quantities of barium the test obtained can hardly be considered conclusive except for traces.

In the light of these facts it is clear that by means of a systematic qualitative analysis it is not possible to detect barium when it occurs to the extent of 5 per cent., if a gram sample be used. This fact has led us to the task of working out another method for the systematic detection of the alkaline earth metals, which will be reported in another communication.

Summary.

It has been shown as a result of a quantitative study that in the ordinary systematic qualitative scheme the test for barium with ammonium carbonate is unreliable in consequence of losses which have been accounted for under the following heads:

1. Loss involved in the precipitation of a typical metal of the copper group, 1.4 mg. Ba.
2. Loss due to the action of ferric chloride on hydrogen sulfide, 14.0 mg. Ba.
3. Loss due to the absorption of carbon dioxide in the precipitation of the iron group with ammonia, 14.7 mg. Ba.
4. Loss involved in the precipitation of a typical metal of the ammonium sulfide group, 2.2 mg. Ba.
5. Loss involved in the precipitation and filtration of zinc sulfide, 2.8 mg. Ba.
6. Failure of the reagent ammonium carbonate to detect as much as 10 mg. barium in the presence of ammonium salts.
7. Presence of sulfates in the reagents employed.

These figures represent the minimum losses, but that they are larger in actual qualitative work is shown by the results of a number of test analyses which failed to disclose the presence of as much as 25 and in some cases 50 milligrams of barium.

METHYLENEDISALICYLIC ACID AND ITS REACTION WITH BROMINE AND IODINE.

By Erik Clemmensen and Arnold H. C. Heitman.

Received February 22, 1911.

This work was undertaken to study the interaction between methylenedisalicylic acid and iodine, and as the results were of a complicated and unexpected nature, we also included the action of bromine to see if similar or more normal conditions would prevail.

Methylenedisalicylic acid was first prepared by Geigy,[1] who obtained it by heating a mixture of salicylic acid and formaldehyde solutions with strong hydrochloric acid.

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[1] D. R. P. 49970.

It was later prepared by Kahl[1] and Madsen[2] in practically the same way. They all used a much larger amount of formaldehyde than theory calls for.

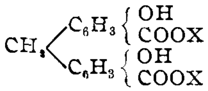
When we prepared it in the same way we obtained an impure product, which after repeated washing with hot water began to melt at 180° and only after careful purification was obtained with the correct melting point of 238°.

When we replaced strong hydrochloric acid by 50 per cent. sulfuric acid and used the theoretical amount of formaldehyde, we at once obtained a product, which after washing with hot water melted at 238°. In this connection it is worth mentioning that by carrying out the reaction in very concentrated solution, and using the theoretical amount of formaldehyde, a product is obtained which, contrary to methylenedisalicylic acid, is insoluble in cold, glacial acetic acid, and on heating does not melt but chars at a temperature above 260°, otherwise, both in reactions and empirical formula is identical with methylenedisalicylic acid.

Methylenedisalicylic acid behaves much like salicylic acid. Aqueous solutions acquire a blue coloration upon the addition of ferric salts.

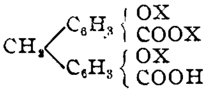
When heated above its melting point methylenedisalicylic acid is decomposed, forming hydroxyphenylmethylenesalicylic acid, and carbon dioxide, and by continued heating yields methylenediphenol.

The acid forms two kinds of salts, *viz.*:



$$CH_2\begin{cases}C_6H_3\begin{cases}OH\\COOX\end{cases}\\C_6H_3\begin{cases}OH\\COOX\end{cases}\end{cases}$$

and



$$CH_2\begin{cases}C_6H_3\begin{cases}OX\\COOX\end{cases}\\C_6H_3\begin{cases}OX\\COOH\end{cases}\end{cases}$$

Normal. Basic.

Of the normal salts which are formed by action of carbonates on the acid, the alkali and alkali earth salts are soluble, while of the basic salts formed with excess of hydroxides, only the alkali salts are soluble.

While studying the different conditions under which formaldehyde was allowed to react on salicylic and methylenedisalicylic acids, we found that formaldehyde when in excess forms an addition product with the phenol groups of methylenedisalicylic acid from which it was readily removed by boiling the product with caustic alkalis. We were unable, however, to obtain this product sufficiently pure for analysis.

