XXII.—*Contributions to the History of the Orcins. Betorcinol and some of its Derivatives.*

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ABOUT 32 years ago (Stenhouse, *Annalen*, **68**, 104), in the course of an extended examination of the lichens with regard to the organic compounds contained in them, and derivatives of these compounds, a quantity of usnic acid obtained from the *Usnea barbata* and *Cladonia rangiferina* was submitted to destructive distillation. The distillate was found to contain a crystalline substance of the composition $C_8H_{10}O_2$, homologous with "orcin," and very closely resembling it in most of its properties. This new member of the orcinol group was named "β-orcin" from this circumstance, and as it was known that the erythrin and lecanoric acid from the *Rocella fuciformis* and the *Lecanoras* yielded orcinol, it was somewhat hastily inferred that the usnic acid in the *Usnea* and *Cladonia* was the source of the so-called β-orcin. Subsequent attempts to prepare the β-orcin by the distillation of pure usnic acid obtained from *Usnea barbata* yielded negative results ; not a trace of the orcinol could be detected. This has been confirmed by other observers.

As there were not only many points of interest connected with this higher homologue of orcinol, but also great uncertainty as to what was the real source of the compound, we obtained a quantity of *Usnea barbata** from the same locality as that which had yielded the original specimen, namely, Roxburghshire (Scotland), and also—through the kindness of our friend Dr. James Young—from Durris, in Kincardineshire. The crude usnic acid extracted from the Usnea, which had previously been most carefully freed from every trace of Evernia or other lichen, was submitted to destructive distillation, and the distillate examined for the orcinol by means of chloride of lime solution. The crimson-red coloration produced at once showed that the Usnea from both localities contained the orcinol-yielding compound. It remained to be determined whether this was the usnic acid, or some other principle accompanying it in the lichen. Destructive distillation of carefully purified usnic acid from the samples of lichen from the two localities at once settled this point; not a trace of β-orcin could be discovered in the distillate. The results of these experiments, therefore, have definitely established that the usnic acid is not

* These lichens were kindly examined for us by Mr. Carruthers, of the British Museum, and also by Sir Joseph Hooker of Kew, both of whom pronounced them to be *Usnea barbata*.

the source from which the β-orcin is derived, but another substance accompanying it in the lichen in the same manner that evernic acid accompanies usnic acid in *Evernia prunastri*.

Betorcinol.

As the prefix α- or β- is now almost universally used to distinguish isomerides, it has been thought advisable to change the name "β-orcin" into betorcinol, so as to bring it more into harmony with the nomenclature employed at the present time.

In preparing betorcinol, $C_8H_{10}O_2$ or $C_6H_2Me_2(OH)_2$, the *Usnea barbata* is first most carefully picked over by hand, so as to free it from every particle of Evernia or other lichen which may be present, and is then steeped in 20 parts of water for 16 hours, in order to thoroughly soften and moisten it.   One-tenth part of lime, equal to 10 per cent. of the original weight of the lichen, is slaked, and after being made into a cream with a sufficient quantity of water, is poured into the mixture, and the whole allowed to stand for an hour with occasional stirring.   The partly exhausted lichen is then taken out, and treated in a precisely similar manner with 10 parts of water, and one-tenth part of lime for one hour, whilst the lime-extract is being filtered, which is most conveniently done through a bag-filter, with a pressure of 6 or 8 feet of the liquid.   The lichen acids are precipitated from the clear solution as soon as possible, by gently acidifying with hydrochloric acid, collected, and washed with a little cold water.   In order to completely exhaust the lichens, it is necessary to treat them four times with lime and water, but the quantity of both employed in the last two extractions may advantageously be diminished by one-fourth. The yield of dry crude lichen acids obtained from the specimens of Usnea examined, gathered in September and October, varied from 3 to $3\frac{1}{2}$ per cent.

