

spheric pressure. It corrodes glass, fumes strongly in the air, and has a characteristic and very powerful dusty odour, not very unlike that of a mixture of chloride of sulphur and sulphurous anhydride. Sulphur rapidly decomposed an aqueous solution of argentic fluoride.

Sulphurous anhydride passed over fluoride of silver at an incipient red heat, produced little or no decomposition of the silver-salt. Vaporous fluoride of sulphur also produced no visible effect.

By passing the vapour of liquid chloride of sulphur over the fluoride in a state of fusion, chemical action occurred, a vapour was evolved which corroded glass and possessed a dusty odour, but did not condense to a liquid; it was probably fluoride of sulphur. The saline residue consisted of argentic chloride and sulphide. A solution of argentic fluoride was decomposed by agitation with liquid chloride of sulphur, hydrofluoric acid being evolved, and argentic chloride and sulphide produced.

Argentic fluoride did not dissolve in bisulphide of carbon. By passing the vapour of the latter substance over the silver-salt at a red heat, a chemical change took place, and a fuming acid vapour was evolved, in accordance with the following equation:— $4\text{AgF} + \text{CS}_2 = 2\text{Ag}_2\text{S} + \text{CF}_4$ . A solution of bromine or iodine in bisulphide of carbon was rapidly decolorized by agitation with particles of argentic fluoride, and the liquid acquired the odour of tetrafluoride of carbon.

*December 21, 1871.*

GEORGE BIDDELL AIRY, C.B., President, in the Chair.

The following communications were read:—

- I. "Contributions to the History of Orcin.—No. II. Chlorine- and Bromine-substitution Compounds of the Orcins." By JOHN STENHOUSE, LL.D., F.R.S., &c.\* Received October 11, 1871.

Schunck†, and subsequently the author of this paper‡, many years ago studied the action of chlorine upon orcin, and obtained more or less crystalline products, contaminated with a brown resinous matter, from which however, they did not succeed in separating the crystals in a state of purity. In the year 1864 De Luynes§ obtained a crystalline substance by acting on orcin with a mixture of potassium chlorate and hydrochloric acid. De Luynes states it to be trichlororcine,  $\text{C}_7\text{H}_5\text{Cl}_3\text{O}_2$ , and in Kekulé's 'Benzolderivate' the melting-point is given at  $159^\circ$ .

\* A preliminary notice of several of the compounds described in this paper appeared in the Chem. News, vol. xxiii. p. 230, and Zeits. Chem. vol. vii. p. 229.

† Ann. Chem. Pharm. vol. liv. p. 271.

‡ Phil. Trans. 1848, p. 88, and Ann. Chem. Pharm. vol. lxxvii. p. 97.

§ Ann. Chem. Pharm. vol. cxxx. p. 34; Kekulé's 'Benzolderivate,' vol. i. p. 388.

*Chlororcin.*

*Pentachlororcin*,  $C_7H_3Cl_5O_2$ .—This compound was obtained by the action of chlorine upon orcin when the former was kept in excess. Two methods of effecting this object were employed,—the first by adding the orcin to chlorine hydrate, the other by the action of potassium chlorate and hydrochloric acid.

A pulpy mixture of the crystalline hydrate of chlorine and water was first prepared by passing a current of chlorine, with occasional agitation, through water to which about one third of crushed ice had been added, until a sufficient quantity of the hydrate was formed. On gradually adding a moderately strong aqueous solution of orcin, a purple colour was produced when the solution first came in contact with the chlorine hydrate, but disappeared immediately on agitation. The addition of the orcin was continued until nearly all the chlorine hydrate was decomposed. It was always advisable to leave a slight excess of the latter, as a purer product was then obtained, and also to have some crushed ice present in the mixture, to avoid decomposition and consequent loss of the hydrate by the heat produced during the reaction. The colourless or pale yellow solution, on standing, yielded a crystalline deposit of crude pentachlororcin.

After many trials, however, it was found that pentachlororcin could generally be more conveniently prepared in quantity by submitting orcin to the chlorinating action of a mixture of hydrochloric acid and potassium chlorate in the following manner:—Four parts of powdered potassium chlorate and a solution of two parts of orcin in seven parts of hydrochloric acid were added to 35 parts of hydrochloric acid, sp. gr. 1.17, placed in a large beaker, and kept cool by immersion in water; a small portion of the potassium chlorate was first added to the hydrochloric acid in the beaker; on pouring in some of the solution of orcin, the same evanescent purple colour made its appearance as when chlorine hydrate was used; the alternate addition of the chlorate and the orcin solution was continued in such a manner that there might always be an excess of chlorate, and that the contents of the beaker never became very hot. It was found necessary to use concentrated hydrochloric acid in this experiment, as otherwise the product was largely contaminated with a viscid oily compound. After twelve to twenty hours the crystalline chlororcin was collected and washed with a small quantity of water. Orcin treated with chlorine hydrate yields nearly twice its weight of crude chlororcin, but with potassium chlorate and hydrochloric acid about 150 per cent. of its weight.

