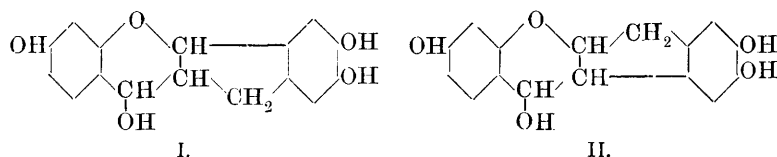


XXIII.—On *Brazilic Acid* and the Constitution of *Brazilin*.

By W. H. PERKIN, jun.

IN Part I. of this research (A. W. Gilbody, W. H. Perkin, jun., and J. Yates, *Trans.*, 1901, **79**, 1401), it was argued that since trimethylbrazilin, on oxidation with permanganate, yields *2-carboxy-5-methoxy-phenoxyacetic acid* and *metahemipinic acid*, the constitution of brazilin must be represented by one of the following formulæ:



These two formulæ are so similar that for a long time it was found impossible to obtain evidence sufficient to afford even a clue as to which was the correct one, but ultimately the detailed examination of *brazilic acid* (*loc. cit.*, p. 1410) led to results which show clearly that formula I is to be accepted as representing the constitution of brazilin.

Brazilic acid, $C_{12}H_{12}O_6$, which is produced in a yield of only 0.7 per cent. by the oxidation of trimethylbrazilin with permanganate, crystallises from water in colourless needles and melts at 129° ; it is a monobasic acid, since its silver salt has the formula $C_{12}H_{11}AgO_6$, and its sodium salt the formula $C_{12}H_{11}NaO_6$; when, however, its solution in water is boiled with baryta, it yields a barium salt of the formula $C_{12}H_{10}BaO_6$, and therefore, under these circumstances, it behaves like a dibasic acid, a point which will be referred to later.

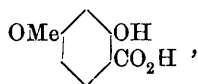
Brazilic acid contains 1 methoxy-group, as shown by Zeisel's method, and when fused with potash, it is decomposed with formation of a readily soluble acid which in aqueous solution gives an intense violet coloration with ferric chloride; it is therefore derived from the resorcylic nucleus in brazilin.

On treatment with hydroxylamine, brazilic acid yields an oxime, and with semicarbazide, a semicarbazone; it therefore contains a carbonyl group, and this group is evidently situated in the γ -position to the carboxyl group, because, when reduced with sodium amalgam, brazilic acid yields *dihydrobrazilic acid*, $C_{12}H_{14}O_6$, and this, when liberated from its sodium salt, spontaneously loses water with formation of the *lactone* $C_{12}H_{12}O_5$.

These facts, although they throw much light on the constitution of brazilic acid, are not sufficient to establish its formula, but the neces-

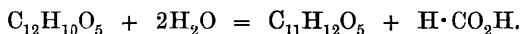
sary further information was ultimately obtained by the examination of the behaviour of the acid with dehydrating agents, especially sulphuric acid. When brazilic acid is warmed with concentrated sulphuric acid, it loses 1 molecule of water and is converted into *anhydrobrazilic acid*, a crystalline substance which melts at 197° , and differs sharply from brazilic acid in being very sparingly soluble even in boiling water.

This new acid is monobasic and still contains a carbonyl group, since with hydroxylamine it yields a crystalline oxime, $C_{12}H_{11}O_5N$; furthermore, a determination by Zeisel's method showed that it still contained the methoxy-group which was present in the brazilic acid. It is also an unsaturated acid, because its solution in sodium carbonate at once decolorises permanganate, and on investigating this oxidation it was found that an almost quantitative yield of *p-methoxysalicylic acid*,

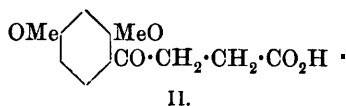
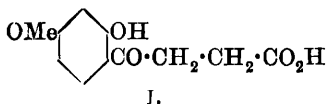


is formed if the oxidation is carried on at a sufficiently low temperature, a fact which affords a valuable clue as to the constitution of the acid.