The crude product, which consists chiefly of usnic acid mixed with but a very small proportion of the acid which yields betorcinol, is boiled with its own weight of lime and 40 parts of water for 3—4 hours.   It is not necessary, in fact it is far better not to dry the acids before boiling them with lime and water ; the amount of lime and water required can be easily reckoned for the quantity of usnic acid taken when the yield of crude acid which the particular sample of lichen gives has once been ascertained.   By this mode of treatment the whole of the usnic acid is converted into the insoluble basic calcium compound described in a former paper (*Proc. Roy. Soc.*, **18**, 223, and *Annalen*, **155**, 51), whilst the other lichen acid splits up, yielding carbonic anhydride and betorcinol, the former combining with the lime to form calcium carbonate, whilst the betorcinol remains dissolved.   As

the latter oxidises with the greatest readiness in alkaline solutions, it is necessary that the operation should be conducted in a flask furnished with an upright condensing tube with a small opening at the top, the heat being so regulated that steam in small quantity issues continuously from the upper end. When the reaction is completed, the solution is at once filtered through a vacuum-filter into dilute hydrochloric acid in quantity just sufficient to neutralise the lime. If this precaution be not taken, loss of the orcinol will occur through oxidation. The feebly acid solution is rendered strongly acid with acetic acid, filtered from a small quantity of flocculent precipitates, and evaporated on the water-bath : as the evaporation proceeds, a black tar is gradually deposited, arising apparently from the oxidation of a product of the action of the lime on the usnic acid or on some substance present in the crude usnic acid. When the solution has been reduced to about one-eighth of its original bulk, it is filtered, and the evaporation of the clear solution is continued, whilst the black tar which separates may be exhausted with boiling water, and the filtrate reserved for subsequent treatment along with the washings of the crude betorcinol. When the solution becomes concentrated, the impure betorcinol separates in the crystalline state, being almost insoluble in the concentrated solution of calcium chloride, derived partly from the calcium chloride in the crude lichen acids, and partly from the neutralisation of the lime by hydrochloric acid. The crystals, which are mixed with more or less of the black tar previously mentioned, are collected, washed with a little water, and dried. As the washings contain betorcinol, they should be reserved, together with the solutions obtained by treating the tar with boiling water, and evaporated with fresh quantities of betorcinol solution ; or they may be concentrated and the betorcinol extracted by agitation with ether. Instead of employing hydrochloric acid to neutralise the solution of betorcinol obtained by boiling the mixture of crude acids with lime and water, sulphuric acid may be used : in this case the solutions, after being concentrated by evaporation and filtered from the calcium sulphate, must be agitated with ether to extract the betorcinol. The process first described is, however, far to be preferred for the preparation of the orcinol, whilst the last mentioned is useful when very small quantities are operated on, as when it is desired to examine a lichen for the acid which yields betorcinol.

In order to purify the crude product, the dry betorcinol is boiled with 50 parts of benzene, and filtered hot from the brown insoluble portion, which is again treated with benzene until nothing more dissolves : the benzene solutions are then concentrated by distillation, and on cooling deposit the nearly pure betorcinol in pale brown crystals, which may be collected, washed with a little benzene, and dried.

A crystallisation or two from boiling water (4 parts) renders it quite pure, although the crystals still retain a brown tinge. The amount of betorcinol obtained from *Usnea barbata* in this way rarely exceeds 0·1 per cent. of the weight of the lichen.

The purified betorcinol was found to have the same melting point (163°) as the original specimen prepared 32 years ago, and to be identical with it in all its properties.

