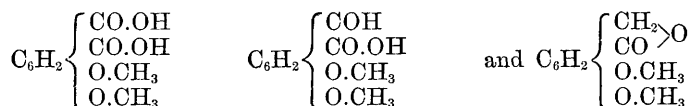281

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XIV.—*On Narcotine, Cotarnine, and Hydrocotarnine.*   (Part III.)

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In Part II (Appendix) of these researches, reasons have been adduced for the ascription to hemipinic acid, opianic acid, and meconin of the respective formulæ :—
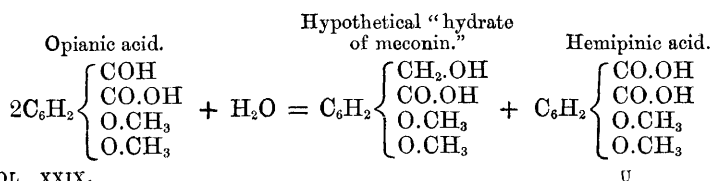
$$C_6H_2\begin{cases}CO.OH\\CO.OH\\O.CH_3\\O.CH_3\end{cases} \qquad C_6H_2\begin{cases}COH\\CO.OH\\O.CH_3\\O.CH_3\end{cases} \qquad \text{and } C_6H_2\begin{cases}CH_2\\CO\end{cases}\!\!>\!O \\ \begin{cases}O.CH_3\\O.CH_3\end{cases}$$

The experiments described below were made with the view of obtaining further evidence on these points, and completely corroborate these formulæ.
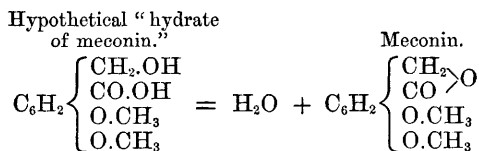
§ 1. *Action of heated Caustic Potash on Opianic Acid.*

Opianic acid was prepared by oxidising narcotine with sulphuric acid and manganese dioxide according to the directions of Matthiessen and Foster (this Journal, 1863, 342) ; the resulting acid was several times recrystallised from water, and was then dissolved in very concentrated caustic potash solution containing about three times as much solid potash as the opianic acid used, and the whole gently boiled down, with constant stirring until quite thick and pasty ; in this way the whole of the opianic acid was converted into meconin and hemipinic acid, as stated by Matthiessen and Foster (*loc. cit.*), in accordance with the reaction :—

$$2C_{10}H_{10}O_5 = C_{10}H_{10}O_4 + C_{10}H_{10}O_6;$$

or assuming the correctness of the above three structural formulæ, in accordance with the pair of reactions :—

Opianic acid.   Hypothetical "hydrate of meconin."   Hemipinic acid.

$$2C_6H_2\begin{cases}COH\\CO.OH\\O.CH_3\\O.CH_3\end{cases} + H_2O = C_6H_2\begin{cases}CH_2.OH\\CO.OH\\O.CH_3\\O.CH_3\end{cases} + C_6H_2\begin{cases}CO.OH\\CO.OH\\O.CH_3\\O.CH_3\end{cases}$$

Hypothetical " hydrate of meconin."

Meconin.

$$C_6H_2\begin{cases} CH_2.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} = H_2O + C_6H_2\begin{cases} CH_2 \\ CO \end{cases}O \\ O.CH_3 \\ O.CH_3 \end{cases}$$

The resulting meconin and hemipinic acid were separated as directed by Matthiessen and Foster; after purification by frequent crystallisation, the pure meconin melted in a capillary tube at $102°$—$102·5°$, but fused below boiling water; $0·2860$ gram of meconin gave $0·6480$ CO_2 and $0·1380$ H_2O.

	Calculated.		Found.
C_{10}...............	120	61·86	61·79
H_{10}	10	5·15	5·36
O_4...............	64	32·99	—
$C_{10}H_{10}O_4$	194	100·00	

The crude hemipinic acid was found to contain, after conversion into lead salt and decomposition by sulphuretted hydrogen, a small quantity of another acid which struck a beautiful blue tint with ferric chloride; this substance was finally traced to the further action of the fused potash on the meconin first formed whereby methyl-normeconin, $C_9H_8O_4$ is formed (*vide* § 8); to free the hemipinic acid completely from this substance, many crystallisations are necessary. By boiling the mixture of acids with dilute sulphuric acid and potassium dichromate solution the methyl normeconin is wholly oxidised together with some hemipinic acid; on agitating the cooled liquid with ether and evaporation of the extract, pure hemipinic acid separates in crystals containing $C_{10}H_{10}O_6$. 2 H_2O; after drying on the water-bath these first melt completely at $181°$—$182°$ (corrected), giving off water and becoming partially converted into hemipinic anhydride in so doing. An acid free from methyl-normeconin may be also obtained by well washing the ammonia salt dried at $100°$ with alcohol, and then acidulating and extracting with ether.

The silver salt gave these numbers :—

$0·6475$ gram gave $0·3190$ Ag   Ag $= 49·26$ per cent.

The formula $C_{10}H_8Ag_2O_6$ requires $49·09$ per cent.

The anhydride prepared by heating the acid to about $180°$ for an hour forms, after crystallisation from absolute alcohol, light shining needles melting at $166°$—$167°$ (corrected) : it is noticeable that hemipinic acid purified only by several recrystallisations and still containing a small quantity of methyl-normeconin, melts $10°$ to $15°$ lower than the

pure acid, and furnishes an anhydride which, even after crystallisation from absolute alcohol, strikes a faint blue with ferric chloride and melts at little above 160°.
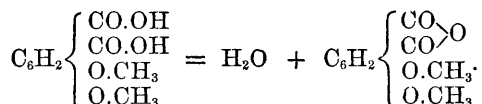
The hemipinic acid prepared and purified as above was employed in the experiments mentioned below ; it may be noticed that the above results fully corroborate the statements of Matthiessen and Foster as to the action of potash on opianic acid; on the other hand, Liechti was unable (*Annalen der Chemie, Suppl.*, vii, 129) to obtain hemipinic acid from opianic acid by heating with caustic potash of sp. gr. 1·38° until foaming up almost ceased ; or rather, he did not succeed in isolating hemipinic acid from the syrupy extract containing meconin and methyl-normeconin obtained by acidulating the mass and treating with ether.

The hemipinic anhydride obtained gave the following numbers :—

0·2380 gram gave 0·4990 CO_2 and 0·0830 H_2O.

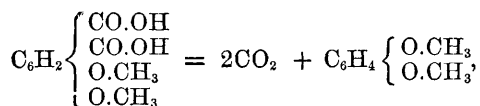|	Calculated.		Found.
C_{10}	120	57·69	57·18
H_8	8	3·85	3·88
O_5	80	38·46	—
$C_{10}H_8O_5$	208	100·00	

and hence was formed, as Matthiessen and Wright first found (*Phil. Trans.*, 1869, 667), in virtue of the reaction,

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} = H_2O + C_6H_2 \begin{cases} CO \\ CO \end{cases} O \\ \begin{cases} O.CH_3 \\ O.CH_3 \end{cases}$$

The readiness with which hemipinic acid forms an anhydride by dehydration probably indicates that it is a phthalic acid derivative, *i.e.*, that the two carboxyl groups are in the 1·2 portion with respect to one another.

§ 2. *Action of heated Soda-lime on Sodium Hemipinate.*

If hemipinic acid be a dimethoxyl-dicarboxyl-benzene, it is possible that by treating its salts with alkalis or alkaline earths the reaction,

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} = 2CO_2 + C_6H_4 \begin{cases} O.CH_3 \\ O.CH_3 \end{cases}$$

might take place, the dimethylic ether of a dioxybenzene resulting. On heating an intimate mixture of dry sodium hemipinate with twice its weight of soda-lime in a retort, a distillate was obtained consisting of an aqueous layer and a heavy oil; on rectification the latter boiled

almost wholly between $200°$ and $210°$, and after one or two distillations the larger portion boiled wholly between $204°$ and $206°$ (corrected), and gave the following numbers:—

0·2820 gram gave 0·7160 CO_2 and 0·1860 H_2O.

	Calculated.		Found.
C_8	96	69·56	69·24
H_{10}	10	7·25	7·33
O_2	32	23·19	—
$C_8H_{10}O_2$	138	100·00	

Hence the product had at any rate the percentage composition of a dimethyl-dioxybenzene: it possessed an agreeable creosote-like odour, was almost insoluble in alkalis and in water, but readily dissolved in alcohol, the solution giving no coloration with ferric chloride; on boiling with neutral silver nitrate a slight reduction ensued; with ammoniacal silver nitrate, a copious reduction: on warming with a few drops of strong nitric acid a liquid was obtained, from which a magnificently crystalline nitro-derivative separated by spontaneous evaporation in a warm place. In all these respects it exactly corresponded with the *dimethyl-pyrocatechin* of Marasse (*Annalen der Chemie*, clii, 59) boiling at $205°$—$206°$.

