination to the known 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde (Rao, Srikantia, and Iyengar, *loc. cit.*), and the mercury is accordingly in position 3.

The constitutions of the mercury compounds from 2-hydroxy-5-methoxybenzaldehyde (VIII) and *o*-vanillin (IX) follow similarly from their conversion into the known 3-bromo-2-hydroxy-5-methoxybenzaldehyde (Rubenstein, J., 1925, **127**, 2000) and 5-bromo-2-hydroxy-3-methoxybenzaldehyde (Davies, J., 1923, **123**, 1586, 2847*)* respectively.

In the preparation of the mercury compounds from 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde, demercuration takes place when the solutions are cooled (compare Henry and Sharp, J., 1926, 2432). The simple explanation that this is in all cases a reversible reaction,

$$R{\cdot}H + Hg(O{\cdot}CO{\cdot}CH_3)_2 \rightleftharpoons R{\cdot}Hg{\cdot}O{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO{\cdot}OH,$$

in which the reaction from left to right takes place at elevated temperatures and that in the reverse direction on cooling, appears to be rendered untenable by the fact that the mercurated product of 2-hydroxy-3-methoxybenzaldehyde can be recrystallised from acetic acid without demercuration, although crystallisation of 5-acetoxymercuri-4-hydroxy-3-methyl-6-*iso*propylbenzaldehyde from the same solvent does induce partial demercuration (*loc. cit.*, p. 2439).

The work described forms part of an investigation into the relation of chemical constitution to bactericidal action in this group of organic mercury compounds (Henry, Sharp, and Brown, *Biochem. J.*, 1925, **19**, 513). Only three of the substances now prepared are suitable for bactericidal tests; these have been kindly examined by Major H. C. Brown, C.I.E., M.B., B.Ch., of the Wellcome Bureau of Scientific Research. They were tested as sodium salts dissolved in water, by the method already described (*loc. cit.*). The minimum concentration required to kill *Bacillus typhosus*, Rawlings, in five minutes is, for the mercury compound from

2-hydroxy-3-methoxybenzaldehyde, 0·004%; from 2-hydroxy-4-methoxybenzaldehyde, 0·025%; from 2-hydroxy-5-methoxybenzaldehyde, 0·0025%.

EXPERIMENTAL.

It has not been possible to find a standard set of conditions suitable for the mercuration of all the aldehydes now dealt with. The modifications in solvents, quantities and methods of working described below have been made to overcome such difficulties as demercuration, formation of intractable colloidal solutions, etc. Solubility of the reaction mixture in aqueous alkali was taken as an indication of complete mercuration.

Resorcylaldehyde.—Resorcylaldehyde (1 mol.) and mercuric acetate (2 mols.) in alcoholic solution were mixed at room temperature. The yellow precipitate, which formed at once, quickly turned white, and on recrystallisation from glacial acetic acid, it separated in faintly pink crystals, which do not melt up to 300°. The compound is 3 : 5-*diacetoxymercuri*-2 : 4-*dihydroxybenzaldehyde* (Found : Hg, 61·4, 61·35; C, 20·15, 20·1; H, 1·5, 1·8. $C_{11}H_{10}O_7Hg_2$ requires Hg, 61·2; C, 20·15; H, 1·5%).

3 : 5-*Dichloromercuriresorcylaldehyde*, made from the foregoing substance by the usual method, crystallises from acetone in colourless slender needles, which on heating turn pink at 240°, darken to red and decompose at 260° (Found : Hg, 65·5. $C_7H_4O_3Cl_2Hg_2$ requires Hg, 66·0%). Bromine in acetic acid (5%) converts it into 3 : 5-*dibromoresorcylaldehyde* (see below), which separates from alcohol in colourless needles, m. p. 204° (corr.); yield, 84% (Found : C, 28·2; H, 1·4; Br, 54·2. $C_7H_4O_3Br_2$ requires C, 28·4; H, 1·4; Br, 54·0%). In a similar manner with iodine (5% solution in 10% aqueous potassium iodide) the mercury compound yields 3 : 5-*di-iodoresorcylaldehyde*, which forms needles from alcohol, m. p. 168° (corr.) (Found : C, 21·65; H, 1·2. $C_7H_4O_3I_2$ requires C, 21·6; H, 1·0%).