In order to purify the crude chlororcin obtained by either of the above-described methods, it was dissolved when dry in a considerable quantity of carbon disulphide (eight measures), filtered and concentrated by distillation (to one half). On being set aside for some time it usually crystallized out; but as it exhibits strongly the phenomenon of supersaturation, especially when impure, it was sometimes necessary to agitate or add a crystal

of the substance. The solution then immediately deposited the chlororcin, and occasionally became hot enough to cause ebullition of the carbon disulphide. Two or three crystallizations rendered it quite pure. Pentachlororcin crystallizes from carbon disulphide in large colourless prisms, melting at  $120^{\circ}\cdot 5$ . It is moderately soluble in bisulphide of carbon and benzol, and readily in ether. It dissolves somewhat in cold alcohol, and when boiled with it for some time undergoes a change which I have not as yet investigated,—water throwing down an oil which only solidifies after having been exposed to the air for some days in a shallow vessel. The pentachlororcin is but very slightly soluble in water, to which, however, it communicates an exceedingly disagreeable and persistent bitter metallic flavour. When boiled with water it is decomposed, an oil and a crystalline solid passing over with the vapour. The oil, which has a peculiar odour, recalling that of chloropicrin, is heavier than water; the solid compound crystallizes in needles, and is identical with the trichlororcin described below. When heated with concentrated sulphuric acid it blackens and decomposes, giving off hydrochloric acid. It dissolves in nitric acid by the aid of heat, and crystallizes out unchanged on cooling. The addition of water to the solution precipitates the pentachlororcin. By long boiling with the acid it is decomposed with evolution of nitrous fumes.

*Analysis of Pentachlororcin.*

I. .901 grm. substance gave .937 grm. carbonic anhydride and .096 grm. of water.

II. .196 grm. substance gave .473 grm. argentic chloride.

III. .360 grm. substance gave .871 grm. argentic chloride.

IV. .229 grm. substance gave .555 grm. argentic chloride.

V. .202 grm. substance gave .488 grm. argentic chloride.

Theory.	I.	II.	III.	IV.	V.	Mean.
$C_7 = 84 = 28\cdot 33$	28·36	..	..	..	..	28·36
$H_3 = 3 = 1\cdot 01$	1·18	..	..	..	..	1·18
$Cl_5 = 177\cdot 5 = 59\cdot 87$	..	59·70	59·85	59·96	59·75	59·82
$O_2 = 32 = 10\cdot 79$	..	..	..	..	..	..
296·5						

V. was prepared by the action of potassium chlorate and hydrochloric acid, I., II., III., and IV. by means of chlorine hydrate. The substance was dried *in vacuo*.

*Trichlororcin*,  $C_7H_5Cl_3O_2$ .—When pentachlororcin was heated with hydriodic acid to  $100^{\circ}$  it was decomposed, trichlororcin being formed and iodine set free. The best method of conducting the operation, so as to obtain a pure product, was to add the pentachlororcin in small portions to a mixture of amorphous phosphorus and hydriodic acid, containing eight or ten per cent. of iodine, and to digest between each addition until