Pure methylenedisalicylic acid does not yield formaldehyde.

We observed that methylenedisalicylic acid when subjected to halogenation in alkaline solution, or in glacial acetic acid, to which mercuric oxide or acetate (serving to react with the hydrogen halide) was added,

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[1] *Ber.*, 31, 148.

[2] *Arch. Pharm.*, 245, 44.

reacted very readily with halogen, but to our surprize found that simple substitution did not follow.

Even though the results obtained in halogenating methylenedisalicylic acid were not entirely satisfactory, for the reason that the halogenated substance lacked uniformity, and that these substances or their salts could not be obtained in crystallin form, nor satisfactorily separated by fractional precipitation, or by the aid of solvents, they do nevertheless serve to indicate what follows during the reaction of methylenedisalicylic acid with bromine and iodine. Of the two, the brominated derivatives were least definit in point of substitution and distinction.

It appears, that before halogen is taken up, a condensation or rearrangement of some kind is first effected after which the halogen enters the newly formed molecule, until a certain point of saturation is reached when additional methylenedisalicylic acid is reacted upon. If, for instance, the acid was treated with halogen in such a way as would naturally introduce n atoms halogen a product would result with only $2n - 1/2$ atoms of halogen in the molecule. This would indicate that two molecules methylenedisalicylic acid united during the reaction forming a condensation product containing $2n - 1$ atoms halogen.

When a moderate amount of halogen was used, compounds of the general empirical formula $C_{30}H_{16-n}O_{10}X_n$ resulted. These compounds are dihydroxydicarboxylic acids, as with carbonates they form dibasic salts, and on treatment with hydroxides they form salts with four equivalents of base.

The acids are insoluble in water but slightly soluble in dilute mineral acids. Their alkaline solutions are strongly colored.

On acetylating, six acetyl groups are added, and these compounds when dissolved in alkalies give practically no color.

This seems to indicate that two of the hydroxyl groups are in quinoid form.

By prolonged boiling with zinc dust and potassium hydroxide all halogen is removed and compounds result with the empirical formula $C_{30}H_{16}O_{10}$, having the same general properties as the halogenated compounds.

When treated with halogen they react very readily (without the necessity of having a substance present to react with the hydrogen halide formed, as in the case of methylenedisalicylic acid) forming halogenated compounds which are identical with those obtained direct from methylenedisalicylic acid.

On heating the calcium salts of these halogenated derivatives, phenol and a small quantity of parabromocresol distil off.

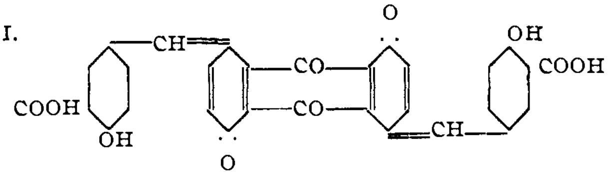
When treating the halogenated dicarboxylic acids $C_{30}H_{16-n}O_{10}X_n$ with dilute alkalies or dilute mineral acids in a sealed tube at 160°, or in an alkaline solution with a large excess of halogen, carbon dioxide is eliminated and halogenated compounds with the empirical formula $C_{29}H_{16-n}O_8X_n$ are formed.

These compounds are monobasic acids, decomposing carbonates with the formation of strongly greenish-colored insoluble salts. Upon treatment with hydroxides, they do not take up additional base nor can they be acetylated.

We were unable to completely remove the halogen from these derivatives. These halogenated monobasic acids can also be obtained direct, *viz.*: by treating methylenedisalicylic acid with a large excess of halogen in the presence of an alkaline carbonate.

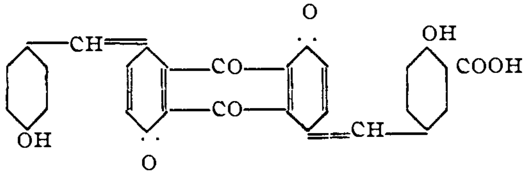
The way these compounds are obtained, and the above mentioned properties and reactions, could be explained by the following structural formulas:

I.



