LXV.—*On Orcinol and some of the other Dihydroxytoluenes.*

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VARIOUS considerations had some time since led us to consider it highly probable that orcinol was a dihydroxytoluene of the constitution 1 : 3 : 5, a supposition which has since been shown to be true by Tiemann and Streng (*Ber.*, 1881, 1999). In order to satisfy ourselves upon this point, and to ascertain if some practicable method for its artificial production could not be found, we undertook the research recorded in the present notes.

As we were endeavouring to obtain satisfactory proof of its exact constitution, we avoided all methods involving the fusion of a compound with a caustic alkali, as this method has in some cases been found to cause the hydroxyl-group to attach itself at a position in the benzene-nucleus different from that occupied by the halogen or other group which has been eliminated.

For this reason we started with the dinitrotoluene 1 : 3 : 5, which has been prepared by Staedel (*Ber.*, 1881, 902), from both dinitro-orthotoluidine and dinitro-paratoluidine. We prepared it from the latter.

As obtained by us it crystallised in bright yellow needles, melting at 92.4° .

Analysis.

Empl. 0.2503 gram; vol. N = 32.5 c.c.; $t = 11^{\circ}$; $b = 743.5 = 15.13$ per cent. N. Theory requires 15.38 per cent.

We obtained a yield of from 60 per cent. to 65 per cent. of the theoretical amount.

On dissolving the dinitrotoluene in an alcoholic solution of ammonium sulphide it gets warm, and the addition of water then causes the precipitation of an orange-red substance. This was dissolved in dilute hydrochloric acid, filtered, and reprecipitated by ammonia.

This nitrotoluidine crystallises from alcohol and ether in red-brown lancet-shaped needles. There is frequently mixed with it a lighter-coloured body which is less easily soluble in ether or dilute hydrochloric acid, and may modify the characteristics of the nitrotoluidine. The best method of purification appears to be to dissolve the nitrotoluidine in hydrochloric acid and leave it for 12–24 hours in a warm place, when a white precipitate gradually forms. This must be filtered out and the liquid again left, and the filtration repeated until no further precipitate separates on standing or warming.

This white substance melts at from 170 – 180° , and appears to be the result of imperfect reduction.

The purified solution will now give, by neutralisation with ammonia, a precipitate which should be washed, dried, and crystallised from ether or alcohol. We thus obtained it in thick needles melting at 98 – 98.4° . It is very easily soluble in ether, also in alcohol and benzene, and somewhat so in water.

The salts appear to dissolve freely in water only, in presence of an excess of acid.

The chloride appears to give up a portion of its acid on drying in the air or washing with ether.

Analysis.

Empl. 0.2893 gram; vol. N = 45.5 c.c.; $t = 13.2^{\circ}$; $b = 758.6 = 18.47$ per cent. N. Theory requires 18.42 per cent. N.

We obtained a yield equal to about 50 per cent. of the dinitrotoluene used.

The nitrotoluidine was now dissolved in a warm mixture of equal volumes of sulphuric acid and water, and cooled, whereupon the sulphate crystallised out. An aqueous solution of potassium nitrite was now gradually added until the sulphate was all redissolved. An equal volume of water was now added, and the mixture warmed, whereupon

the diazo-compound was decomposed with evolution of gas, and nitro-cresol formed. This separated as a brown oil. This oil and the ethereal extract of the mother-liquid were boiled with water and filtered hot. By this means most of the pitch, &c., was left on the filter, and the filtrate, on cooling, gave thick bright yellow needles of nearly pure nitro-cresol. These were purified by crystallisation from benzene or water.

Thus obtained it crystallised in bright yellow needles or prisms, very soluble in ether or alcohol, less so in benzene, and still less in water, easily soluble with a dark yellow colour in alkalis or their carbonates. It does not distil with steam. When crystallised from benzene its melting point is 90—91°, but when crystallised from water, 60—62°. This arises from its crystallising with water, as will be seen below.

By heating to 100° a sample which melted at 60—62°, or by drying it over sulphuric acid, or by recrystallising it from ether or benzene, its melting point was raised to 90—91°. If this was left long in the open air it attracted moisture, and then again melted at 60—62°.

In order to determine the amount of water of crystallisation some was left over sulphuric acid for various times.