In order to see if the product were really dimethyl-pyrocatechin, a known weight was heated with a large excess of strong hydriodic acid and a little amorphous phosphorus, the vapours evolved being passed first through a well cooled condenser to prevent the passage of the original oil or of pyrocatechin vapour, and finally through a combustion-tube filled with lead chromate. Methyl iodide was readily evolved at $100°$. The vapours still retained in the flask were swept out after three hours by aspirating a little air freed from carbonic acid, and the residue in the flask was then heated to boiling for half an hour, after which the vapours were again swept out by a current of air. This process was again repeated, the following numbers being finally obtained, 0·7910 gram of substance being used:—

	Total CO_2 collected. gram.	Percentage of carbon evolved as methyl iodide.
After 3 hours, at $100°$	0·4570	15·76
„ $3\frac{1}{2}$ „	0·4810	16·58
„ ditto, and boiling for $\frac{1}{2}$ an hour....	0·4930	17·00
„ „ „ 1 hour	0·5030	17·34
Calculated for dimethyl pyrocatechin....	0·5044	17·39

Probably the number finally obtained is exact only through the mutual compensation of several small errors, the loss of carbon from

incomplete decomposition being just about equal to the gain from the carrying over to the combustion-tube of traces of vapours other than methyl iodide. After the conclusion of the experiment a few milligrams of pyrocatechin were found condensed in the tube of the condenser.

The pyrocatechin thus produced by the action of hydriodic acid on the hemipinic acid product was extracted by diluting the acid liquid with water, agitating with ether, distilling off the ether and dissolving the residue in water, precipitating by lead acetate, decomposing the precipitate with sulphuretted hydrogen, evaporating, and crystallising the residue from boiling benzene. The crystals thus obtained melted at $101°$—$102°$ when perfectly dry, but at a little lower temperature if exposed to the air for a short time so as to take up hygroscopic moisture.

[Fittig and Remsen have shown (*Annalen der Chemie*, clix, 129) that *pure* pyrocatechin crystallised from toluene melts at $102°$, or some $10°$ lower than the temperature usually stated as its melting point in text-books. Lautemann also found (*ibid*, 120, 311), that sublimed pyrocatechin fused at $100°$, uncorrected; whilst recently Tiemann has corroborated the results of Fittig and Remsen (*Deut. Chem. Ges. Ber.*, viii, 509).] The following numbers were obtained :—

$0·2870$ gram gave $0·6880$ CO_2 and $0·1470$ H_2O.

	Calculated.		Found.
C_6.	72	65·45	65·37
H_6	6	5·45	5·69
O_2.	32	29·10	—
$C_6H_4(OH)_2$	110	100·00	

With ferric chloride the substance gave the usual pyrocatechin reaction. With reference to this it may be noticed that the tint assumed by a solution of pyrocatechin to which ferric chloride and ammonia have been added varies somewhat with the amounts of these reagents added; with only a small amount of ferric chloride a dirtier green coloration is produced than with protocatechuic acid, but on addition of ammonia the same dirty purplish red is produced in each case; whilst with larger quantities of ferric chloride, pyrocatechin gives, on addition of ammonia, a shade much more inclining to violet than that given by pyrocatechuic acid. Tiemann and Haarmann state (*Deut. Chem. Ges. Ber.*, vii, 618) that an aqueous solution of pyrocatechin gives with ferric chloride a dark green *precipitate*, and one of pyrocatechuic acid a dark green *coloration*, the former becoming a turbid violet and the latter a clear red on further addition of ammonia. This distinction is marked only in comparatively strong solutions, a

dilute pyrocatechin solution giving no visible precipitate with ferric chloride.

The above results clearly establish that the oily product of the distillation of hemipinate of sodium with soda lime is dimethyl-pyrocatechin. The methyl iodide evolved by the action of nydriodic acid boiled between 40° and 45°. The yield of dimethyl-pyrocatechin was only about 40 per cent. of the calculated quantity, but it was of considerable purity.

It may be noticed that Koelle prepared dimethyl-pyrocatechin from dimethyl pyrocatechuic acid by distillation with lime (*Annalen der Chemie*, clix, 230). His product, however, boiled at 210°—215°, and gave a deep green coloration with ferric chloride, from which it seems probable that it contains either some pyrocatechin or some monomethyl pyrocatechin (guiacol) ; the raised boiling point would rather indicate the former, since guiacol boils at 200° and pyrocatechin at 245° ; moreover, Tiemann has already pointed out (*Deut. Chem. Ges. Ber.*, viii, 509), that in all probability Koelle's dimethyl protocatechuic acid contains some of a monomethyl acid (vanillic acid), as it had the odour of vanilla, which is not possessed by pure dimethyl-protocatechuic acid.

§ 3. *Action of Melting Caustic Potash on Hemipinic Acid.*

When hemipinic acid is heated with caustic potash to 240°, the following reaction takes place :—

$$C_{10}H_{10}O_6 + 3KOH = K_2CO_3 + 2CH_4O + C_7H_5O_4.K,$$
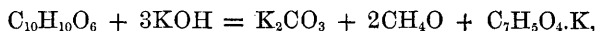
the methylic alcohol being probably further altered whilst still in the nascent state. The resulting potassium salt is that of *protocatechuic acid*. Powdered caustic potash is mixed with a few drops of water and heated to fusion (about 200°—220°). Hemipinic acid (one-sixth or one-seventh of the weight of the potash) is then dropped in with continual stirring ; after 10—15 minutes a thermometer immersed in the fused mass rises to 235°—240°. The heat is then discontinued, and, after cooling, the fused mass is dissolved in hydrochloric acid and the solution agitated with ether. The ethereal extract obtained on evaporation yields, after solution in water and digestion with animal charcoal, crystals of nearly pure protocatechuic acid. After recrystallisation from water, these gave the following numbers :—

> 0·5335 gram lost at 100° 0 0575 = 10·78 per cent.
> Calculated for $C_7H_6O_4,H_2O \ldots = 10·47$,,
> 0·2710 gram gave 0·5420 CO_2 and 0·1000 H_2O.

	Calculated.		Found.
C_7	84	54·54	54·55
H_6	6	3·90	4·10
O_4	64	41·56	—
$C_7H_6O_4$	154	100·00	

The acid dried at 100° melted at 198°—199° (corrected), and gave with ferric chloride and ammonia the characteristic protocatechuic reaction.

From the results described in this and the previous section it follows that hemipinic acid is a *carboxyl-dimethyl protocatechuic acid*,

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases}.$$ Hence it must have one of the two structures—
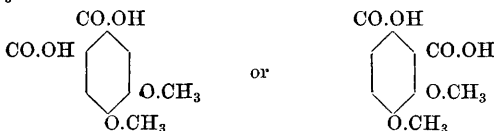

since the two CO.OH groups are presumably in the 1 . 2 positions with respect to one another, and since protocatechuic acid must be regarded as a 1 . 3 . 4 benzene derivative (the CO.OH group being in the position 1), inasmuch as it can be formed by hydroxylating either oxybenzoic acid (1 . 3) or paroxybenzoic acid (1 . 4).—Barth.

§ 4. *Action of Heated Soda-lime on Sodium Opianate.*

It results from the composition of hemipinic acid, and the fact that opianic acid gives rise to that body by addition of oxygen, that

opianic acid must be represented by the formula $C_6H_2 \begin{cases} COH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases}$,

whence it seems not improbable that under suitable conditions it might undergo the reaction—

$$C_{10}H_{10}O_5 = CO_2 + C_6H_3 \begin{cases} COH \\ O.CH_3, \\ O.CH_3 \end{cases}$$
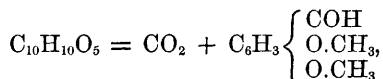
thus giving rise to the dimethylic ether of the aldehyde of either proto-catechuic acid or one of its isomerides; and in point of fact this is found to be the case, the yield, however, of the product being but small, owing to the tendency of the opianic acid to form meconin and hemipinic acid, the former of which is charred by the heat, whilst the latter gives rise (as shown above) to dimethyl-pyrocatechin. Con-

trary to expectation, a better yield was obtained by heating sodium opianate with soda-lime than by heating barium opianate with barium hydrate. The opianate and the soda-lime should be thoroughly dried at 130°—140°, intimately mixed, and gently heated in a retort. The distillate, like that from hemipinic acid, consisted of an aqueous liquid with a heavy oil at the bottom. In one experiment the oil almost all boiled above 260°, but in several others the greater part boiled below 200°, only small quantities being obtained boiling above 260°. The portions boiling above 260° yielded on fractional distillation a distillate at 280°—285° (not corrected), of which the larger portion boiled at 283°. This portion was a heavy viscid oil, of odour recalling that of vanilla, though different therefrom. On placing in a freezing mixture, it solidified to a crystalline mass, which (after keeping in the solid state for several weeks) melted at 41° (corrected). The following numbers were obtained :—

0·2455 gram gave 0·5840 CO_2 and 0·1410 H_2O.

