

IV.—*On some New Derivatives of Coumarin.*

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IN May last I had the honour of laying before the Society a short account of some derivatives of this interesting product. Since that time I have procured further information upon the substances I then described, and have also obtained a number of new derivatives of coumarin. I now beg leave to bring an account of my results before the Society.

Dibromide of Coumarin.

When preparing this product I originally mixed a solution of coumarin in disulphide of carbon with a similar solution of bromine, using these substances in theoretical proportions. The resulting solution was then allowed to evaporate spontaneously, and the product purified. By this method I obtained a very poor yield of the dibromide. I have since found that if the solution of bromine and coumarin be kept for twelve hours or more previous to the evaporation of the disulphide, a much larger yield of product is obtained, 5 grms. of coumarin generally yielding from $7\frac{1}{2}$ to 8 grms. of dibromide.

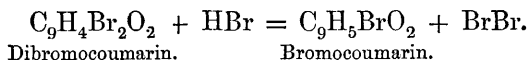
Dibromide of coumarin, when mixed with an alcoholic solution of potassic iodide, becomes brown, and on evaporation deposits metallic-looking needles, apparently consisting of a mixture of iodine and coumarin crystallised together.

a. Bromocoumarin.

Upon referring to the previous method given for the preparation of this body, it will be found that it was obtained from the mother-liquors of dibromocoumarin. If, however, a mixture of bromine and coumarin (mixed with disulphide of carbon) in the proportion of two parts of the former to one of the latter, be heated in a sealed tube to about 200° C. for three or four hours, the resulting product will consist almost entirely of monobromocoumarin.

In this reaction dibromocoumarin is undoubtedly first produced, but at the high temperature employed it is decomposed

by the hydrobromic acid produced, losing half of its bromine, thus—

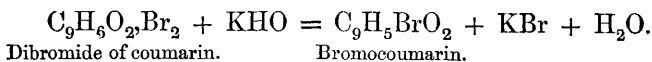


The bromocoumarin obtained by this process sometimes crystallises from alcohol in long slender needles; these, however, on standing in the mother-liquor for a few days become short and hard, like those described in my previous paper; in fact, so different was the appearance of this body when freshly crystallised from that which I had previously obtained, that I subjected it to analysis. The following are the results obtained:—

- I. 4440 of substance gave
 3710 of AgBr.
 II. 3436 of substance gave
 5986 of CO₂, and
 0702 of H₂O.

	Theory.		Experiment.	
			I.	II.
C ₉	108	48·00	—	47·51
H ₅	5	2·22	—	2·27
Br	80	35·56	35·56	—
O ₂	32	14·22	—	—
	225	100·00		

I have, however, found a still more simple process for the preparation of bromocoumarin than the above. It consists in the decomposition of the dibromide of coumarin with alkalis, the following reaction taking place:—



When this process is employed the dibromide of coumarin is powdered and suspended in alcohol, and rather more than enough alcoholic potash is added than is required to complete the above reaction. The decomposition takes place rapidly, the mixture becoming quite hot, and of a pale yellow colour. After it has stood for some time water is gradually added, until it ceases to throw down any more bromocoumarin. When sufficiently diluted the product is collected upon a filter, washed,

dried, and crystallised from spirit. In this way it is generally obtained in transparent needles, about half-an-inch in length. An analysis of this product gave the following numbers:—

·4102 of substance gave
·7242 of CO₂, and
·0872 of H₂O.

	Theory.		Exp.
C ₉	108	48·00	48·15
H ₅	5	2·22	2·36
Br	80	35·56	—
O ₂	32	14·22	—
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	225	100·00	

The alkaline filtrate from the above contains a quantity of this substance in solution, which may be precipitated with acid, and if a large excess of alkali has been used, most of the bromocoumarin will be found in solution; it is, however, apparently not usually so pure as that precipitated with water, and generally forms smaller crystals.

From the difference in the appearance of the products obtained by the above processes, I was at first inclined to think they were isomeric forms of bromocoumarin, but as the melting points are nearly identical, as are also the products of decomposition, I am induced to believe that these variations are due to the presence of small amounts of impurities.