Betorcinol is distinguished from orcinol not only by its higher melting point and in being much less soluble in cold water, but also in its chemical reactions, especially with hypochlorites and with ammonia. Betorcinol gives a characteristic bright crimson coloration with hypochlorites, very different from the purplish-red obtained with orcinol. Its reaction with ferric chloride is also more marked, a green coloration being produced at first, which gradually becomes darker with formation of a flocculent precipitate. In contact with ammonia solution, betorcinol rapidly acquires a bright red colour on exposure to the air, whilst the corresponding orcinol solution is but slowly changed. Schwarz (*Ber.*, **13**, 543) has recently shown that when orcinol is gently heated with dilute soda solution and a little chloroform, an orange-coloured solution is produced, which has a most brilliant green fluorescence when viewed by reflected light. We find, however, that betorcinol behaves very differently when treated in a similar manner, giving a deep red solution which is almost entirely destitute of fluorescent properties.

Chlorobetorcinols.

Tetrachlorobetorcinol, $C_6H_6Cl_4O_2$, or $C_6Me_2Cl_2(OCl)_2$.—This compound may be prepared by the action of chlorine on the orcinol, taking care that the former is always kept in excess, as when a solution of betorcinol is added to chlorine hydrate. A mixture of the crystalline chlorine hydrate with water is first prepared by passing a current of chlorine with occasional agitation through water to which about one-fourth of crushed ice has been added: betorcinol is then dissolved in 50 parts of boiling water, and the cooled solution is gradually added to a portion of the chlorine hydrate mixture, leaving the latter in slight excess. This is most conveniently effected by first adding the betorcinol solution in very slight excess, which is easily ascertained, as the orange coloration disappears instantly on agitation as long as the chlorine is in excess, but becomes permanent when all the free chlorine has been removed. A little more chlorine hydrate is then added, and the almost colourless mixture allowed to stand for 12—20 hours, when colourless tetrachlorobetorcinol is deposited in the crystalline state. If sufficient chlorine hydrate has not been employed, the crystals will be coloured yellow more or less: any very great

excess of chlorine should be avoided, however, as it is apt to oxidise the chlororcinol and occasion loss.* The yield in successfully conducted operations is about 160—165 per cent. of the weight of the betorcinol originally taken. Attempts were also made to prepare the tetrachlorobetorcinol by the method which had been so successfully applied to the chlorination of orcinol and resorcinol, namely, the action of potassium chlorate and hydrochloric acid on the orcinol, but the results were not satisfactory : apparently the molecule of the betorcinol is completely broken up by the powerful oxidising action of the chlorine peroxide produced by the action of the hydrochloric acid on the chlorate.

The tetrachlorobetorcinol may easily be purified by one or two crystallisations from boiling light petroleum (16 parts). It forms large white prismatic crystals which melt at 109°, and are easily soluble in benzene and in ether, but insoluble in water. The chlorine was estimated in the substance dried in a vacuum, with the following result :—

0·262 gram of substance gave 0·544 gram of silver chloride.

	Theory.	Found.
Cl in $C_8H_6Cl_4O_2$	51·45	51·37

The action of excess of chlorine on betorcinol, therefore, gives rise to the tetrachlorinated derivative, $C_8H_6Cl_4O_2$.

Dichlorobetorcinol, $C_8H_8Cl_2O_2$, or $C_6Me_2Cl_2(OH)_2$.—The tetrachlorinated derivative just described is readily acted on by reducing agents, 2 atoms of chlorine being displaced by hydrogen : the best agent for this purpose is a solution of hydriodic acid containing 15 per cent. of iodine. The finely powdered tetrachlorobetorcinol is added in small portions at a time to a boiling solution of hydriodic acid of the strength indicated and a small quantity of red phosphorus, in a flask furnished with reversed condenser : care should be taken that each portion of the tetrachloro-derivative is reduced before adding the next, which may be known by the disappearance of the yellow colour due to the liberated iodine, and any lumps that may form must be broken up. After all the tetrachlorobetorcinol has been added, the boiling is continued for a few minutes until the last portions are reduced, and the dichloro-compound assumes the appearance of a mass of slender colourless needles. It is then collected, washed with water, and dried. One or two crystallisations from light petroleum (50 parts) suffice to render it pure. It forms long colourless needles which melt at 142°, and are soluble in carbon bisulphide, benzene,

* We wish to direct particular attention to the use of chlorine hydrate as a chlorinating agent, especially in those cases where it is desirable that excess of chlorine should be constantly present during the reaction.

and ether. A chlorine determination was made of the substance dried in a vacuum.

