

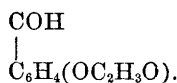
XI.—*On the Formation of Coumarin and of Cinnamic and of other Analogous Acids from the Aromatic Aldehydes.*

By W. H. PERKIN, F.R.S.

IN November, 1875 (*Chem. News*, vol. xxxii, p. 258), I brought before the Society a short preliminary account of the experiments on this subject in which I was then engaged. Since then I have been further working in the same direction, and will now give an account of my results up to the present time.

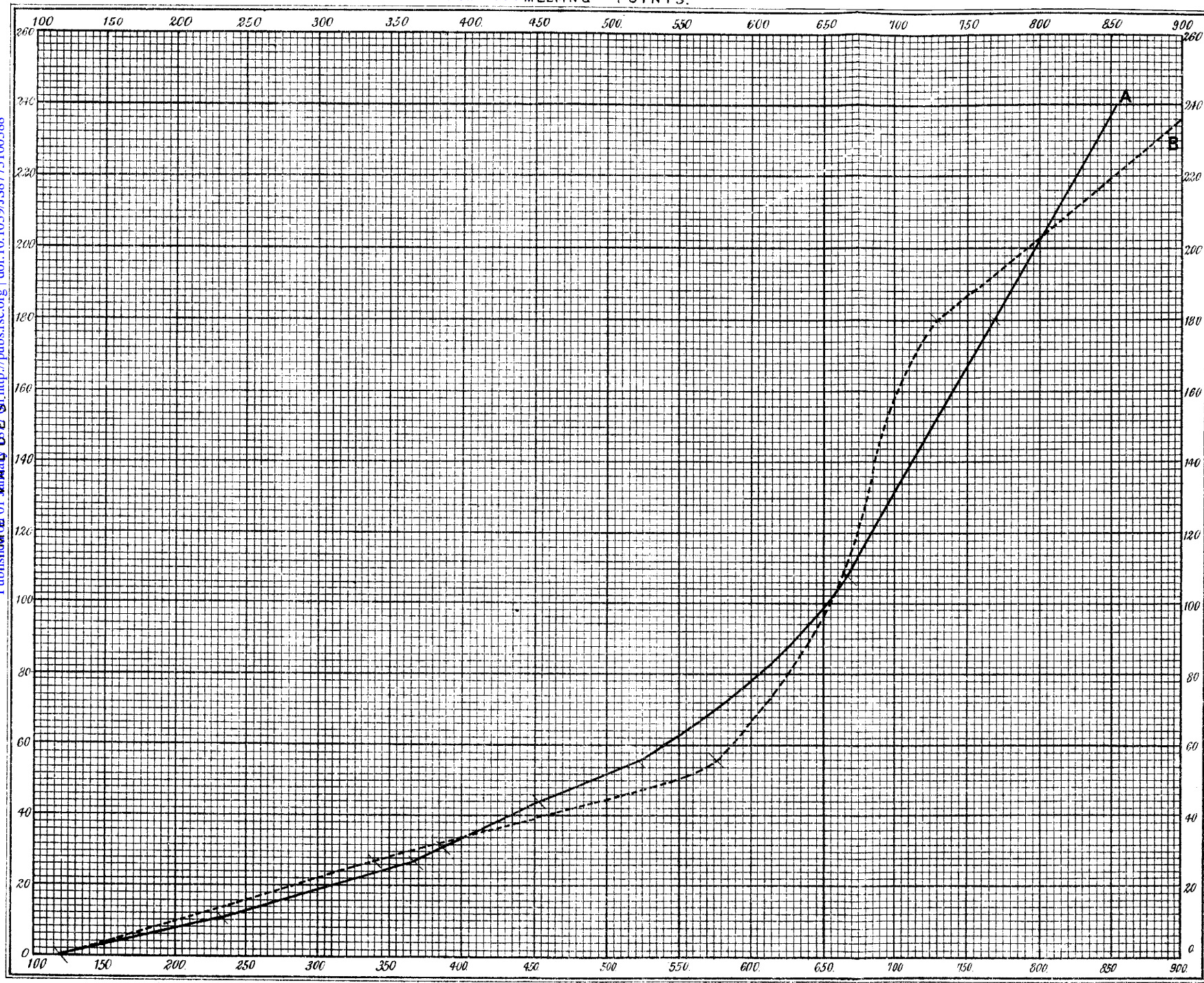
These experiments were at first commenced with the hope of obtaining some light upon the peculiar reactions by which the coumarins are formed. It will be remembered that in the process by which I succeeded in preparing these bodies, the products employed were the sodium-derivative of the hydride of salicyl and the anhydrides of the fatty acids (*Journ. Chem. Soc.*, xxi, 53).

It is known that when acetic anhydride acts upon the sodium-compound of the hydride of salicyl, acetate of sodium and hydride of aceto-salicyl are produced (*Journ. Chem. Soc.*, xxi, 181), the former having the composition—



The phenolic hydrogen of the aldehyde having been thus replaced

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by acetyl, this substance would consequently have the properties of an ordinary aldehyde.

This being the case, it appeared probable that the next part of the reaction in the formation of coumarin took place between the aldehydic group, the sodium acetate, and the acetic anhydride, the resulting product then splitting up into acetic acid and coumarin.

It was obvious that neither the hydride of aceto-salicyl nor the hydride of salicyl would yield coumarin if heated with acetic anhydride *only*, as they are known to form other compounds with this substance. (*Journ. Chem. Soc.*, xxi, 183, and xx, 587.)

A quantity of hydride of salicyl was, therefore, boiled with acetic anhydride and sodium acetate, and then treated as described in my paper already referred to, when, to my surprise, I found that coumarin had been produced in quantity.

Thinking it unlikely that the sodium of the acetate used could have replaced the phenolic hydrogen of the salicylic aldehyde and thus have influenced the reaction, I was induced to try similar experiments with other aromatic aldehydes, the first I selected being benzoic aldehyde.

#### ACIDS FROM BENZOIC ALDEHYDE.

##### I.—*Cinnamic Acid.*

On boiling this aldehyde with acetic anhydride and sodium acetate, chemical action took place, but much more slowly than when hydride of salicyl was employed; nevertheless, after heating the mixture for about a day, a good deal of change was found to have taken place, and on separating the sodium acetate with water, and treating the oily residue with an alkaline carbonate, a considerable quantity of an organic acid dissolved, which, when precipitated by an acid and purified by crystallisation from dilute spirit, was found to be pure cinnamic acid. Similar operations were then made in sealed tubes, a temperature of about 180° C. being employed and continued for five or six hours. On opening the tubes, carbonic anhydride escaped,\* and on examining the solid crystalline mass, it was found to contain cinnamic acid in large quantities; in some experiments as much as 84 per cent. of acid has been obtained from the benzoic aldehyde employed.