α Bromocoumarin, when left in contact with cold alcoholic ammonia, decomposes with formation of ammoniac bromide, and a non-crystalline sticky mass easily soluble in water. Heated with potassic hydrate it yields potassic bromide and a new acid. It decomposes when heated with potassic cyanide and alcohol in a sealed tube, forming a brown solution, from which water throws down a drab coloured amorphous precipitate. When it is heated with alcohol to 200° C. in a sealed tube for five or six hours, slight decomposition takes place, with formation of hydrobromic acid. A similar change takes place if water be used instead of alcohol.

\alpha. Dibromocoumarin.

The method I previously gave for the preparation of this body consisted in heating in a sealed tube to 140° C. a mixture

of one part of coumarin, two parts of bromine, and four or five parts of disulphide of carbon. I have since found, however, that this process is greatly improved by the addition of iodine to the mixture, as it is then only necessary to heat the sealed tube for four or five hours in a bath of salt and water to complete the reaction. The product is freed from disulphide of carbon by evaporation, and from iodine by means of a solution of potassic iodide, and finally purified by two or three crystallisations from alcohol. A specimen prepared in this manner gave the following numbers :—

·2584 of substance gave
 ·3330 of CO_2 and
 ·0371 of H_2O .

	Theory.		Exp.
C_9	108	35·53	35·15
H_4	4	1·31	1·59
Br_2	160	52·63	—
O_2	32	10·53	—
	304	100·00	

The melting point of this substance is 183°C ., and not 174°C . as I previously gave it. It is, however, not so definite as might be desired, as it generally shows signs of fusion below 183°C .

α Dibromocoumarin is easily decomposed by boiling alcoholic or aqueous potassic hydrate, with formation of potassic bromide, and the potassic salt of a new acid.

When suspended in cold alcoholic ammonia, α dibromocoumarin becomes of a pale yellow colour, and gradually dissolves with formation of ammoniac bromide; on standing a crystalline product is deposited. It is volatile when heated, and evolves ammonia when treated with potash. The resulting alkaline solution does not deposit any product when acidified. It is soluble in water and crystallises in beautiful white needles.

The alcoholic solution upon evaporation yields a second crystalline body soluble in water. It cannot be volatilized without undergoing decomposition. A syrupy body is also produced.

I hope to return to the examination of these products at a future period.

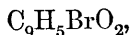
β Bromocoumarin.

It will be remembered that the sodium derivative of the hydride of salicyl, when digested with acetic anhydride, yields ordinary coumarin. It therefore appeared to be of interest to treat the sodium compound of brominated hydride of salicyl in a similar manner, to see whether a brominated coumarin could be obtained.

The hydride of sodium-bromosalicyl, when submitted to the action of acetic anhydride, rapidly changes colour and dissolves, the mixture becoming quite hot. After the reaction has moderated, the product is well boiled for ten or fifteen minutes, and then poured into water, in which it sinks as a heavy oil, acetate of sodium dissolving. On distilling this oil, acetic anhydride and acetic acid first come over, then a quantity of oily product, which rapidly solidifies; the first half of this contains a large quantity of the hydride of bromosalicyl, the remaining portion, however, when crystallised from alcohol two or three times, yields colourless flat prisms, apparently rhombic. This substance gave the following numbers on analysis:—

- I. ·5170 of substance gave
 ·9071 of CO₂, and
 ·1036 of H₂O.
 II. ·3576 of substance gave
 ·6276 of CO₂, and
 ·0735 of H₂O.

The numbers give percentages agreeing with those required by the formula—



as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C ₉	108	48·00	47·84	47·86
H ₅	5	2·22	2·22	2·28
Br	80	35·56	—	—
O ₂	32	14·22	—	—
	225	100·00		

This substance is therefore monobromocoumarin. It is

moderately soluble in spirit, and when fused has an odour somewhat similar to that of coumarin. It greatly differs in properties from the bromocoumarin previously described. Its melting point is 160° C., or 50 degrees higher, and when boiled with alcoholic or aqueous potassic hydrate it does not decompose with formation of potassic bromide, but simply dissolves like ordinary coumarin, I have therefore termed it β bromocoumarin.

