# XIV.—*Corydaline.  Part VII.  The Constitution of Corydaline.*

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THE results obtained by oxidising corydaline with potassium permanganate and nitric acid have been described in previous communications. In the present paper, some additional experimental details are given, and the whole of the results are discussed in their bearing on the constitution of the alkaloid.

Attention has already been drawn to the resemblance which corydaline bears to berberine (Trans., 1899, **75**, 670). This resemblance is not merely superficial ; the two alkaloids probably differ only in some of the details of their structure. The comparison, however, must be drawn, not between corydaline and berberine, but between corydaline and tetrahydroberberine, or between dehydrocorydaline (which differs from corydaline by 4 atoms of hydrogen) and berberine. The conclusion, based on the chemical investigation, that the two alkaloids are closely related, has been confirmed by an examination of their absorption spectra, which we have found to be almost identical. The spectroscopic results will form the subject of a separate communication.

Corydaline has been analysed in recent years by various chemists, with results practically identical with those which we published in 1892 (Trans., **61**, 244 ; Freund and Josephi, *Annalen*, 1893, **277**, 1 ; Ziegenbein, *Arch. Pharm.*, 1896, **234**, 492 ; Martindale, *ibid.*, 1898, **236**, 214). From the analytical results, we deduced the formula $C_{22}H_{29}O_4N$, and Freund and Josephi the formula $C_{22}H_{27}O_4N$. The latter is probably the correct formula.

By the action of mild oxidising agents such as dilute nitric acid or iodine in alcoholic solution, 4 atoms of hydrogen are removed from the corydaline molecule and an intensely yellow base, dehydrocorydaline, $C_{22}H_{23}O_4N$, is produced, from which, by reduction, an optically inactive modification of the alkaloid may be obtained (Ziegenbein, *loc. cit.* ; E. Schmidt, *Arch. Pharm.*, 1896, **234**, 489 ; Dobbie and Marsden, Trans., 1897, **71**, 657). The ease with which corydaline can be oxidised to dehydrocorydaline, and dehydrocorydaline reduced to corydaline, shows that these two substances are very closely related to one another. It will be remembered that berberine, which is a yellow base like dehydrocorydaline, and tetrahydroberberine, which resembles corydaline in being colourless, can also be readily converted the one into the other.

When corydaline is heated with a concentrated solution of hydrogen iodide, it is converted into a phenolic derivative containing four hydr-

oxyl groups, each molecule of corydaline yielding 4 molecules of methyl iodide. The alkaloid has therefore all its four oxygen atoms present in methoxyl groups (Trans., 1892, **61**, 605).

By oxidising corydaline with potassium permanganate at the boiling point, the chief products of oxidation are hemipinic and *m*-hemipinic acids :
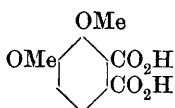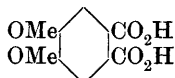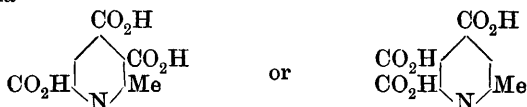