To procure the cinnamic acid in the pure state by this process.

\* The formation of carbonic anhydride in this and in the other analogous operations described in this paper is believed to be due to the decomposition of the organic acid by heat, this gas and a hydrocarbon resulting, which in this case would be cinnamene.

I have found it convenient first to boil the product of the reaction with water in a retort; by this means, any unconverted aldehyde is separated, being carried over by the steam. The residue is then allowed to cool, during which time the crude oily cinnamic acid solidifies, and any dissolved in the aqueous saline solution crystallises out. It is then collected on a filter, washed from sodium acetate, boiled with sodium carbonate, and after cooling, filtered from the oily impurities which are always present. On acidifying the alkaline solution, the cinnamic acid separates as a white pasty crystalline precipitate; this is further purified by two or three crystallisations from dilute alcohol.

Experiments have been made in which the sodium acetate has been replaced by other salts, such as sodium valerate, and also by lead acetate, but in all cases cinnamic acid resulted, the formation of the acid being apparently due to the anhydride employed, and not to the acid of the salt used.

The following are the results of the analysis of the cinnamic acid obtained by these methods:—

- I. ·2465 of substance gave  
·657 of CO<sub>2</sub> and  
·122 of H<sub>2</sub>O.
- II. ·264 of substance gave  
·7013 of CO<sub>2</sub> and  
·1322 of H<sub>2</sub>O.
- III. ·244 of substance gave  
·6535 of CO<sub>2</sub> and  
·118 of H<sub>2</sub>O.
- IV. ·3684 of substance gave  
·9815 of CO<sub>2</sub> and  
·184 of H<sub>2</sub>O.

		Experiment.			
Theory for C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> .		I.	II.	III.	IV.
Carbon	72·97	72·70	72·88	73·04	72·73
Hydrogen	5·47	5·49	5·60	5·40	5·54

The substance employed for No. I was prepared with sodium acetate and acetic anhydride. In Nos. II and III, the sodium acetate was replaced by sodium valerate, and in No. IV by sodium butyrate.

The proportions I have generally employed are one of sodium salt, two of aldehyde, and three of anhydride. The amount of sodium salt is important. I have found that by reducing it to about a fourth part of the aldehyde used, that only 50 per cent. of cinnamic acid was obtained; but when it was increased to the same weight as the aldehyde, the yield was not greater than when half that quantity was used.

The product found in the sealed tubes after heating, is a clear pale-brown fluid which, on cooling, becomes a solid or semi-solid crystalline mass, through which small pale-coloured opaque nodules separate; more particularly when sodium valerate is used in place of acetate. Some of these were separated by the addition of acetic anhydride, which dissolves out the crystalline substance consisting apparently of the compound of sodium acetate and acetic anhydride. After being further washed with fresh anhydride, the product, consisting of these opaque masses, was obtained moderately pure. It was freed from anhydride under a bell-jar over potassium hydrate, and then at  $100^{\circ}$ .

This substance, when treated with water, decomposes, yielding cinnamic acid and sodium cinnamate. It dissolves in strong aqueous ammonia without forming cinnamide. On analysis, it gave the following numbers:—

- I.  $\cdot 317$  of substance gave  
 $\cdot 070$  of  $\text{Na}_2\text{SO}_4 = 7\cdot 12$  per cent. sodium.  
 II.  $\cdot 456$  of substance gave  
 $\cdot 102$  of  $\text{Na}_2\text{SO}_4 = 7\cdot 24$  per cent. sodium.

From these results the product is undoubtedly a compound of sodium cinnamate with cinnamic acid,  $\text{C}_9\text{H}_7\text{NaO}_2, \text{C}_9\text{H}_8\text{O}_2$  (which requires  $7\cdot 2$  per cent. sodium), corresponding to the already known acid potassium benzoate,  $\text{C}_7\text{H}_5\text{KO}_2, \text{C}_7\text{H}_6\text{O}_2$ .

#### II.—*Phenylcrotonic Acid.*

Cinnamic acid having been so easily produced by the process just described, I naturally made further experiments in this direction, substituting other anhydrides for acetic. The following results were obtained when propionic anhydride was employed.

Sealed tubes were charged with one part of sodium propionate, two parts of benzoic aldehyde, and three parts of propionic anhydride, and then heated to  $180^{\circ}$  for six or seven hours; the tubes, on cooling, contained a nearly solid mass, consisting of two kinds of crystals moistened with an oily product. On opening the tubes, carbonic anhydride escaped.

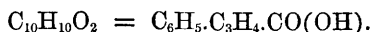
The product of this reaction was mixed with water and boiled in a retort until oily matter nearly ceased to distil off. The residue was left for some time until quite cold, and then thrown on a filter and washed with cold water to remove sodium propionate. It was then boiled with a solution of sodium carbonate, filtered from a small quantity of neutral oil, and treated with ether to remove the last traces of this product. The clear alkaline solution was afterwards heated, and acidified with hydrochloric acid, which caused a copious white precipitate to separate. When cold, this was collected on a filter, washed

with cold water, and then twice crystallised from alcohol, after which it was submitted to analysis.

- I. ·268 of substance gave  
·7257 of CO<sub>2</sub> and  
·151 of H<sub>2</sub>O.
- II. ·2785 of substance gave  
·757 of CO<sub>2</sub> and  
·155 of H<sub>2</sub>O.

Theory for C <sub>10</sub> H <sub>10</sub> O <sub>2</sub> .		Experiment.	
		I.	II.
Carbon . . . . .	74·07	73·85	74·12
Hydrogen . . . . .	6·17	6·33	6·19

This acid is, therefore, phenyl-crotonic acid—



In one operation, sodium acetate was employed in place of sodium propionate, but the same result was obtained.

Phenylcrotonic acid melts at 82° to a clear oil, but as the temperature falls, it becomes a beautifully crystalline mass. It is easily soluble in alcohol, especially when hot, from which it separates as the solution cools in transparent oblique crystals. It is also slightly soluble in boiling water, and crystallises from it on cooling in fine needles.

*Barium salt*, C<sub>20</sub>H<sub>18</sub>BaO<sub>4</sub>Aq. When boiled with a solution of barium hydrate the acid dissolves, and on cooling deposits this salt in beautiful fern-like crystals; these were collected, washed, and recrystallised. It is a beautifully white salt, and when examined by the lens, the crystals appear to be plates. Cold water dissolves it to a small extent only. The crystals become opaque when dried in the water-oven, from loss of water of crystallisation. It gave the following numbers on analysis. The combustions were made with lead chromate :—

- I. ·2805 of substance dried at 150° C. gave  
·535 of CO<sub>2</sub> and  
·1047 of H<sub>2</sub>O.
- II. ·1408 of substance dried at 150° C. gave  
·0712 of BaSO<sub>4</sub>.