Methylation of dibromoresorcylaldehyde. Treatment of the dibromo-aldehyde (5 g.) with excess of methyl sulphate (3·5 c.c.) in presence of sodium hydroxide (20 c.c. of 10% solution) furnished a mixture of the mono- and di-methyl ethers. After being heated on the water-bath for 20 minutes, the reaction mixture was made alkaline and then on extraction with ether furnished 3 : 5-*dibromo*-2 : 4-*dimethoxybenzaldehyde* (0·8 g.), which crystallised from alcohol in long colourless needles, m. p. 101—102° (corr.) (Found : C, 33·4; H, 2·8; Br, 49·15. $C_9H_8O_3Br_2$ requires C, 33·35; H, 2·5; Br, 49·3%). The alkaline mother-liquor on acidification and extraction with ether yielded a brown solid (4·2 g.), which was separated by steam distillation into two products. The volatile substance crystallised from alcohol in colourless needles (0·5 g.), m. p. 96—97°, identical with 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde (p. 2287). The non-volatile product was brown and, after purification through the bisulphite compound, crystallised from alcohol in thin plates, m. p. 172—174° (corr.). It is doubtless 3 : 5-dibromo-4-hydroxy-2-methoxybenzaldehyde, which according to Lindemann and Forth (*loc. cit.*) melts at 170—171° (Found : C, 31·2; H, 2·2; Br, 51·8. Calc. for $C_8H_6O_3Br_2$: C, 31·0; H, 1·95; Br, 51·6%).

Other Dihydroxybenzaldehydes.—The only other dihydroxybenzaldehydes tried were 2 : 3-, 2 : 5- (gentisinaldehyde), and 3 : 4- (protocatechualdehyde). Admixture of any one of these in solution with mercuric acetate at room temperature led to immediate mercuration. In a few minutes the clear liquids formed with the first two aldehydes began to deposit greenish-brown precipitates, which, while still moist, remained soluble in aqueous alkali, forming solutions from which metallic mercury quickly began to separate. After drying, the precipitates were no longer completely soluble in aqueous alkali, acetic acid or pyridine. Though these substances could not be purified, analysis of the product from 3 : 4-dihydroxybenzaldehyde indicates that it consists of a hydroxymercuriacetoxymercuri-3 : 4-dihydroxybenzaldehyde (Found : Hg, 66·3. $C_9H_8O_6Hg_2$ requires Hg, 65·4%). With gentisinaldehyde, the initially clear solution soon began to deposit mercurous acetate, this process being complete in about 3 days.

iso*Vanillin.*—*iso*Vanillin (10·15 g.; 1 mol.) in alcohol (100 c.c.) was boiled under reflux for ½ hour with mercuric acetate (20·35 g.; 1 mol.) in hot alcohol (400 c.c.) containing acetic acid (15 c.c.). A white amorphous solid (2·85 g.) slowly separated; the filtrate from this on cooling deposited more of the substance (10·35 g.) and on concentration crops of needle-shaped crystals separated amounting to 9·45 g.; finally an oil was obtained from which on extraction with ether 1·12 g. of *iso*vanillin were recovered. The first two crops were monohydroxymercuri*iso*vanillin, and the later ones mixtures of this and monoacetoxymercuri*iso*vanillin. The whole was converted by solution in acetic acid into 2-*acetoxymercuri*iso-*vanillin*. This crystallised from the solvent in bright colourless needles which do not melt up to 300° (Found : C, 28·9, 29·05; H, 2·45, 2·4; Hg, 48·7, 48·95. $C_{10}H_{10}O_5Hg$ requires C, 29·2; H, 2·45; Hg, 48·85%). The corresponding *chloromercuri*-compound crystallises from alcohol in colourless needles, m. p. 255—256° (Found : Hg, 51·7. $C_8H_7O_3ClHg$ requires Hg, 51·8%). Bromomercuri*iso*vanillin (0·9 g.), prepared in the usual manner, was converted by bromine in acetic acid into a bromo*iso*vanillin (0·35 g.), crystallising from alcohol in colourless needles, m. p. 211—212° (Found: C, 41·4; H, 3·2; Br, 34·75. $C_8H_7O_3Br$ requires C, 41·6; H, 3·1; Br, 34·6%). This is identical with the supposed 6-bromo*iso*vanillin prepared by Pauly (*loc. cit.*), which is now shown (see below) to be 2-bromo*iso*vanillin.