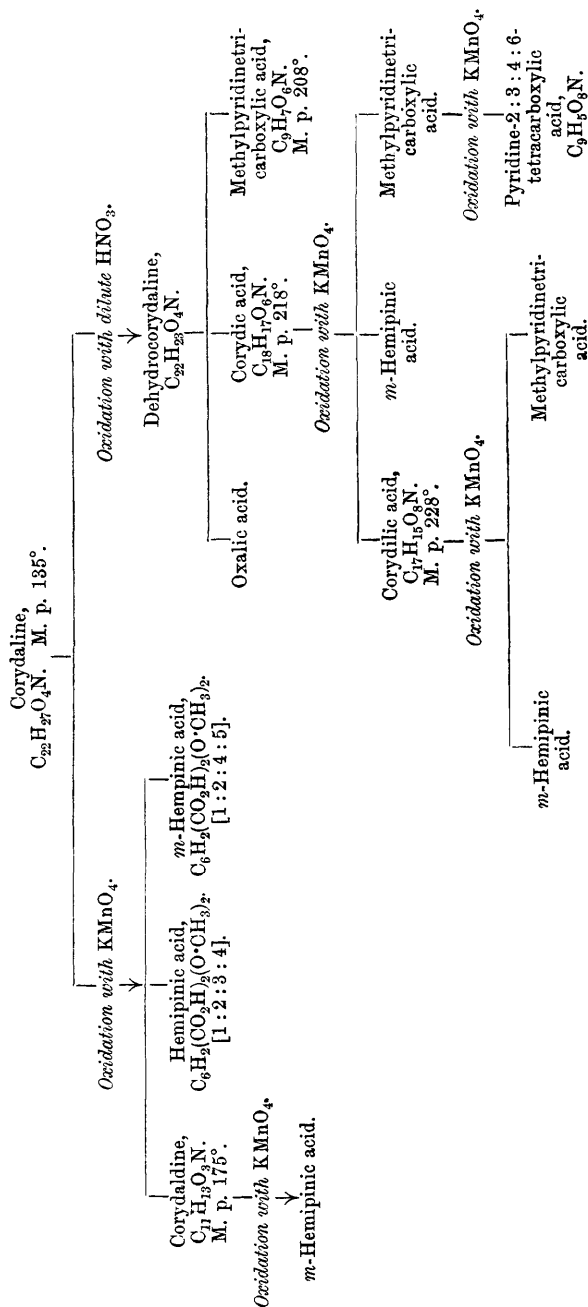Hemipinic acid.                    *m*-Hemipinic acid.

The presence of two benzene nuclei in the molecule is thus established (Trans., 1894, **65**, 57 ; 1897, **71**, 657 ; 1899, **75**, 670). Along with the hemipinic acids, a small quantity of corydaldine is also obtained, the yield of which is considerably increased by conducting the oxidation at the ordinary temperature. Corydaldine has been shown to have the following constitution, $\mathrm{CH_3 \cdot O \atop CH_3 \cdot O}{>}C_6H_2{<}{CO-NH \atop CH_2 \cdot CH_2}$, which proves the presence of an *iso*quinoline nucleus in the alkaloid (Trans., 1899, **75**, 670).

When nitric acid is used as the oxidising agent in place of permanganate, dehydrocorydaline is first produced ; one of the benzene nuclei is next destroyed, and the beautiful, yellow, dibasic corydic acid, $C_{18}H_{17}O_6N + \frac{1}{2}H_2O$, formed. When corydic acid is in turn oxidised with permanganate at the boiling point, it is resolved into an insoluble, colourless, tribasic acid, $C_{17}H_{15}O_8N$, which we propose to term corydilic acid, a methylpyridinetricarboxylic acid, and *m*-hemipinic acid (Dobbie and Marsden, Trans., 1897, **71**, 657). In the present paper, it is shown that the methylpyridinetricarboxylic acid has either the formula

           or           

Corydilic acid, on continued boiling with potassium permanganate, is gradually split up into a mixture of the methylpyridinetricarboxylic acid and *m*-hemipinic acid.

These results afford a basis for the discussion of the constitution of corydic acid. This acid is derived from dehydrocorydaline by the destruction of one of the benzene nuclei, and since it yields *m*-hemipinic acid as one of its oxidation products, the nucleus which is destroyed must be that from which hemipinic acid is derived. The 2-methylpyridinetricarboxylic acid, which is also one of the oxidation products of corydic acid, contains 6 atoms of carbon, exclusive of the

*Oxidation products of corydaline.*

Corydaline,
$C_{22}H_{27}O_4N$.   M. p. 135°.