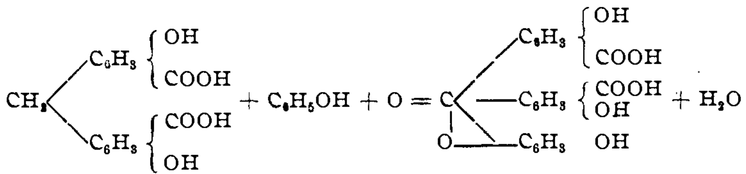
I. Representing the halogenated dihydroxydicarboxylic acids which would be designated as 1,5-anthratriquinone-4,8-dihomo-[5,5]salicylic acid.

II.



II. Representing the halogenated monocarboxylic acids, which would be designated as 4-hydroxy-8-benzylidene-1,5-anthratriquinone-4-homo-[5] salicylic acid.

Caro[1] found when reacting with an oxidizing and dehydrating mixture (nitrous acid in concentrated sulfuric acid) upon a mixture of one molecule phenol or phenolcarboxylic acid, and one molecule methylenedisalicylic acid, hydroxyaurins and their carboxylic acids are formed:



Hydroxyaurin.

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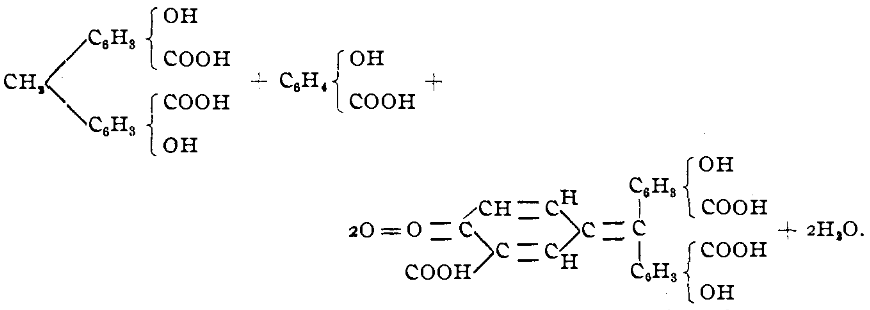
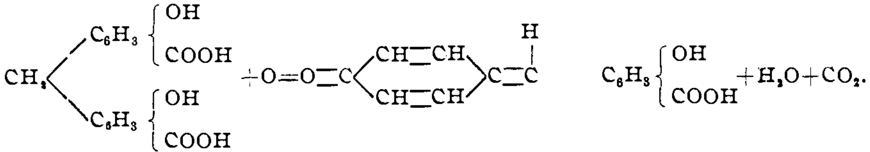
[1] *Ber.*, **25**, 939–943.

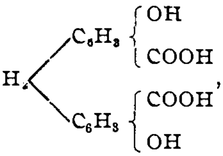


Aurintricarboxylic acid.

and Kahl[1] observed by reacting on methylenedisalicylic acid with a similar oxidizing mixture that the acid is converted into formaurin:



Experimental.

Methylenedisalicylic acid,  was prepared by mixing 32 grams salicylic acid, 10 grams formaldehyde 40 per cent. (theory) and 180 grams 50 per cent. sulfuric acid and gently boiling the mixture 10 hours under reflux condenser. The reaction product was powdered, washed with cold water and finally several times with boiling water to remove any uncondensed salicylic acid, collected and dried. The yield was theoretical. The resulting methylenedisalicylic acid is a white powder, having a strong bitter taste and melting at 238° with decomposition. It could not be obtained in good crystallin form.

It is readily soluble in ether, acetone, alcohol, ethyl acetate, glacial acetic acid, very slightly in hot water and insoluble in benzene, chloroform, carbon disulfide and petroleum ether.

From solutions in alcohol, acetone and glacial acetic acid it is imperfectly precipitated on addition of water.

Its aqueous solutions are colored blue by ferric chloride. On heating methylenedisalicylic acid by itself above the melting point or with caustic alkalies, it is decomposed into hydroxyphenylmethylenesalicylic acid, methylenediphenol and carbon dioxide.

Alkali and alkali earth carbonates are readily decomposed by it, forming

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[1] *Ber.*, 31, 143–151.

soluble salts, none of which could be obtained in distinct crystallin form. They are precipitated from concentrated solutions on addition of alcohol, or sodium chloride.