	Calculated.		Found.
C_9	108	65·06	64·87
H_{10}	10	6·02	6·38
O_3	48	28·92	—
$C_9H_{10}O_3$	166	100·00	

The ethereal solution of this substance when shaken up with sodium hydrogen sulphite, was almost wholly deprived of the dissolved matter, the ether leaving only faint traces of it on evaporation. On decomposing the sulphite solution with sulphuric acid, the substance was set free unaltered and was readily dissolved out by ether. On treating it with strong nitric acid and allowing the product to evaporate spontaneously in a warm place, a well crystallised nitro-derivative was formed. In all these properties, with the sole exception of the melting point, this product exactly agrees with the methyl-vanillin, or dimethyl-protocatechuic aldehyde, recently obtained by Tiemann by methylating vanillin (*Deut. Chem. Ges. Ber.*, viii, 1123). Tiemann's product boiled at about 285° (uncorrected), and distilled as a yellowish viscid oil solidifying in a freezing mixture to a crystalline mass melting at 15°—20°. That the product from opianic acid really is methyl vanillin is clearly proved by the following experiments :—

(A.) *Oxidation of Methyl-vanillin.*

Methyl-vanillin from opianic acid was boiled in a flask with an inverted condenser with about 1000 parts of water containing a little sulphuric acid, and potassium dichromate solution was gradually

added; after an hour a considerable amount of reduction had taken place; the acid liquid was treated with ether and the ethereal solution shaken up with ammonia; the ammoniacal solution yielded to ether, after acidification, an acid sparingly soluble in cold water, more readily in hot water, crystallising therefrom in shining small prisms on cooling; the melting point of this acid was found to be 171°. [Koelle, *Annalen der Chemie*, 159—240, states that dimethyl protocatechuic acid synthesized from protocatechuic acid, melts at 170°—171°; Graebe and Borgmann, *ibid*, 158—282, give 179°—180°; and Church (this Journal), 1875, 113, gives 179·5° as the melting point of dimethyl-protocatechuic acid obtained by the oxidation of methyl eugenol; Tiemann gives 174°, *uncorrected*, as the melting point of di-methyl-protocatechuic acid from methyl-vanillin, methyl-creosol, &c.] With ferric chloride it gave no coloration, but after fusion at 210°— 220° with caustic potash, it formed an acid readily dissolved out by ether (after acidification of the solution of the fused mass), and giving with ferric chloride the well-known protocatechuic acid reaction, viz., dark-green coloration becoming dark-red, or purplish-red on further addition of ammonia. Hence, although the quantity of substance was insufficient for analysis, there can be no doubt that it was dimethyl-protocatechuic acid formed from the corresponding aldehyde (methyl-vanillin) by oxidation.

(B.) *Action of Hydrochloric Acid on Methyl-vanillin.*

Methyl-vanillin was heated with a large excess of strong hydro-chloric acid to boiling for ten hours, an inverted condenser being attached. Methyl chloride was eliminated, and a dark tarry mass separated on cooling: this was dissolved in ether and the solution agitated with potash; and the dark-coloured alkaline liquid was sepa-rated, acidified with hydrochloric acid, and exhausted with fresh ether. On evaporating down the ethereal solution, an oily residue was left, which on standing became crystalline; the crystals, freed from a little adhering oily matter by pressure in blotting-paper, melted at close upon 80°, smelt and tasted exactly like vanilla, dissolved very sparingly in cold water, but more readily in hot water, crystallising from the solution on standing. The following numbers were obtained:

0·2765 gram gave 0·6330 CO_2 and 0·1440 H_2O.

	Calculated.		Found.
C_8	96	63·16	62·44
H_8	8	5·26	5·78
O_3	48	31·58	---
$C_8H_8O_3$	152	100·00	

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Hence this product was *vanillin*, identical with the odorous principle of vanilla, and with that obtained by Tiemann and Haarmann (*Deut. Chem. Ges. Ber.*, vii, 608) from coniferin, its production from methyl vanillin being brought about in virtue of the reaction—

$$C_6H_3\begin{cases}COH\\O.CH_3\\O.CH_3\end{cases} + HCl = CH_3Cl + C_6H_3\begin{cases}COH\\O.CH_3.\\OH\end{cases}$$
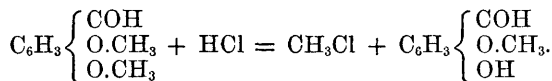
It is, therefore, evident that by the action of heat on a mixture of sodium opianate and soda-lime, dimethyl-protocatechuic aldehyde is formed; and hence the COOH radical eliminated from opianic acid by the action of soda-lime is in the same position as that removed from hemipinic acid by the action of caustic potash at 240°.

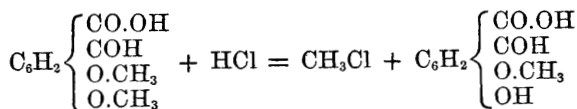From the character of the alternative formulæ thus deducible for opianic acid, viz.,
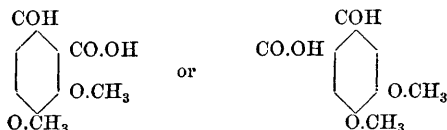
it results that narcotine must possess one of the two structures—
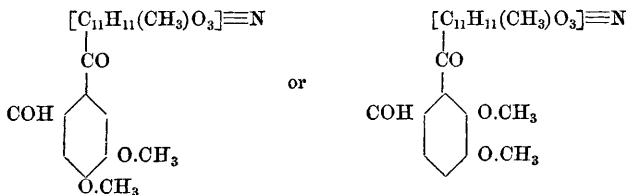
the CO group linking the benzene-radical to the cotarnine nucleus, corresponding in position to the CO.OH eliminated from opianic acid by soda-lime, and to that removed from hemipinic acid by heating with potash at 240°.

Attempts have been made on the part of Messrs. Macfarlan of Edinburgh, to utilise the above-described process for the preparation of vanillin commercially, but without much success owing to the extremely small yield of vanillin obtainable; even in the most favourable experiments yet made only a very small fraction of the calculated quantity of methyl vanillin was obtainable from opianic acid, whilst the yield of vanillin from methyl vanillin is but small.
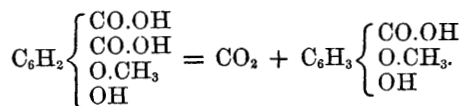
Mathiessen and Foster have shown that by acting on opianic acid with hydrochloric acid, methyl chloride is formed together with " methyl-noropianic acid " thus—

$$C_6H_2\begin{cases}CO.OH \\ COH \\ O.CH_3 \\ O.CH_3\end{cases} + HCl = CH_3Cl + C_6H_2\begin{cases}CO.OH \\ COH \\ O.CH_3 \\ OH\end{cases}$$

By distilling this acid with soda-lime, it might be *à priori* anticipated that either vanillin or an isomeride thereof might result; we did not succeed, however, in isolating any such product from the distillate obtained; much less heavy oil was formed than with opianic acid, and the greater part of the acid used appeared to be completely charred: probably this result is due to the phenolic character of methyl noropianic acid. That methyl-noropianic acid is capable, under other circumstances, of splitting up into carbon dioxide and vanillin (methylprotocatechuic aldehyde) is rendered highly probable by the observation of Dr. Armstrong, verbally communicated to us during the progress of these experiments, that on heating opianic acid with zinc chloride a little vanillin is formed; probably the reaction is brought about by the elimination of methyl from opianic acid by the agency of nascent hydrochloric acid formed from the zinc chloride (which has a tendency to become basic at a high temperature) thus producing methyl-noropianic acid, which then splits up into carbon dioxide and vanillin, thus—

$$C_6H_2\begin{cases}CO.OH \\ COH \\ O.CH_3 \\ OH\end{cases} = CO_2 + C_6H_3\begin{cases}COH \\ O.CH_3 \\ OH\end{cases}$$
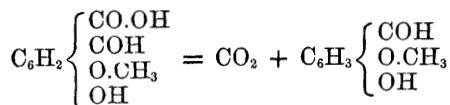
this reaction being parallel with that described in § 6, where methyl norhemipinic acid splits up into carbon dioxide and methyl protocatechuic acid—

$$C_6H_2\begin{cases}CO.OH \\ CO.OH \\ O.CH_3 \\ OH\end{cases} = CO_2 + C_6H_3\begin{cases}CO.OH \\ O.CH_3. \\ OH\end{cases}$$

It is noteworthy that whereas opianic acid thus gives rise to a monomethyl-protocatechuic derivative having the residual methyl group in one of the two positions with reference to the COH group deducible from the 1 . 3 . 4 protocatechuic acid formula, hemipinic acid by analogous processes gives rise to a monomethyl protocatechuic derivative where the residual methyl group is *in the other position* (so-called "methyl-hypogallic acid." Vide *infra*).