β Dibromocoumarin.

On treating the hydride of sodium-dibromosalicyl with acetic anhydride in exactly the same manner as for the preparation of β bromocoumarin, a beautifully crystalline product is obtained. It gave the following numbers on analysis:—

- I. .3639 of substance gave—
 .4714 of CO_2 and
 .0463 of H_2O
 II. .2020 of substance gave—
 .2623 of CO_2 and
 .0266 of H_2O .

These numbers give per centages agreeing with those required by the formula—



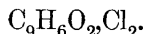
as will be seen by the following comparison:—

	Theory.		Experiment.	
			I.	II.
C_9	108	35.53	35.33	35.41
H_4	4	1.31	1.41	1.46
Br_2	160	52.63	—	—
O_2	32	10.53	—	—
	304	100.00		

The substance is therefore dibromocoumarin. It is rather difficultly soluble in alcohol. It crystallises in short hard needles. It is not the same body as that obtained by acting on coumarin with bromine and iodine. It melts at 176° C., and is not decomposed by boiling with a solution of potassic hydrate. I have, therefore, designated it as β dibromocoumarin.

Dichloride of Coumarin.

A solution of coumarin in chloroform absorbs chlorine gas, very minute quantities of hydrochloric acid being formed. On allowing the solution to evaporate spontaneously after the chlorine has been passed through it for an hour or two, a syrupy product is obtained very like new honey. This is the dichloride of coumarin. I have not analysed it, as there is no way of judging of its purity; but from its products of decomposition, there can be no doubt that it possesses the formula—



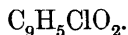
On keeping, it appears to decompose; when heated, it gives off hydrochloric acid, and, on distillation, is converted into chlorocoumarin. With alcoholic potash it decomposes in the same way as the dibromide.

a. Chlorocoumarin.

When a mixture of one part of coumarin and three parts of pentachloride of phosphorus is heated in a retort placed in an oil-bath, the two bodies slowly react upon each other as the temperature rises, and when the oil has reached about 200°C ., the product becomes a dark brown liquid (at a few degrees higher it is converted into a carbonaceous mass); during this reaction a volatile liquid, consisting chiefly of tetrachloride of phosphorus distils over. The contents of the retort after treatment with water, become a pasty mass of crystals, which is first purified by distillation, and then by several crystallisations from alcohol. The substance gave the following numbers on analysis:—

- I. .3904 of substance gave—
 .8546 of CO_2 and
 .1050 of H_2O .
- II. .4006 of substance gave—
 .8760 of CO_2 and
 .1047 of H_2O .
- III. .3364 of substance gave—
 .2703 of AgCl .

These numbers give percentages agreeing with those required by the formula—

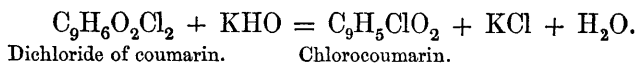


The following is a comparison of the theoretical and experimental numbers—

	Theory.		Experiment.		
			I.	II.	III.
C ₉	108.0	59.83	59.70	59.64	—
H ₅	5.0	2.77	2.98	2.90	—
Cl	35.5	19.67	—	—	19.88
O ₂	32.0	17.73	—	—	—
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	180.5	100.00			

From these results it is evident that the pentachloride of phosphorus has simply given up chlorine to the coumarin. It is very curious that if half the amount of pentachloride of phosphorus mentioned above be employed, the product of the reaction suddenly carbonizes, sometimes when the oil-bath is at a temperature as low as 150° C. I have had this happen twice, whereas with the *excess* of pentachloride the product may be heated in an oil-bath standing at 200° C.