the liberated iodine had been reconverted into hydriodic acid. When all the pentachlororcin had been introduced, the digestion was continued until the trichlororcin appeared as a colourless oily layer at the bottom of the flask. On cooling, a considerable portion more crystallized out of the hydriodic acid in colourless needles. The oily trichlororcin, which solidified on cooling, was dissolved in a small quantity of spirit, filtered to separate it from the excess of amorphous phosphorus, and the alcoholic solution precipitated by water. The amount of crude product thus obtained was about 75 per cent. of the weight of the pentachlororcin originally employed. One or two crystallizations from boiling water slightly acidified with acetic acid rendered it quite pure. If very pure pentachlororcin had not been employed in the preparation the crude product was more or less coloured, and could only be purified with considerable difficulty, as the colouring-matter adheres to the trichlororcin with great obstinacy. It was found, however, that several alternate crystallizations from benzol and petroleum-oil, and a final crystallization from water, almost entirely removed the brown colouring-matter. It fuses to an oil under boiling water, in which it is moderately soluble, crystallizing out almost completely on cooling in long colourless transparent needles, which become white and opaque when exposed to the air. It is but sparingly soluble in carbon disulphide, moderately in petroleum-oil, rather more so in benzol, and excessively soluble in ether and alcohol. It is soluble in boiling glacial acetic acid, and crystallizes out on cooling in thin transparent plates, which become white and opaque on the addition of water. Trichlororcin melts at  $123^{\circ}$ , and when heated to a very much higher temperature it blackens and gives off hydrochloric acid, even under diminished pressure. It cannot, therefore, be distilled *in vacuo*, but it passes over readily with the vapour of water. When heated for several hours to  $180^{\circ}$  with moderately strong hydriodic acid and phosphorus, it was found to be reconverted into orcin, which could be extracted from the solution by agitating it with ether. The addition of alcoholic ammonia to a solution of the trichlororcin in alcohol threw down a white crystalline precipitate, but slightly soluble in water or alcohol. This compound, when dissolved in a large excess of dilute aqueous ammonia, and submitted to the action of metallic zinc in a close vessel at the ordinary temperature, yielded a colourless solution. On exposing this to the air, however, it acquired a fine blue colour, which was changed to red by the action of acids. Further investigation will no doubt show the nature of this compound.

*Analysis of Trichlororcin.*

- I. .257 grm. substance gave .486 grm. argentic chloride.
- II. .302 grm. substance gave .572 grm. argentic chloride.
- III. .216 grm. substance gave .293 grm. carbonic anhydride and .046 grm. water.

Theory.	I.	II.	III.	Mean.
$C_7 = 84 = 36.93$	..	..	37.00	37.00
$H_5 = 5 = 2.20$	..	..	2.37	2.37
$Cl_3 = 106.5 = 46.81$	46.78	46.86	..	46.82
$O_2 = 32 = 14.06$	..	..	..	..
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227.5	100.00			

I. was from the pentachlororcin prepared by the action of chlorine hydrate on orcin; II. and III. from that prepared by hydrochloric acid and potassium chlorate. The substance was dried *in vacuo*.

This trichlororcin differs considerably in its melting-point and other properties from that described by De Luynes\* as formed by the action of hydrochloric acid and potassium chlorate on orcin. Moreover, although many attempts were made to prepare trichlororcin by his method with varying proportions of the materials, pentachlororcin was invariably obtained, contaminated, however, in some instances, with a large amount of viscid oily impurities. I conclude, therefore, that De Luynes's trichlororcin was either isomeric with that above described, or that it was an impure substance.

#### *Bromorcin.*

*Pentabromorcin*,  $C_7H_3Br_5O_2$ .—This compound was readily formed by the action of an excess of bromine on orcin. Seven parts of bromine and about 200 of water were placed in a stoppered bottle, and a moderately strong aqueous solution of one part of orcin added by small portions, with constant agitation. The yellow crystalline product thus obtained, amounting to 370 per cent. of the weight of the orcin, was then collected, and purified by repeated crystallization from carbon disulphide, in a manner similar to the corresponding chlorine compound. It is almost insoluble in water, very soluble in alcohol and ether, and moderately so in benzol and carbon disulphide, from the latter of which it may be obtained in very large and almost colourless transparent crystals. It melts at  $126^\circ$ , and when boiled with water appears to undergo a decomposition similar to the pentachlororcin. Heated with concentrated sulphuric acid it gradually dissolves, and on continuing the heat hydrobromic acid and bromine are evolved in abundance. Like the corresponding chlorine compound, it dissolves in hot nitric acid, crystallizing out again on cooling, but is at the same time far more readily decomposed. When boiled with amorphous phosphorus and moderately strong hydriodic acid it is rapidly decomposed, and passes into solution probably as orcin. With very weak hydriodic acid, however, containing about one per cent. of iodine and excess of amorphous phosphorus, the decomposition takes place more gradually, and a heavy oily layer is obtained, which solidifies on cooling. This, after purification, was

\* Ann. Chem. Pharm. vol. cxxx. p. 34; Kekulé's 'Benzolderivate,' vol. i. p. 388.

found to be identical with the tribromorcin described by Stenhouse\*, and subsequently examined by Laurent and Gerhardt†, and by Lamparter‡.

*Analysis of Pentabromorcin.*

I. .578 substance gave 1.046 argentic bromide, which is equivalent to 77.00 per cent. bromine, the formula  $C_7H_3Br_5O_2$  requiring 77.07 per cent.