§ 5. *Action of Hydriodic Acid on Hemipinic Acid.*

From the character of the two alternative formulæ arrived at in § 3 for hemipinic acid, it results that if by any reaction one of the
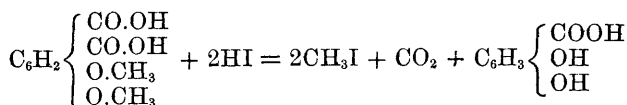
two CO.OH groups be eliminated, nothing but dimethyl protocatechuic acid can be formed if the hemipinic acid formula be 1 . 2 . 4 . 5, or

$$\begin{array}{c} \text{CO.OH} \\ \text{CO.OH} \; \hexagon \\ \text{O.CH}_3 \\ \text{O.CH}_3 \end{array}$$
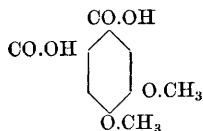
whilst either dimethyl-protocatechuic acid or a dimethylised isomeride of protocatechuic acid can result if the formula be 1 . 2 . 3 . 4, or

$$\begin{array}{c} \text{CO.OH} \\ \hexagon \; \text{CO.OH} \\ \text{O.CH}_3 \\ \text{O.CH}_3 \end{array}$$
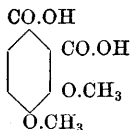
If, therefore, the production (by further removal of methyl) of an isomeride of protocatechuic acid such as the supposed "hypogallic acid" of Matthiessen and Foster, be substantiated, manifestly the first formula is excluded, and the second demonstrated to be appropriate. As stated in Part II (Appendix), however, the conclusions arrived at by Matthiessen and Foster have not been confirmed by the experiments of Liechti: the former chemists (this Journal, 1863, 342) represent the action of hydriodic acid on hemipinic acid as being in accordance with the equation—

$$C_6H_2 \begin{cases} \text{CO.OH} \\ \text{CO.OH} \\ \text{O.CH}_3 \\ \text{O.CH}_3 \end{cases} + 2HI = 2CH_3I + CO_2 + C_6H_3 \begin{cases} \text{COOH} \\ \text{OH} \\ \text{OH} \end{cases}$$
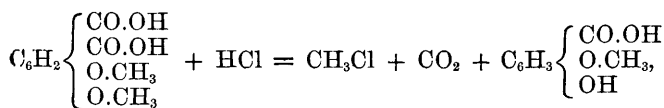
"hypogallic acid" isomeric with protocatechuic acid resulting, whilst Liechti (*Annalen der Chemie, Suppl.*, vii, 129) regards the action as being represented by the equation—

$$2C_{10}H_{10}O_6 + 4HI = 4CH_3I + C_2H_2O_4 + C_{14}H_{10}O_8,$$
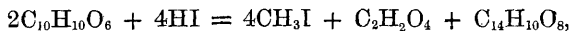
oxalic acid (subsequently decomposed) and *two* isomeric acids $C_{14}H_{10}O_8$ being formed, termed by him respectively "opinic acid" and "isopinic acid." Of these the latter was regarded by Liechti as identical with the "hypogallic acid" of Matthiessen and Foster notwithstanding that he observed a difference of upwards of 30° in melting point and of several tenths in hydrogen percentage, whilst the solubilities in cold water and in ether are by no means identical, "isopinic acid" being described as readily soluble in cold water, and only very slightly soluble in ether, whilst "hypogallic acid" is stated to be only slightly soluble in cold water and readily soluble in ether.
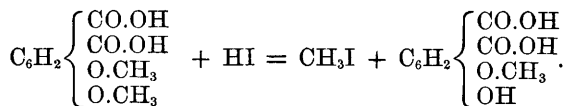
Again, if the so-called "methyl hypogallic acid" of Matthiessen and Foster, produced by the action of hydrochloric acid on hemipinic acid, be really formed, as supposed by them, in virtue of the reaction,

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} + HCl = CH_3Cl + CO_2 + C_6H_3 \begin{cases} CO.OH \\ O.CH_3, \\ OH \end{cases}$$

and really have the composition of a methylated isomeride of protocatechuic acid, the first hemipinic acid formula is equally excluded, and the second demonstrated as correct.
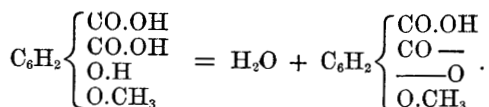
On investigating these points, we have obtained results which lead us to the conclusion that the first action of hydriodic acid on hemipinic acid is represented, neither by the equation of Matthiessen and Foster nor by that of Liechti; as regards the results of the latter chemist, they are susceptible of entirely different interpretations ; whilst although the equation of Matthiessen and Foster represents a reaction actually taking place, yet the body formed in virtue of it appears, as far as our experiments have gone, to be simply protocatechuic acid, and *not* an isomeride thereof. Similarly we find that "methyl hypogallic acid" is simply a monomethyl-protocatechuic acid.

The first action of hydriodic acid on hemipinic acid appears to be just that which might be expected from the character of the action of that acid on opianic acid and on meconin as studied by Matthiessen and Foster, viz., the elimination of *one* methyl group only, in virtue of the reaction—

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} + HI = CH_3I + C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases}.$$

In accordance with the nomenclature of Matthiessen and Foster, this body may be termed *methyl normal hemipinic acid*, or, briefly, *methyl-norhemipinic acid*.

By continuing the action, this body appears to undergo further changes : the numerical values obtained by Liechti in the case of his "opinic acid," and to some extent those of Matthiessen and Foster with their "hypogallic acid," render it very probable that under certain conditions methyl norhemipinic acid loses the element of water, yielding a body which cannot well be the analogue of hemipinic anhydride, as it crystallises from water with water of crystallisation, but which may readily be the analogue of salicylide, being possibly formed thus—

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.H \\ O.CH_3 \end{cases} = H_2O + C_6H_2 \begin{cases} CO.OH \\ CO \!\!-\!\! \\ \overline{\qquad} O \\ O.CH_3 \end{cases}.$$
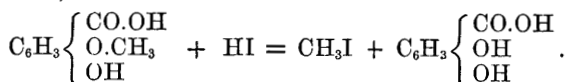
We do not insist, however, on the occurrence of this reaction, nor on the formation of this body, as we have not been able to reproduce the conditions under which a crystalline body having the properties ascribed to "opinic acid" is generated directly from hemipinic acid, although we have obtained indications of the formation of such a substance on heating methylnorhemipinic acid (§ 6).

A change which methylnorhemipinic acid certainly undergoes we find to be represented by the equation—
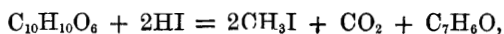
$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} = CO_2 + C_6H_3 \begin{cases} CO.OH \\ O.CH_3 \\ OH \end{cases}$$
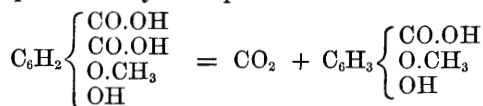
the resulting body being the "methylhypogallic acid" of Matthiessen and Foster, or as it may be more appropriately termed, *methylprotocatechuic acid;* this body also loses methyl, forming ordinary protocatechuic acid, thus :—

$$C_6H_3 \begin{cases} CO.OH \\ O.CH_3 \\ OH \end{cases} + HI = CH_3I + C_6H_3 \begin{cases} CO.OH \\ OH \\ OH \end{cases}.$$
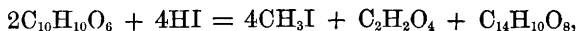
These three acids, methylnorhemipinic, methylprotocatechuic, and protocatechuic acids are the only bodies that we have been able to isolate from the products of the action of hydriodic acid on hemipinic acid; this circumstance, however, does not necessarily exclude the possibility of an acid isomeric with protocatechuic acid (the "hypogallic acid" of Matthiessen and Foster) being formed under other conditions; only, the results of these chemists may be otherwise interpreted.

The data from which these conclusions are drawn are the following. Pure hemipinic acid was gently heated with 6—7 times its weight of 50 per cent. hydriodic acid and a little amorphous phosphorus in a flask provided with a well cooled condenser; the evolution of methyl iodide commenced speedily, but not more than traces of carbon dioxide were evolved at first; after some minutes' very gentle boiling, the evolution of methyl iodide diminished greatly, that of carbon dioxide simultaneously increasing, and after a quarter of an hour altogether no appreciable quantity of methyl iodide globules condensed, whilst the evolution of carbon dioxide was greater than ever.

The theoretical amount of methyl iodide for the equation of Matthiessen and Foster—

$$C_{10}H_{10}O_6 + 2HI = 2CH_3I + CO_2 + C_7H_6O,$$

and for that of Liechti—

$$2C_{10}H_{10}O_6 + 4HI = 4CH_3I + C_2H_2O_4 + C_{14}H_{10}O_8,$$

is 125 per cent. of the hemipinic acid employed (dried at 100°); in two experiments the total quantities collected were 65 and 75 per cent. only.   The amount of carbon dioxide collected from first to last during a very carefully conducted experiment did not amount to more than one-fifth of that requisite for the former of these two reactions; whilst, on the other hand, no trace of oxalic acid could be found in the product, and no trace of carbon monoxide was evolved during the reaction.