*Oxidation with KMnO₄.*

Hemipinic acid,
$C_6H_2(CO_2H)_2(O\cdot CH_3)_2$.
[1:2:3:4].

m-Hemipinic acid,
$C_6H_2(CO_2H)_2(O\cdot CH_3)_2$.
[1:2:4:5].

Corydaldine,
$C_{11}H_{13}O_3N$.
M. p. 175°.

*Oxidation with KMnO₄.*

m-Hemipinic acid.

*Oxidation with dilute HNO₃.*

Dehydrocorydaline,
$C_{22}H_{23}O_4N$.

*Oxidation with KMnO₄.*

Corydic acid,
$C_{18}H_{17}O_6N$.
M. p. 218°.

Oxalic acid.

Methylpyridinetri-
carboxylic acid,
$C_9H_7O_6N$.
M. p. 208°.

Corydilic acid,
$C_{17}H_{15}O_8N$.
M. p. 228°.

*Oxidation with KMnO₄.*

m-Hemipinic
acid.

Methylpyridinetri-
carboxylic
acid.

*Oxidation with KMnO₄.*

m-Hemipinic
acid.

Methylpyridinetri-
carboxylic
acid.

*Oxidation with KMnO₄.*

Pyridine-2:3:4:6-
tetracarboxylic
acid,
$C_9H_5O_8N$.

carbon atoms of the carboxyl groups.    It cannot, therefore, be derived from the pyridine ring of the *iso*quinoline nucleus, since the investigation of corydaldine has shown that this pyridine ring has no side chain attached to it.    The 2-methylpyridinetricarboxylic acid represents, therefore, a second ring to which the nitrogen atom, as in the case of berberine, must be common.    We thus arrive at the following formula for corydic acid :
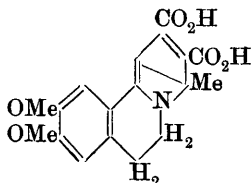


FIG. 1.—Corydic acid.

This formula accounts for the relation of the molecular formula of corydic acid to that of dehydrocorydaline ; for the presence of the two carboxyl groups, and for the formation, on oxidation, of corydilic acid, the 2-methylpyridinetricarboxylic acid, and *m*-hemipinic acid.    The formation of the last-named acid establishes the position of the methoxyl groups.    There is no direct experimental evidence to prove that the positions of the carboxyl groups are those which we have assigned to them, rather than the positions 4 : 5, but we shall presently state our reasons for introducing a direct link between the carbon atoms 2 and 5, which limits the carboxyl groups to the positions shown in the formula.

The formula (2), which we have assigned to dehydrocorydaline follows from that of corydic acid.    Perkin's formula for berberine is placed side by side for comparison (Perkin, Trans., 1889, **55**, 63) :
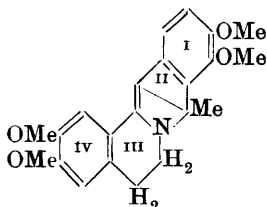


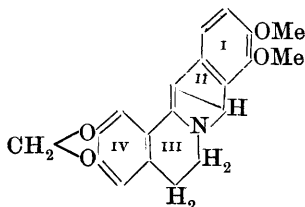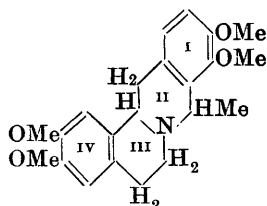FIG. 2.—Dehydrocorydaline.



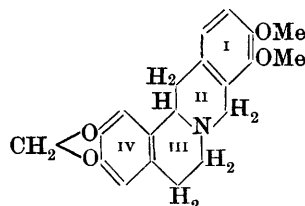FIG. 3.—Berberine.



FIG. 4.—Corydaline.



FIG. 5.—Tetrahydroberberine.