Chlorocoumarin may be easily prepared by treating the dichloride of coumarin with alcoholic potash in exactly the same manner as described for the preparation of α bromocoumarin, the reaction being analogous—



Obtained by either of the above processes, this substance forms flat needles about half an inch long. It is moderately soluble in alcohol, and slightly so in hot water, from which it crystallises on cooling.

It melts at 122°–123° C., and when heated emits an agreeable aromatic odour. When boiled with alcoholic potassic hydrate, it decomposes with formation of potassic chloride, and forms the same product as α bromocoumarin when treated in the same manner.

From this description, α chlorocoumarin is evidently a substance different from that obtained by Dr. Båsecke, his product is in fact the β chlorocoumarin corresponding to the β bromocoumarin, and was obtained from the hydride of chlorosalicyl.

Tetrachlorocoumarin.

Chlorine gas, when passed through a solution of coumarin and iodine in tetrachloride of carbon, is rapidly absorbed, hydrochloric acid being evolved; if the gas be passed for two or three hours, a quantity of a reddish body separates, on evaporating the product so as to separate the tetrachloride of carbon, an oily residue is obtained, the red substance having fused with the impurities.

On mixing this substance with alcohol, it soon becomes a white paste. This is then pressed in a small linen bag, when a white product is obtained, which is further purified by being several times crystallised from spirit. It gave the following numbers on analysis :—

·3877 of substance gave—
·5309 of CO₂ and
·0355 of H₂O.

These numbers give per centages approximating to those required by the formula—



as will be seen from the following comparison :—

	Theory.		Exp.
C ₉	108	38·03	37·32
H ₂	2	0·70	1·02
Cl ₄	142	50·00	—
O ₂	32	11·27	—
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	284	100·00	

It is therefore a tetrachlorocoumarin. This substance melts at 144°—145° C. It is difficultly soluble in spirit from which it crystallises in small white needles. When heated with alcoholic potassic hydrate, it decomposes, with formation of potassic chloride and the salt of a new acid not yet examined.

Coumarilic Acid.

I have already mentioned that α bromocoumarin when boiled with a solution of potassic hydrate decomposes, yielding potassic bromide and the salt of a new acid. To prepare this acid in a

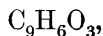
pure state, I have found it best to proceed in the following manner: A quantity of pure α bromocoumarin is mixed with an excess of the ordinary solution of potassic hydrate. On heating this mixture, the bromocoumarin gradually dissolves, but on reaching the boiling-point, the solution rapidly becomes a pasty crystalline mass. Sufficient water is then added to dissolve this, and the boiling continued for about an hour. The solution on cooling, deposits the potassic salt of the new acid in small needles. If any quantity of this salt remains in the mother-liquor, the addition of potassic hydrate will precipitate it. The crystalline salt thus obtained is collected upon a linen filter and well pressed, to remove as much of the alkaline-mother liquor as possible. It is then crystallised once or twice from alcohol and dried.

To obtain the acid from this salt it is dissolved in water, and hydrochloric acid is added in excess. The new acid is then thrown down as a snow white crystalline precipitate, which is purified first by washing with water on a filter, and then by crystallisation from boiling water.

It gave the following numbers on analysis:—

- I. .2112 of substance gave—
 .5146 of CO_2 and
 .0734 of H_2O .
 II. .2561 of substance gave—
 .6266 of CO_2 and
 .0846 of H_2O .

These percentages give numbers agreeing with those required by the formula—



as the following comparison will show:—

	Theory.		Experiment.	
			I.	II.
C_9	108	66.67	66.45	66.72
H_6	6	3.70	3.86	3.67
O_3	48	29.63	—	—
	162	100.00		

This acid, which I have proposed to call *coumarilic acid*, melts at 192° — 193° C. It distils without leaving any residue, but decomposes partially with formation of an oily body smelling

like naphthaline. When gently heated, it sublimes. The vapour is very suffocating. It is excessively soluble in alcohol, but difficultly so in chloroform and disulphide of carbon. It is moderately soluble in boiling water, from which it crystallises on cooling in beautiful long needles like benzoic or cinnamic acid. Its aqueous solution has a bitter taste. It is not decomposed when heated with potassic hydrate to 180°C . for an hour.