0·199 gram of substance gave 0·276 gram of silver chloride.

	Theory.	Found.
Cl in $C_8H_8Cl_2O_2$	34·30	34·31

The result of the analysis corresponds almost exactly with that required for dichlorobetorcinol, $C_8H_8Cl_2O_2$.

Bromobetorcinols.

Tetrabromobetorcinol, $C_8H_6Br_4O_2$, or $C_6Me_2Br_2(OBr)_2$.—The tetrabrominated derivative may be prepared in a manner similar to that employed for converting orcinol into pentabromorcinol (*Proc. Roy. Soc.*, **20**, 76, and *Annalen*, **163**, 179) by adding a solution of the orcinol to bromine and water, taking care to keep the bromine in excess; the action, however, does not take place so readily with betorcinol as with orcinol itself. The most convenient method of conducting the operation is to place 5 parts of bromine and 100 of water in a stoppered bottle, and add a solution of 1 part of betorcinol in 50 of water in successive portions, with agitation between each addition, so that there may always be excess of bromine in the liquid. As soon as the reaction is completed, the whole is allowed to stand for a few minutes, and then violently agitated, when the bromobetorcinol will collect into a soft pasty mass, which becomes hard after a time. The solution of betorcinol should be made with boiling water and cooled rapidly just before being used, agitation being avoided as much as possible, otherwise the betorcinol is apt to crystallise out. The crude tetrabromobetorcinol is dissolved in carbon bisulphide—in which it is very soluble—a slight excess of bromine added, and the solution allowed to evaporate spontaneously in a loosely covered beaker. The large colourless prisms of the bromobetorcinol which form may readily be separated from the traces of brown resinous matter, and purified by crystallisation from boiling light petroleum. In this way, betorcinol yields about 320 per cent. of its weight of tetrabromobetorcinol.

Another and perhaps more convenient method of converting betorcinol into the tetrabrominated derivative is to treat it with bromine in carbon bisulphide solution. For this purpose a mixture of 5 parts of bromine and 30 parts by measure of carbon bisulphide are poured on to 1 part of betorcinol in fine powder, and gently heated in a flask furnished with condensing tube; the betorcinol gradually disappears, whilst torrents of hydrobromic acid are given off. As soon as the whole of the betorcinol is dissolved, the dark red-brown

solution containing dibromobetorcinol and excess of bromine is poured off from traces of black tar into a clean flask, and agitated with its own bulk of warm water, when the colour gradually becomes lighter or entirely disappears. In the latter case sufficient bromine has not been employed, and it is necessary to add more. The carbon bisulphide solution of the tetrabromobetorcinol separated from the supernatant liquid is concentrated by distillation and allowed to evaporate spontaneously, the crystals which form being purified in the manner formerly described. A very pure tetrabromobetorcinol may at once be obtained by acting on pure colourless dibromobetorcinol with bromine and water at a gentle heat, and crystallising the product from carbon bisulphide and light petroleum. It crystallises in large colourless prisms melting at 101°, and very similar in appearance to tetrachlorobetorcinol. It is very soluble in ether, benzene, and carbon bisulphide, less so in petroleum. The analysis of the substance dried in a vacuum gave the following results :—

0·267 gram substance gave 0·442 gram silver bromide.