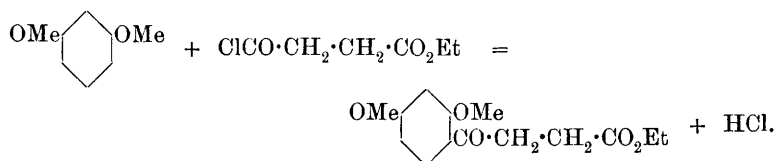
A further clue was obtained by the discovery that, when boiled with baryta water, anhydrobrazilic acid is readily decomposed into formic acid and a new acid, $C_{11}H_{12}O_5$, thus :



This new acid crystallises from water in colourless needles and melts at 155° ; it is a monobasic, ketonic acid and its aqueous solution gives, with ferric chloride, an intense violet coloration. Since anhydrobrazilic acid gives no coloration with ferric chloride, it was probable that the elimination of formic acid had been accompanied by the formation of a free hydroxyl group in the benzene ring. That this is the case was proved by the fact that the methyl ester of the acid $C_{11}H_{12}O_5$, when heated with sodium methoxide and methyl iodide, is converted into the methyl ester of an acid, $C_{12}H_{14}O_5$, which gives no coloration with ferric chloride; the hydroxy-group of the former acid had therefore been converted into a methoxy-group in the latter. The further consideration of the properties of the acid $C_{11}H_{12}O_5$, taken in conjunction with the fact that anhydrobrazilic acid on oxidation yields *p-methoxysalicylic acid*, seemed to indicate that the acid $C_{11}H_{12}O_5$ is 6-hydroxy-4-methoxybenzoylpropionic acid (I), and that its methyl derivative, $C_{12}H_{14}O_5$, is therefore dimethoxybenzoylpropionic acid (II),



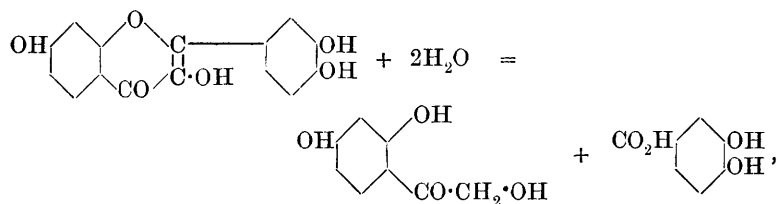
In order to prove this point, it was decided to attempt the synthesis of the dimethoxy-acid, and after a number of failures this was ultimately accomplished (in conjunction with Mr. E. Ormerod) by treating a mixture of dimethylresorcinol and the ester of the half-chloride of succinic acid with aluminium chloride, thus :



The product of this reaction yielded, on hydrolysis, an acid melting at 147° , which was identical with the dimethoxy-acid, $\text{C}_{12}\text{H}_{14}\text{O}_5$, obtained from brazilin, and the constitutions of this acid and of the hydroxy-methoxy-acid, $\text{C}_{11}\text{H}_{12}\text{O}_5$, from which it was obtained are consequently proved to be represented by the formulæ II and I given above.

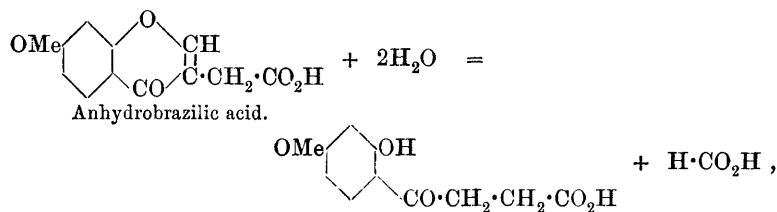
Referring again to the conversion of anhydrobrazilic acid by hydrolysis with baryta into hydroxymethoxybenzoylpropionic acid and formic acid, $\text{C}_{12}\text{H}_{10}\text{O}_5 + 2\text{H}_2\text{O} = \text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{H} \cdot \text{CO}_2\text{H}$, we see that we have here a case of a decomposition which has repeatedly been observed in the *pheno-γ-pyrone* series.

Thus fisetin, which is somewhat similarly constituted to brazilin, when digested with alcoholic potash is decomposed into fisetol and protocathechuic acid,

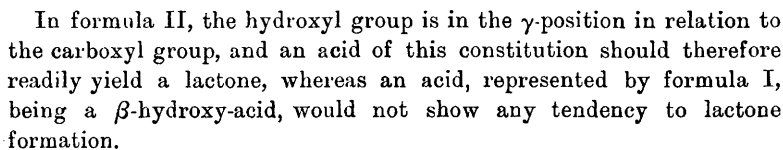


and many other similar examples might be given.