	Gram.	M. p.		Gram.	Per cent.	M. p.
Empl.	0.1549	60—61°	left for 7 days	lost 0.0161	= 10.39	81—86°
„	0.5307	60—61	„ 6 „	0.0534	= 10.06	81—85
„	0.3160	61—62	„ 5 „	0.0330	= 10.44	87—89

1 molecular proportion of water would amount to 10.52 per cent.

Analysis of some Crystallised from Benzene and then Dried over Sulphuric Acid.

Empl. 0.2171 gram; vol. N = 17.5 c.c.; $t = 12.5^\circ$; $b = 742.2 = 9.3$ per cent. N. Theory requires 9.15 per cent.

The yield was about 65 per cent. of the theoretical amount.

The nitro-cresol was now reduced with tin and hydrochloric acid: after removal of the tin the liquid was evaporated, during which process it turned brown. The crystalline chloride was washed with ether to remove unreduced nitro-cresol, and was then used for conversion into dihydroxytoluene.

The base itself was not isolated. In order to obtain dihydroxytoluene 1 : 3 : 5 from the chloride, 1 gram of this latter was dissolved in a hot mixture of 13 grams sulphuric acid with an equal volume of water, the solution was diluted with 100 grams of water, cooled by a freezing mixture, and a solution containing 0.6 gram of potassium nitrite added. The decomposition of the diazo-compound

thus formed commences between 30° and 50°. The liquid was warmed to expel all the gas and complete the decomposition; then filtered and extracted with ether.

In this way we obtained a red-brown oil, which was purified by frequent distillation and crystallisation from benzene or chloroform. Thus we obtained it from chloroform in glittering white leaves, and from benzene in long needles or prisms. After drying for 14 days over sulphuric acid it melted at 106—108°.

Analysis.

	H	C
Empl. 0·1653 H ₂ O = 0·0932	= 6·26 p. c.	
„ 0·1611 H ₂ O = 0·0911	= 6·28 „	CO ₂ = 0·4007 = 67·83 p.c.
Theory for C ₆ H ₃ .CH ₃ .(OH) ₂		
requires.....	= 6·45 „	67·74 „

The question now remained, was this identical with the orcinol obtained in other ways? We compared it in all its reactions (viz., ammonia and moist air, chloride of lime, ferric chloride, sodium hydrate in air, sodium hydrate in chloroform) with orcinol otherwise obtained, and found them all to agree perfectly, with the exception of the melting point.

Lamparter (*Jahresb.*, 1865, 589) gives as the melting point of anhydrous orcinol, obtained from lichens, 86°, and when crystallised from water, 58°. Vogt and Henniger (*Jahresb.*, 1872, 410) find for the melting point of the orcinol they obtained from chlorotoluene-sulphonic acid, 57·1°, when crystallised from water.

We examined some orcinol obtained from Messrs. Hopkin and Williams, and found that although it agreed in all other respects with the descriptions usually given of orcinol, yet that the melting point varied from 56° to 107°, accordingly as crystals or fine powders were taken, and according to whether the temperature was raised slowly or fast. It appears certain that by very slow raising of the temperature the combined water is driven off, and then the orcinol melts at the higher point.

In trying the dihydroxytoluene prepared by our method (when crystallised from water) we got sometimes from 54—56°, sometimes 54—105°.

By distilling the orcinol from Hopkin and Williams between two watch-glasses, and by fractionating the distillate by changing the upper glass, we got—

For 1st	distillate	m. p.	54— 81·6°
„ 2nd	„	„	82— 83·0
„ 3rd	„	„	107—108·5
„ 4th and 5th	„	„	107—108·0

Treating the substance obtained by us in a similar way we got—

For 1st distillate	m.p.	54—55°
„ 2nd	„	90—98
„ 3rd	„	98—103
„ 4th	„	97—104

It does not appear that by merely raising the temperature to 100° the whole of the water can be satisfactorily driven off.

On placing Messrs. Hopkin and Williams' orcinol in a partial vacuum over sulphuric acid, the melting point after 24 hours was—

	106·5—107·5°
After 8 days	106·5—108·0
and the same after 14 days.	