The salts of the heavy metals, made by double decomposition cf the soluble salts, are obtained as insoluble colored precipitates. Methylenedisalicylic acid, when precipitated from a soluble salt with a mineral acid, separates in gelatinous form, particularly if the solution is warm.

A mixture of salicylates and methylenedisalicylates, in solution, when fractionally precipitated by mineral acids will first yield most of the salicylic acid, although the entire separation in this way is not possible.

Methylenedisalicylic acid for analysis was prepared over the barium salt, precipitated with dilute hydrochloric acid taken up with ether, the ether evaporated and the substance dried at 100° for 5 hours.

Calculated for $C_{15}H_{12}O_6$: C, 62.48; H, 4.20.
Found: C, 62.36; H, 4.01.

Calcium methylenedisalicylate was prepared by decomposing calcium carbonate with methylenedisalicylic acid in boiling water; filtering, concentrating the solution and precipitating with alcohol. Dried to constant weight over sulfuric acid *in vacuo* the salt contains two molecules water of crystallization. It is a white, bitter-tasting substance, soluble in water.

Calculated for $C_{15}H_{10}O_6Ca + 2H_2O$: Ca, 11.07; found 11.20.

Dried at 110° for 24 hours it gave the following results:

Calculated for $C_{15}H_{10}O_6Ca$: Ca, 12.22; found, 12.54.

Dicalcium methylenedisalicylate was prepared by treating a solution of the normal calcium salt with the calculated quantity of potassium hydroxide, when the basic salt was precipitated with eight molecules water of crystallization. It is a white voluminous powder. For analysis it was dried to constant weight over sulfuric acid *in vacuo*.

Calculated for $C_{15}H_8O_6Ca_2 + 8H_2O$: Ca, 15.78; found, 15.73.

The salts of barium, magnesium and zinc were prepared and found to have the same general properties.

Barium methylenedisalicylate............	$C_{15}H_{10}O_6Ba + 3H_2O$.
Dibarium methylenedisalicylate...........	$C_{15}H_8O_6Ba_2 + 8H_2O$.
Magnesium methylenedisalicylate.........	$C_{15}H_{10}O_6Mg + 2H_2O$.
Zinc dimethylenedisalicylate..............	$C_{15}H_{10}O_6Zn + 4H_2O$.

Diacetylmethylenedisalicylic acid was prepared by dissolving 15 grams methylenedisalicylic acid in glacial acetic acid and boiling for several hours with either 16 grams acetic anhydride or 10 grams acetyl chloride. When cold it was poured into water and separated out as a heavy oil.

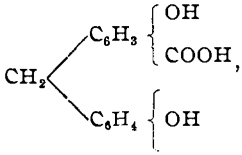
It was purified by taking it up in ether, the solution washed with water, the ether evaporated and the substance dried at 50° *in vacuo* over calcium chloride and potassium hydroxide sticks. It is a white powder, permanent in air, melting at 142°, and decomposing carbonates forming soluble salts.

It is very soluble in ether, alcohol, acetone, acetic ether and glacial acetic acid, insoluble in water, chloroform, carbon disulfide, benzene and petroleum ether.

The substance is not colored with ferric chloride, and could not be obtained in crystallin form.

Calculated for $C_{15}H_{10}O_6(CH_3CO)_2$: C, 61.29; H, 4.33.
Found: C, 61.21; H, 4.19.

0.4484 required 48 cc. 0.1 *N* KOH corresponding to 0.4464 or 99.5% for $C_{15}H_{10}O_6(CH_3CO)_2$ with four equivalents.

Hydroxyphenylmethylenesalicylic acid, or *hydroxyphenylhomosalicylic acid,*  $CH_2\left\langle\begin{array}{l} C_6H_3\left\{\begin{array}{l}OH\\ COOH\end{array}\right. \\ C_6H_4\left\{OH\right.\end{array}\right.$, was prepared by two methods: first, by dissolving 10 grams of methylenedisalicylic acid and 30 grams potassium hydroxide in 50 cc. of water, heating the mixture at 140° in a sealed tube for two hours, diluting the solution with water, filtering and saturating with carbon dioxide, extracting the separated phenols with ether and acidifying the aqueous solution with dilute hydrochloric acid, when it separated as a sticky mass; secondly, by heating methylenedisalicylic acid above its melting point for a short time, dissolving when cold in potassium hydroxide, saturating the solution with carbon dioxide, extracting with ether and acidulating.