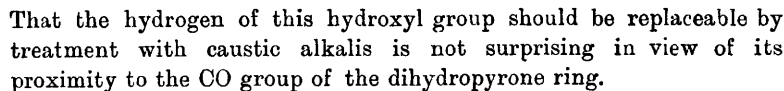
Arguing, then, from analogy, it is evident that the formula of *anhydrobrazilic acid* and its decomposition into methoxyhydroxybenzoylpropionic acid must be represented thus :



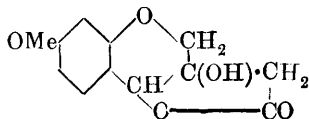
Since, then, anhydrobrazilic acid is produced from brazilic acid by the elimination of 1 molecule of water and consequent formation of a double-linking, it follows that there are only two formulæ which can represent brazilic acid, namely,



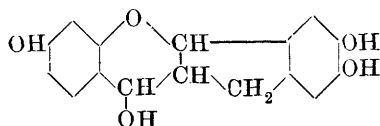
It has been shown by the preparation and analysis of its sodium, silver, and barium salts that brazilic acid is a well-characterised, monobasic acid, but it is also pointed out (p. 228) that when boiled with baryta water it yields a very sparingly soluble barium salt of the formula $C_{12}H_{10}O_6Ba$, which is quite different from the normal salt, $(C_{12}H_{11}O_6)_2Ba$, obtained by precipitating the solution of the sodium salt with barium chloride. The formation of the salt $C_{12}H_{10}BaO_6$ is evidently due to the hydrogen of the hydroxyl group, as well as that of the carboxyl group, being replaceable by barium, that is to say, the salt has the constitution :



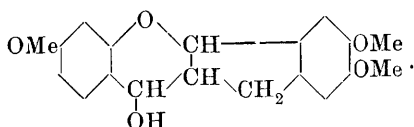
When brazilic acid is reduced by sodium amalgam, it is converted into the lactone of dihydrobrazilic acid, and the constitution of this substance must therefore be represented thus :



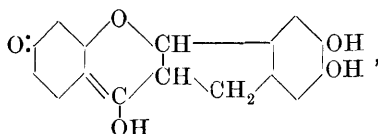
If, now, the two formulæ for brazilin given at the beginning of this paper be examined, it will be seen that only formula I can yield braziliic acid in a simple manner, and there seems, therefore, to be no reason to doubt that the constitution of brazilin is :



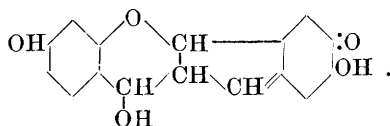
This formula accounts for all the known properties of brazilin in a satisfactory manner, and of the four hydroxyl groups three are represented as phenolic and the other one as alcoholic ; it is thus obvious that three only should be converted into methoxy-groups on treating brazilin with sodium methoxide and methyl iodide, and this is actually the case. The trimethylbrazilin so produced, which has been so largely employed in this investigation, will have the constitution :



In the previous paper (*loc. cit.*, p. 1403), it was suggested that the constitution of the dye-stuff, *brazileïn*, $C_{16}H_{12}O_5$ —which contains two atoms of hydrogen less than brazilin and is produced from it by oxidation—may probably be :



the two atoms of hydrogen being removed, one from the $CH(OH)$ group and one from the OH group of the resorecyl nucleus. It must, however, be pointed out that it is quite possible that the two atoms of hydrogen may be derived from the CH_2 group and the parahydroxy-group of the catechol nucleus, and the formula of *brazileïn* would then be :



Since, however, *brazileïn* yields such complicated, salt-like compounds with sulphuric acid (A. G. Perkin and Hummel, *Ber.*, 1882, 15, 2343), it

is not improbable that it may be derived from several molecules of brazilin, and therefore have a constitution much more complex than represented by the formulæ given above. This view receives some support from the fact that it has so far not been found possible to reconvert brazilein into brazilin by reduction.

Brazilic Acid, $C_{12}H_{12}O_6$.

This acid was mentioned in the previous paper (Trans., 1901, 79, 1411), and the method employed in isolating it from the products of the oxidation of trimethylbrazilin with potassium permanganate was briefly described. Two analyses were also given, the mean of which ($C=57.1$; $H=5.0$) agrees with the numbers required by the formula $C_{12}H_{12}O_6$ ($C=57.2$; $H=4.8$). The molecular weight of the acid has since been determined by the cryoscopic method, when two experiments gave 265 and 276, whereas the molecular weight of $C_{12}H_{12}O_6$ is 254.