α chlorocoumarin may be employed instead of α bromocoumarin in the preparation of this acid. It is monobasic.

Ammonic Coumarilate.—This salt is easily obtained by dissolving coumarilic acid in aqueous ammonia, and evaporating in vacuo over sulphuric acid. It is a beautiful salt, crystallising in flat prisms, radiating from a common centre. It is easily soluble in water.

Sodic Coumarilate.—Coumarilic acid dissolves in a solution of sodic carbonate with effervescence, forming a salt which crystallises in transparent rectangular tables. It is easily soluble in water.

Potassic Coumarilate.—The preparation of this salt has already been given. It is difficultly soluble in cold alcohol, but moderately soluble in this menstruum when boiling; nearly insoluble in solutions of potassic hydrate of about 20 per cent. It crystallises in prisms half an inch long which break up into small plates. Its taste is bitter. A determination of the potassium in this salt gave the following numbers:—

·1781 of salt gave—

·0759 of $\text{K}_2\text{SO}_4 = 19\cdot07$ per cent. of potassium.

The formula $\text{C}_9\text{H}_5\text{KO}_3$ requires 19·5 per cent. of potassium.

Calcic Coumarilate is thrown down as a precipitate on addition of calcic chloride to potassic coumarilate. It is crystalline and difficultly soluble in water.

Baric Coumarilate is somewhat like the calcic compound.

Argentie Coumarilate.—On adding argentic nitrate to a solution of potassic coumarilate, this salt is thrown down as a white curdy precipitate, slightly soluble in water. The following determinations were made of the silver in this salt:—

I. ·1118 of substance gave—

·0443 silver = 39·62 per cent.

II. ·1608 of substance gave—
·0648 of silver = 40·29.

The formula $C_9H_5AgO_3$ requires 40·15. Analysis II was made from coumarilic acid prepared from α chlorocoumarin. I from α bromocoumarin.

Plumbic Coumarilate is a white curdy precipitate.

Mercurous Coumarilate is also a white precipitate.

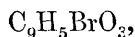
Ferric Coumarilate is a pale brown precipitate.

Bromocoumarilic Acid.

This acid is produced in the same manner as coumarilic acid, but substituting α dibromocoumarin for α bromocoumarin. The acid is also purified by crystallisation from spirit and water instead of water. It gave, on analysis, the following numbers:—

I. ·2504 of substance gave—
·4109 of CO_2 and
·0489 of H_2O .
II. ·3260 of substance gave—
·5357 of CO_2 and
·0658 of H_2O .

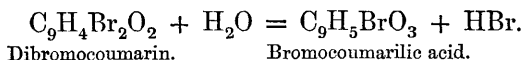
These numbers give percentages agreeing with the formula—



as the following comparison will show:

	Theory.		Experiment.	
			I.	II.
C_9	108	44·81	44·75	44·82
H_5	5	2·08	2·17	2·24
Br	80	33·19	—	—
O_3	48	19·92	—	—
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	241	100·00		

I therefore propose to call this acid *bromocoumarilic acid*; its formation may be expressed thus:—



Bromocoumarilic acid melts above $250^\circ C$. It crystallises

from a mixture of spirit and water in needles. It is very soluble in alcohol, and but little so in water. When heated to 180°C . with potassic hydrate, it decomposes and becomes brown, potassic bromide being formed. It has a bitter taste, and is monobasic.

Ammonic Bromocoumarilate is easily soluble in water, and crystallises in needles.

Sodic Bromocoumarilate is easily soluble in water, but does not produce good crystals.

Potassic Bromocoumarilate.—This salt is prepared like the corresponding coumarilate. It is easily soluble in water, but is almost wholly thrown down from its aqueous solution by strong solutions of potassic hydrate. It crystallises from alcohol in beautiful long needles. Determinations of the potassium in the salt gave the following numbers:—

- I. $\cdot 3215$ of substance gave—
 $\cdot 1026$ of $\text{K}_2\text{SO}_4 = 14\cdot 30$ per cent. of K.
 II. $\cdot 1897$ of substance gave—
 $\cdot 0600$ of $\text{K}_2\text{SO}_4 = 14\cdot 17$ per cent. of K.