The resulting sticky substance was taken up in ether, the solution washed well with water, the ether evaporated, and the resulting red-colored transparent mass dried at 50° *in vacuo* over calcium chloride.

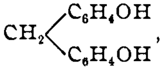
It appears as a slightly red-colored electrical substance, melting above 60° and very slightly soluble in boiling water, readily soluble in ether, acetone, ethyl acetate, glacial acetic acid, and insoluble in chloroform, carbon disulfide, benzene and petroleum ether. It could not be obtained in crystallin form.

Its aqueous solution is colored blue by ferric chloride, and it decomposes alkali carbonates forming soluble salts, which are separated as viscid liquids with sodium chloride.

Calculated for $C_{14}H_{12}O_4$: C, 68.82; H, 4.95.
Found: C, 68.62; H, 5.27.

1.2580 required 50.6 cc. 0.1 *N* KOH corresponding to 1.23909 or 98.48%.

When the substance was made according to the second method, it contained small quantities of methylenedisalicylic acid. It is interesting to note that this substance is isomeric with the quinoid formaurin discovered by Kahl.[1]

Methylenediphenol,[2] 
$CH_2 < \begin{matrix} C_6H_4OH \\ C_6H_4OH \end{matrix}$, represented the major portion of the phenols which separated by saturating the potassium hydroxide solution with carbon dioxide. It was obtained pure by boiling the ether-soluble residue with water and filtering the solution hot, when on cooling it crystallized in thin colorless plates. It agrees with the properties given in the literature with one exception, having a melting point of 148° instead of 158° as given. For analysis it was dried at 100° for two hours.

Calculated for $C_{13}H_{12}O_2$: C, 77.96; H, 6.00.
Found: C, 77.40; H, 6.29.

Tribromoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}Br_3$, was prepared by dissolving 36 grams of methylenedisalicylic acid and 20 grams of sodium hydroxide in 1000 cc. water and adding to this a solution of 35 grams of bromine and 50 grams of sodium bromide in 500 cc. of water. The mixture was gently warmed to 45°, cooled and acidulated with dilute hydrochloric acid. The resulting reddish-colored product was washed with water, boiled with an excess of calcium carbonate suspended in dilute alcohol, and the solution filtered and concentrated, when the calcium salt separated as a dark heavy liquid. It was obtained pure by redissolving it in dilute alcohol, and concentrating the solution.

The calcium salt was decomposed with dilute hydrochloric acid and the substance taken up with ether, the ether solution washed with water, the ether evaporated and the residue dried at 100°.

It appears in the form of hard, brittle, colored lumps. When freshly prepared, it is slightly soluble in dilute mineral acids, readily in acetone, alcohol, ether and alkalies with a red color. It is insoluble in chloroform, benzene and carbon disulfide. Heated above 200° it is decomposed.

Calculated for $C_{30}H_{13}Br_3O_{10}$; Br, 31.02; found, 31.02.

The neutral calcium salt was prepared by boiling the substance with a large quantity of dilute alcohol in which finely precipitated calcium carbonate was suspended, filtering the hot solution, evaporating to one-fourth the original volume, collecting the precipitate which was first dried at ordinary temperature and finally for one hour at 100°.

It is a dark reddish-colored, hard, lumpy substance.

Calculated for $C_{30}H_{11}Br_3O_{10}Ca$; Ca, 4.93; found, 4.85.

The basic potassium salt was prepared by dissolving 9 grams of the acid in 100 cc. of alcohol containing 3.5 grams potassium hydroxide, when it was precipitated in gelatinous form. It was obtained pure by dissolving it in the least possible amount of water and precipitating with alcohol.

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[1] *Ber.*, **31**, 143.

[2] Beck, *Ann.*, **194**, 318; Eberhardt-Welter, *Ber.*, **27**, 1814; Steadel, *Ann.*, **283**, 163.

Dried at 50° over sticks of potassium hydroxide and calcium chloride *in vacuo*, it appears in the form of dark, brittle lumps soluble in water with a red color, and insoluble in acetone.