Brazilic acid melts at $129-130^\circ$ and is only sparingly soluble in cold water; it dissolves readily in hot water and separates, on slowly cooling, in long, colourless needles. It dissolves readily in alcohol, ether, or acetic acid, but less readily in chloroform, and is almost insoluble in cold light petroleum; in hot benzene, it is readily soluble, and separates, on cooling, in long needles. That brazilic acid is a saturated substance is shown by the fact that its solution in cold sodium carbonate does not decolorise permanganate, oxidation taking place, indeed, only very slowly on warming. Bromine dissolved in chloroform is also without action on the acid in the cold. An aqueous solution of brazilic acid gives no coloration with ferric chloride, but when fused with potash the acid is readily decomposed, and, on acidifying and extracting with ether, a syrupy substance is obtained which is very soluble in water and gives, with ferric chloride, an intense violet coloration.

When boiled with acetic anhydride, brazilic acid dissolves, forming a yellow solution, but this rapidly becomes brown and then quite black, decomposition evidently taking place. If a small quantity of the dry acid is heated in a test-tube, it chars and gives an oily distillate which has a strong odour of coumarin.

Brazilic acid contains one methoxy-group, as is shown by the following determinations made by Zeisel's method:

0.1429 gave 0.1370 AgI. $OCH_3 = 12.6$.

0.1892 „ 0.1795 AgI. $OCH_3 = 12.5$.

$C_{12}H_{12}O_6$, containing one OCH_3 , requires $OCH_3 = 12.3$ per cent.

The residues from these methoxy-determinations were decolorised by sulphurous acid and extracted with ether, when a substance was

obtained which crystallised from water in pale yellow crystals and melted at about 178° ; it was not further examined.

Salts of Brazilic Acid.—That this acid is monobasic was first proved by titration with decinormal sodium hydroxide, using phenolphthalein as the indicator.

0.21 gram, dissolved in warm water, required for neutralisation 8.1 c.c. of sodium hydroxide solution = 0.0324 gram, whereas this amount of an acid, $C_{12}H_{12}O_6$, if monobasic, would neutralise 0.033 gram NaOH.

The solution was then mixed with a further quantity of 11.9 c.c. of the sodium hydroxide (making 20 c.c. in all) and boiled for 5 minutes, when, on titrating back, it was found that the amount neutralised was practically the same as before, namely, 0.034 gram.

The *sodium* salt, $C_{12}H_{11}O_6Na$, separates in glistening plates when a hot solution of the acid is neutralised with sodium carbonate and then allowed to cool. The salt was recrystallised from water, dried at 100° , and analysed:

0.1602 gave 0.0405 Na_2SO_4 . $Na = 8.2$.

$C_{12}H_{11}O_6Na$ requires $Na = 8.4$.

This salt, which does not appear to contain water of crystallisation, is comparatively sparingly soluble in cold water, although it dissolves readily on warming. On account of the facility with which it crystallises even when impure, it proved to be very valuable as a means of isolating brazilic acid from mixtures with other acids and resinous products. The corresponding potassium salt appears to be readily soluble in water.

The *silver* salt, $C_{12}H_{11}O_6Ag$, is obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white precipitate which is very sparingly soluble in water. On analysis

0.1613 gave 0.2352 CO_2 , 0.0496 H_2O , and 0.0484 Ag. $C = 39.8$;
 $H = 3.4$; $Ag = 30.1$.

0.201 gave 0.2932 CO_2 , 0.0608 H_2O , and 0.0605 Ag. $C = 39.8$;
 $H = 3.3$; $Ag = 30.1$.

$C_{12}H_{11}O_6Ag$ requires $C = 40.1$; $H = 3.1$; $Ag = 30.1$ per cent.

The *barium* salt, $(C_{12}H_{11}O_6)_2Ba \cdot 2H_2O$.—When a neutral solution of the ammonium salt of brazilic acid is mixed with barium chloride, an amorphous, almost gelatinous, precipitate is at first produced, but this rapidly becomes crystalline. This salt is readily soluble in hot water, and separates, on cooling, in slender needles; after draining on porous porcelain and exposing to the air for 3 days, it appears to contain 2 molecules of water of crystallisation:

0.2228 air-dried salt lost, at 100° , $0.0118 = 5.3$.

$(C_{12}H_{11}O_6)_2Ba, 2H_2O$ requires 5.3 per cent. of water.