Theory for C <sub>20</sub> H <sub>18</sub> BaO <sub>4</sub> .		Experiment.	
		I.	II.
Carbon . . . . .	52·28	52·01	—
Hydrogen . . . . .	3·92	4·15	—
Barium . . . . .	29·84	—	29·73

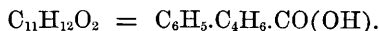
III.—*Phenylangelic Acid.*

This acid was discovered by Fittig and Bieber (*Zeitschr. f. Chem.*, 1869, p. 332), they obtained it by heating butyric chloride and benzoic aldehyde in sealed tubes to 120—130° for a long time. It is produced easily by heating butyric anhydride, butyrate of sodium, and benzoic aldehyde to 180° in sealed tubes. The proportions I have used correspond to those for the preparation of phenylcrotonic acid already given. The purification of the crude product from the sealed tube was also conducted in a similar manner. The specimen analysed was twice crystallised from alcohol.

·235 of substance gave  
·6455 of CO<sub>2</sub> and  
·146 of H<sub>2</sub>O.

	Theory for C <sub>11</sub> H <sub>12</sub> O <sub>2</sub> .	Experiment.
Carbon .....	75·00	74·89
Hydrogen .....	6·83	6·90

It is therefore phenylangelic acid—



It melts at 104° to a colourless liquid, and on cooling, crystallises in small needles (Fittig and Bieber give the fusing point as 81°). It is very soluble in alcohol, and is deposited from this solvent in small white needles, but the mother-liquors on standing sometimes give beautiful transparent solid crystals several millimetres in diameter. It dissolves easily in hot petroleum spirit, but only to a small extent when this solvent is cold. It also dissolves slightly in boiling water, from which it is deposited on cooling in white crystals. When boiled with water it is carried over to a small extent with the steam.

In one experiment ten grams of oil of bitter almonds gave eight and a half grams of this acid before crystallisation from alcohol.

If isobutyric anhydride and sodium isobutyrate be heated with benzoic aldehyde, a crystalline acid is produced; it has not yet, however, been much examined.

*Silver salt.*—On addition of silver nitrate to a solution of the sodium salt of phenylangelic acid, a white precipitate is formed slightly soluble in cold water.

*Chloride of Phenylangelyl*, C<sub>11</sub>H<sub>11</sub>O.Cl.—A mixture of phenylangelic acid and phosphorus pentachloride, in the proportions of one molecule of each, was gently warmed: chemical action set in energetically, with evolution of hydrochloric acid, and the mixture became fluid. The product was heated in an oil-bath to 140°, and dry air passed through it to remove the phosphorous oxychloride. The resulting product was a pale yellow oil. With water it gradually decomposes, forming a

crystalline mass of phenylangelic acid, and with alcohol it produces an oily ether. Its composition was determined by converting it into the amide.

*Phenylangelamide*,  $C_{11}H_{13}(NH_2)$ . — The preceding chloride when shaken with strong aqueous ammonia, yields a yellowish-white solid product which, when washed, dried, and dissolved in boiling alcohol, separates out on cooling in very beautiful prismatic crystals. It gave the following numbers on analysis :—

- I. ·2795 of substance gave  
 ·7685 of  $CO_2$  and  
 ·2005 of  $H_2O$ .
- II. ·2516 of substance gave  
 ·6945 of  $CO_2$  and  
 ·168 of  $H_2O$ .

Theory for $C_{11}H_{11}O(NH_2)$ .		Experiment.	
		I.	II.
Carbon .....	75·45	74·98	75·28
Hydrogen .....	7·42	7·97	7·42

No. II was first crystallised from alcohol, and then from petroleum spirit.

Phenylangelamide is easily soluble in alcohol, but rather difficultly so in petroleum spirit. Boiling water dissolves it to a small extent, from which it crystallises on cooling. It melts at  $128^\circ$ .

*Products of the Action of Succinic Anhydride and Sodium Succinate on Benzoic Aldehyde.*

Having obtained the results already described, by acting upon benzoic aldehyde with the anhydride and the corresponding salt, of monobasic acids it was thought that it would be interesting to make similar experiments, using anhydrides of dibasic acids.

For this purpose succinic anhydride was selected, and heated with sodium succinate and benzoic aldehyde in sealed tubes, to about  $180^\circ$ , for seven or eight hours. The product was a brownish-red sticky substance, and on opening the tubes very large quantities of carbonic anhydride escaped, the product at the same time swelling up to a spongy mass.

The product had no smell of benzoic aldehyde; when boiled with water it fused to a red-brown thick oil, a pale yellow solution being formed. The oily product after repeated boiling with water became, on cooling, a brittle mass, soluble in alkalis.

The aqueous solution on cooling, after standing for some time, deposited nearly colourless crystals, which were in the form of beautiful leafy plates or long needles; these were collected, well washed with



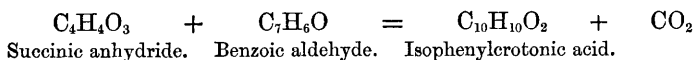
water, and afterwards boiled in water. At first the crystals fused to an oil, but after some time almost entirely dissolved. The solution was filtered and allowed to cool, when it deposited beautiful white needles of the new product. This substance gave the following numbers on analysis:—

- I. ·254 of substance gave  
     ·690 of CO<sub>2</sub> and  
     ·141 of H<sub>2</sub>O.
- II. ·256 of substance gave  
     ·694 of CO<sub>2</sub> and  
     ·144 of H<sub>2</sub>O.

		Experiment.	
The formula C <sub>10</sub> H <sub>10</sub> O <sub>2</sub> requires		I.	II.
Carbon .....	74·07	74·08	73·91
Hydrogen .....	6·17	6·16	6·25

This substance, which is an acid, has therefore the composition of phenylcrotonic acid already described. It is, however, very different in properties; I have therefore named it *isophenylcrotonic acid*.

The formation may be expressed thus, leaving out the succinate, the presence of which is necessary, but its action at present not understood.



Isophenylcrotonic acid melts at about the same temperature as its isomeride obtained from benzoic aldehyde, propionic anhydride, &c., viz., at 83—84°, and when strongly heated it gives off vapours of a suffocating character, somewhat like succinic acid. The fused acid on cooling solidifies to a beautiful crystalline mass. It is excessively soluble in alcohol.