	Theory.	Found.
Br in $C_8H_6Br_4O_2$	70·48	70·44

Although the analyses left but little doubt that the compound obtained by the action of excess of bromine on betorcinol in presence of water was really the tetrabromo-derivative of the formula $C_6Me_2Br_2(OBr)_2$, it was considered advisable for the sake of confirmation to ascertain the amount of hydrobromic acid produced in the reaction. With this object two quantities of betorcinol of 0·2 gram each were treated with excess of bromine in presence of water, according to the method first described, and the amount of hydrobromic acid determined in the aqueous solution, after removal of the excess of bromine. The results were as follows :—

I.	II.	III.
0·4525 gram	0·4536 gram	0·4696 gram

In I, the excess of bromine was removed by exposing the liquid to a gentle heat in an open basin, until it had become colourless ; whilst in II, the excess of bromine was removed by agitation with carbon bisulphide ; III is the amount of hydrobromic acid which should be obtained theoretically from 0·2 gram of betorcinol, according to the equation—

$$C_6Me_2H_2(OH)_2 + 4Br_2 = C_6Me_2Br_2(OBr)_2 + 4HBr.$$
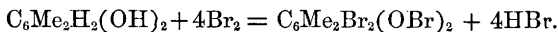
Dibromobetorcinol, $C_8H_8Br_2O_2$, or $C_6Me_2Br_2(OH)_2$.—Like the tetrachlorinated derivative, tetrabromobetorcinol is readily acted on by hydriodic acid, even in the cold, dibromobetorcinol being formed ; if,

however, the acid is concentrated, and the mixture is boiled for some time, the action goes farther, and betorcinol is regenerated. Some care is required, therefore, to convert the tetrabromo- into the dibromo-derivative, but even under the most favourable circumstances, the yield obtained falls far short of the theoretical. The finely powdered tetrabromobetorcinol is first treated in the cold with a little red phosphorus and a solution of hydriodic acid containing 12 per cent. of iodine; after 15—20 minutes, the dark brown mixture is heated in a water-bath at 60°, with occasional agitation, until the free iodine has been entirely reconverted into hydriodic acid by the action of the phosphorus, care being taken to break up any lumps of dibromobetorcinol that may be formed. Finally the whole is boiled for a minute or two to complete the reaction, and the nearly colourless dibromobetorcinol collected, washed thoroughly with cold water, and dried at a gentle heat. It may be purified by successive crystallisation from carbon bisulphide and light petroleum (100 parts).

A far more productive and less troublesome process, however, is to treat the orcinol with bromine diluted with carbon bisulphide, for under these circumstances the action goes no further than the production of the dibrominated derivative, even when the bromine is in excess; the presence of water being necessary to convert the dibromo-into tetrabromo-betorcinol. A mixture of 8 parts of bromine, with 100 parts by measure of carbon bisulphide, is poured on to 3 parts of betorcinol in fine powder, and the mixture digested for some time in a flask furnished with a condensing tube; hydrobromic acid is given off, and the betorcinol gradually dissolves. After about thirty minutes' boiling, the carbon bisulphide solution becomes of a pale brown colour, and the reaction may be considered as completed. The digestion is then stopped, the clear solution poured off from the traces of dark coloured impurity adhering to the sides of the vessel, and the solution concentrated by distillation, until the dibromo-compound begins to crystallise out. When cold, the nearly colourless crystals are collected, and after being washed with a little cold carbon bisulphide, they are purified by crystallisation from light petroleum. The carbon bisulphide mother-liquors and washings, when distilled to dryness, yield a farther quantity of dibromobetorcinol, but it has a brown colour, and cannot be rendered colourless by simple crystallisation from any of its solvents; if, however, it is finely powdered and boiled for a minute or two with dilute hydriodic acid, the brown impurity is rendered insoluble in light petroleum, so that the bromobetorcinol may readily be obtained perfectly pure by one or two crystallisations from that solvent. It forms long needles, of melting point 155°, and closely resembles the corresponding chlorinated derivative in its relation to solvents. Dried in a vacuum—

0·219 gram substance gave 0·280 gram silver bromide.

	Theory.	Found.
Br in $C_8H_8Br_2O_2$	54·05	54·41

The percentage of bromine found indicates that the compound is dibromobetorcinol, $C_8H_8Br_2O_2$.