Bromination of iso*vanillin.* A solution of *iso*vanillin (10 g.) in acetic acid (60 c.c.) was treated gradually with bromine (10·7 g.) in acetic acid (15 c.c.). After standing for 1½ hours, the white crystals which had separated were filtered off (4·6 g.), m. p. 190—210°; the filtrate on concentration yielded a further crop (6·7 g., m. p. 120—180°) and finally on evaporation to dryness in a desiccator left a pale brown solid (3·2 g.), m. p. 75—85°. Recrystallisation of the first crop from alcohol furnished stout colourless needles, m. p. 211—212°, identical with the bromo-derivative obtained from the mercury compound, and a final crop, m. p. 110—120°. The lower-melting fractions were crystallised from 50% alcohol, giving a first crop (1·7 g.), m. p. 209—210°, and later crops, m. p. 100—110°. On crystallisation to constant melting point the latter were obtained as a *monohydrate* in colourless needles, m. p. 112—114° (corr.) (Found on air-dried substance: C, 38·55; H, 3·7. $C_8H_7O_3Br,H_2O$ requires C, 38·55; H, 3·6%. Found on substance dried by sublimation at 140° in a vacuum: C, 41·6; H, 3·3; Br, 34·8, 34·8. $C_8H_7O_3Br$ requires C, 41·6; H, 3·1; Br, 34·6%). This compound is shown (see below) to be *6-bromo*iso*vanillin.*

*Conversion of bromo*iso*vanillin,* m. p. 211—212°, *into 2-bromo-3 : 4-dimethoxybenzoic acid.* The product resulting from heating the bromo*iso*vanillin (5 g.) with methyl iodide (5 c.c.) and sodium (0·5 g.) in methyl alcohol (100 c.c.) during 3 hours was worked up in the usual way and yielded unchanged bromo*iso*vanillin (0·3 g.) and a substance (5 g.) which, as shown below, must be *2-bromo-3 : 4-dimethoxybenzaldehyde.* It crystallised from 50% alcohol in colourless needles, m. p. 80° (corr.), and sublimed slowly at 70° in a vacuum (Found: C, 44·4; H, 3·7; Br, 32·9. $C_9H_9O_3Br$ requires C, 44·1; H, 3·7; Br, 32·6%). To this aldehyde (4·5 g.), suspended in a boiling solution of magnesium sulphate (18 g.) in water (450 c.c.), potassium permanganate (3·6 g.) in water (180 c.c.) was added gradually, followed, after cooling, by 2*N*-sodium hydroxide (180 c.c.). The liquid was filtered, and the precipitate (2·7 g.) formed on acidifying the filtrate was crystallised from alcohol; it formed colourless needles, m. p. 203—204° (corr.). 2-Bromo-3 : 4-dimethoxybenzoic acid has m. p. 201—202° (Zincke and Francke, *loc. cit.*). The substance sublimes slowly at 120° in a vacuum (Found: C, 41·6; H, 3·6; Br, 30·7. Calc. for $C_9H_9O_4Br$: C, 41·4; H, 3·5; Br, 30·6%). The methyl ester forms colourless needles from light petroleum, m. p. 46°, which agrees with the recorded melting point (Found : Br, 29·4. Calc. for $C_{10}H_{11}O_4Br$: Br, 29·1%).

*Conversion of bromo*isovanillin, m. p. 112—114°, *into* 6-*bromo*-3 : 4-*dimethoxybenzoic acid.* This change was effected by the methods described in the preceding paragraph. The 6-bromo-3 : 4-dimethoxybenzaldehyde obtained crystallised from alcohol in colourless needles, m. p. 150—151° (corr.), agreeing with the figure 149—150° recorded by Pschorr (*loc. cit.*) (Found on substance dried at 80° in a vacuum : C, 44·4; H, 3·75; Br, 32·75. Calc. for $C_9H_9O_3Br$: C, 44·1; H, 3·7; Br, 32·6%). The acid produced on oxidation crystallised from 50% alcohol in colourless needles, m. p. 185° (corr.), in agreement with the recorded m. p. of 6-bromoveratric acid (Found on substance dried at 120° in a vacuum : C, 41·2; H, 3·5; Br, 30·75. Calc. for $C_9H_9O_4Br$: C, 41·4; H, 3·5; Br, 30·6%). The methyl ester formed faintly yellow needles, m. p. 81—82° (corr.).