*Pentachlororcin hypochlorite*,  $C_7H_4Cl_6O_3 = C_7H_3Cl_5O_2, HClO$ .—A white crystalline substance was obtained in endeavouring to prepare pentachlororcin by the action of calcium hypochlorite and hydrochloric acid on orcin; but as it appeared to differ somewhat from that compound it was carefully examined. After some trials the following was found to be the best method of preparation:—Five parts of orcin were dissolved in a mixture of four measures of hydrochloric acid, sp. gr. 1.17, with four measures of water; and this solution was then gradually added to a moderately strong clear solution of calcium hypochlorite, taking care to leave the latter in excess. The liquid, which has a milky appearance, was then strongly acidulated with hydrochloric acid, and allowed to stand 24 hours, when it deposited a considerable quantity of white crystals. These were collected, dried, and purified by crystallization from benzol, as, unlike pentachlororcin, they are but sparingly soluble in carbon disulphide. When pure it crystallizes in transparent prisms of great dispersive power. It is very soluble in ether, moderately so in light petroleum-oil, and almost insoluble in water. When heated with hydriodic acid and phosphorus it is decomposed, but apparently without the formation of trichlororcin. It is very soluble in alcohol, and after boiling the solution for some time the addition of water causes the precipitation of an oil, which solidifies if exposed to the air for a few days. When the substance is boiled with water the latter becomes milky, and gives off pungent vapours. The hypochlorite dissolves in hot nitric acid, and crystallizes out on cooling; hot concentrated sulphuric acid decomposes it. It has a considerably higher melting-point than pentachlororcin, namely  $140^{\circ}5$ . The following results were obtained by analysis:—

I. .272 grm. substance gave .240 grm. carbonic anhydride and .033 grm. water.

II. .274 grm. substance gave .242 grm. carbonic anhydride and .032 grm. water.

III. .257 grm. substance gave .633 grm. argentic bromide.

IV. .147 grm. substance gave .361 grm. argentic bromide.

\* Phil. Trans. 1848, p. 87.

† Ann. Chim. Phys. [3] vol. xxiv. p. 317.

‡ Ann. Chem. Pharm. vol. cxxxiv. p. 257.

Theory.	I.	II.	III.	IV.	Mean.
$C_7 = 84 = 24.07$	24.06	24.08	..	..	24.07
$H_4 = 4 = 1.15$	1.31	1.34	..	..	1.32
$Cl_5 = 213 = 61.03$	..	..	60.94	60.75	60.85
$O_3 = 48 = 13.75$	..	..	..	..	..
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349	100.00				

The rational formula deduced from the percentage composition of the substance is  $C_7H_4Cl_5O_3$ ; and I propose to give it the provisional name of *pentachlororcin hypochlorite*,  $C_7H_3Cl_5O_2$ ,  $HClO$ , until its constitution is more satisfactorily made out by an examination of the products of its decomposition.

#### *Chlorresorcin.*

*Pentachlorresorcin*,  $C_6HCl_5O_2$ .—An attempt was made to obtain a chlorresorcin by submitting resorcin to the action of chlorine hydrate in a manner similar to that which had been so successfully employed in preparing pentachlororcin; but the results obtained were unsatisfactory, the product being very small in comparison to the resorcin taken, and even that so contaminated with oily impurities that further examination was deemed inexpedient. The action of potassium chlorate and hydrochloric acid, however, gave a much more favourable result. Five parts of potassium chlorate and a solution of two parts of resorcin in eight of hydrochloric acid were gradually added to forty parts of hydrochloric acid, which was prevented from becoming very hot by immersion in cold water. The operation was conducted in a manner similar to that previously described in the preparation of pentachlororcin; but more care was required to obtain a successful result, and the amount of product was comparatively small, about 70 per cent. of the resorcin. The crystalline compound which is deposited on standing was collected, and, after being simply pressed to remove some of the mother-liquor, boiled with a considerable quantity of carbon disulphide. The supernatant aqueous layer was then separated by means of a separating-funnel, and the greater portion of the carbon disulphide removed by distillation. When sufficiently concentrated the anhydrous chlorresorcin crystallized out in brilliant colourless plates or flattened prisms. One or two recrystallizations rendered it pure. The crude product of the action of the chlorate and hydrochloric acid on resorcin appeared to consist principally of a hydrate of the chlorresorcin, as when it was rapidly heated for a short time with a comparatively small proportion of carbon disulphide, and the solution filtered, it deposited a white crystalline compound in minute scales, sparingly soluble in the disulphide. On submitting the solution to distillation, however, to remove the excess of carbon disulphide, water passed over with the latter, and the solution, when sufficiently concentrated, deposited large crystals of the anhydrous substance. Pure pentachlorresorcin is colourless, and melts at  $92^\circ.5$ . It is moderately soluble in warm water,

from which it separates, on cooling, in a white opaque mass of indistinct crystals, apparently the hydrate. It is readily soluble in carbon disulphide, benzol, and petroleum-oil, and very soluble in alcohol and ether.