The fact that the action of bromine on betorcinol, when every trace of water is carefully excluded, only displaces two atoms of hydrogen in it, yielding a dibrominated derivative, whilst if water is present a tetrabrominated derivative is produced, is readily accounted for, if we take into consideration the great difference between the energy involved in the formation of gaseous hydrobromic acid by the union of bromine and hydrogen, and the formation of hydrobromic acid in aqueous solution; for, according to Thomsen (*Ber.*, **5**, 770)—

$$H + Br \qquad = \quad 8440 \text{ units}$$
$$\text{whilst } H + Br + Aq = 28376 \quad ,,$$
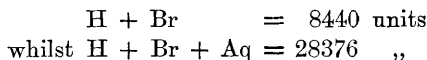
In the betorcinol, the two hydrogen atoms, which are united with carbon in the benzene-nucleus, are comparatively easily displaced by bromine, so that the dibrominated derivative, $C_6Me_2Br_2(OH)_2$, is produced with evolution of gaseous hydrobromic acid. In the case of the two hydrogen-atoms united with oxygen in the OH groups, however, it is only when the much greater energy involved in the formation of hydrobromic acid in the presence of water is brought into operation, that displacement takes place with formation of the tetrabrominated derivative.

We have examined the behaviour of orcinol under the same conditions, and find that it is precisely similar to that of betorcinol, nothing but tribromorcinol being formed, unless water is present.

Iodobetorcinol.

Moniodobetorcinol, $C_8H_9IO_2$, or $C_6Me_2HI(OH)_2$.—This derivative may be prepared in a manner similar to moniodorcinol by the action of lead oxide on betorcinol and iodine in ethereal solution. The betorcinol is dissolved in 50 parts of dry ether, 2 parts of iodine are added, and as soon as it has completely dissolved, lead oxide in very fine powder is gradually added with constant agitation, until the solution is decolorised; the operation is most conveniently conducted in a stoppered bottle. The nearly colourless ethereal solution is separated from the lead iodide and excess of lead oxide, and after washing the residue with ether until nothing more is dissolved, the washings are added to the original solution, and the whole is distilled to dryness in the water-bath. The oily residue, which solidifies on standing, is boiled with

light petroleum ; this dissolves all but a little brown matter, and on cooling, the impure moniodobetorcinol is deposited in the crystalline state.   It may be purified by repeated crystallisation from light petroleum, when it melts at 93°.   Iodobetorcinol is very soluble in ether, benzene, or carbon bisulphide, as is also the brown impurity which accompanies it.   It is only very sparingly soluble in boiling water, more so in dilute spirit, but it does not crystallise well from the latter.   The results of an iodine determination made on the substance, dried in a vacuum, were as follows:—

0·250 gram substance gave 0·222 gram silver iodide.

	Theory.	Found.
I in $C_8H_9IO_2$	48·11	47·99

This corresponds very closely with what is required by the formula $C_8H_9IO_2$.

Nitrosobetorcinol.

Mononitrosobetorcinol, $C_8H_9NO_3$, or $C_6Me_2H(NO)(OH)_2$, is readily prepared by the action of nitrosyl sulphate, $SO_2(NO).OH$, on betorcinol in aqueous solution ; 2 parts of betorcinol is dissolved in 100 parts of boiling water, and the solution, after being filtered and cooled, is poured into a mixture of 7 parts of nitrosyl sulphate solution (*Journ. Chem. Soc.*, 1877, i, 545), containing 15 per cent. N_2O_3, with 200 parts of water, when a brilliant, orange-red precipitate almost immediately makes its appearance.   After allowing the mixture to stand for five minutes, the precipitate is collected on a vacuum filter, and washed by stirring it up with 100 parts of water, and again collecting ; repeating the washing once more in the same manner, so as to remove the last traces of free acid, and finally drying at a gentle heat.   The amount of nitrosobetorcinol obtained in this way is about equal to that of the betorcinol taken.   Nitrosobetorcinol is moderately soluble in boiling water, and easily in alcohol, but it cannot readily be recovered in the crystalline state.   It is very soluble in hot glacial acetic acid, and on cooling, separates in small bright red prismatic crystals.   It is sparingly soluble in light petroleum and in carbon bisulphide, somewhat more so in hot benzene, crystallising out on cooling, and easily soluble in ether.