Corydaline differs from dehydrocorydaline in containing four more atoms of hydrogen. Having regard to the great ease with which corydaline can be oxidised to dehydrocorydaline and the latter substance reduced to corydaline, it may be assumed that we have to do here with a group similar to that which exists in certain anthracene and acridine derivatives, and such as Perkin has assumed to be present in berberine. The existence of a double bond between the carbon atoms 5 and 6 and of a direct bond between the carbon atoms 2 and 5 in ring II of the formula for dehydrocorydaline (Fig. 2) would explain the ease with which the one substance passes into the other.

The formula proposed for corydaline, (Fig. 4), explains the reactions and accounts for the formation of all the derivatives of the alkaloid which have been examined. By oxidation, the rings, which for convenience of reference we have numbered I and IV on the diagram, would yield hemipinic and $m$-hemipinic acids respectively, and ring II methylpyridinetricarboxylic acid. Corydaldine, $C_{11}H_{13}O_3N$ (Fig. 6), containing rings III and IV, would result from the oxidation of corydaline in the same way as $\omega$-aminoethylpiperonylcarboxylic anhydride (Fig. 7) results from the oxidation of berberine :
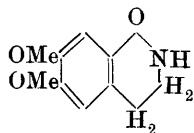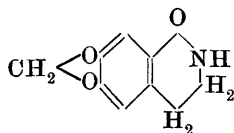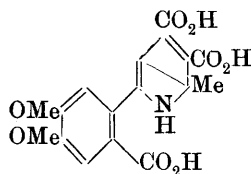
FIG. 6.—Corydaldine.

FIG. 7.—$\omega$-Aminoethyl-piperonyl carboxylic anhydride.

FIG. 8.—Corydilic acid.

Corydic acid (Fig. 1) would be formed by the destruction of ring I, and corydilic acid (Fig. 8) from corydic acid by the oxidation of ring III.

If our formulæ are correct, they incidentally prove that Perkin's formula, which we have quoted, is to be preferred to the alternative formula suggested by him for berberine, in which the carbon atoms 2 and 5 are connected by a double bond, because, on account of the presence of the methyl group in dehydrocorydaline, no double bond is possible between the carbon atoms 2 and 5, and if a double bond existed in berberine in this position the very close resemblance between the two substances would not be satisfactorily explained.

When the decomposition products of berberine are compared with those of corydaline, a close parallelism is observed between them. Both alkaloids yield hemipinic acid as a derivative of ring I. From rings III and IV, ω-aminoethylpiperonylcarboxylic anhydride is obtained in the case of berberine, just as corydaldine is obtained from the corre-

sponding rings of corydaline. Ring IV of berberine yields hydrastic acid :

$$CH_2 <^O_O \bigcirc ^{CO_2H}_{CO_2H} \text{ ,}$$
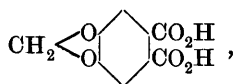
the corresponding decomposition product of corydaline being $m$-hemipinic acid. The oxidation product obtained from ring II is of special interest in the case of both alkaloids. Weidel (*Ber.*, 1879, **12**, 410), by oxidising berberine with strong nitric acid, obtained as chief oxidation product berberonic acid :

$$\begin{array}{c} CO_2H \\ \bigcirc {}^{CO_2H} \\ CO_2H \quad N \end{array}$$
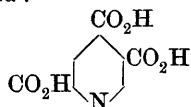
We have also obtained the same acid from a new derivative of berberine, which is described in another communication. In discussing the constitution of berberine, Perkin does not take into account the occurrence of berberonic acid amongst its decomposition products. It is clear, however, that its occurrence affords important confirmation of the correctness of his formula, since it would result from ring II by the oxidation of the attached rings I and III, but could not result from ring III, which would yield cinchomeronic acid. There is thus direct evidence in the case of berberine, as well as in the case of corydaline, of the existence of a fourth closed chain in the molecule of the alkaloid. It is remarkable that both in the case of berberine and of corydaline, ring II is the more stable of the rings to which the nitrogen atom is common. From neither alkaloid has any acid corresponding to ring III been obtained. A further instance of the comparative ease with which ring III in corydaline is broken up is afforded by the formation of corydilic acid from corydic acid.