0.211, dried at 100° , gave 0.0773 $BaSO_4$. Ba = 21.6.

$(C_{12}H_{11}O_6)_2Ba$ requires Ba = 21.7 per cent.

A neutral solution of the ammonium salt of brazilic acid gives no precipitate with calcium chloride, a pale blue precipitate with copper sulphate, and a white, amorphous, very insoluble precipitate with lead acetate.

The *barium* salt, $C_{12}H_{10}O_6Ba$, the constitution of which is discussed in the introduction to this paper, was prepared as follows.

A hot solution of brazilic acid was rapidly mixed with a large excess of hot baryta water, when a white, granular precipitate rapidly separated and increased, apparently, on boiling. After boiling for a few minutes out of contact with air, the salt was rapidly collected on the pump, washed repeatedly with boiling water, dried at 100° , and analysed:

0.4653 gave 0.2689 $BaSO_4$. Ba = 34.0.

0.1449 „ 0.0824 $BaSO_4$. Ba = 33.5.

$C_{12}H_{10}O_6Ba$ requires Ba = 35.5.

$C_{12}H_{10}O_6Ba, H_2O$ requires Ba = 33.9 per cent.

These results, which agree better with the latter formula, clearly show that brazilic acid, when boiled with baryta, yields a dibasic barium salt. In order to be certain that no change in constitution had taken place during this treatment, the barium salt was ground in a mortar with a little dilute hydrochloric acid, and the crystalline precipitate collected on the pump, washed with water, and dried at 100° . It then melted at 129° and consisted of pure brazilic acid.

Oxime of Brazilic Acid, $C_{12}H_{13}O_6N$.—In preparing this oxime, the pure acid (0.5 gram) was dissolved in dilute caustic potash (containing 2 grams KOH), a solution of 2 grams of hydroxylamine hydrochloride was then added, and the whole allowed to stand for 24 hours. On acidifying, a flocculent precipitate separated; this was extracted with ether, the ethereal solution dried over calcium chloride and evaporated, and the syrupy residue left over sulphuric acid in a vacuum desiccator for several days, when it gradually solidified. As all attempts to recrystallise the substance were unsuccessful, it was analysed in its crude form:

0.2376 gave 12.1 c.c. nitrogen at 22° and 756 mm. N = 5.7.

$C_{12}H_{13}O_6N$ requires N = 5.3 per cent.

This oxime dissolves readily in hot water and, on cooling, separates as an oil.

Semicarbazone of Brazilic Acid, $C_{13}H_{15}O_6N_3$.—Brazilic acid appar-

ently combines with semicarbazide only with difficulty, as the following experiment shows. About 1 gram of the acid was dissolved in hot water and mixed with 1.5 grams of semicarbazide hydrochloride and 1.5 grams of sodium acetate and allowed to stand. After a few days, a thick oil had separated, which, on vigorous stirring, soon solidified to a mass of minute crystals; these appeared to consist of the semicarbazone mixed with small quantities of unchanged brazilic acid, since the substance contained only 11 per cent. of nitrogen, instead of 13.6 per cent. required by the formula $C_{13}H_{15}O_6N_3$. The filtrate from the crystals deposited, in the course of a few days, a hard, compact crust of crystals, which were collected, washed well, and dried at 100° . On analysis:

0.165 gave 18.4 c.c. nitrogen at 17° and 747 mm. $N = 12.7$.

$C_{13}H_{15}N_3O_6$ requires $N = 13.6$ per cent.

The substance began to decompose at $125\text{--}126^\circ$, then at about $150\text{--}160^\circ$ it became quite solid, and a few degrees higher it again decomposed and was converted into a black mass. That this substance, although not quite pure, is the semicarbazone of brazilic acid was proved by dissolving it in hot hydrochloric acid, when, on cooling, the solution became filled with needle-shaped crystals of pure brazilic acid.

Lactone of Dihydrobrazilic Acid.

Brazilic acid is readily reduced by sodium amalgam with formation of the sodium salt of dihydrobrazilic acid, and on acidifying this the γ -hydroxy-acid at once loses water with formation of its lactone.

The pure sodium salt of brazilic acid (0.5 gram) was dissolved in water, the solution placed in a flat, porcelain dish cooled by running water, and treated with 3 per cent. sodium amalgam (100 grams) in small quantities at a time. On acidifying the product, an oily substance separated which was at first partly soluble in sodium carbonate and therefore probably contained some hydroxy-acid. In order to convert the whole into the lactone, the strongly acid liquid was warmed for a few minutes on the water-bath.