The formula $\text{C}_9\text{H}_4\text{BrKO}_3$ requires $14\cdot 00$ per cent. of potassium.

Baric Bromocoumarilate may be obtained by the addition of a solution of baric chloride to the above potassic salt as a crystalline precipitate, difficultly soluble in water.

Argentio Bromocoumarilate is a white precipitate.

Plumbic Bromocoumarilate is a white precipitate.

Sulphocoumarilic Acid.

On digesting a mixture of about one part of coumarin and five parts of fuming sulphuric acid in the water-bath for an hour or two, the product will be found to dissolve perfectly in water. This, when diluted and neutralized with baric carbonate, yields, besides baric sulphate, a soluble salt which, when evaporated, crystallises in tufts of transparent prisms. This is rendered pure by recrystallisation from water. To obtain the new acid from this salt, it is dissolved in water, and sulphuric acid added in exactly the quantity necessary to precipitate all the barium as sulphate. The solution is then filtered and evaporated, first over the water-bath and then in vacuo. In this way the acid is usually obtained in needles, easily soluble in water. It has not been burnt, but from the

analysis of its salts, its formula, when anhydrous, is $C_9H_6O_2SO_3$. Determinations of its water of crystallisation gave the following numbers :—

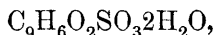
- I. ·9330 of crystallised acid lost
 ·1305 of water at $100^\circ C.$ = 13·99 per cent.
 II. ·5635 of crystallised acid lost
 ·0783 of water at $100^\circ C.$ = 13·9 per cent.

In one experiment I obtained this acid in octahedra, which were very brilliant whilst in the mother-liquor, but became opaque as soon as exposed to the air. A determination of the water of crystallisation gave the following results :—

- 3792 of substance lost
 ·0527 of water at $100^\circ C.$ = 13·90 per cent.

This preparation when recrystallised, was deposited on the palm of needles. It is, therefore, probable that they originally crystallised with more water than is contained in the needles.

These numbers correspond with those required by the formula—



which theoretically contains 13·74 per cent. of H_2O . The crystallised acid does not lose any more weight at $200^\circ C.$ than at $100^\circ C.$

This acid, which I propose to call sulphocoumarilic acid, possesses a strongly acid and bitter taste; it is very soluble in water, and may be evaporated to a thin syrup before it shows any signs of crystallisation. It is monobasic. When its salts are mixed with an excess of alkali, a yellow solution is obtained similar in appearance to that produced by dissolving coumarin in alkali.

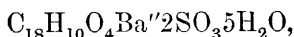
Ammonic Sulphocoumarilate.—This salt is obtained by evaporating a solution of the above acid, to which an excess of ammonia has been added. It crystallises in satiny needles, very soluble in water, and also soluble in alcohol.

Sodic Sulphocoumarilate.—On adding a solution of sodic carbonate to a solution of sulphocoumarilic acid, effervescence takes place, and on evaporating the resulting solution when neutral, beautiful crystals are obtained, very transparent and derived from the rhombic octahedron. It is easily soluble in water, but nearly insoluble in alcohol.

Potassic Sulphocoumarilate crystallises in flat prisms, easily soluble in water, insoluble or nearly so in alcohol.

Baric Sulphocoumarilate.—The preparation of this salt has already been given. It contains a considerable quantity of water of crystallisation, the crystals efflorescing rapidly in vacuo.

The formula is—



as the following results will show :—

- I. 1.0232 of crystallised salt lost in vacuo—
 ·1067 of $H_2O = 10.43$ per cent., and from vacuo to $180^\circ C$.
 ·0279 = 2.90 per cent.
- II. ·7420 of crystallised salt lost in vacuo—
 ·0777 of $H_2O = 10.50$ per cent., and from vacuo to 180
 ·0198 = 2.66 per cent.