*Silver salt*, C<sub>10</sub>H<sub>9</sub>AgO<sub>2</sub>.—A portion of the acid was mixed with sodium carbonate in the proportions of two molecules of acid to one of carbonate. On heating the mixture the acid dissolved with effervescence. Silver nitrate was added to this solution when cold, in small quantities, and the resulting precipitate filtered off. The filtrate was then mixed with an excess of silver nitrate, which caused the formation of an extremely bulky and very curdy precipitate. After standing for some time, with repeated stirring to ensure complete mixing, it contracted somewhat in bulk. It was then collected on a filter, thoroughly washed with cold water and dried. On analysis it gave the following numbers:—

- I. ·383 of substance gave  
 ·154 of silver = 40·2 per cent.  
 II. ·3535 of substance gave  
 ·1415 of silver = 40·02 per cent.

The formula  $C_{10}H_8AgO_2$  requires 40·14 per cent. of silver.

It is proposed to continue the investigation of this acid, in order to obtain a more complete account of its history, and to endeavour to produce some of its homologues by the use of other dibasic anhydrides, &c.

Having obtained the foregoing results with benzoic aldehyde, experiments were made in a similar manner with

Cuminic  
 Cinnamic  
 Anisic  
 and Methylsalicylic aldehydes.

The following results were obtained.

#### ACIDS FROM CUMINIC ALDEHYDE.

##### I. *Cumenylacrylic or Isopropylphenylacrylic Acid.*

The cuminic aldehyde employed in the following experiments was obtained by simply fractioning oil of cumin, the presence in it of a small quantity of cymene being of no consequence.

A mixture of the aldehyde with dry sodium acetate and acetic anhydride in the proportions of two parts of aldehyde, one part of sodium acetate and three parts of acetic anhydride, was heated in sealed tubes to a temperature of 175° for five or six hours; the resulting product on cooling was a pale brown radiating crystalline mass, and on opening the tubes, carbonic anhydride escaped, but not in very large quantities.

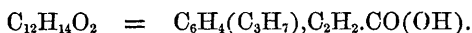
The solid product, when boiled in a retort with water, gave a distillate containing a small quantity of unchanged cuminic aldehyde. When this had ceased to come over, the distillation was stopped. The remaining product in the retort was a brownish oil mixed with an aqueous fluid, the former on cooling solidified to a crystalline mass, and the latter deposited fine white needles. The entire product was thrown on a filter and washed with water. It was then boiled with a solution of sodium carbonate, in which it mostly dissolved, leaving but a small quantity of a neutral brown oil. On filtering the alkaline solution and acidifying it with hydrochloric acid, an acid separated as a nearly white precipitate, which was collected, washed, dried, and

then purified by two or three crystallisations from alcohol. At first the crystals were of a somewhat drab colour, but a few recrystallisations rendered them perfectly white. By this process I have obtained fifty-five per cent. of crystallised acid from the aldehyde employed. It gave the following numbers on analysis:—

- I. .2235 of substance gave
  - .618 of CO<sub>2</sub> and
  - .154 of H<sub>2</sub>O.
- II. .2595 of substance gave
  - .720 of CO<sub>2</sub> and
  - .174 of H<sub>2</sub>O.
- III. .252 of substance gave
  - .698 of CO<sub>2</sub> and
  - .168 of H<sub>2</sub>O.

		Experiment.		
Theory for C <sub>12</sub> H <sub>14</sub> O <sub>2</sub>	I.	II.	III.	
Carbon . . . . .	75·78	75·36	75·66	75·55
Hydrogen . . . . .	7·36	7·65	7·43	7·41

This acid I propose to call *cumenylacrylic acid*—



It crystallises in beautiful pure white needles, which appear to consist of oblique prisms. It is freely soluble in alcohol, and in hot glacial acetic acid, but in boiling water it is only slightly soluble.

At 157—158° it melts, forming a clear fluid, which solidifies to a crystalline mass on cooling. When heated until it boils, carbonic anhydride is given off, a hydrocarbon being formed at the same time.

Cold fuming nitric acid dissolves it, small crystals of a nitro-acid soon separating out from the solution. This, when freed from nitric acid, crystallises from alcohol in yellow needles.

Cumenylacrylic acid is not rapidly acted upon by an aqueous solution of chromic acid, even when boiling; it is, however, gradually decomposed, and an oil distils over, having the odour and properties of cuminic aldehyde.

A solution of this acid in carbon disulphide, when treated with bromine, deposits crystals of a new derivative, which is decomposed when heated with alkalis. This is under examination.

Cinnamic acid, when treated with hypochlorous acid, yields phenylchlorolactic acid. A similar experiment was made with cumenylacrylic acid, but on passing chlorine into its alkaline solution, it became turbid, and oily products containing chlorine separate out.

*Ammonium salt*.—A solution of cumenylacrylic acid in aqueous ammonia, when evaporated in a vacuum over sulphuric acid, dries up to a mass of silky asbestos-like crystals, which give off ammonia with caustic alkalis. This salt is not easily soluble in water.

*Sodium salt*.—Obtained by boiling the acid with the theoretical quantity of a solution of sodium carbonate. It quickly dissolves, with evolution of carbonic anhydride, and when evaporated in a vacuum the solution dries up to a white mass, very indistinctly crystalline. It is moderately soluble in water, but precipitated from its solution by sodium chloride; when strongly heated a good deal of a hydrocarbon distils off. Hydrochloric acid precipitates the cumenylacrylic acid from this salt as a beautiful snow-white flocculent powder.

*Calcium salt*,  $C_{24}H_{26}CaO_4$ .—This is obtained by adding calcium chloride to an aqueous solution of the sodium salt. It comes down as a white crystalline bulky precipitate, which is collected, washed with cold water, and crystallised from boiling water. In this manner it is obtained in small but beautifully white needles. It is difficultly soluble in water; dried in a vacuum it gave the following numbers:—

- |     |  |
|-----|--|
| I.  | ·297 of substance gave                 |
|     | ·0955 of $CaSO_4 = 9.45$ p.c. calcium. |
| II. | 416 of substance gave                  |
|     | ·137 of $CaSO_4 = 9.68$ p.c. calcium.  |

The formula  $C_{24}H_{26}CaO_4$  requires 9.58 p.c. of calcium.

This salt when heated to between  $90^\circ$  and  $100^\circ$  in air free from carbonic anhydride, rapidly increases in weight owing to the absorption of oxygen until an amount of that gas has been taken up equal to about one atom. On decomposing this oxidised salt with hydrochloric acid, a white easily decomposable acid is obtained, which is now under investigation. It is believed to be *oxycumenylacrylic acid*,  $C_{12}H_{14}O_3$ .