Our substance similarly treated gave, after

24 hours	m.p.	104—105°
After 8 days	„	105—107
„ 14	„	106—108

Some of Messrs. Hopkin and Williams' orcinol, which had been dried for 14 days, and which melted at 106·5—108°, was analysed—

Empl. 0·2261 gram; $\text{CO}_2 = 0·5561 = 67·08$ p.c. C. Theory = 67·74
 $\text{H}_2\text{O} = 0·1253 = 6·16$ „ H. „ = 6·45

It appears therefore certain that the dihydroxytoluene, 1 : 3 : 5, obtained in the manner we have described, is identical with orcinol.

The melting point of orcinol, when containing water, seems to be about 56°, but the actual point of complete fusion is very hard to determine. When the compound is anhydrous, or nearly so, the melting point seems to be 106·5—108°. It appears very hard to remove the last traces of water. Some orcinol from Messrs. Hopkin and Williams was placed *in vacuo* over sulphuric acid.

Empl. 0·3230 gram; after 45 hours it had lost 0·0254 = 7·86 per cent.
 (m.p. 106·5—107·5°).
 5 days „ „ 0·0301 = 9·32 per cent.
 12 „ „ „ 0·0373 = 11·55 „
 (m.p. 106·5—108°).

Again—

Empl. 0·3496 gram; after 25 hours it had lost 0·0321 = 9·18 per cent.
 10 days „ „ 0·0402 = 11·5 „
 (m.p. 107—108°).
 12 „ „ „ 0·0411 = 11·73 per cent.
 (m.p. 107—108°).

Theory for $\text{C}_6\text{H}_3\text{CH}_3(\text{OH})_2 + \text{H}_2\text{O}$ requires 12·67 per cent.

The artificially-prepared orcinol appears to behave in the same way.

Empl. 0.1 gram; after 4 days it had lost $0.0114 = 11.4$ per cent.

„ 12 „ „ $0.0125 = 12.5$ „

In further prosecution of our researches, we have succeeded in preparing orcinol by other methods, viz., from metabromo-toluene-metasulphonic acid. This was described by us in this Journal, 1880, 627, and *Ber.*, 1880, 1944—1948. By taking the potash salt of this and fusing it with twice its weight of caustic potash at a temperature of about $280-300^{\circ}$ for from half-an-hour to one hour, a mass was obtained which was dissolved in water and acidulated, extracted first with benzene to remove bye-products, and then with ether. The ethereal extract, on evaporation, left a brown oil, which, by distillation, gave a white distillate, slowly becoming crystalline. A fractional distillation of this substance, after crystallisation from water, gave distillates as follows:—

1st m. p.	54—56°
2nd „	54—100
3rd „	98—103
4th „	100—104

Some dried over sulphuric acid had the melting point $103-103^{\circ}$.

Analysis.

Empl. 0.1863 gram $\text{H}_2\text{O} = 0.1057 = 6.31$ per cent. H; 6.45 per cent. $\text{CO}_2 = 0.4648 = 67.92$ „ C; 67.74 „

Theory for
 $\text{C}_6\text{H}_3\text{CH}_3(\text{OH})_2$.

It gave all the reactions of orcinol with chloride of lime, ferric chloride, sodium hydrate and air, sodium hydrate and chloroform, and ammonia and moist air; and we may therefore conclude that it is identical with the above. We have also prepared orcinol from metabromometatoluidine (described by us in this Journal, 1880, 432).

We dissolved it in a warm mixture of equal volumes of sulphuric acid and water; on cooling, the sulphate crystallised out. A solution of potassium nitrite was now gradually added until the crystals were dissolved. Water was now added and the solution warmed, when gas was evolved and an oil separated out. This was purified by distillation with steam. The oil slowly solidifies into a mass of white crystals, which may be completely purified by solution in dilute caustic soda, filtration, short boiling, acidification, and then repeated distillations with steam. The boiling with caustic soda seems to drive off a substance, volatile with steam and insoluble in the soda. As the

substance is slightly soluble in water, the mother-liquids should be extracted with ether.

This substance melts at $56-57^{\circ}$, is very easily soluble in ether and alcohol, and somewhat in water.

Analysis.

Empl. 0.4120 gram; AgBr = $0.4097 = 42.32$ per cent. Br. Theory requires 42.78 per cent. for monobromocresol.