These numbers show that this salt loses four molecules of water in vacuo, the fifth being given off entirely at $180^\circ C$.

	Theory.	Experiment.	
		I.	II.
4 mol.	10.63	10.43	10.50
1 mol.	2.66	2.90	2.66

Determinations of barium in the anhydrous salt gave the following numbers:—

- I. ·2456 of substance gave—
 ·0969 of baric sulphate = 23.20 per cent. of barium.
- II. ·1192 of substance gave—
 ·0474 of baric sulphate = 23.38 per cent. of barium.
- III. ·0994 of substance gave—
 ·0393 of baric sulphate = 23.25 per cent. of barium.

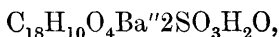
The formula $C_{18}H_{10}O_4Ba''2SO_3$ requires 23.34 per cent. of barium.

Combustion of barium salt containing one molecule of water.

- I. ·2911 of substance gave—
 ·3818 of CO_2 , and
 ·0570 of H_2O .

II. .3850 of substance gave—
 .5010 of CO₂, and
 .0787 of H₂O.

These give numbers agreeing with the formula—



as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C ₁₈	216	35·70	35·77	35·70
H ₁₂ ..	12	1·98	2·17	1·98
O ₁₁	176	29·09	—	—
Ba....	137	22·65	—	—
S ₂	64	10·58	—	—
	605	100·00		

Strontic Sulphocoumarilate.—This salt is easily soluble in water, and crystallises very nicely. It contains water of crystallisation, becoming opaque at 100° C., the last quantities of water not being expelled until a much higher temperature is used.

A determination of the strontium in the anhydrous salt gave the following numbers:—

.1698 of substance gave—
 .0574 of strontic sulphate = 16·15 per cent. strontium.

The formula C₁₈H₁₀O₄Sr''2SO₃ requiring 16·27 per cent.
 .0769 of a second specimen, dried at about 110° C., gave
 .0253 of strontic sulphate = 15·69 per cent. of strontium.

The formula C₁₈H₁₀O₄Sr''2SO₃, H₂O requiring 15·75 per cent.

Disulphocoumarilic Acid.

On heating a mixture of about eight parts of fuming sulphuric acid and one part of coumarin to a temperature of 150° or 160° C. for an hour or two, the product contains two sulphoacids, viz., sulphocoumarilic and disulphocoumarilic acids. On treating this with baric carbonate in the usual manner, the solution contains the barium salts of these two acids. To separate them the solution is evaporated to dryness, and treated

with warm water, which removes the baric sulphocoumarilate, leaving the less soluble salt of the new acid behind. This is purified by crystallisation from boiling water, in which it is not very soluble.

Thus obtained it is a white slightly crystalline product nearly insoluble in cold water.

Dried at 100° C. it gave on analysis the following numbers :—

·3258 of substance gave—

·1648 of baric sulphate = 29·76 per cent. of barium.

The formula $C_9H_4O_2Ba''2SO_3, H_2O$ requires 29·85 per cent. of barium.

Determinations of water of crystallisation—

I. 1·4226 of salt dried at 100° C. lost

·0486 of H_2O at 180° C. = 3·42 per cent.

II. ·5612 of salt dried at 100° C. lost

·0235 of H_2O at 180° C. = 4·18 per cent.

The above formula requires 3·92 per cent.

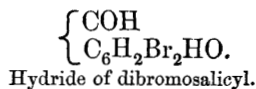
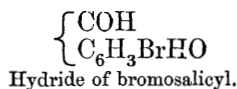
Determination of barium in anhydrous salt—

·1904 of substance gave

·0994 of baric sulphate = 30·7 per cent.

The formula $C_9H_4O_2Ba''2SO_3$ requires 31·06 per cent.

From what has been said of the bromine and chlorine derivatives of coumarin, it is evident that the bromine or chlorine introduced must be related to different carbon groups, according as the product belongs to what has been termed the α or β derivative. In the case of the latter it is evident that it is contained in the C_6 group, as these bodies are produced from the brominated hydride of salicyl; those employed in this paper being represented thus :—



The bromine in the bromocoumarin obtained from these bodies by means of acetic anhydride is not attacked by boiling with potash.