2-*Hydroxy*-4-*methoxybenzaldehyde*.—A hot filtered solution of mercuric acetate (16 g.; 1 mol.) in alcohol (100 c.c.) containing acetic acid (2·5 c.c.) was added to 2-hydroxy-4-methoxybenzaldehyde (7·6 g.; 1 mol.) (Ott and Nauen, *Ber.*, 1922, **55**, 925) and the solution after boiling under reflux for 5 minutes was filtered from a trace of mercurous acetate. On cooling, it deposited bundles of needle-shaped crystals (13·25 g.) consisting of almost pure 3-*acetoxymercuri*-2-*hydroxy*-4-*methoxybenzaldehyde*, and on concentration yielded a further 5·5 g. Finally there remained a sticky oil from which a little unchanged aldehyde was recovered. One recrystallisation of the first crop from alcohol containing 1% of acetic acid sufficed for purification. The remaining crops on fractional crystallisation from the same solvent furnished further quantities, leaving a residue of 1·5 g. which appeared to contain a little more highly mercurated substance. The monoacetoxymercuri-derivative melts at 159—160° (corr.) (Found on substance dried in a desiccator : Hg, 48·7; C, 29·3; H, 2·8. $C_{10}H_{10}O_5Hg$ requires Hg, 48·85; C, 29·2; H, 2·45%).

The corresponding bromomercuri-compound on treatment with bromine in acetic acid yielded a substance which, as shown below, must be 3-*bromo*-2-*hydroxy*-4-*methoxybenzaldehyde*. It crystallises from alcohol in bright colourless needles, m. p. 119—121° (corr.), and sublimes on heating at 100° in a vacuum. The melting point is depressed to 90° on admixture with 5-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 120—121° (Rao, Srikantia, and Iyengar, *loc. cit.*) (Found : C, 41·75; H, 3·2; Br, 34·7. $C_8H_7O_3Br$ requires C, 41·6; H, 3·1; Br, 34·6%). The phenylhydrazone forms colourless platelets from alcohol, m. p. 166—167° (corr.), which on admixture depress the melting point of 5-bromo-2-hydroxy-4-methoxybenzaldehydephenylhydrazone to 140—150°. The latter is described as pale yellow leaflets, m. p. 177—178°; our specimen was colourless and melted at 183° (corr.). The new bromo-compound on further bromination yielded a product which crystallised from alcohol in colourless needles, m. p. 96—97°, and did not depress the melting point of 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde prepared by Rao, Srikantia, and Iyengar's method (Found: C, 30·9; H, 2·1. Calc. for $C_8H_6O_3Br_2$: C, 31·0; H, 1·95%).

2-Hydroxy-5-methoxybenzaldehyde.—In the earlier attempts to mercurate this aldehyde, the reaction in boiling 50% alcohol was found to be complete in 50 minutes but difficulty was experienced in isolating the mercury compound owing to demercuration taking place when the reaction mixture was worked up. The following procedure was found satisfactory, although the yield varied slightly in different experiments. A mixture of 2-hydroxy-5-methoxybenzaldehyde (6 g.) and mercuric acetate (48 g.) in 50% alcohol (200 c.c.) containing acetic acid (3 c.c.) was boiled under reflux for an hour. The hot solution was filtered from mercurous acetate (5·25 g.) into 600 c.c. of 3% aqueous sodium hydroxide. The mercuric oxide was filtered off (21·0 g.), and the clear orange-coloured filtrate acidified with hydrochloric acid. The yellow precipitate was collected, washed well with water, and dried in a desiccator (9·4 g.). From the filtrate 2-hydroxy-5-methoxybenzaldehyde (1·3 g.) was recovered by steam distillation. The yellow precipitate consisting of *3-chloromercuri-2-hydroxy-5-methoxybenzaldehyde* is slightly soluble in alcohol, acetone, and chloroform, rather more so in benzene. From the last solvent it crystallises in three forms: (a) rosettes of rather wide, flat, yellow needles, (b) yellow spherical crystals, and (c) fine, hair-like, yellow needles. The conditions under which these forms arise have not been definitely elucidated, but they appear to separate as follows: (a) when solutions at a temperature below about 50° are left to cool, (b) from solutions above that temperature, and (c) when solutions saturated at room temperature are allowed to evaporate spontaneously. The compound melts at 242—243° (corr.; decomp.) (Found: C, 24·7; H, 1·9; Hg, 51·8. $C_8H_7O_3ClHg$ requires C, 24·8; H, 1·8; Hg, 51·8%).