*Barium salt*.—Obtained by double decomposition. It is a white powder, apparently slightly crystalline. Sometimes it conglomerates to a plastic mass when boiled with water, in which it is slightly soluble.

*Strontium salt*,  $C_{24}H_{26}SrO_4, 2H_2O$ .—Similar to the barium salt, being a white powder slightly soluble in water. A specimen dried in a vacuum gave on analysis 17.62 per cent. of strontium; the above formula requires 17.42 per cent.

*Copper salt*.—This is obtained as a beautiful green precipitate on adding a solution of copper sulphate to the sodium salt.

The *ferric salt* is precipitated as a bulky light brown product on adding iron perchloride to a solution of the sodium salt.

*Silver salt*,  $C_{12}H_{13}AgO_2$ .—On adding silver nitrate to a hot solution

of the sodium salt, a copious and bulky precipitate forms; after a short time this contracts, and when viewed under the microscope is seen to be crystalline; when dry it is extremely electric. It gave the following numbers on analysis:—

- I. ·368 of substance gave  
     ·133 of silver = 36·14 per cent.
- II. ·258 of substance gave  
     ·094 of silver = 36·43 per cent.

The above formula requires 36·36 per cent. of silver.

*Chloride of Cumenylacryl*,  $C_{12}H_{13}OCl$ .—Cumenylacrylic acid when heated with phosphorus pentachloride (in the calculated proportions) rapidly changes, the mixture becoming fluid, and hydrochloric acid being given off in abundance. On distilling off the oxychloride of phosphorus by heating the product to  $130^\circ$  in an oil-bath, and finally by passing dry air through it at the same temperature, the liquid becomes pale red, and exhibits a blood-red fluorescence. This coloration is undoubtedly due to some slight decomposition, caused by over heating.

When cold, the chloride of cumenylacryl solidifies to a beautifully crystalline mass, fusible at about  $25^\circ$ . On exposure to the air, the moisture soon reconverts it into the acid. On mixing it with alcohol, heat is evolved, and an oil heavier than water is produced; this is undoubtedly the ether.

The formula of this substance was determined by converting it into the amide.

*Cumenylacrylamide*,  $C_{12}H_{13}O(NH_2)$ .—Aqueous ammonia acts quickly on the chloride of cumenylacryl, producing a white powder, insoluble, or nearly so, in water. This, when washed and dried, was purified by crystallisation from alcohol, in which it is moderately soluble. In this manner it is obtained in beautiful satiny plates, not unlike flakes of sublimed naphthalene. It gave the following numbers on analysis:—

- 272 of substance gave
- 7575 of  $CO_2$  and
- 196 of  $H_2O$ .

Theory for $C_{12}H_{13}O(NH_2)$ .	Experiment.
Carbon . . . . .	76·19
Hydrogen . . . . .	75·95
	8·0

This amide melts at  $185$ — $186^\circ$ , and when further heated, distils with apparently but little decomposition, though small quantities of ammonia are given off.

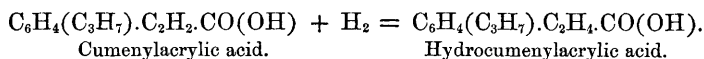
Boiling aqueous potash does not decompose it, unless the solution be a saturated one, when ammonia is freely given off.

*Hydrocumenylacrylic or Cumenylpropionic Acid.*—To a quantity of cumenylacrylic acid, mixed with about 15 times its weight of water a sufficient amount of sodium amalgam (containing 2 per cent. of sodium) was added, to form its sodium salt. The mixture was frequently agitated. The acid then gradually dissolved, very little hydrogen being given off; excess of sodium amalgam was afterwards introduced, and the mixture left for several hours until hydrogen was pretty freely evolved. After the separation of the amalgam, the solution was acidified with hydrochloric acid, which precipitated the new acid in a crystalline condition. It was collected, washed with water, and pressed between bibulous paper, then dissolved in warm glacial acetic acid, and the solution filtered from a small amount of an amorphous insoluble product. To the clear filtrate water was added by degrees, which caused the new acid to separate in satiny scales, enough water being eventually added to cause nearly the whole of the acid to separate. After standing for several hours, it was collected on a filter, well washed with water, dried in a vacuum, and then fused. On analysis, it gave the following numbers :—

·2627 of substance gave  
·7175 of CO<sub>2</sub> and  
·194 of H<sub>2</sub>O.

	Theory for C <sub>12</sub> H <sub>16</sub> O <sub>2</sub> .	Experiment.
Carbon . . . . .	75·0	74·48
Hydrogen . . . . .	8·3	8·19

The production may be expressed thus :—



*Hydrocumenylacrylic Acid* fuses at 70° to a clear oil crystallising very beautifully on cooling. It is very soluble in hot alcohol, petroleum-spirit, and glacial acetic acid, but insoluble, or nearly so, in water.

It dissolves in boiling sodium carbonate, forming a clear solution of its sodium salt.

The barium and calcium salts are white precipitates, which when rubbed with a glass rod, become tenacious.

The copper-salt is a bright blue-green precipitate.

*Silver salt*, C<sub>12</sub>H<sub>15</sub>AgO<sub>2</sub>.—This was prepared by double decomposition with the sodium salt and silver nitrate, rejecting the first portions thrown down. It is a white precipitate, nearly insoluble in water. Dried in a vacuum, and then at 100°, it gave the following numbers on analysis :—

- I. 4025 of substance gave  
     ·145 of silver = 36·00 per cent.
- II. 3082 of substance gave  
     ·111 of silver = 36·05 per cent.

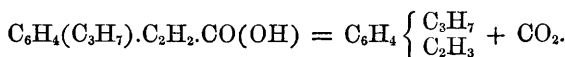
Theory for the above formula requires 36·12 per cent. silver.

*Isopropylcinnamene, or Isopropylvinylbenzene.*—When cumenylacrylic acid is gently boiled in a bulb-tube with a long neck, into which a side delivery-tube is fixed, the heat being so moderated that a thermometer placed in the upper part of the neck does not indicate more than about 200—210°, a colourless oil distils over, and eventually scarcely anything is left in the bulb-tube. This oil, when washed with aqueous potash, dried over solid potash, and finally distilled from sodium, begins to boil at about 190°, the greater portion coming over between 195—200°. A specimen collected between these temperatures gave the following numbers:—

- 2256 of substance gave
- 747 of CO<sub>2</sub> and
- 205 of H<sub>2</sub>O.