After repeatedly extracting with pure ether, the solution was dried over calcium chloride and evaporated to a small bulk, when, on standing, small, colourless, glistening crystals separated: these were collected, washed with ether, and analysed.

0.1753 gave 0.3949 CO_2 and 0.0831 H_2O . $C = 61.4$; $H = 5.3$.

0.1052 „ 0.2354 CO_2 „ 0.0498 H_2O . $C = 61.0$; $H = 5.2$.

$C_{12}H_{12}O_5$ requires $C = 61.0$; $H = 5.1$ per cent.

The lactone of dihydrobrazilic acid melts at $142\text{--}144^\circ$ and is sparingly soluble in dry ether; it dissolves readily in warm water and

separates on cooling as an oil which, however, soon crystallises ; it is readily soluble in alcohol, moderately so in chloroform and benzene, and sparingly soluble in light petroleum. When heated in small quantities in a test-tube, it decomposes to a large extent and gives an oily distillate smelling of coumarin ; this solidifies on rubbing, and on crystallising from water some of the lactone is recovered, showing that it distils to some extent without decomposition.

The lactone dissolves in baryta water, yielding a readily soluble barium salt, but is insoluble in cold sodium carbonate ; on boiling, however, it dissolves, and the solution, if well cooled and acidified, remains clear and evidently contains the hydroxy-acid, since, if heated to boiling and again cooled, the lactone separates. Concentrated sulphuric acid colours the crystals an intense crimson, and on standing a deep crimson solution is produced ; this, on warming, becomes at first more intensely coloured, and then the crimson changes to dark brown.

Anhydrobrazilic Acid.

This acid is obtained when brazilic acid is treated with sulphuric acid under the following conditions. Pure brazilic acid (0.3 gram) is dissolved in 5 c.c. of sulphuric acid and the test-tube containing the solution plunged into boiling water for $1\frac{1}{2}$ to 2 minutes ; the dark brown solution is then cooled and mixed with 2 vols. of water when, on rubbing with a glass rod, a pale yellow, crystalline substance quickly separates. The sparingly soluble precipitate is collected on the pump, washed well, and dissolved in boiling water, a little purified animal charcoal being added, when, on cooling the filtered solution, a sandy, crystalline powder is deposited which consists of pure anhydrobrazilic acid.

In the preparation of this acid, it was found best to always work with the quantities given above ; if larger quantities are used, the yield obtained is not nearly so good. From the sulphuric acid mother liquors, small quantities of the anhydro-acid mixed with some unchanged brazilic acid may be extracted with ether and the two acids may then be separated by crystallisation from water.

The total yield of anhydrobrazilic acid obtained is, however, not more than 50 per cent. of the brazilic acid used, the loss being apparently due to some of the latter acid becoming sulphonated during the process of preparation. On analysis :

0.1635 gave 0.3681 CO_2 and 0.0645 H_2O . $\text{C} = 61.4$; $\text{H} = 4.4$.

0.1472 „ 0.3319 CO_2 „ 0.0580 H_2O . $\text{C} = 61.5$; $\text{H} = 4.4$.

$\text{C}_{12}\text{H}_{10}\text{O}_5$ requires $\text{C} = 61.5$; $\text{H} = 4.3$ per cent.

Anhydrobrazilic acid is very sparingly soluble in water and melts at 197° . When heated in a test-tube, it decomposes and gives a brown

oily distillate which, on cooling, solidifies and has an odour strongly resembling that of coumarin. It dissolves readily in alcohol, but is sparingly soluble in benzene, chloroform, or ether, and almost insoluble in light petroleum. It behaves like an unsaturated acid, since its solution in sodium carbonate rapidly decolorises permanganate. That it is a monobasic acid is shown by the results obtained by titrating it with decinormal sodium hydroxide.

0.1536 required for neutralisation 0.0264 NaOH, whereas this amount of a monobasic acid, $C_{12}H_{10}O_5$, should neutralise 0.0263 NaOH.

Oxime of Anhydrobrazilic Acid, $C_{12}H_{11}NO_5$.—In preparing this oxime, a small quantity of the acid was dissolved in sodium bicarbonate, mixed with an excess of a solution of hydroxylamine hydrochloride which had been neutralised with sodium carbonate, and the whole allowed to stand for 24 hours. On acidifying, the product deposited an oil, but this rapidly solidified to a granular precipitate, which was collected, washed well, and recrystallised from boiling water. It was thus obtained as a sandy powder consisting of microscopic needles, which melted with decomposition at about 175–180°. On analysis:

0.1533 gave 0.3260 CO_2 and 0.0629 H_2O . C = 57.9; H = 4.5.