Whilst our formula for corydaline satisfactorily accounts for the similarity between this alkaloid and berberine, it also explains the absence from amongst the decomposition products of corydaline of derivatives corresponding to berberal, $C_{20}H_{17}O_7N$, berberilic acid, $C_{20}H_{19}O_9N$, oxyberberine, $C_{20}H_{17}O_5N$, &c., all of which have an atom of oxygen attached to the carbon atom 2 of ring II. On account of the presence of the methyl group in combination with the corresponding carbon atom in corydaline, it would be impossible for an oxygen atom to occupy this position in similar derivatives of corydaline. On the other hand, the formation of corydic acid from corydaline suggested that it might be possible to obtain a similar acid from berberine. We show in a separate communication that by the oxidation of berberine with dilute nitric acid such an acid is readily produced.

One further point remains to be dealt with, the stability of the

methyl group in ring II. With the exception of the pyridinetetra-carboxylic acid (see below), all the oxidation products in which ring II is present, so far examined by us, contain this group. This is not remarkable when it is recalled that prolonged treatment with potassium permanganate in alkaline solution is required for the preparation of 2 : 3 : 4 : 6-pyridinetetracarboxylic acid, either from 2 : 4 : 6-trimethylquinolinecarboxylic acid (Michael, *Annalen*, 1884, **225**, 121) or from flavinol (Fischer and Täuber, *Ber.*, 1884, **17**, 2925). When, however, large quantities of corydaline are oxidised it might be expected that small quantities of a monocarboxylic acid should be obtained. We believe that we have had such an acid in our hands. In our earlier experiments, in which several hundred grams of cory-daline were oxidised with potassium permanganate at the boiling point, a small quantity (about 1·5 grams) of a colourless nitro-genous acid which crystallised in tufts of delicate, silky needles and melted sharply at 156° (Trans., 1895, **67**, 17) was obtained. We were only able to make a slight examination of this substance. A nitrogen determination gave a result agreeing with that required by the formula $C_{21}H_{24}O_4N\cdot CO_2H$ (nitrogen, found, 3·55 ; calculated, 3·50 per cent.). A determination of the methoxyl groups by Zeisel's method showed that the four methoxyl groups present in corydaline were also present in this acid, and the analysis of a silver salt showed that the acid possessed a high molecular weight.

We leave over for the present the full discussion of the relation be-tween the constitution and the colour of some of the corydaline deriva-tives. The further investigation of the products obtained by the oxidation of corydic acid with potassium permanganate at the ordinary temperature, described below, promises to throw further light on this question. It may, however, be mentioned now that the colour seems to depend on the presence of rings II and III, since only the derivatives which contain these rings are coloured.

<div align="center">EXPERIMENTAL.</div>

The oxidation of corydic acid with potassium permanganate (Dobbie and Marsden, Trans., 1897, **71**, 657) has been repeated on a larger scale, and the results already published have been confirmed; the pro-ducts of oxidation are corydilic acid, $C_{12}H_6N(O\cdot CH_3)_2(CO_2H)_3$, a methyl-pyridinetricarboxylic acid, $C_9H_7O_6N$, and *m*-hemipinic acid.

### *Examination of the Methylpyridinetricarboxylic Acid.*

This acid can be obtained, not only by the oxidation of corydic acid with permanganate, but also by the oxidation of corydaline with strong nitric acid in the manner followed by Weidel in the preparation of