	Theory for C <sub>11</sub> H <sub>14</sub> .	Experiment.
Carbon.....	90·41	90·3
Hydrogen.....	9·58	10·0

The formation of this substance may be expressed thus:—



Isopropylvinylbenzene has a pleasant fragrant odour. It resinifies when exposed to the air, and seems to be easily changed, forming a tenacious product which probably corresponds with metacinnamene.

### II.—*Cumenylcrotonic Acid.*

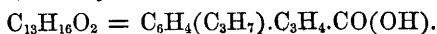
On heating a mixture of two parts of cuminic aldehyde, one part of sodium acetate, and three parts of propionic anhydride in sealed tubes for about five or six hours to 180°, a viscid product was obtained, which, on cooling, became a pale yellow crystalline mass. This, when boiled with water in a retort to remove unaltered cuminic aldehyde, left with the solution of sodium propionate an oily body, which, on standing, became a crystalline mass. This was collected, washed, dissolved in dilute boiling sodium carbonate, and filtered through a wet filter to separate it from a neutral brownish semi-resinous impurity; the clear solution was then boiled and acidified with hydrochloric acid, which caused the new acid to separate as an oil, solidifying on cooling to a

crystalline mass. This was washed and crystallised from alcohol, from which it separated in crystalline nodular masses. Subsequently, it was found better to use petroleum-spirit as the solvent; from this it crystallises in beautiful oblique prisms. The above process has usually given about 50 per cent. of pure acid from the aldehyde employed. It gave the following numbers on analysis:—

- I. ·257 of substance gave  
 ·723 of CO<sub>2</sub> and  
 ·179 of H<sub>2</sub>O.
- II. ·280 of substance gave  
 ·785 of CO<sub>2</sub> and  
 ·198 of H<sub>2</sub>O.

Theory for C <sub>13</sub> H <sub>16</sub> O <sub>2</sub> .		Experiment.	
		I.	II.
Carbon.....	76·42	76·72	76·5
Hydrogen .....	7·84	7·73	7·86

It is, therefore, *cumenylcrotonic acid*,



Cumenylcrotonic acid melts at about 90—91°. On cooling, it crystallises, and then swells up in a most remarkable manner into leaf-like scales. It is easily soluble in alcohol and in boiling petroleum-spirit, though but little so when the solvent is cold.

*Silver salt*, C<sub>13</sub>H<sub>15</sub>AgO<sub>2</sub>.—A quantity of cumenylcrotonic acid was dissolved in a solution containing the theoretical weight of sodium carbonate. A few drops of silver nitrate were added, and the resulting precipitate filtered off; excess of silver nitrate was then added to the filtrate, which caused a copious white curdy precipitate to form, rendering the fluid semi-solid, but by stirring and after standing for some time, it became more dense. It was collected on a filter, washed with cold water in which it is nearly insoluble, and dried. It is of a very pure white colour. On analysis, it gave the following numbers:—

- I. ·301 of substance gave  
 ·104 of silver = 34·55 per cent.
- II. ·2355 of substance gave  
 ·0815 of silver = 34·6 per cent.

The above formula requires 34·72 per cent. silver.

### III.—*Cumenylangelic Acid*.

A mixture of cuminic aldehyde, butyric anhydride, and sodium butyrate, in proportions corresponding to those used for the previous acids, was heated to 180° for five or six hours in a sealed tube.



The product was a thick pale-brown fluid, and on opening the tube, a little carbonic anhydride was given off. In a second operation, sodium acetate was substituted for butyrate. As in the other experiments, the products were purified by distilling off the unchanged aldehyde with water and dissolving the crude acid in sodium carbonate (having previously washed it with water to remove the saline matter), then precipitating the acid from the filtered solution, and finally crystallising two or three times from alcohol. The resulting product gave the following numbers on analysis:—

- I. ·313 of substance gave  
·880 of CO<sub>2</sub> and  
·229 of H<sub>2</sub>O.
- II. ·258 of substance gave  
·727 of CO<sub>2</sub> and  
·190 of H<sub>2</sub>O.

	Theory for C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> .	Experiment.	
		I.	II.
Carbon .....	77·06	76·68	76·90
Hydrogen .....	8·25	8·11	8·18

(Analysis II was made with the product in which sodium acetate was employed.)

This acid is, therefore, *cumenylangelic acid*,



It melts at 123°. Alcohol dissolves it freely, especially when hot, and on cooling deposits it in colourless needles.

#### ACIDS FROM CINNAMIC ALDEHYDE.

In most of the following experiments pure cinnamic aldehyde was used, prepared from oil of cassia or of cinnamon, by means of a bisulphite. (The pure aldehyde was found to boil at 247—248°.) Oil of cinnamon, however, if of the best quality, answered the purpose very well.

#### I.—*Cinnamencilrylic Acid*.

A mixture of two parts of cinnamic aldehyde, three parts acetic anhydride, and one part of sodium acetate, heated to 160—167° in a sealed tube, yields a brown product, which, on cooling becomes a radiated crystalline mass. On opening the tube, carbonic anhydride escapes. On mixing the product with water, the saline matter dissolves and leaves a resinous substance, which, when boiled with sodium carbonate, only partially dissolves. The alkaline solution, after filtration, when acidified with hydrochloric acid, gives a white

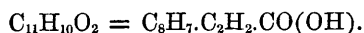
precipitate of the new acid, which is purified by crystallisation from alcohol, and then from petroleum-spirit

A flask, with a condensing-tube, may be used with advantage instead of a sealed tube, in the preparation of this acid, heating it by placing it in a paraffin-bath. The amount of resinous matter produced is always large, and up to the present time I have been unable to obtain more than twenty-five per cent. of this acid from the aldehyde employed. It gave the following numbers on analysis:—

I.	·2565 of substance gave
	·713 of CO <sub>2</sub> and
	·141 of H <sub>2</sub> O.
II.	·3415 of substance gave
	·948 of CO <sub>2</sub> and
	·180 of H <sub>2</sub> O.

	Theory for C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> .	Experiment.	
		I.	II.
Carbon . . . . .	75·85	75·81	75·71
Hydrogen . . . . .	5·74	6·09	5·83

I propose to call this acid *cinnamerylacrylic*, giving the name cinnameryl to the radical C<sub>8</sub>H<sub>7</sub> = C<sub>6</sub>H<sub>5</sub>.C<sub>2</sub>H<sub>2</sub>, which is related to cinnamene in the same manner as cumenyl is to cumene:—



Cinnamerylacrylic acid melts at 165—166°. It is easily soluble in alcohol, from which it crystallises in thin plates. In petroleum-spirit, it is difficultly soluble, but crystallises from it better than from alcohol.