0.1567 „ 7.9 c.c. nitrogen at 20° and 760 mm. N = 5.8.

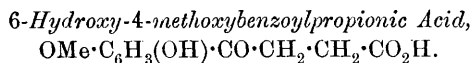
$C_{12}H_{11}NO_5$ requires C = 57.8; H = 4.4; N = 5.6 per cent.

Oxidation of Anhydrobrazilic Acid. Formation of p-Methoxysalicylic Acid, $OMe \cdot C_6H_3(OH) \cdot CO_2H$.—The pure acid (0.5 gram) was dissolved in dilute sodium carbonate and a cold saturated solution of permanganate added drop by drop with constant shaking until the pink colour remained permanent. After sufficient sodium sulphite had been added to destroy the excess of permanganate, the whole was boiled, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk. On acidifying, a colourless acid separated which crystallised from water in colourless needles. On analysis:

0.1104 gave 0.2299 CO_2 and 0.0495 H_2O . C = 56.8; H = 4.9.

$C_8H_8O_4$ requires C = 57.1; H = 4.8 per cent.

This acid melted at 156°, and its aqueous solution gave, with ferric chloride, an intense violet coloration. That it was *p*-methoxysalicylic acid was further proved by mixing it with an equal quantity of this acid, when the mixture melted at 155–156°.



Anhydrobrazilic acid dissolves readily in warm barium hydroxide solution, and if the solution is boiled a thick, crystalline precipitate of the

barium salt of hydroxymethoxybenzoylpropionic acid rapidly forms, the separation being complete after 15 to 20 minutes.

If the solution is dilute, the separation does not take place until it is concentrated sufficiently, and then the barium salt separates in stellate groups. The barium salt is collected on the pump, washed with water, and dissolved in warm dilute hydrochloric acid, when, on standing, the free acid separates in colourless needles, and by recrystallisation from water is readily obtained pure, in long threads somewhat resembling crystals of sublimed phthalic acid. On analysis :

0.1714 gave 0.3702 CO_2 and 0.0840 H_2O . $\text{C} = 58.9$; $\text{H} = 5.4$.

0.1541 „ 0.3329 CO_2 „ 0.0756 H_2O . $\text{C} = 58.9$; $\text{H} = 5.4$.

$\text{C}_{11}\text{H}_{12}\text{O}_5$ requires $\text{C} = 58.9$; $\text{H} = 5.3$ per cent.

6-Hydroxy-4-methoxybenzoylpropionic acid melts at $155-156^\circ$ and dissolves readily in hot, but is rather sparingly soluble in cold, water ; its aqueous solution gives an intense violet coloration with ferric chloride.

The barium salt, obtained by the action of barium hydroxide on anhydrobrazilic acid in the way described above, after drying at 100° , was analysed with the following results :

0.3987 gave 0.2440 BaSO_4 . $\text{Ba} = 36.1$.

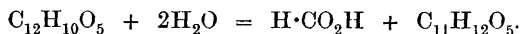
$\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}, \text{H}_2\text{O}$ requires $\text{Ba} = 36.4$ per cent.

From this it would appear that the barium salt prepared in this way has the formula $\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}, \text{H}_2\text{O}$, that is to say, that the barium has replaced, not only the hydrogen of the carboxyl group, but also that of the phenolic hydroxyl group.

Such cases as this have often been observed before ; thus salicylic acid yields a barium salt, $\text{C}_7\text{H}_4\text{O}_3\text{Ba}, 2\text{H}_2\text{O}$, which is very sparingly soluble in water.

The filtrates from several preparations of the barium salt of hydroxymethoxybenzoylpropionic acid were mixed and the excess of barium hydroxide removed by passing carbon dioxide through the boiling solution.