berberonic acid from berberine (*Ber.*, 1879, **12**, 410). The yield by this method is, however, unsatisfactory. The analysis and general properties of this acid have already been given (Trans., 1897, **71**, 657). The copper salt, obtained by adding copper acetate to a neutral solution of the acid is blue in colour, and not yellow, as previously stated. This acid is undoubtedly a methylpyridinetricarboxylic acid, as is shown by its analysis and the analysis of its salts, but it is not identical with any of the known acids of this constitution. Freund and Josephi (*Annalen*, 1893, **277**, 10), from the similarity in behaviour of methyl-corydaline and hydrohydrastinine, inferred that corydaline, like hydrastine, contains a methyl group attached to the nitrogen atom. By heating the acid with sodium amalgam, we failed to obtain any evidence of the formation of methylamine, and concluded from this that the methyl group was not attached to the nitrogen atom, as Freund and Josephi suggested. This conclusion was confirmed by the investigation of corydaldine which has no methyl group attached to its nitrogen atom. Further, Herzig and Meyer (*Monatsh.*, 1897, **18**, 385) showed that there are only four methyl groups altogether in corydaline which can be split off by the action of hydrogen iodide, and since we have shown that there are four methoxyl groups, there can be no methyl in union with the nitrogen atom.

The methylpyridinetricarboxylic acid is an exceedingly stable substance and can be boiled for some time with a dilute solution of potassium permanganate without undergoing any appreciable amount of oxidation. When, however, it is dissolved in excess of potassium hydroxide and a solution of potassium permanganate added, it slowly undergoes oxidation, the operation requiring from eight to nine days at the temperature of the water-bath for completion. Two experiments were made, one with 3 grams and the other with 2 grams of the acid. The excess of permanganate was reduced, the alkaline solution filtered, neutralised with nitric acid and treated with calcium nitrate to remove a small quantity of oxalic acid which had been formed. After filtering from the precipitated calcium oxalate, the solution was treated with lead acetate and the precipitate filtered off and washed. On decomposing this precipitate with hydrogen sulphide, a strongly acid solution was obtained, which on evaporation yielded a residue very soluble in water and insoluble in alcohol. This residue contained inorganic matter. Its solution was found to give an insoluble salt with copper acetate which remained undissolved even when heated with acetic acid. It was therefore precipitated with copper acetate with the object of removing the inorganic matter, the blue copper precipitate filtered, well washed first with strong acetic acid and then with water, and decomposed with hydrogen sulphide. The acid obtained from the filtrate was still found, however, to be contaminated with a

small quantity of inorganic matter, from which by reprecipitation we were unable completely to purify it. We were thus unable to get an accurate determination of the melting point or a specimen of the acid in a sufficiently pure state for analysis.

So far as the qualitative examination was concerned, the acid showed all the properties and gave all the reactions of $2:3:4:6$-pyridinetetracarboxylic acid obtained by Michael (*Annalen*, 1884, **225**, 121) from $2:4:6$-trimethylquinolinecarboxylic acid, and by Fischer and Täuber (*Ber.*, 1884, **17**, 2925) from flavinol. It agreed with this acid in being very easily soluble in water and very sparingly so in alcohol; in giving with ferrous sulphate a dark cherry-red colour, and with ferric chloride a yellow precipitate. With calcium chloride, the free acid gave no precipitate, but with barium chloride a copious white precipitate. The copper salt, as already mentioned, was insoluble even in boiling acetic acid. The silver salt on ignition decomposed suddenly, swelling up and filling the crucible with reduced silver which resembled a mass of tea leaves, exactly as described both by Michael and by Fischer and Täuber.