In the alpha series the bromine or chlorine must be connected

with the carbon of what may perhaps be called the acetic residue. These are easily decomposed with caustic alkali.

I have endeavoured to produce a bromocoumarin of this class by employing bromoacetic anhydride instead of acetic anhydride in the preparation of coumarin from the hydride of salicyl, but have not yet succeeded.

In α dibromocoumarin one half of the bromine appears to be in union with the C_6 group, the other being connected with the acetic residue, as only one atom of bromine is removed by boiling with potassic hydrate.

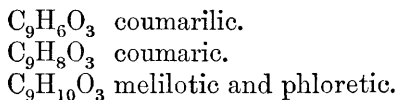
α Bromo- and chlorocoumarins, from their decomposition by caustic alkali, and production of coumarilic acid, would appear to be bromide and chloride of an acid radical (coumaryl). If it were so, however, these substances should give with ammonia an amide, which would decompose on boiling with alkali, yielding ammonia and coumarilic acid; but although the substances are easily acted upon by ammonia, the product when boiled with potassic hydrate does not yield this acid. It is therefore possible that coumarilic acid is not a true acid containing the group COHO, but is only coumarin with one of hydrogen replaced by hydroxyl, unless some molecular change takes place during its formation; and it is perhaps worth remarking that coumarin and its bromine, chlorine, and sulphuric derivatives give yellow solutions with caustic alkali, whereas coumarilic acid forms colourless ones; this may perhaps point to a change in structure. I hope, however, to replace the hydroxyl in coumarilic acid by bromine, and see if the resulting compound is ordinary α bromocoumarin.

Fittig and others consider coumarin as the anhydride or glycollide of oxycinnamic acid, and it appeared to me probable that if it were so it should yield with phosphoric chloride the chloride of chlorocinnamyl. I have not, however, as yet succeeded in obtaining this body, chlorocoumarin being the principal product found.

I must say that if coumarin be a glycollide it is a very anomalous one in its properties, as it may be kept *dissolved* in caustic alkali for months without formation of any appreciable quantity of coumaric acid; neither does it form an amide when heated alone in gaseous ammonia, or in a sealed tube with alcoholic ammonia; whereas salicylide, the glycollide of salicylic acid, is converted into a salicylate as quickly as it dissolves in

an alkali, and from the description given it would appear that it cannot exist in *solution* in alkali.

Coumarilic acid differs in composition from coumaric acid by H_2 , and from melilotic and phloretic acids by H_4 , so that we have the following series :—



These acids are, however, very different in properties : for example, phloretic and melilotic acids distil with formation of their anhydrides, and coumarilic acid distils with only partial decomposition, whereas the intermediate compound, coumaric acid, when heated, forms a brown resinous mass, and when distilled is entirely split up ; if coumarin were its anhydride, we should expect it to be produced, especially as it is very stable and easily volatilized.

The following is a list of the new products described in this paper :—

Dibromide of coumarin	$C_9H_6O_2Br_2$.
Dichloride of coumarin	$C_9H_6O_2Cl_2$.
α . Bromocoumarin	$C_9H_5BrO_2$.
β . Bromocoumarin	$C_9H_5BrO_2$.
α . Chlorocoumarin	$C_9H_5ClO_2$.
β . <i>Chlorocoumarin</i>	$C_9H_5ClO_2$ (<i>Bäsecke</i>).
α . Dibromocoumarin	$C_9H_4Br_2O_2$.
β . Dibromocoumarin	$C_9H_4Br_2O_2$.
Tetrachlorocoumarin	$C_9H_2Cl_4O_2$.
Coumarilic acid	$C_9H_6O_3$.
Bromocoumarilic acid	$C_9H_5BrO_3$.
Sulphocoumarilic acid	$C_9H_6O_2SO_3$.
Disulphocoumarilic acid	$C_9H_6O_2^2SO_3$.