These results clearly show that neither of the above equations correctly expresses the change taking place, since oxalic acid, if formed at all and subsequently split up, must necessarily evolve not only more carbon dioxide than that found, but carbon monoxide in addition.   On the other hand, they are completely in harmony with the reactions stated above to occur, viz., where methylnorhemipinic acid is first produced by elimination of one methyl group, and is subsequently partially converted into methylprotocatechuic acid (" methylhypogallic acid ") by loss of CO_2, and this partially into protocatechuic acid by elimination of a second methyl group: in this way 100 parts of hemipinic acid dried at 100° should form somewhat more than 62 parts of methyl iodide, together with a comparatively small quantity of carbon dioxide, the latter being formed only to a minute extent during the first portion of the reaction, but more copiously afterwards, as the amount of methylnorhemipinic acid increases.

In one experiment (A) the acid liquid obtained by heating hemipinic acid with hydriodic acid until the evolution of methyl iodide all but ceased, was diluted with water and filtered, and the filtrate agitated with a large bulk of ether; the ethereal extract left on evaporation a syrupy residue, which was dissolved in water, treated with animal charcoal, and set aside to crystallise by spontaneous evaporation over sulphuric acid.   No crystals resembling the well-defined crystals of " opinic acid " separated, but as the liquid evaporated, crusts of minute crystals formed on the sides of the vessel resembling an efflorescence, and becoming brownish on the surface by exposure to air; on separating these from the mother-liquor by the filter-pump, and attempting to recrystallise from a very small quantity of hot water, no crystals at all formed, but on allowing the liquid to stand over sulphuric acid, the same minute efflorescence-like crystals again appeared. In this and other respects this product exactly corresponded with Liechti's " isopinic acid."

In another experiment (B) the mode of treatment of the product followed by Liechti was adopted; the acid liquid was diluted with

water and boiled with excess of well-washed freshly precipitated mercuric oxide; the filtrate was then treated with animal charcoal, concentrated to a small bulk and set aside to crystallise. By operating in this way, Liechti obtained two successive crops of crystals, the first consisting of what he termed " opinic acid," expressed by the formula, $C_{14}H_{10}O_8,3H_2O$, losing its water of crystallisation at $100°$, but not by standing over sulphuric acid; the second substance, termed by him " isopinic acid," was much more soluble in water; when air-dry it was expressed by the same formula, but lost two-thirds of its water of crystallisation over sulphuric acid. Our results, however, led to very different conclusions.

On standing over sulphuric acid for a couple of days, the concentrated liquor deposited a small quantity of crystals difficultly soluble in cold water : these were washed with cold water and recrystallised from boiling water; the crystals thus obtained, so far from possessing the composition of " opinic acid," were simply " methyl-hypogallic acid " (*vide* § 7); they were anhydrous, and melted at $249°$—$250°$ (corrected—Liechti states that " opinic acid " first completely melts at $148°$) : they gave no coloration with ferric chloride (Liechti states that his " opinic acid " strikes a beautiful lilac [bluish violet] with that reagent) : and finally they gave numbers wholly different from those required for Liechti's formula.

$0·1800$ gram gave $0·3800$ CO_2 and $0·0800$ H_2O.

		Calculated.		Found.
C_8		96	57·14	57·57
H_8		8	4·76	4·93
O_4		64	38·10	—
$C_8H_8O_4$		168	100·00	

The filtrate from these crystals deposited on standing a crop of very soluble crystals precisely resembling those obtained in experiment (A) : from these specimens the following numerical values were obtained.

It was found, as stated by Liechti in the case of " isopinic acid," that no constant weight was obtainable on drying at $100°$; the loss of weight after the first hour was found to be but slight, but was still sufficiently perceptible to exercise a marked effect on the results; this loss was finally traced to the decomposition of the methylnor-hemipinic acid into carbon dioxide and methylprotocatechuic acid (*vide* § 6). On the other hand, it was found that the crystals, when exposed to the air for a few hours in a thin layer till dry to the touch, lost considerably in weight by further exposure to air, whilst over sulphuric acid they ultimately lost so much that only 2—3 per cent

further was lost on heating to $100°$ for one hour.   The following com-
bustions were made with substances dried several days over sulphuric
acid, and finally kept in the water-bath one hour; it was found that
the loss during a second hour's exposure on the water-bath did not
exceed $0·7$ per cent., and this was apparently due entirely to loss of
carbon dioxide.

Sample from experiment A :—

    $0·2650$ gram gave $0·5035$ CO_2 and $0·0935$.
    $0·3060$,,   of air dry substance lost $0·0395$.

Sample from experiment B :—

    $0·2510$ gram gave $0·4735$ CO_2 and $0·0910$ H_2O.
    $0·3130$,,   of air dry substance lost at $100°$ $0·0440$.
    $0·4075$,,   ,,   ,, $0·0535$.

	Calculated.		Found.	
			A.	B.
C_9	108	50·94	51·82	51·45
H_8	8	3·78	3·92	4·03
O_6	96	45·28	—	—
$C_9H_8O_6$ ..	212	100·00		

Calculated loss at $100°$ for $C_9H_8O_6,2H_2O$.

		Found.	
	A.	B.	
14·52	12·91	14·06	13·13

These numbers agree with the formula as well as could be expected
with so efflorescent and decomposible a substance ; they do not, how-
ever, agree at all with the formulæ of Matthiessen and Foster and
of Liechti, which require respectively—

	M. and F.: $C_7H_6O_4.1\tfrac{1}{2}H_2O$.	Liechti: $C_{14}H_{10}O_8.3H_2O$.
Water of crystallisation	14·92	15·00
Carbon in dry substance	54·54	54·90
Hydrogen ,,	3·90	3·27

Attempts to control the formula of methylnorhemipinic acid by
means of its salts led to no certain results, owing to their ready
decomposibility ; a lead salt was precipitated by adding the aqueous
solution of the acid to neutral lead acetate solution, filtering and
washing, drying over sulphuric acid, and finally at $100°$; this con-
tained $56·7$ per cent. of PbO, whilst the percentage reckoned on the salt
dried over sulphuric acid was $54·5$: the formula, $C_9H_6O_6.Pb$, requires
$53·5$ per cent., whilst the neutral salt of an acid of formula,

$C_6H_3\begin{cases} CO.OH \\ OH \\ OH \end{cases}$, or $(C_7H_5O_4)_2Pb$, would require only $43·4$ per cent,

The " isopinic acid " described by Liechti agrees closely in
physical properties and reactions with methylnorhemipinic acid; the
samples A and B of the latter melted completely at about 150° and
155° respectively, with considerable decomposition; Liechti's product
melted with decomposition at 148°; moreover, the percentages of car-
bon and hydrogen obtained by Liechti with a specimen dried by
long standing over sulphuric acid (one combustion only) agree
tolerably with those calculated, viz. :—

|	Calculated.	Found (Liechti).
Carbon..........	50·94	51·74
Hydrogen	3·78	3·79

whilst the loss at 100° of the air-dried sample amounted to 16 per
cent. and upwards on further heating : it may hence be fairly con-
cluded that " isopinic acid " is simply more or less pure methylnor-
hemipinic acid.

As regards " opinic acid," although the above results would seem
to indicate that this product may have been simply a mixture of
methylprotocatechuic acid (" methylhypogallic acid ") and methyl-
norhemipinic acid, yet the statement of Liechti that his body, when
dried over sulphuric acid, lost no water of crystallisation, but lost
15·16 per cent. on further heating at 100°, is quite opposed to this
view.   The non-formation of oxalic acid or its decomposition product,
carbon monoxide, in our experiments, however, tends to show that the
mode of formation of this substance could not be that deduced by
Liechti, and it therefore seems more reasonable to suppose that his
product had the composition, $C_9H_6O_5.2H_2O$, with which formula his
numbers agree well; he obtained the following values.

0·2546 gram lost at 100° 0·0386, and the residue gave on combus-
tion 0·4340 CO_2 and 0·0624, or altogether 0·1010 H_2O.

Calculated for $C_9H_6O_5.2H_2O$.	Found (Liechti).
Carbon .... 46·96	46·49
Total hydrogen .... 4·35	4.41
Water of crystallisation .... 15·65	15·16

Admitting this view to be correct, " opinic acid " would be, as
above stated, a body derived from methylnorhemipinic acid by the
reaction—

$$C_9H_8O_6 = H_2O + C_9H_6O_5.$$
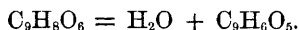
The description of " hypogallic acid " given by Matthiessen and
Foster renders it very probable that, notwithstanding the close agree-
ment between the analytical figures found and those required for the
formula, $C_7H_6O_4.1\frac{1}{2}H_2O$, the body may yet have been simply impure

" opinic acid," the admixture being probably unaltered hemipinic acid.