Calculated for $C_{30}H_9Br_3O_{10}K_4$: K, 16.90; found, 17.23.

Triiodoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}I_3$ was prepared by two methods: first, by dissolving 5 grams sodium hydroxide and 9 grams of methylenedisalicylic acid in 100 cc. of water, and adding this to a cold solution of 25 grams of iodine and 40 grams of sodium iodide in 1000 cc. water. The mixture was gently warmed to 80° on a steam bath, allowed to cool, the reaction product salted out with sodium chloride and acidulated with dilute sulphuric acid. Secondly, by dissolving 9 grams of methylenedisalicylic acid and 25 grams of iodine in 500 cc. of glacial acetic acid, adding 15 grams of yellow mercuric oxide, and warming the mixture to 75° until all free iodine had disappeared. The acetic acid was then removed under reduced pressure, the residue treated with sodium carbonate solution, filtered and acidulated.

The resulting iodinated product was purified by boiling it with a large quantity of dilute alcohol containing in suspension finely precipitated calcium carbonate, the clear liquid poured off, the insoluble residue collected, warmed with dilute hydrochloric acid and the insoluble product washed with water and dried. It is a reddish-colored substance, decomposing above 230° and when freshly prepared slightly soluble in dilute mineral acid and readily soluble in alcohol, acetone, ethyl acetate and glacial acetic acid. It is insoluble in water, chloroform, benzene, carbon disulfide and petroleum ether.

Alkali carbonates and alkali hydroxides yield soluble salts which dissolve with a red color.

From concentrated solutions they are precipitated in gelatinous form with alcohol.

The salts of the alkali earths and the heavy metals are insoluble in water.

Iodine is liberated by heating the substance in dry form or with concentrated sulfuric acid, and by boiling with potassium hydroxide and zinc dust it is entirely removed. When heated in a sealed tube with a one per cent. alkali carbonate or 2 per cent. mineral acid solution carbon dioxide is broken off and the substance is transformed to a monocarboxylic acid derivative. For analysis the substance was dried at 100°.

Calculated for $C_{30}H_{13}I_3O_{10}$: C, 38.84; H, 1.43; I, 42.05.
Found: C, 39.07; H, 1.67; I, 41.48.

The calcium and basic potassium salts made in the usual manner gave the following results:

Calculated for $C_{30}H_{11}I_3O_{10}Ca$: Ca, 4.20; found, 3.78.
Calculated for $C_{30}H_9I_3O_{10}K_4$: K, 14.67; found, 14.38.

An acetylated product was prepared by boiling for 5 hours 9 grams of the substance with 10 grams of acetic anhydride dissolved in 200 cc. glacial acetic acid. The reaction mixture was poured into water, the precipitate collected, dissolved in alcohol and precipitated with water, collected and dried over potassium hydroxide sticks *in vacuo*. It is then obtained as a yellow substance, soluble in alcohol, ether, ethyl acetate and glacial acetic acid, and insoluble in benzene, chloroform, and petroleum ether.

Calculated for $C_{30}H_{11}I_3O_{10}(CH_3CO)_6$: I, 32.50; found, 31.32.

During acetylation the substance lost iodine, but it shows that a change from a quinoid configuration to a regular form has resulted and that the acetyl radical has also entered the methylene group.

Heptabromoanthratriquinonedihomosalicylic acid, $C_{30}H_9O_{10}Br_7$, was prepared by dissolving 18 grams of methylenedisalicylic acid and 10 grams of sodium hydroxide in 800 cc. water and then adding 12 grams of sodium carbonate. This solution was added to 500 cc. of water containing 60 grams of bromine and 80 grams of sodium bromide, and the mixture slowly warmed to 60°, when the reaction product separated as a yellow mass, which was collected and extracted with alcohol, the alcohol-insoluble residue dissolved in acetone and precipitated from the acetone solution with alcohol, collected and dried at 80°. The yield was 4 grams.

It is a light yellow fine, electrical powder, decomposing above 200°.

It is very soluble in acetone, slightly soluble in alcohol, and insoluble in chloroform, benzene, carbon disulfide and petroleum ether. Alkalies dissolve it with a red color. It could not be acetylated without decomposition.