When boiled in a retort with aqueous chromic acid, it gives a distillate containing an oil which appears to be cinnamic aldehyde.

The acid, when heated and boiled, decomposes, yielding an oil which burns with a very smoky flame.

*Sodium salt.*—Cinnamerylacrylic acid dissolves slowly in a dilute boiling solution of sodium carbonate, and if theoretical quantities are employed, the solution, on evaporation, dries up to a white, almost amorphous mass, not very soluble in cold water.

*Calcium salt.*—This is obtained by adding calcium chloride to a solution of the sodium salt. It is obtained as a white precipitate, dissolving to a small extent in boiling water, from which it separates in small glistening crystals on cooling.

*Barium salt.*—Barium chloride gives, with the sodium salt, a white precipitate slightly soluble in water, and separating from the boiling solution on cooling in small needles.

*Magnesium salt.*—Magnesium sulphate added to a dilute solution of

the sodium salt produces a white milky precipitate, which almost immediately redissolves, but on standing, the salt is deposited in a crystalline state.

*Silver salt*,  $C_{11}H_9AgO_2$ .—Obtained by double decomposition as a white, somewhat curdy, precipitate, slightly soluble in water, and blackening gradually in sunlight. It gave the following numbers on analysis :—

- I. 4265 of substance gave  
1635 of silver = 38·33 per cent.
- II. 309 of substance gave  
119 of silver = 38·51 per cent.

The above formula requires 38·07 per cent. of silver.

*Lead salt*, a white curdy precipitate.

*Copper salt*, a pale green precipitate.

*Ferric salt*, a pale brown precipitate.

*Chloride of Cinnamethylacryl*,  $C_{11}H_9OCl$ .—Cinnamethylacrylic acid, when heated gently with phosphorus pentachloride, is rapidly acted upon with evolution of hydrochloric acid, the mixture becoming fluid. On cooling, the chloride separates out in small crystals, rendering the product nearly solid.

*Cinnamethylacrylamide*,  $C_{11}H_9O(NH_2)$ .—On agitating the above chloride with strong aqueous ammonia a white product, insoluble in water, is obtained; this, when washed and dried, crystallises from alcohol in flat needles like benzoic acid. It is rather easily soluble in alcohol. On analysis it gave the following numbers :—

- 2595 of substance gave
- 725 of  $CO_2$  and
- 151 of  $H_2O$ .

	Theory for $C_{11}H_9O(NH_2)$ .	Experiment.
Carbon .....	76·30	76·19
Hydrogen .....	6·35	6·46

*Hydrocinnamethylacrylic acid*. On treating cinnamethylacrylic acid with sodium-amalgam by degrees (the acid being suspended in a large excess of water) it dissolved; excess of amalgam was then added, and the mixture allowed to stand about twelve hours. The clear solution was then decanted, acidified with hydrochloric acid, and agitated with ether. The ethereal solution thus obtained left the new acid on evaporation as an oily fluid, which was analysed and gave the following numbers :—

- 2695 of substance gave
- 7365 of  $CO_2$  and
- 162 of  $H_2O$ .

	Theory for $C_{11}H_{12}O_2$ .	Experiment.
Carbon .....	75·0	74·52
Hydrogen .....	6·81	6·68

*Silver salt*,  $C_{11}H_{11}AgO_2$ .—This is a white precipitate, and gave the following numbers on analysis:—

·400 of substance gave  
 ·1505 of silver = 37·62 per cent.

The above formula requires 38·16 per cent. of silver.

The analytical results obtained with this acid are not so satisfactory as could be desired, but I had but little product at my disposal. The numbers, however, indicate that only two atoms of hydrogen united with the cinnamylacrylic acid, and not four, as was thought probable.

If the formula given be correct, this acid is isomeric with phenyl-angelic acid.

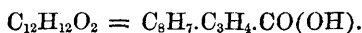
## II. *Cinnamylcrotonic Acid*.

In the preparation of this acid the proportions used were six grams of sodium propionate, fifteen grams of cinnamic aldehyde, and fifteen grams of propionic anhydride. The mixture was heated in a sealed tube to 160—165° C. for about six hours. On opening the tube only a small quantity of carbonic anhydride escaped. The product was boiled with water to remove volatile products, and allowed to cool, then thrown on a filter to separate sodium propionate, boiled with sodium carbonate, and the resulting solution filtered. The new acid was then precipitated with hydrochloric acid, washed, crystallised once from alcohol, and finally twice from petroleum spirit. The above quantities yielded five grams of acid. It gave the following numbers on analysis:—

·2710 of substance gave  
 ·7585 of  $CO_2$  and  
 ·158 of  $H_2O$ .

	Theory for $C_{12}H_{12}O_2$ .	Experiment.
Carbon .....	76·59	76·31
Hydrogen .....	6·39	6·48

This acid is therefore *cinnamylcrotonic acid*,—



It melts at 157—158°. It is nearly insoluble in cold, and difficultly in hot petroleum spirit. From this solvent it crystallises in flat, oblique, transparent prisms, which become opaque on keeping. It is easily soluble in alcohol.

*Sodium salt*.—The above acid dissolves slowly in a boiling dilute solution of sodium carbonate. On evaporating it in a vacuum it forms a distinctly crystalline product only moderately soluble in water.

*Calcium salt*.—This separates from the sodium salt on the addition of calcium chloride, as a flocculent white precipitate, which dissolves if boiled in a very large excess of water, and crystallises out on cooling in groups of minute needles.

*Barium salt*.—Obtained by double decomposition, is a flocculent precipitate, difficultly soluble in boiling water. It is deposited from its aqueous solution on cooling in minute crystals, which, when seen with a lens, appear like crystals of benzoic acid.

The *magnesium salt* is a crystalline body more easily soluble than the two preceding.

The *ferric salt* is a pale drabish-brown precipitate.

The *copper salt* is a very pale green precipitate.

*Silver salt*,  $C_{12}H_{11}AgO_2$ .—This is of a pure white colour, slightly soluble in cold water, and but slowly acted upon by light. It gave the following numbers on analysis:—

- I. .410 of substance gave  
    .149 of silver = 36.34 per cent.
- II. .4055 of substance gave  
    .1475 of silver = 36.37 per cent.

The above formula requires 36.6 per cent. silver.