The metabromo-metacresol thus obtained was heated to $280-300^{\circ}$ with twice its weight of caustic potash for one hour. The melt was acidified and extracted by ether. The ethereal extract was distilled, and in this way we obtained a distillate, solidifying into crystals, and possessing all the characteristics of orcinol.

Orcinol was also obtained from metadibromotoluene by heating it in a closed iron tube, with twice its weight of potassium hydrate, dissolved in a small quantity of water for two hours from $280-300^{\circ}$.

It was further obtained from toluene-metadisulphonic acid.

As a starting point, we took ortho-amido-toluene-metasulphonic acid, and heated 5 grams of it with 15 grams of strongly fuming sulphuric acid to $150-170^{\circ}$ for between half-an-hour and an hour.

The mass then dissolved easily in water, and was treated with barium carbonate to remove the excess of sulphuric acid. The barium salt filtered, a very small excess of sulphuric acid added to remove the barium, and the filtered solution evaporated to dryness and dissolved in alcohol, re-evaporated to dryness, and redissolved in alcohol and again evaporated. The mass thus obtained was very easily soluble in water or alcohol, but not in benzene.

Analysis.

Empl. 0.4720 gram; BaSO₄ = $0.8234 = 59.89$ per cent. SO₃. Theory for amido-toluol-disulphonic acid requires 59.92 per cent.

In a previous communication (this Journal, 1880, 625) we have pointed out that the sulpho-group in the monosulphonic acid occupies the position para to NH₂ and meta to CH₃. In order to determine the position of the other sulpho-group, we converted the amido-sulphonic acid into a diazo-compound by introducing nitrous gas into a mixture of it with alcohol or benzene. The diazo-compound was boiled with water, a few drops of nitric acid then added, and the whole boiled until crystals appeared on cooling. These were filtered out, a few drops more nitric acid added, and the liquid boiled again, this operation being repeated as often as any further crop of crystals was obtained. In this manner six crops of crystals were obtained,

which all had the melting point 85° , and possessed all the properties of dinitroorthocresol.

Now this last has the two nitro-groups in the two positions meta to CH_3 , as was pointed out by us in a former communication (this Journal, 1880, 631), also by Staedel (*Ber.*, 1881, 901).^{*} Hence we conclude that the two sulpho-groups displaced by the nitro-groups had the same position, and that the acid thus obtained is ortho-amido-toluene-metadisulphonic acid. The para-amidotoluene-metadisulphonic acid may be obtained in an analogous manner. When the diazo-compound of either of these acids is heated with absolute alcohol under pressure, the toluene-metadisulphonic acid is formed. The solution is then evaporated, after neutralisation with an alkali or alkaline carbonate, and on heating the resulting salt with caustic alkali to from 200° to 300° , orcinol is produced, in all respects identical with that produced by the other methods described.

In pursuing these researches, we prepared also the dihydroxytoluene 1 : 2 : 4, proceeding as follows:—We start from ortho-nitro-para-toluidine (m. p. $77-78^{\circ}$). 40 grams of this was dissolved in 300 grams of a mixture of 1 vol. sulphuric acid with $1\frac{1}{2}$ vols. of water, and the solution cooled. This causes the separation of crystals of the sulphate.

A solution of potassium nitrite was now gradually added until all the crystals of sulphate were dissolved. It is best to add the potassium nitrite by a tube reaching to the bottom of the vessel. 3200 grams of a mixture of equal parts of sulphuric acid and water were now added, and the whole heated gradually until the evolution of gas ceased. On cooling, crystals of nitrocresol separated out. The mother-liquor was extracted with ether after the addition of water; and by evaporation of the ether a further quantity of nitrocresol was obtained. In this manner the total yield of nitrocresol reached about 80 per cent. of the theoretical quantity. In order to purify it, the ethereal solution was shaken with animal charcoal, or the nitrocresol was crystallised from water. By slow evaporation of an ethereal solution it was obtained in hard yellow prisms of m. p. $77-77.4^{\circ}$. It dissolves in alkalis and their carbonates with an orange-red colour, but the aqueous solutions of the salts partially decompose on heating. It is easily soluble in ether and alcohol.

Analysis.

Empl. 0.3313 gram; vol. N = 25.5 c.c.; $t = 8^{\circ}$; $b = 747.5$ mm.