The attempts to prepare nitrobetorcinol, both from the nitroso-compound, and also by the direct action of nitric acid on betorcinol, gave unsatisfactory results, nothing but amorphous flocculent substances being obtained.

A nitrogen determination of nitrosobetorcinol gave the following results :—

0·368 gram substance gave 24·6 c.c. nitrogen at 2°, and 770 mm. = 24·574 c.c. at 0°, and 760 mm. = 0·03083 gram of nitrogen.

	Theory.	Found.
N in $C_8H_9NO_3$	8·383	8·378

The numbers are identical with those required by the formula $C_8H_9(NO)O_2$.

It will be seen from these results, that in the action of nitrous acid on betorcinol, only one of the hydrogen atoms is displaced by the nitrosyl group, giving rise to mononitrosobetorcinol although resorcinol and orcinol under similar circumstances give dinitroso-derivatives. Considering that the action of nitrous acid on phenol—the *mono*hydroxy-derivative of benzene—gives a *mono*nitrosophenol in which the NO group occupies the para position with respect to the OH group, and that of the three meta*di*hydroxy-derivatives of phenol, resorcinol and orcinol yield *di*nitroso-derivatives, whilst betorcinol yields only a *mono*-nitroso-derivative, it is not improbable that in the latter, the para position with respect to one of the OH groups is occupied by a CH_3 group.

Of the four possible formulæ for betorcinol or dimethyldihydroxyben-zene, I is capable of yielding a dinitroso-derivative, in which the NO groups can occupy a para position with respect to the OH groups, and in IV the para positions are occupied by CH_3 groups, so that it could not yield a nitroso-derivative of this class, whilst in II and III there is *only one* para position, in which the NO-group could enter, and consequently they would yield *mono*nitroso-derivatives. Although our knowledge of the laws which govern the introduction of the nitrosyl group into the hydroxyl-derivatives of benzene is far too elementary to enable us to pronounce with certainty on this point, it seems more probable that the constitution of betorcinol is represented either by II or by III than by I or IV.
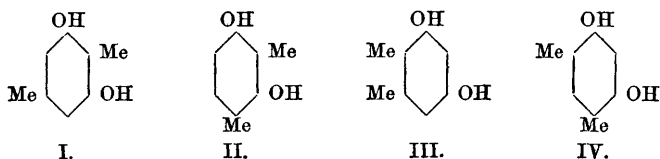
The Acid which yields Betorcinol.

Barbatic Acid, $C_{19}H_{20}O_7$.—As the crude mixed acids obtained from the *Usnea* contain but a very small quantity of the acid which yields betorcinol in comparison with the usnic acid present, great difficulty was experienced at first in separating the two, and it was only after

many fruitless trials of fractional precipitation and crystallisation that a process was discovered which permitted the new acid to be isolated with certainty.   The mixture of crude acids extracted from the *Usnea barbata* by lime in the manner described in the earlier part of this paper is collected, stirred up with water strongly acidified with hydrochloric acid, and allowed to stand for an hour or so; this treatment is necessary to completely decompose any lime salt of barbatic acid that may be present.   The crude acids are then collected, washed, and dried at a gentle heat.   After being powdered, 1 part of the mixed acids is digested with 40 parts of hot benzene, which dissolves all but a small quantity of dark-coloured mucilaginous matter.   The filtered benzene solution is then distilled down to about one-sixth of its bulk, and the crystals which separate on cooling are collected and treated three times successively with ether, the first and second times in the cold, whilst the third time the acid is boiled for half an hour with the ether, and allowed to cool (using 10 parts of ether in all).   The ethereal solutions, which contain all the barbatic and some usnic acid, are distilled to dryness, the residue treated in the cold with sufficient ether to dissolve the barbatic acid, and filtered from the residue of usnic acid, which is only sparingly soluble in cold ether; an equal bulk of benzene is then added to the clear ethereal solution, and the mixture is distilled down until all the ether has passed over, and also some of the benzene.   On standing for some time, nearly pure barbatic acid is deposited in the crystalline state, whilst the small quantity of usnic acid present remains in the benzene solution.