Further information as to the identity of the oxidation product of the methylpyridinetricarboxylic acid was obtained by boiling it with strong acetic acid. When $2:3:4:5$-pyridinetetracarboxylic acid is heated at $160°$, $3:4:5$-pyridinetricarboxylic acid is obtained, and $2:3:5:6$-pyridinetetracarboxylic acid decomposes at $150°$ into $3:5$-pyridinedicarboxylic acid. In both cases, the carboxyl groups which are eliminated are adjacent to the nitrogen atom. It was therefore to be anticipated that, under similar treatment, the tetracarboxylic acid obtained by the oxidation of the methylpyridinetricarboxylic acid would yield cinchomeronic acid by the elimination of the carboxyl groups 2 and 6, if we had rightly identified it. As a matter of fact, we found that cinchomeronic acid was produced by boiling with acetic acid, and identified without difficulty. The tetracarboxylic acid was boiled for some time with strong acetic acid and the solution evaporated to dryness. The residue was insoluble in cold and only dissolved with difficulty in hot water. The aqueous solution deposited the acid on cooling in colourless, prismatic crystals, which after purification by recrystallisation melted at $260°$. The acid was insoluble in chloroform, almost insoluble in ether, and only very slightly soluble in alcohol. It gave no reaction with ferrous sulphate or with ferric chloride. Silver nitrate and lead acetate gave white precipitates when added to its aqueous solution. Calcium and barium chlorides gave no precipitate even on the addition of ammonia. The copper salt was more soluble in cold than in hot water and was precipitated by warming a cold aqueous solution; the precipitate redissolved again on cooling. The last reaction which is characteristic of cinchomeronic (pyridine-3 : 4-

dicarboxylic) acid, taken in conjunction with the melting point, solubility, and the reactions above described, left no doubt as to the identity of the acid which we had obtained.  Cinchomeronic acid might be formed either from pyridine-2 : 3 : 4 : 5-tetracarboxylic acid or -2 : 3 : 4 : 6-tetracarboxylic acid, by the elimination of the carboxyl groups 2 and 5 or 2 and 6 respectively.  It could not be derived from the 2 : 3 : 5 : 6-acid.  The tetracarboxylic acid which we obtained not only agreed in every respect with the 2 : 3 : 4 : 6-acid, but differed from the 2 : 3 : 4 : 5-isomeride in giving no precipitate with zinc sulphate in neutral solution.  The difficulty of removing inorganic matter from the tetracarboxylic acid which we obtained is characteristic of the 2 : 3 : 4 : 6-acid.

The methylpyridinetricarboxylic acid from corydaline must therefore have one or other of the following formulæ (Figs. 9 and 10) :
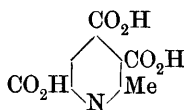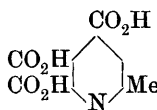


FIG. 9.                           FIG. 10.

The position of one of the carboxyl groups must be adjacent to the nitrogen atom, since it follows that, when the *iso*quinoline nucleus is destroyed in the formation of methylpyridinetricarboxylic acid, the carbon atom 1, next to the nitrogen atom, must have a carboxyl group attached to it representing carbon atom 9, which is common to the benzene and pyridine rings of the *iso*quinoline nucleus (see Fig. 2).

The two remaining carboxyl groups must represent one of the rings of the corydaline molecule which has been destroyed by oxidation and must therefore occupy positions adjacent to one another.

The position of the methyl group is fixed by the following considerations.  It cannot occupy the position 4, because, in that case, the only arrangement possible would be $[CH_3 : (CO_2H)_3 = 4 : 2 : 5 : 6]$.  This acid is known, and is not identical with the acid under investigation.  The position 3 is likewise excluded, since, in that case, the tetracarboxylic acid obtained on oxidation would be $[(CO_2H)_4 = 2 : 3 : 4 : 5$ or $2 : 3 : 5 : 6]$, having regard to the fact that two of the carboxyl radicles represent a ring destroyed by oxidation, and must therefore be adjacent to one another.  By similar reasoning, position 5 is excluded ; the methyl group must therefore occupy the position which is assigned to it in the formula.  It is shown earlier in this paper that the methyltricarboxylic acid is probably $[CH_3 : (CO_2H)_3 = 2 : 3 : 4 : 6]$, but we have no direct experimental evidence which enables us to decide between this formula and $[CH_3 : (CO_2H)_3 = 2 : 4 : 5 : 6]$.

*Examination of Corydilic Acid*, $C_{12}H_6N(O\cdot CH_3)_2(CO_2H)_3$.