The filtrate deposited, on evaporation, a further small quantity of the insoluble barium salt ; this was removed by filtration, and the concentrated solution, which contained a considerable quantity of a barium salt, carefully tested for formic acid. This was easily proved to be present, not only by the fact that the solution blackened silver nitrate, but also because it readily reduced mercuric chloride to mercurous chloride. There can, therefore, be no doubt that anhydrobrazilic acid is decomposed by boiling with barium hydroxide into formic acid and hydroxymethoxybenzoylpropionic acid, according to the equation



Dimethoxybenzoylpropionic Acid, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

It was necessary to prepare this acid, in order to compare it with the acid obtained synthetically by the action of aluminium chloride on the mixture of dimethylresorcinol and the ester of the half-chloride of succinic acid (see next section).

Hydroxymethoxybenzoylpropionic acid (1 gram) was dissolved in 12 grams of methyl alcohol, 3 grams of concentrated sulphuric acid added, and the whole heated to boiling in a reflux apparatus for 4 hours.

On adding water, a crystalline substance separated, which, since it was insoluble in sodium carbonate, evidently consisted of the methyl ester, $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2Me$. In this condition, it melted at about 85° , and its alcoholic solution gave an intense violet with ferric chloride; it was, however, not further purified, owing to the necessity for using the whole quantity for further methylation. The dry methyl ester (0.8 gram) was dissolved in dilute sodium methoxide (containing 0.1 gram Na) and heated in a sealed tube with 3 grams of methyl iodide at 120° for 2 hours; the tube was then opened, the same quantity of sodium methoxide and methyl iodide again added, the tube resealed, and heated at 120 — 130° for 3 hours. The product was poured into water, the oily precipitate extracted with ether, the ethereal solution well washed with water, and then three times with dilute soda in order to extract some unmethylated ester which was present. The ethereal solution was then evaporated and the residual oil hydrolysed by boiling for a few minutes with methyl alcoholic potash. Water was then added and the clear solution evaporated until free from methyl alcohol, when, on the addition of hydrochloric acid, a crystalline acid was deposited, which was collected, washed with water, dried on a porous tile, and recrystallised twice from benzene. On analysis:

0.1250 gave 0.2779 CO_2 and 0.0673 H_2O . $C = 60.6$; $H = 6.0$.

$C_{12}H_{14}O_5$ requires $C = 60.5$; $H = 5.9$ per cent.

Dimethoxybenzoylpropionic acid melts at 146 — 148° , with slight previous softening, and when kept a short time a few degrees above its melting point, it becomes a deep violet colour. It is readily soluble in alcohol and in hot benzene, but sparingly so in cold benzene; its alcoholic solution gives no coloration with ferric chloride.

Synthesis of Dimethoxybenzoylpropionic Acid.

[With E. ORMEROD.]

In synthesising this acid, a process was employed which is somewhat similar to that recommended by L. Bouveault (*Bull. Soc. Chim.*, 1897, [iii], 17, 333) as suitable for cases of this kind.

Dimethylresorcinol (8.4 grams) was dissolved in nitrobenzene (17 grams) and carbon disulphide (35 grams), and then mixed with the ester of the half-chloride of succinic acid, $\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (10 grams). Powdered aluminium chloride* (8 grams) was then added in small quantities and, after standing for some hours, the mixture was gently heated on the water-bath for a few minutes.

The product was treated with water, the oily layer well washed with water, and the carbon disulphide removed on the water bath; the residue was then distilled in steam until the nitrobenzene and small quantities of unchanged dimethylresorcinol had been removed. The non-volatile oil was extracted with ether, the ethereal solution evaporated, and the brown oil hydrolysed with a slight excess of alcoholic potash. After evaporating off the alcohol, the residue was dissolved in water and acidified, when a brown solid separated, which was collected on the pump and purified by repeated recrystallisation from benzene. On analysis:

0.1559 gave 0.3465 CO_2 and 0.0834 H_2O . $\text{C} = 60.6$; $\text{H} = 5.9$.

$\text{C}_{12}\text{H}_{14}\text{O}_5$ requires $\text{C} = 60.5$; $\text{H} = 5.9$ per cent.

The synthetical dimethoxybenzoylpropionic acid thus obtained melted at $146\text{--}148^\circ$ with slight previous softening, and the melted mass became a deep violet colour a few degrees above this temperature. That it is identical with the acid of this composition obtained from anhydrobrazilic acid as described above, was further proved by mixing the two acids, when no alteration in the melting point could be observed.

In conclusion, I wish to express my thanks to Mr. J. Yates for his valuable assistance in carrying out this investigation, and I wish also to state that much of the expense incurred was defrayed by repeated grants from the Royal Society Fund.

THE OWENS COLLEGE,
MANCHESTER.

* Prepared from aluminium.