	Calculated for		Found (Matthiessen and Foster).		
	$C_{10}H_{10}O_6.2H_2O.$	$C_9H_6O_5.2H_2O.$			
Carbon in dry sub-					
stance	53·10	55·67	54·34	54·46	54·35
Hydrogen in dry					
substance	4·42	3·09	3·97	3·95	3·82
Water of crystal-					
lisation........	13·73	15·65	14·80	14·63	15·08

A mixture of about equal quantities of " opinic acid " and hemipinic acid would therefore give numbers exactly agreeing with those found. " Hypogallic acid " is described as slightly soluble in cold water, easily in hot water, alcohol and ether, separating from hot water in small prismatic crystals united into stellate groups : melting point about 180°, with previous decomposition. " Opinic acid " is stated by Liechti to crystallise in colourless shining prisms, about 1 centimeter long, melting at 148°, readily soluble in water, especially on heating, soluble in alcohol, sparingly soluble in ether. Hemipinic acid often crystallises in stellate prisms, is sparingly soluble in cold water and ether, readily in hot water and alcohol; it melts at 182°. In some qualitative reactions " opinic " and " hypogallic " acids agree, viz., in reactions with ammoniacal silver nitrate, and ferric chloride : " opinic acid," however, did not reduce an alkaline copper solution, whilst " hypogallic acid " did reduce it.

Much as we should have liked to solve the question as to the true constitution of this " hypogallic acid," we were unable to do so, not succeeding in obtaining a sufficient quantity for examination of any substance possessing the properties of " opinic " or of " hypogallic acid."

It may be further remarked that possibly protocatechuic acid was present in the "hypogallic acid" of Matthiessen and Foster; we have found that methyl-norhemipinic acid may be mixed with fully its own weight of protocatechuic acid without causing any marked greenish shade in the coloration given with ferric chloride. That protocatechuic acid is actually formed by the action of hydriodic acid on hemipinic acid is not only rendered probable by the quantity of methyl iodide evolved, and from the production of methylproto-catechuic ("methyl-hypogallic") acid, a body readily demethylised by hydracids, but is also proved by the following observations : the mixture of mercuric iodide and oxide obtained in Experiment B was treated with sulphuretted hydrogen, and the filtrate agitated with ether : on evaporisation and crystallisation from water of the residue, crystals were obtained melting at 190° after drying at 100°, giving

x 2

the protocatechuic reaction with ferric chloride, forming a sublimate of pyrocatechin on heating with pumice-stone, and yielding the following numbers after drying at 100°.

0·1680 gram gave 0·3320 CO_2 and 0·0680 H_2O.

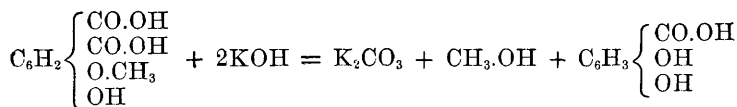|	Calculated.		Found.
C_7	84	54·54	53·90
H_6	6	3·90	4·49
O_4	64	41·56	—
$C_7H_6O_4$	154	100·00	

Vide also § 6.

§ 6. *Decompositions of Methyl-norhemipinic Acid.*

(A.) *Action of Fusing Caustic Potash.*

When methyl-norhemipinic acid is fused with caustic potash at 240° no charring takes place, but the power of striking a blue tint with ferric chloride is completely destroyed; on acidulating and extracting with ether nothing but protocatechuic acid is obtained, a result evidently predicable *à priori* from the nature of the reaction which ensues when hemipinic acid is similarly treated (§ 3).
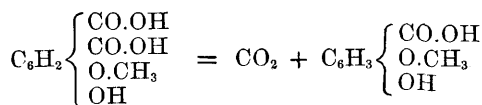
The action may be represented by the equation

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} + 2KOH = K_2CO_3 + CH_3.OH + C_6H_3 \begin{cases} CO.OH \\ OH \\ OH \end{cases}$$

the methylic alcohol being probably further acted on whilst still nascent.

(B.) *Action of Heat.*

When methyl norhemipinic acid is heated to 100° for some time, as stated above, a small amount of carbon dioxide is evolved; at higher temperatures, and especially above the melting point, this evolution becomes more rapid: on heating with a large excess of pumice-stone powder, a sublimate is obtained of which a portion is sparingly soluble in cold water, more readily in boiling water, crystallising in small prisms on cooling: these prisms gave no coloration with ferric chloride, and melted at 249° (corrected), and hence were evidently methyl protocatechuic acid ("methyl hypogallic acid"—*vide* § 7) formed by the reaction—

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} = CO_2 + C_6H_3 \begin{cases} CO.OH \\ O.CH_3 \\ OH \end{cases}$$

Besides methyl protocatechuic acid, an oily substance was also present in the sublimate, giving a green coloration with ferric chloride after solution in alcohol; in all probability this was guiacol (mono-methyl pyrocatechin), formed from the methyl-norhemipinic acid by the reaction

$$C_6H_2 \begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} = 2CO_2 + C_6H_4 \begin{cases} O.CH_3 \\ OH \end{cases}$$
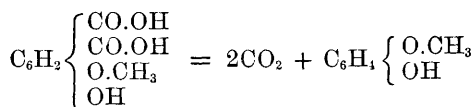
parallel with that whereby dimethyl pyrocatechin is formed from hemipinic acid (§ 2).

Tiemann has recently shown that vanillic acid, the second modification of methyl-protocatechuic acid (*vide* § 7), when heated with slacked lime yields a distillate of pure guiacol (*Deut. Chem. Ges. Ber.*, viii, 1123).

When methyl-norhemipinic acid is kept for half an hour in the fused state at a temperature of about 160°—170°, a dark-coloured residue is left, soluble in ammonia; on evaporation to dryness of the ammoniacal solution, much humus-like matter is left behind when the residue is dissolved in water; by addition of a drop of hydrochloric acid to the filtered solution, evaporation to dryness, and treatment of the residue with a little cold water, crystalline flakes are left undissolved, soluble in hot water, and yielding a bluish-violet coloration with ferric chloride, quite different from the pure blue shade given by methyl-protocatechuic acid; only minute quantities of this product were obtained, so that it could not be studied, but from its mode of production, and the colour given with ferric chloride, it seems highly probable that this substance is the " opinic acid " of Liechti, formed, as indicated above (§ 5), in accordance with the equation—

$$C_9H_8O_6 = H_2O + C_9H_6O_5.$$

(C.) *Action of Hydracids.*

When methyl-norhemipinic acid is boiled for five hours with diluted hydrochloric or hydriodic acid (1 part saturated acid to 2 or 3 water), crystals of impure methyl-protocatechuic acid separate on cooling and standing; the filtrate on shaking with ether yields, after evaporation of the extract, a crystalline residue consisting chiefly of protocatechuic acid, melting at 196°, together with a little unaltered methyl-norhemipinic acid: the protocatechuic acid is evidently formed by the elimination of methyl from the methyl-protocatechuic acid first produced by the elimination of CO_2 through the action of the heat (§ 7).

§ 7. *Action of Hydrochloric Acid on Hemipinic Acid.*

Pure hemipinic acid was heated with ten times its weight of strong hydrochloric acid under paraffin on the water-bath for twelve hours; the liquid was then evaporated nearly to dryness, largely diluted with water and boiled; the filtrate was dark brown, and deposited, on cooling and standing, highly coloured crystals, very sparingly soluble in water; the humus-like residue was treated with ammonia, and evaporated nearly to dryness, and then washed well with warm water; much humus was thus left insoluble, and a dark solution obtained, containing the ammonia salt of an acid very sparingly soluble in water. This ammonia salt, and that formed by dissolving in ammonia the dark-coloured crystals from the aqueous liquid, were partially decolorised by cautious addition of dilute acid, until all excess of ammonia was neutralised, and a small quantity of the sparingly soluble acid precipitated; and the filtrate was finally boiled with purified animal charcoal, whereby a nearly colourless solution was obtained, from which hydrochloric acid precipitated a mass of fine needles. When air-dry, these were anhydrous; they melted at 251° *corrected* [Matthiessen and Foster found that "methylhypogallic acid" supported a temperature of 245° unchanged, but melted at a somewhat higher temperature, solidifying on cooling to a crystalline mass]; with ferric chloride they gave no coloration. The following numbers were obtained:—

0·2970 gram gave 0·6240 CO_2 and 0·1310 H_2O.

	Calculated.		Found.
C_8	96	57·14	57·29
H_8	8	4·76	4·90
O_4	64	38·10	—
$C_8H_8O_4$	168	100·00	

It is hence manifest that this body is the "methyl-hypogallic acid" of Matthiessen and Foster; the following experiments, however, show that this acid is really a *monomethyl-protocatechuic acid*.
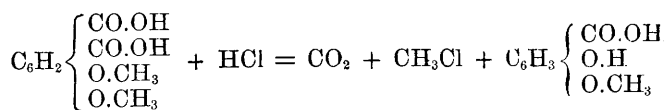
(A.) When heated with dilute hydrochloric acid (sp. gr. 1·04) to 150° for three hours, the acid is scarcely affected at all, and no darkening in colour occurs; on agitating with ether the aqueous liquid filtered from the undecomposed acid which separates on cooling, an extract is obtained which yields on evaporation a minute amount of a substance giving with ferric chloride the protocatechuic acid reaction, but no blue coloration like that of hypogallic acid.