The analysis and description of this acid have already been published (Dobbie and Marsden, Trans., 1897, **71**, 657). Corydilic acid is obtained along with *m*-hemipinic and 2-methylpyridinetricarboxylic acids when corydic acid is oxidised with potassium permanganate at the boiling point. From the former it is easily separated, but it is more difficult than we at first supposed to free it entirely from the latter. Repeated recrystallisations are necessary to effect complete purification. This explains why the specimens which we analysed gave results slightly lower than the theoretical numbers. In addition to the reactions already described for this acid, we have made the following observations. Its aqueous solution gives no reaction with ferrous sulphate or ferric chloride, and no precipitate with barium chloride, calcium chloride, cadmium chloride, or copper acetate, even in presence of ammonia. From alkaline solution, corydilic acid is precipitated by the addition of excess of strong hydrochloric acid. If, however, the alkaline solution is exactly neutralised with dilute hydrochloric acid, no precipitation takes place, and a slight excess of hydrochloric acid may be added without causing the acid to separate. The solution so obtained has a faint green colour, and on standing, sometimes deposits pale, greenish-yellow crystals, which apparently consist of a hydrochloride of the acid. The crystals are very unstable, and decompose on the addition of water, leaving a residue of corydilic acid. Owing to its instability, we were unable to get this substance in a fit condition for analysis.

*Oxidation of Corydilic Acid with Potassium Permanganate.*

Corydilic acid is very stable, but on heating for several hours with potassium permanganate in alkaline solution it gradually undergoes oxidation. The acid employed was carefully purified from every trace of the methylpyridinetricarboxylic acid. About 6 grams of the pure acid were oxidised in quantities of 2 grams at a time. After removal of the manganese oxides, the alkaline solution was concentrated and precipitated with lead acetate. This precipitate, on decomposition with sulphuretted hydrogen, yielded a mixture of acids, which, on separation by fractional crystallisation, was found to consist of undecomposed corydilic acid, *m*-hemipinic acid, and the 2-methylpyridinetricarboxylic acid. The two latter acids were compared with specimens prepared directly from corydaline and found to agree in every respect.

It has already been shown that corydilic acid is tribasic, and that it contains two methoxyl groups. The following formula explains its

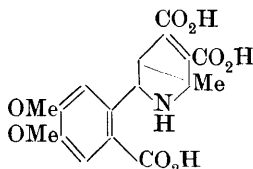formation from corydic acid as well as all the facts connected with its decomposition products:



FIG. 11.

### *Oxidation of Corydic Acid with Potassium Permanganate at the Ordinary Temperature.*

Corydic acid was suspended in cold water and about twice its weight of potassium permanganate added in aqueous solution in small quantities at a time.    The alkaline solution was precipitated with silver nitrate and the precipitate decomposed with sulphuretted hydrogen in the usual way.    The filtrate, on evaporation, deposited a bright yellow acid which, after purification by repeated recrystallisation from water, melted at 212—215°.    This acid is anhydrous, and differs from corydic acid in being more soluble in cold water and in giving a precipitate with silver nitrate in neutral solution.    It was dried at 100° and analysed, with the following results :

0·2503 gave 0·5506 $CO_2$ and 0·1207 $H_2O$.    C = 59·99 ; H = 5·36.
0·2086    ,,    0·4621 $CO_2$    ,,    0·0990 $H_2O$.    C = 60·42 ; H = 5·27.
0·2748    ,,    10·6 c.c. nitrogen at 16° and 758 mm.    N = 4·55.
   $C_{16}H_{17}O_6N$ requires C = 60·18 ; H = 5·33 ; N = 4·39 per cent.

This acid is dibasic and forms both a normal and an acid silver salt. Its precise relation to corydic acid is still under investigation.

We have limited our investigation of corydaline derivatives and decomposition products to those substances which seemed most important for the determination of the constitution of the alkaloid, as the expense entailed has been very heavy.    For the same reason, our account of some of the substances actually described is less complete than we could have wished.    We hope in a future paper to supplement the information on some of the more important points which require fuller elucidation.

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