Calculated for $C_{30}H_9Br_7O_{10}$: Br, 51.41; found, 50.80.

A basic potassium salt was prepared by dissolving 6 grams of the acid in 20 cc. of acetone and adding it to a solution of 1.7 grams potassium hydroxide in absolute alcohol.

The resulting dark, gelatinous substance was dissolved in the least possible amount of warm water and precipitated with absolute alcohol, collected and dried over potassium hydroxide sticks *in vacuo*, at 50°.

It appears in the form of dark-colored brittle lumps, soluble in water and insoluble in alcohol and acetone.

Calculated for $C_{30}H_5Br_7O_{10}K_4$: K, 12.72; found, 12.62.

Pentabromohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8Br_5$, was prepared by dissolving 18 grams of methylenedisalicylic acid, 10 grams of sodium hydroxide and 90 grams of sodium borate in 1000 cc. of water and adding the solution to 120 grams of bromine and 150 grams of sodium bromide in 1000 cc. of water. The mixture was gradually warmed to 75°, when a strong reaction followed, after which the yellow reaction product was collected and purified by dissolving it in acetone and precipitating with alcohol.

It is a yellow powder, practically insoluble, except in acetone and caustic alkalies. It is not precipitated from the latter solution with carbon dioxide.

When a warm acetone solution is treated with warm benzene and the solvent allowed to evaporate at ordinary temperature, a deposit is formed, which under the microscope appears to consist of small round plates.

For analysis it was dried at 100°.

Calculated for $C_{29}H_{11}Br_5O_8$: Br, 45.12; C, 39.29; H, 1.14.
Found: Br, 45.90; C, 38.47; H, 1.91.

Pentaiodohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8I_5$, was obtained in a similar manner, by treating methylene disalicylic acid in alkaline solution with an excess of iodine in the presence of sodium borate.

The resulting iodinated substance was purified by boiling it with very dilute (0.5 per cent.) potassium hydroxide solution, washing the greenish-colored potassium salt until the washings were neutral to litmus paper, and acidulating with dilute hydrochloric acid. The product was thoroughly washed with water and alcohol successively, collected, and dried at 100°.

The substance is a reddish-yellow colored, amorphous powder, practically insoluble in all ordinary solvents, possessing a slight quinonelike odor. On heating it does not melt, but yields iodine and a phenol, leaving a charred residue.

Iodine is also liberated on heating with concentrated sulfuric acid. Alkalies do not remove the iodine but form insoluble greenish-colored salts. All efforts to acetylate the product failed, even with sulfuric acid present. By suspending the substance in glacial acetic acid and boiling for 48 hours with concentrated hydriodic acid, a tarlike mass soluble in caustic alkalies was obtained.

Calculated for $C_{29}H_{11}O_5I_5$: C, 31.03; H, 0.99; I, 56.58.
Found: C, 31.12; H, 1.66; I, 56.49.

$C_{28}H_{10}O_6I_5COOK$. This potassium salt was prepared by two methods, first by warming the substance with an excess of dilute potassium hydroxide; and second with an excess of potassium carbonate. The greenish-colored product was collected and dried. It is an olive-green insoluble powder, permanent in the air.

The analyses of the substance obtained by both methods are given.

Calculated for $C_{29}H_{10}O_8I_5K$: K, 3.37. Found: 1, 4.20; 2, 3.14.

Anthratriquinonedihomosalicylic acid, $C_{30}H_{16}O_{10}$, was prepared by boiling the tribromo derivative with 600 cc. of 25 per cent. potassium hydroxide and 200 grams zinc dust under reflux condenser for 24 hours.

The cold reaction mixture was diluted with water, filtered, acidulated with 50 per cent. sulfuric acid, when the dehalogenated substance separated, as a white precipitate which darkened rapidly on exposure to air. By dissolving it in acetone and precipitating with water it was obtained as a brown powder, which decomposes at 185° and behaves like the original halogenated substance.

Dissolved in glacial acetic acid and treated with bromine or iodine, substitution follows, yielding halogenated products similar to those obtained by treating methylenedisalicylic acid with halogen in the presence of a neutralizing substance.

Calculated for $C_{30}H_{16}O_{10}$: C, 67.15; H, 3.01.
Found: C, 66.55; H, 3.98.