The substance formed on replacement of the chloromercuri-group by bromine crystallised from light petroleum (b. p. 40—60°) in bundles of stout yellow needles, m. p. 110—111° (corr.), which did not depress the melting point of 3-bromo-2-hydroxy-5-methoxybenzaldehyde prepared by Rubenstein's method (*loc. cit.*) and described by him as brown needles, m. p. 107° (Found: C, 41·9; H, 3·5; Br, 34·65. Calc. for $C_8H_7O_3Br$: C, 41·6; H, 3·1; Br, 34·6%).

o-*Vanillin.*—The *o*-vanillin used was prepared by the Reimer–Tiemann process and consisted of yellow needles, m. p. 42—43° (corr.). The following process was devised to avoid demercuration on cooling, which takes place with alcohol as solvent. *o*-Vanillin (5 g.), dissolved in water (250 c.c.), was boiled under reflux for an hour with mercuric acetate (31·8 g.; 3 mols.) dissolved in water (30 c.c.) containing acetic acid (3 c.c.). The yellow precipitate was filtered off, washed with water, and dried in a desiccator (10·9 g.). Longer boiling caused the separation of a further small amount of mercuri-compound. The substance crystallises from glacial acetic acid in pale yellow needles, which do not melt up to 300°, consisting probably of the acetoxymercuri-derivative. The crystals, however, slowly lose acetic acid on drying, even in a desiccator at room temperature, but the loss is not complete in 6 weeks. Dried at 100° in a vacuum, it loses its acetoxy-group completely with the formation of 2 : 5-*anhydro*-5-*hydroxymercuri*-2-*hydroxy*-3-*methoxybenzaldehyde* (IX) (Found: Hg, 57·2; C, 27·5; H, 1·95. $C_8H_6O_3Hg$ requires Hg, 57·2; C, 27·4; H, 1·7%). The compound formed by replacement of the hydroxymercuri-group by bromine was crystallised from light petroleum (b. p. 40—60°) and then from alcohol; it then separated in pale yellow needles, m. p. 127—129°, which did not depress the melting point of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (Davies, *loc. cit.*) (Found: C, 41·8; H, 3·0; Br, 34·5. Calc. for $C_8H_7O_3Br$: C, 41·6; H, 3·1; Br, 34·6%).

Vanillin.—The mercury compound was prepared by Paolini's method (*loc. cit.*). On treatment with bromine in acetic acid it is converted into 5-bromovanillin, m. p. 166—169° (corr.), which does not depress the melting point of an authentic specimen of that substance (Found: C, 41·4; H, 3·1; Br, 34·8. Calc. for $C_8H_7O_3Br$: C, 41·6; H, 3·1; Br, 34·6%).

Phloroglucinaldehyde.—The following process was found to avoid the formation of colloidal solutions which are particularly troublesome with this substance. The aldehyde (0·513 g.) in 50% alcohol (10 c.c.) was mixed with mercuric acetate (2·12 g.; 2 mols.) in water (10 c.c.) containing acetic acid. The pale yellow precipitate, which formed at once, was washed with alcohol and ether and dried in a desiccator (1·95 g.). When dry, it was insoluble in organic solvents and only partly soluble in sodium hydroxide. For analysis it was dried at 70° in a vacuum (Found: Hg, 68·6; C, 15·6; H, 0·9. $C_7H_4O_5Hg_2$ requires Hg, 70·5; C, 14·8; H, 0·7%). It is evidently not pure but clearly contains two atoms of mercury.

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