When the benzene mother-liquor from which the first crop of mixed usnic and barbatic acids has separated is distilled with water to remove all the benzene, a brown crystalline mass is left, consisting principally of usnic, with some barbatic acid, the latter of which may be separated by treatment with ether, &c., in the manner just described.

The acid as thus obtained is usually slightly coloured, and contains traces of usnic acid, but it may be purified by crystallising it from benzene.   Advantage may also be taken of the facility with which it forms a very sparingly soluble acid potassium salt.   For this purpose, the nearly pure barbatic acid is dissolved in a slight excess of very dilute potash, and carbonic anhydride is passed into the solution; as soon as the excess of potash is saturated, a white curdy precipitate of the acid potassium compound of barbatic acid is produced.   The passing of the carbonic anhydride must then at once be stopped, as otherwise any usnic acid which may be present will also be precipitated. The potassium compound after being collected and washed, is dissolved in cold water by the aid of a few drops of potash solution, and the clear liquid strongly acidified with hydrochloric acid.   The pure bar-

batic acid may then be collected, washed, dried, and crystallised from benzene. It crystallises in colourless needles or long plates, and sometimes in short prisms; these melt at 186°, and at a somewhat higher temperature decompose with evolution of carbonic anhydride, and formation of betorcinol.

The acid dried at 100° was submitted to analysis, with the following results:—

I. 0·142 gram substance gave 0·330 gram carbonic anhydride, and 0·072 gram water.

II. 0·244 gram substance gave 0·567 gram carbonic anhydride, and 0·129 gram water.

		Theory.	I.	II.	Mean.
C_{19}	= 228	63·33	63·38	63·38	63·38
H_{20}	= 20	5·56	5·63	5·87	5·75
O_7	= 112	31·11	—	—	—
	360	100·00			

The analyses of this acid correspond with the formula $C_{19}H_{20}O_7$, which bears the same relation to betorcinol, $C_8H_{10}O_2$, that evernic acid, $C_{17}H_{16}O_7$, does to orcinol, $C_7H_8O_2$, and it is therefore not improbable that this acid is a dimethylevernic acid. As, however, this cannot be considered to be definitely established, we have provisionally named the new acid *barbatic acid*, from the circumstance that it exists along with usnic acid in the *Usnea barbata*. We have also examined *Cladonia rangiferina*, and find that it contains an acid which yields betorcinol when boiled with lime, and is in all probability identical with barbatic acid.

A short time ago Hesse (*Ber.*, **10**, 1326) succeeded in obtaining an acid, which he termed "usnetic acid," (m. p. 172°) by treating an Usnea found on Calisaya bark with lime and dilute alcohol, and although this acid resembles barbatic acid in many of its properties, the much lower melting point, and the higher percentage of carbon (65·08) in the former renders it improbable that they are the same, especially as he states that his acid gave no sublimate when heated. It may be as well, however, to call attention to the well-known fact, that those lichen acids which may be regarded as derived from orcinol, such as lecanoric and evernic acids, yield ethereal salts with great readiness when boiled with alcohol, and that whilst we studiously avoided the use of alcohol in the preparation of barbatic acid, Hesse not only employed dilute alcohol and lime for the extraction of the mixed acids from the lichen, but purified his usnetic acid by dissolving it in hot dilute alcohol, and evaporating the solution.