N per cent. = 9.14 . Theory for $\text{C}_6\text{H}_3\text{CH}_3\text{NO}_2\text{OH} = 9.15$.

^{*} We, in common with Nölting and Salis (*Ber.*, 1881, 982), found the melting point of pure dinitro-ortho-cresol higher than did Staedel, viz., 85.8° ; Nölting and Salis give 86° .

This nitrocresol is easily reduced by tin and hydrochloric acid. The solution may be freed from tin by hydrogen sulphide, and the filtered liquid evaporated to dryness. In this way a crystalline residue of chloride of amidocresol is obtained, but it is always coloured brown in the process of evaporation. Any unreduced nitrocresol remaining may be removed by washing with ether. The chloride is easily soluble in water, but on the addition of an alkali, or alkaline carbonate or ammonia, the liquid becomes brown or green.

In order to prepare from this the dihydroxytoluene 1 : 2 : 4, one gram of it was dissolved in 13 grams of a warm mixture of equal volumes of sulphuric acid and water. The mixture was now diluted with 100 grams of water, cooled by a freezing-mixture, and a dilute solution of potassium nitrite added until a slight smell of nitrous acid remained permanent; an excess of nitrite injures the reaction. The liquid was now warmed from 90° to 95°, filtered, and exhausted with ether. The ether by evaporation left a brown oil, which was boiled with benzene. The benzene was decanted off and distilled, and the residue remaining after the benzene had distilled off further distilled. In this way an oily distillate was obtained, which after some time crystallised. This was purified by frequent sublimations and crystallisations from benzene or toluene, and was thus eventually obtained of melting point 104—105°.

Analysis.

Empl. 0.0953 gram; $\text{H}_2\text{O} = 0.0566 = 6.61$ per cent. H.

$\text{CO}_2 = 0.2364 = 67.65$ „ C.

Theory for $\text{C}_6\text{H}_3\text{CH}_3(\text{OH})_2$

requires..... H = 6.45 per cent.

C = 67.74 „

The reactions agree pretty closely with those described by Håkanson (*Ber.*, 1872, 1087) for the dihydroxytoluene obtained by him from the toluenedisulphonic acid prepared from toluene and fuming sulphuric acid, and it is probable that they are identical.

Since this paper was written, Knecht (*Ber.*, 1882, 298) has obtained this dihydroxytoluene in a similar manner, and gives 103° as the melting point.

We have also prepared the dihydroxytoluene 1 : 2 : 5.

For this purpose we start from the nitro-orthotoluidine produced by the nitration of ortho-acetotoluid, and which we showed (this *Journal*, 1880, 436) had that constitution.

40 grams of metanitro-orthotoluidine (m. p. 127—129°) were dissolved in 300 grams of a warm mixture of equal volumes of sulphuric acid and water. The mixture cooled, and a solution of potassium nitrite carefully added until the crystals of sulphate

deposited on cooling were all dissolved. 1600 grams of a mixture of 1 vol. sulphuric acid to 2 vols. of water were then added, and the mixture gently warmed. The decomposition of the diazo-compound takes place at a temperature of 70—90°. A brown oil separates out which crystallises on cooling, and fine needles form in the liquid. These crystals and a further portion extracted from the mother-liquid with ether were dissolved in ether, and purified with animal charcoal.

Owing to the formation by the above process of dinitro-ortho cresol as well as mono-nitrocresol, the perfect isolation of the latter is difficult. We found that the best method was to dissolve the mixed cresols in potash solution, and separate the more from the less soluble portion. (The potassium salt of dinitro-orthocresol is much less soluble in cold potash-solution than the salt of the mono-nitrocresol). We then reprecipitated the cresol with sulphuric acid. By repeating these operations we got the compound tolerably pure.

The metanitro-orthocresol thus obtained crystallises from water in fine glittering bright yellow needles, melting at 30—34°; but by drying it on paper or on a water-bath, or by crystallising it from ether, its melting point is raised to 94·6—95°.

It is not freely soluble in water, but easily in alcohol or ether, and also in solutions of alkalis or their carbonates. The salts of the alkalis dissolve in water with an orange-yellow colour.

Analysis.

Empl. 0·2267 gram; vol. N = 17·5 c.c.; $t = 7·8^\circ$; $b = 750·3$ mm. = 9·02 per cent. N. Theory for C_6H_3, CH_3, NO_2, OH requires 9·15 per cent. N.