*Analysis of the Chlorresorcin.*

I. .476 grm. substance gave .447 grm. carbonic anhydride and .020 grm. water.

II. .308 grm. substance gave .289 grm. carbonic anhydride and .013 grm. water.

III. .193 grm. substance gave .490 grm. argentic chloride.

IV. .259 grm. substance gave .659 grm. argentic chloride.

	Theory.	I.	II.	III.	IV.	Mean.
$C_6 = 72$	$= 25.49$	25.56	25.60	..	..	25.58
$H = 1$	$= 0.35$	0.47	0.47	..	..	0.47
$Cl_5 = 177.5$	$= 62.84$	..	..	62.81	62.95	62.88
$O_2 = 32$	$= 11.32$	..	..	..	..	..
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	282.5	100.00				

The results of the analysis correspond very nearly to the formula  $C_6HCl_5O_2$ , that of pentachlorresorcin. This somewhat anomalous composition was, however, confirmed by the analyses of the corresponding bromine compound.

*Bromresorcin.*

*Pentabromresorcin*,  $C_6HBr_5O_2$ .—This compound was prepared by adding resorcin solution to a mixture of bromine and water, in a manner similar to that employed in the preparation of pentabromorcin. It is, however, advantageous to use considerably less water (about one fifth), and to moderate the heat produced during the reaction by occasionally immersing the bottle in cold water. Two or three crystallizations from carbon disulphide serve to purify the product, which then forms large colourless or faintly yellow prismatic crystals. The pure pentabromresorcin melts at  $113^{\circ}.5$ . It is almost insoluble in water, but readily soluble in ether and alcohol, from the latter of which it is precipitated on the addition of water. It is also moderately soluble in cold benzol and in hot petroleum-oil, from which it crystallizes out in great part on cooling. Treated with hydriodic acid it yields a colourless compound, crystallizing in needles, probably tribromresorcin.

*Analysis of Pentabromresorcin.*

I. .382 grm. substance gave .712 grm. argentic bromide.

II. .292 grm. substance gave .544 grm. argentic bromide.

Theory.	I.	II.	Mean.
$C_6 = 72 = 14.25$	..	..	..
$H = 1 = 0.20$	..	..	..
$Br_5 = 400 = 79.21$	79.30	79.27	79.28
$O_2 = 32 = 6.34$	..	..	..
<hr/> 505	<hr/> 100.00		

The analyses of those chlorine and bromine derivatives of resorcin that have just been described thoroughly establish the existence of the compounds  $C_6HCl_5O_2$  and  $C_6HBr_5O_2$ , which closely resemble in their properties the corresponding pentachlororcin,  $C_7H_3Cl_5O_2$ , and pentabromorcin,  $C_7H_3Br_5O_2$ , obtained from ordinary orcin. The view of the constitution of the orcins put forth by Kekulé, who regards them as dihydroxyl derivatives of the benzols, is scarcely in accordance with the method of formation and composition of these compounds, as in the case of the pentabromoresorcin five hydrogen atoms in the resorcin are undoubtedly directly replaced by bromine, although one of them, according to Kekulé's view, exists as hydroxyl.

An attempt was made to prepare the resorcin body corresponding to that obtained from orcin by the action of calcium hypochlorite and hydrochloric acid, and which I have designated pentachlororcin hypochlorite, but without success. The product was a very viscid oil, which showed no signs of solidification even after standing for some weeks, and from which I was unable to obtain any crystalline compound.

## II. "Note on Fucusol." By JOHN STENHOUSE, LL.D., F.R.S. Received October 11, 1871.

In a paper which I communicated to the Royal Society of London in 1850\*, "On the Oils produced by the Action of Sulphuric Acid upon various Classes of Vegetables," after describing the sources, method of preparation, and characteristic properties of furfural and its educts, I described another isomeric substance closely resembling furfural, both in its physical and chemical properties, and which I named fucusol from the source whence it had been obtained, namely, *Fucus nodosus*, *F. vesiculosus*, *F. serratus*, &c.

The nature of the substance which yielded furfural was involved in considerable obscurity until the publication of Gudkow's paper "On the Furfural-yielding Substance in Bran"†, which he found to be present in it to the amount of from 15 to 20 per cent., and which, when boiled with dilute sulphuric acid, was converted into a brownish sweet syrup. This is the substance from which furfural is obtained by distillation with sulphuric acid or hydrochloric acid.

\* Phil. Trans. 1850, p. 467.

† Zeits. Chem. 1870, p. 360.