(B.) When heated to 160°—170° for three hours with acid of sp gr. 1·09 (about equal bulks of ordinary commercial pure acid and water), a considerable portion of the acid is decomposed; on opening

the tube, methyl chloride and carbon dioxide escape with some
violence; the aqueous solution yields to ether a mixture of protoca-
techuic acid and pyrocatechin, the latter greatly predominating: these
were separated by adding ammonia to the residue left on evaporating
the ethereal solution, and again evaporating to dryness; on boiling
with benzene the mixture of ammonium protocatechuate and pyro-
catechin left, the latter was dissolved out, and obtained in crystals
on cooling the solution: the insoluble residue was dissolved in water,
agitated with ether to remove traces of adhering pyrocatechin, and
finally acidified and exhausted with ether: on evaporation, crystals
exactly resembling protocatechuic acid were obtained, giving the ordi-
nary ferric chloride reaction, and melting at 191°; the pyrocatechin
melted at 102°—102·5°, gave (in comparatively concentrated solution)
a green colour and greenish-black precipitate with ferric chloride,
becoming dirty purple-violet on further addition of ammonia, and
furnished on combustion numbers agreeing with those required theo-
retically for pyrocatechin.

(C.) When heated to 210°—220° with fusing caustic potash, the
acid furnishes protocatechuic acid identified by its iron reaction after
acidification and treatment with ether; the greater part of the acid,
however, is undecomposed at this temperature.

There can, therefore, be little doubt that the so-called "methyl-
hypogallic acid" is simply a *monomethyl-protocatechuic acid*, its forma-
tion from hemipinic acid being represented by the equation—

$$C_6H_2\begin{cases}CO.OH\\CO.OH\\O.CH_3\\O.CH_3\end{cases} + HCl = CO_2 + CH_3Cl + C_6H_3\begin{cases}CO.OH\\O.H\\O.CH_3\end{cases}$$

Two acids having the composition of methyl-protocatechuic acid
have been recently briefly described by Tiemann and Reimer (*Deut.
Chem. Ges. Ber.*, viii, 509): of these, one, vanillic acid, is manifestly
not identical with "methyl-hypogallic acid," as it has an odour of
vanilla, is more soluble in water, and melts at 211°—212°; the other,
however, is described as less soluble in water than vanillic acid, and
is not improbably identical with "methyl-hypogallic acid:" to settle
this point, methyl-protocatechuic acid was prepared by heating
together one proportion of protocatechuic acid, two of caustic potash,
and two of methyl iodide with some methylic alcohol in a sealed tube
at 140°—160° for four hours, and boiling the resulting methyl-proto-
catechuic methylic ether with potash; on addition of hydrochloric acid
to the product of this saponification, crystals were thrown down which,
after purification by conversion into ammonia salt, treatment with
animal charcoal, precipitation by hydrochloric acid, and crystallisation

from boiling water, were anhydrous, melted at 250°—251° (corrected), corresponded in all other respects perfectly with "methyl-hypogallic acid," and gave the following numbers on combustion : —

0·2015 gram gave 0·4260 CO_2 and 0·0950 H_2O.

	Calculated.		Found.
C_8	96	57·14	57·11
H_8	8	4·76	5·24
O_4	64	38·10	—
$C_8H_8O_4$	168	100.00	

As a further proof of the identity of " methyl-hypogallic acid " with the acid obtained by methylating protocatechuic acid, the former was converted into dimethyl-protocatechuic acid by heating in a sealed tube to 140°—160° for three hours with two proportions of caustic potash and two of methyl iodide with some methylic alcohol, and saponifying the resulting methylic ether by boiling with potash; on addition of hydrochloric acid, crystals separated which, after purification, melted at 172°—173°.   After crystallisation from boiling water and drying at 100° the acid gave the following numbers :—

0·2200 gram gave 0·4790 CO_2 and 0·1100 H_2O.

	Calculated.		Found.
C_9	108	59·35	59·38
H_{10}	10	5·49	5·56
O_4	64	35·16	—
$C_9H_{10}O_4$	182	100·00	

According to Kölle (*Annalen der Chemie*, 159, 240) dimethylprotocatechuic acid crystallises anhydrous; the above product, however, after crystallisation from boiling water and drying in the air till constant in weight, gave the following numbers : —

0·3460 gram lost at 100° 0·0350 $= 10·12$ per cent.
0·1670   ,,   ,,   0·0175 $= 10·48$,,
Calculated for $C_9H_{10}O_4,H_2O$ $= 9·00$,,

The mother-liquors from which the " methyl-hypogallic acid " had separated (from the reaction of hydrochloric acid on hemipinic acid, as above described) were evaporated to a small bulk during which a little more " methyl-hypogallic acid " separated, and were then exhausted with ether; the ethereal solution left on evaporation a crystalline mass which was dissolved in water, decolorised with animal charcoal, and set aside to crystallise by spontaneous evaporation over sulphuric acid; a small quantity of fine crystals was thus obtained, chiefly in the form of a crust, which crept up the side of the vessel ;
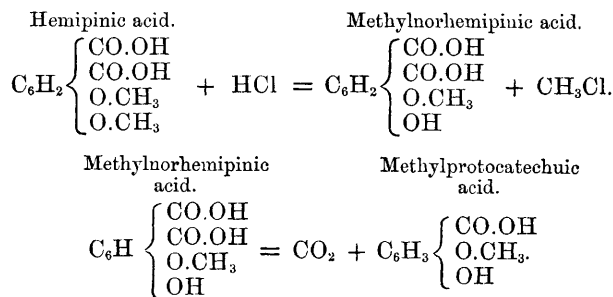
these were excessively soluble in water and alcohol, and very closely resembled methyl-norhemipinic acid.   With a small quantity of ferric chloride these gave a beautiful blue coloration, becoming dark bluish-green on adding a little more ; a further addition of ammonia changed the colour to a purplish blood-red ; in this respect they behaved precisely like a mixture of methyl-norhemipinic acid with about twice its weight of protocatechuic acid, the green coloration due to the latter not becoming visible until enough ferric chloride has been added to convert the whole of the methyl-norhemipinic acid into blue compound ; and this conclusion is borne out by the observed melting temperatures, a portion fusing at near $150°$ (the melting point of methyl-norhemipinic acid), whilst the remainder did not melt till the temperature rose to upwards of $180°$ (protocatechuic acid melts at $198°$) ; also by the following analytical figures :—

0·2610 gram gave 0·5110 CO_2 and 0·0935 H_2O.

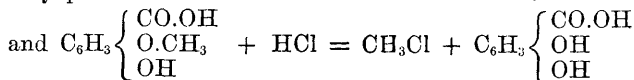|	Calculated.		Found.
	$C_9H_8O_6$.	$C_7H_6O_4$.	
Carbon	50·94	54·54	53·39
Hydrogen	3·78	3·90	3·98

and by the facts that on fusion with caustic potash at $240°$, no charring ensued, but only protocatechuic acid could be detected in the product on acidifying and extracting with ether; and that on heating with pumice-stone, a mixture of pyrocatechin and "methylhypogallic" acid sublimed, the former being identified by its solubility in water forming crystals on evaporation to dryness, and its reaction with ferric chloride ; the latter by its almost insolubility in cold water, and melting point ($249°$ corrected) and want of colour reactions with ferric chloride [*vide* § 6].

It may therefore be concluded that the end-products of the action of hydrochloric acid on hemipinic acid are the same as those of hydriodic acid, viz., methyl-norhemipinic, methyl-protocatechuic ("methylhypogallic") and protocatechuic acids, formed respectively by the reactions—

$$\text{Hemipinic acid.} \qquad\qquad \text{Methylnorhemipinic acid.}$$

$$C_6H_2\begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ O.CH_3 \end{cases} + HCl = C_6H_2\begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} + CH_3Cl.$$

$$\text{Methylnorhemipinic acid.} \qquad\qquad \text{Methylprotocatechuic acid.}$$

$$C_6H\begin{cases} CO.OH \\ CO.OH \\ O.CH_3 \\ OH \end{cases} = CO_2 + C_6H_3\begin{cases} CO.OH \\ O.CH_3. \\ OH \end{cases}$$

Methyl-protocatechuic acid.   Protocatechuic acid.

$$\text{and } C_6H_3 \left\{ \begin{array}{l} CO.OH \\ O.CH_3 \\ OH \end{array} \right. + HCl = CH_3Cl + C_6H_3 \left\{ \begin{array}{l} CO.OH \\ OH \\ OH \end{array} \right.$$

In this way the first action of hydrochloric acid on hemipinic acid is just analogous to that on meconin and on opianic acid, viz., elimination of *one* methyl group.