An easier way of obtaining the pure mononitrocresol was found to consist in boiling the metanitro-orthotoluidine with moderately concentrated solution of soda until it dissolved. In this way few, if any, bye-products, except a little pitch, seem to be formed. The pitch is easily removed by filtration, and by then precipitating the nitrocresol with sulphuric acid, extracting with ether and shaking with animal charcoal, it may be obtained at once nearly pure, and the yield is very nearly theoretical. The nitrocresol obtained in this manner presented exactly the same characteristics as that obtained in the other manner—

Analysis.

Empl. 0·2895 gram; vol. N = 23·25 c.c.; $t = 9·6^\circ$; $b = 757$ mm. = 9·60 per cent. N. Theory requires 9·15 per cent. N.

It appears from the above that the fluid nitro-orthocresol which Hofmann and Miller (*Ber.*, 1881, 571) consider to have the constitution 1 : 2 : 5 must have some other constitution.

The nitrocresol obtained by either of the above processes is easily reduced by tin and hydrochloric acid. After the tin has been removed by hydrogen sulphide, the chloride of the amidocresol is easily obtained by evaporation in good crystals coloured brown by the slight products of decomposition. These were washed with ether to free them from undecomposed nitrocresol.

The free amidocresol was not obtained, as it decomposed immediately on being set free from its salts, giving a greenish-yellow or red-brown colour to the solution from which ether extracted nothing but a red-brown pitch.

In order to obtain the dihydroxytoluene 1 : 2 : 5 the chloride of the amidocresol was dissolved in a considerable quantity of a very dilute sulphuric acid. To this was added a dilute solution of potassium nitrite until the smell of nitrous acid remained permanent for a short time. More water was then added, and the mixture boiled until all disengagement of gas ceased. The cooled and filtered liquid was then exhausted with ether. On evaporation, the ether gave red-brown crystals, which were purified by sublimation and recrystallisation from benzene in which they are not freely soluble. It was obtained from benzene, in white pearly leaves, melting at $124-125^{\circ}$, freely soluble in alcohol, ether, or water. From water it crystallises in colourless crystals, which melt at $123-125^{\circ}$, and do not appear to contain any water of crystallisation.

This dihydroxytoluene was prepared from the nitrocresol obtained from nitro-orthotoluidine by both the above-mentioned methods, and in both cases appeared identical.

Analysis.

Theory for
 $C_6H_3CH_3(OH)_2$
 requires

Empl. 0.2247 gram; $H_2O = 0.1480 = 7.31$ p. c. H. H = 6.45 p. c.
 $CO_2 = 0.5567 = 67.56$ „ C. C = 67.74 „

This dihydroxytoluene appears to be identical with the hydrotoluquinone of Nietzki (*Ber.*, 1877, 834) prepared from toluquinone from orthoamidoazotoluene. With soda-solution it gives a pretty blue-green colour, which very quickly turns to dark brown. With chloride of lime it turns blue-green, as with soda, then brown; but with a weak solution of chloride of lime a brownish-red. Chloroform and soda produce a brown colour; ferric chloride a brownish-red, or in a dilute solution, yellow. Ammonia in presence of moisture changes it into a dark brown mass, which dissolves in alkalis with a brown colour, and the addition of acetic acid to the solution causes the precipitation of brown flocks.

We also made some investigations into the preparation of hydroxy-toluene 1 : 3 : 4, starting from metanitroparatoluidine (m. p. 114—115°).

Armstrong and Thorpe (*Jahresb.*, 1876, 452) obtained, by nitration of paracresol, a nitrocresol identical with that which Wagner (*Ber.*, 1874, 537) obtained by heating metanitroparacetotoluid with sodium hydrate. This nitrocresol must have the required constitution, viz., 1 : 3 : 4, unless some molecular change takes place. Wagner by this method, however, obtained only small quantities. We therefore tried to prepare it from the diazo-compound, in the hopes of getting a better yield.