The calcium salt and basic potassium salt were made in the same manner and had the same general properties as the salts of the original halogenated substance. The analyses gave the following results:

Calculated for $C_{30}H_{14}O_{10}Ca$: Ca, 6.98; found, 7.08.
Calculated for $C_{30}H_{12}O_{10}K_4$: K, 22.72; found, 21.95.

The ethyl ester of anthratriquinonedihomosalicylic acid was prepared by heating the silver salt with an excess of ethyl iodide and absolute alcohol in a sealed tube for 5 hours at 160°. The alcohol and excess of ethyl iodide were evaporated, the sustance taken up in ether, the solution washed with potassium carbonate and the ether evaporated. The ester was then obtained as a colorless, resinous mass which in contradistinction to the acid was soluble in benzene but could not be obtained in crystallin form.

In the hope of getting a crystallin acetyl derivative the ester was treated with a large excess of acetic anhydride and the resulting product in ether solution washed with potassium carbonate and the ether evaporated.

The acetylated ester was then obtained as a brown solid which melts above 70° to a liquid possessing a slight ethereal odor. It could however not be crystallized.

It is very soluble in alcohol, acetone, benzene, chloroform, ether and ethyl acetate, only slightly so in carbon disulfide and insoluble in petroleum ether.

Calculated for $C_{28}H_{12}O_6(CH_3CO)_6(COOC_2H_5)_2$: C, 66.80; H, 3.51.
Found: C, 66.02; H, 5.06.

The acetylated derivative must therefore be hexaacetyldihydroxy anthraquinone dihomoethylsalicylate.

40 grams of the calcium salt of the tribromo derivative was mixed with an equal quantity of potassium carbonate and subjected to dry distillation, when 12 grams of phenols distilled. They were fractionated, 75 per cent. coming over at 180–185° while the last fraction distilled above 220°. The first fraction was identified as phenol, and the second as bromoparacresol.

Summary.

1. Methylenedisalicylic acid is obtained pure and in good yield by the interaction of formaldehyde and salicylic acid in molecular proportions, in the presence of 50 per cent. sulfuric acid.
2. Heated above the melting point methylenedisalicylic acid decomposes into hydroxyphenylmethylenesalicylic acid, methylenediphenol and carbon dioxide.
3. When treated with bromine or iodine, methylenedisalicylic acid as such is not halogenated.
4. The action of bromine or iodine on methylenedisalicylic acid effects a condensation in which two molecules of acid are involved, resulting in the formation of a molecule which may be designated as a halogenated anthratriquinonedihomosalicylic acid.
5. This was dehalogenated with zinc dust and potassium hydroxide.
6. When halogenated anthratriquinonedihomosalicylic acid is heated with a solution of alkaline carbonates or mineral acids, under pressure, it is decomposed yielding a monobasic acid, which may be considered as halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid.
7. Halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid is also formed by reacting on methylenedisalicylic acid with a large excess of halogen in the presence of a neutralizing substance like borax or an alkaline carbonate.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

SYNTHESES OF PYRROLE COMPOUNDS FROM IMIDO ACIDS. *N*-PHENYL-α,α'-DICARBETHOXY-β,β'-DIKETOPYRROLIDINE.

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In a paper entitled "Researches on Furfurans," Johnson and Johns[1] showed that diethyl diglycolate condenses with diethyl oxalate, in the presence of sodium ethylate, giving practically a quantitative yield of 2,5-dicarbethoxy-3,4-diketotetrahydrofurfurane (II). The formation of this cyclic compound, in this manner, was perfectly analogous to that of dimethyl diketocamphorate (I)[2] from diethyl oxalate and dimethyl β,β-dimethylglutarate. The authors also stated, in this same paper, their intention of continuing this work and also of examining the behavior of diethyl oxalate towards esters of thiodiglycolic and diglycolamidic acids. These esters would be expected to condense in a manner similar to the glutarates or diglycolates giving the corresponding diketotetrahy-

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[1] *Am. Chem. J.*, 31, 290 (1906).

[2] Komppa, *Ber.*, 32, 1421; 34, 2472; 36, 4332; Dieckmann, *Ibid.*, 32, 1933.