The results detailed in this and the two preceding sections do not decisively disprove the view of Matthiessen and Foster that hemi-pinic acid is capable of giving rise to an isomeride of protocatechuic acid, although they show that the evidence of the formation of such a substance is very incomplete; even, however, if it were fully proved that "hypogallic acid" is not an isomeride of protocatechuic acid, it would not be possible to decide which of the two alternative formulæ—
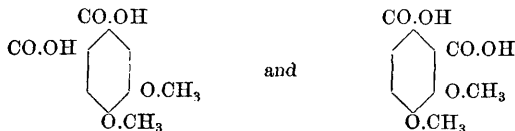
for hemipinic acid is to be adopted, since the formation of nothing but protocatechuic acid and its derivatives from hemipinic acid is not inconsistent with the second formula, although the production of an isomeride of protocatechuic acid would be quite inconsistent with the first.

As regards the names "methyl-hypogallic acid" and "isopinic acid," the above results show that both are misnomers : the first acid may in future be preferably termed *methyl-protocatechuic acid* (the other monomethylic protocatechuic acid of Tiemann and Reimer, being distinguished as *vanillic acid*), whilst the second is more correctly designated as *methyl-norhemipinic acid.*

§ 8. *Action of fused Caustic Potash on Meconin.*

If meconin be the anhydride of an alcoholo-acid, $C_6H_2 \left\{ \begin{array}{l} CO.OH \\ CH_2.OH \\ O.CH_3 \\ O.CH_3 \end{array} \right.$, the

first product of the action of potash on this anhydride, $C_6H_2 \left\{ \begin{array}{l} CO \\ CH_2 \\ O.CH_3 \\ O.CH_3 \end{array} \right.$,

will probably be $C_6H_2 \left\{ \begin{array}{l} CO.OK \\ CH_2.OH \\ O.CH_3 \\ O.CH_3 \end{array} \right.$; by the further action on this of pot-

ash, the production of various substances might be anticipated; thus, one or both methyl groups may be eliminated, the $CH_2.OH$ group may be oxidised to $CO.OH$, and if the heat be high enough, CO_2 may be eliminated. In order to see what reaction, if any, ensues at a temperature of 200°—210°, a strong caustic potash solution was evaporated down till a thermometer in it marked about 190° and then as much dry meconin as represented one-third of the weight of solid potash used was gradually stirred in, and the whole kept hot, with continual stirring, for some 10—15 minutes, by which time the thermometer marked 210°. After cooling the mass was dissolved in water and acidulated with sulphuric acid, whereby oily drops of unaltered meconin were thrown down, together with some crystals of potassium sulphate; the aqueous filtrate was agitated with ether and the ethereal extract with dilute ammonia, whereby a solution of a sparingly soluble ammonia salt was formed; this was then acidified and treated with fresh ether, the extract evaporated to dryness, and the residue boiled with animal charcoal and water; on evaporation of the only slightly yellowish aqueous solution thus obtained, well-defined crystals separated; after draining and drying in the air, these were anhydrous and melted at 125° (corrected); with ferric chloride their aqueous solution gave a beautiful blue tint, becoming red on further addition of ammonia. The following numbers were obtained:—

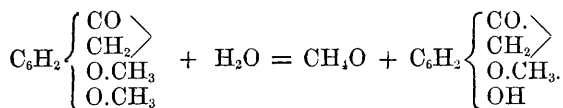0·3370 gram gave 0·7425 CO_2 and 0·1425 H_2O.

	Calculated.		Found.
C_9	108	60·00	60·09
H_8	8	4·44	4·70
O_4	64	35·56	—
$C_9H_8O_4$	180	100·00	

Hence this product is *methyl-normeconin*, apparently identical with that obtained by Matthiessen and Foster by the action of hydrochloric or hydriodic acid on meconin (this Journal, 1868, 360); as noticed above, the formation of an acid yielding a blue coloration with ferric salts by fusing opianic acid with potash was observed by Liechti, who, however, did not succeed in isolating the substance, or in tracing out the nature of the reactions by which it is formed; he thought it proceeded from the decomposition of the hemipinic acid first formed, and that it was probably "hypogallic acid."

On treating narcotine with caustic potash to 200°—210°, stirring well the while, acidifying the product and treating with ether, a small quantity of an acid is obtained, yielding with ferric chloride and ammonia the reactions of methyl-normeconin, and becoming converted into protocatechuic acid when heated with potash to 240°;

without doubt this substance is actually methyl-normeconin, since Matthiessen and Wright have shown that on heating narcotine to incipient decomposition, a little meconin is formed; probably this is produced by the reduction of nascent opianic acid, the first decomposition-product, as shown in Part I.

The first action of fusing potash on meconin, then, is (as with the two methyl-protocatechuic acids and dimethyl-protocatechuic acid) simply to eliminate methyl: the reaction may be represented as—

$$C_6H_2\begin{cases} CO \\ CH_2 \\ O.CH_3 \\ O.CH_3 \end{cases} + H_2O = CH_4O + C_6H_2\begin{cases} CO. \\ CH_2 \\ O.CH_3 \\ OH \end{cases}$$

The resulting body is, as Matthiessen and Foster have shown, a weak acid (*i.e.*, a phenol); an ethereal solution shaken with a little ammonia solution forms a jelly-like compound sparingly soluble in water and reproducing the original substance when treated with acids; pure meconin gives no such reaction: this compound loses much ammonia whilst drying, the whole of the remainder escaping on heating to 100°. A specimen prepared by adding excess of strong ammonia solution to a warm alcoholic solution of methyl-normeconin, cooling, and drying the mass which separated in the air, gave off at 100°, 3·62 per cent. of ammonia (weighed as ammonium chloride), the formula $C_9H_7(NH_4)O_4$ requiring 8·63 per cent.

When methyl-normeconin is heated with 6—7 times its weight of caustic potash to 230°—240°, much frothing ensues and hydrogen is given off copiously: the product when dissolved in water and acidified yields to ether a crystalline acid giving a green coloration with ferric chloride, becoming purple-red with ammonia, and agreeing in all other respects with protocatechuic acid; after treatment with animal charcoal and recrystallising, the acid melted at 199° (corrected) after drying at 100°, and gave the following numbers :—

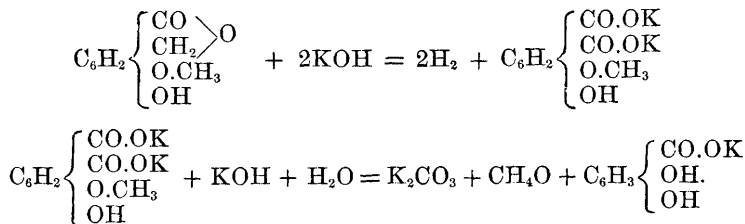0·6730 gram of air-dry crystals lost at 100° 0·0715 gram = 10·62 per cent.

Calculated for $C_7H_6O_4,H_2O = 10·47$ per cent.

0·2830 gram gave 0·5705 CO_2 and 0·1030 H_2O.

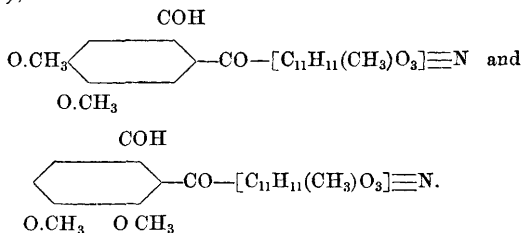|	Calculated.		Found.
C_7	84	54·54	54·98
H_6	6	3·90	4·04
O_4	64	41·56	—
$C_7H_6O_4$	154	100·00	

Hence, in all probability the action of heated potash on methyl-

normeconin is to oxidize it to methyl-norhemipinic acid, which is then converted (as shown in § 6) into protocatechuic acid by elimination of CO.OH and of methyl; thus:—

$$C_6H_2\begin{cases}CO \\ CH_2 \\ O.CH_3 \\ OH\end{cases}\!\!\!\!O \quad + \ 2KOH \ = \ 2H_2 \ + \ C_6H_2\begin{cases}CO.OK \\ CO.OK \\ O.CH_3 \\ OH\end{cases}$$

$$C_6H_2\begin{cases}CO.OK \\ CO.OK \\ O.CH_3 \\ OH\end{cases} + \ KOH + H_2O = K_2CO_3 + CH_4O + C_6H_3\begin{cases}CO.OK \\ OH. \\ OH\end{cases}$$

It may be inferred from these results and those detailed in §§ 1 and 3 that the end-product of the action of fusing potash on opianic acid is simply protocatechuic acid, as each of the substances first formed, viz., meconin and hemipinic acid, becomes converted into that acid by continuance of the action.

The foregoing results do not suffice to decide which of the two formulæ (§ 4),

$$O.CH_3\left\langle\right\rangle\!\!-\!\!CO\!-\![C_{11}H_{11}(CH_3)O_3]\!\equiv\!N \quad \text{and}$$

with COH above, and O.CH_3 below.

$$\left\langle\right\rangle\!\!-\!\!CO\!-\![C_{11}H_{11}(CH_3)O_3]\!\equiv\!N.$$

with COH above, and O.CH_3 O CH_3 below.

belongs to narcotine; the formation of nothing but protocatechuic acid derivatives from opianic acid and its derivatives by various reactions is not inconsistent with the second formula, although the production of isomerides of protocatechuic acid derivatives would, if established, tend to show that the first formula is inapplicable.