10 grams metanitroparatoluidine was dissolved in 100 grams of a mixture of equal parts of sulphuric acid and water, and a solution of potassium nitrite was added until a sample of the solution no longer gave a precipitate of nitrotoluidine on addition of water. The solution was then decomposed by heating, 800 grams of a mixture of 1 vol. sulphuric acid and 1½—2 vols. of water having first been added. The result, however, was unsatisfactory, as neither in the distillate nor in the ethereal extract was any large quantity of nitrocresol obtained, but only a very little melting at 33°.

We therefore tried Wagner's method, and after some experiments succeeded in getting a very good yield. The best plan is to take say 10 grams, and heat it with about 50—100 grams of a 20 per cent. solution of sodium hydrate for 15 hours; then pour off the liquid, and boil the remaining nitrotoluidine with a fresh charge of sodium hydrate, repeating this process until it is all dissolved. All the sodium hydrate liquors are then mixed, acidified with sulphuric acid, and distilled. In this way an almost theoretical yield is obtained; from 20 grams of nitrotoluidine we obtained 19 grams of nitrocresol. This good yield allows us to assume that no molecular change takes place, and that the nitrocresol has the constitution 1 : 3 : 4. The substance when purified was obtained from benzene in yellow crystals, melting at 33—33·4°, easily soluble in caustic alkalis, ether, or alcohol, but scarcely soluble in water. A portion of this nitrocresol was reduced by tin and hydrochloric acid. After removal of the tin by a current of hydrogen sulphide, the filtrate was evaporated to dryness. The chloride (1 gram), dissolved in 100 grams water and 13 grams sulphuric acid, cooled by a freezing mixture, and 0·6 gram of potassium nitrite in solution added. The solution was then warmed, filtered, and extracted with ether. An oil was thus obtained, which dissolved easily in water. The aqueous solution was coloured green by ferric chloride, on adding ammonia or sodium carbonate gradually the colour became first blue and then violet.

This oil is probably the dihydroxytoluene, 1 : 3 : 4. Its properties

coincide with those of homocatechol, which Tiemann (*Ber.*, 1877, 210; and 1878, 672) obtained by heating the calcium salt of α -homoprotocatechuic acid, and from coniferyl alcohol. They also regarded it as a dihydroxytoluene, 1 : 3 : 4.

It would appear from our investigations, as well as those of others, that inasmuch as orcinol evidently has the constitution 1 : 3 : 5, those reactions by which it has been obtained from substances of other constitution, such as chlorotoluene-sulphonic acid (1 : 2 : 4), must have involved a molecular change.

We subjoin a table of the reactions of the different dihydroxytoluenes above described. Circumstances have prevented us from investigating the dihydroxytoluene 1 : 3 : 4 as fully as we could have wished, as also the two others, viz., 1 : 2 : 3 and 1 : 2 : 6; but we hope to resume the investigation at some later date.

Reagent.	Orcinol, 1·3·5.	1·2·5.	1·2·4.	1·3·4.
Ammonia and damp air.	Intense red violet, diss. in alkalis with red-violet colour. Acetic acid precipitates red flocks.	Dark brown, dissolves in alkalis with brown colour. Acetic acid precipitates brown flocks.	Reddish, then brown, then green, then blue. Blue changing to red by addition of acetic acid, without any precipitation.	
Chloride of lime.	Deep violet-red, then brown and yellow.	Blue-green, then brown. When dilute, brownish-red.	Yellow.	
Ferrie chloride.	Deep black-violet.	Brownish-red, yellow in dilute solutions.	Blue, scarcely changing.	Green; on gradual addition of NH_3 or Na_2CO_3 , became blue and then violet.
Sodium hydrate and air.	Red.	Pretty blue-green, changing to dark-brown.	Rose-red, then brownish.	
Chloroform and sodium hydrate on heating.	Red, after a while a green fluorescence, yellow by transmitted light.	Brown.	Rose-red.	

NOTE.

The above paper was written principally in the autumn of 1881, but its publication has been delayed, owing to our having applied for protection for the method of manufacturing orcinol, and since it was written, independent workers have published some of the above results. We have, however, thought it better to publish the paper in its entirety, at the risk of repeating work already done. We may perhaps take this opportunity of noticing a paper by C. Langer (*Ber.*, 1882, 1061—1065), on the law of substitution of aromatic amines, and point out that the law he there enunciates is really nothing else than the law which we showed to be true in a communication to this Society in 1880 (this Journal, 1880, 430), stated in other words.