### III. *Cinnamylangelic Acid*.

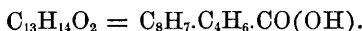
The products used in the preparation of this acid were employed in the proportion of one of sodium butyrate, two of cinnamic aldehyde, and three of butyric anhydride, and the sealed tubes were heated to 160—165° for about six hours. The resulting substance was boiled with water until oily products ceased to distil over. The residue in the retort was allowed to cool, and the crude acid collected on a filter and washed with water, boiled with sodium carbonate, the solution filtered, and the acid precipitated with hydrochloric acid. It was then dried and crystallised from petroleum spirit. On analysis, however, it did not give satisfactory numbers. It was then further purified by conversion into the calcium salt, which was boiled with water, thrown on a filter, and washed with hot water. The salt was then decomposed with hydrochloric acid, the product washed, dried, and crystallised from petroleum spirit. There was first formed a bulky mass of minute crystals almost filling the liquid; in a few hours, however, they changed, becoming brilliant and occupying a small space. They were very beautiful when viewed under the microscope.

The following numbers were obtained on analysis:—

- I. ·254 of substance gave  
 ·7177 of CO<sub>2</sub> and  
 ·1544 of H<sub>2</sub>O.
- II. ·2388 of substance gave  
 ·673 of CO<sub>2</sub> and  
 ·146 of H<sub>2</sub>O.

	Theory for C <sub>13</sub> H <sub>14</sub> O <sub>2</sub>	Experiment.	
		I.	II.
Carbon .....	77·22	77·04	76·84
Hydrogen .....	6·93	6·75	6·79

It is, therefore, *cinnamenylangelic acid*,—



This acid melts at 125—127°. It is easily soluble in alcohol, but not very freely so in petroleum spirit.

*Silver salt*, C<sub>13</sub>H<sub>13</sub>AgO<sub>2</sub>.—On adding a small quantity of silver nitrate to a solution of the sodium salt of this acid, a precipitate forms, but redissolves in the excess of the sodium salt. On adding a large quantity, however, a white precipitate is obtained, slightly soluble in cold water. It gave the following numbers on analysis:—

- I. ·315 of substance gave  
 ·1105 of silver = 35·08 per cent.
- II. ·218 of substance gave  
 ·0765 of silver = 35·05 per cent.

The above formula requires 34·95 per cent. silver.

#### ACIDS FROM ANISIC ALDEHYDE.

##### I. *Methylparoxyphenylacrylic Acid*.

A mixture of two parts of anisic aldehyde, two of acetic anhydride, and one of sodium acetate, heated to about 170° in sealed tubes for eight hours, gave a dark-coloured product, and on opening the tubes carbonic anhydride escaped. The contents of the tubes were boiled with water in a retort until the distillate was nearly free from oil, the residue was then allowed to cool, and the crystalline product collected on a filter and washed from saline matter. It was then boiled with sodium carbonate, filtered through a wet filter to remove neutral oily products, and the new acid precipitated with hydrochloric acid. After being washed and dried, it was twice crystallised from alcohol. It gave on analysis the following numbers:—

- I. .283 of substance gave  
 .696 of CO<sub>2</sub> and  
 .145 of H<sub>2</sub>O.  
 II. .205 of substance gave  
 .5065 of CO<sub>2</sub> and  
 .105 of H<sub>2</sub>O.

	Theory for C <sub>10</sub> H <sub>10</sub> O <sub>3</sub> .	Experiment.	
		I.	II.
Carbon . . . . .	67·41	67·07	67·33
Hydrogen . . . . .	5·61	5·69	5·66

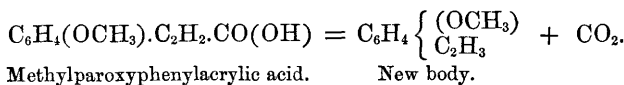
It is, therefore, *methylparoxyphenylacrylic acid*,—



and, therefore, the methylic derivative of paracoumaric acid, which is paroxyphenylacrylic acid.

Methylparoxyphenylacrylic acid melts at about 171°. It is moderately soluble in alcohol, from which it crystallises in very pale yellow needles. It also dissolves rather freely in hot glacial acetic acid. In boiling water it is soluble, but only to a small extent, this solution on cooling deposits the acid in small white crystals.

On heating till it boils, decomposition takes place, an oil having a strong but pleasant odour of fennel being produced; when cooled it solidifies to a crystalline mass. It is most probably a homologue of anethol, and produced thus:—



Methylparoxyphenylacrylic acid, when boiled in a retort with dilute chromic acid, is slowly oxidised, and an oil distils over, which is apparently anisic aldehyde.

*Sodium salt*, C<sub>10</sub>H<sub>9</sub>NaO<sub>3</sub>.—This is obtained by boiling a weighed quantity of the acid with the theoretical quantity of a standard solution of sodium carbonate. It is deposited on cooling as a white mass, appearing under the microscope to consist of minute crystals with a satiny lustre. It is rather difficultly soluble in water. An analysis of the crystals dried in a vacuum gave the following result:—

- .328 of substance gave  
 .117 of sodium sulphate = 11·67 p.c.

The above formula requires 11·50 p.c. of sodium.

*Calcium salt*.—Obtained in the form of transparent needles on

adding calcium chloride to a weak boiling solution of the sodium salt, filtering, and leaving the mixture to cool.

*Barium salt.*—Prepared in an analogous manner to the calcium salt, is obtained as a crystalline precipitate.

*Strontium salt.*—Deposited from its boiling aqueous solution on cooling in small crystals, more soluble than the barium salt.

*Copper salt.*—Obtained by double decomposition. It is a pale bluish-green precipitate.

*Ferric salt.*—A brown precipitate.

*Silver salt, C<sub>10</sub>H<sub>4</sub>AgO<sub>3</sub>.*—A dilute solution of the sodium salt was treated with silver nitrate until a small quantity of a precipitate was produced, and not redissolved on stirring; the solution was then filtered, and silver nitrate added in excess. The pure white precipitate then produced was collected, washed and dried in a vacuum. It gave on analysis the following numbers:—

I.	·3137 of substance gave
	·1185 of silver.
II.	·3815 of substance gave
	·588 of CO <sub>2</sub> and
	·1118 of H <sub>2</sub> O and
	·144 of silver.

	Theory for C <sub>10</sub> H <sub>4</sub> AgO <sub>3</sub> .	Experiment.	
		I.	II.
Carbon .....	42·10	—	42·03
Hydrogen .....	3·16	—	3·23
Silver .....	37·89	37·77	37·74

This salt is slightly soluble in water.

*Chloride of Methylparoxyphenylacryl.*—When methylparoxyphenylacrylic acid and phosphorous pentachloride are heated together in a flask by means of a water-bath, chemical action quickly sets in, hydrochloric acid is evolved, and the mixture becomes fluid. After removing the phosphorous oxychloride by heating the product in an oil-bath to 120—130°, and then passing dry air, the new product is left as a somewhat dark yellowish oil, which on cooling solidifies to a beautifully crystalline mass, fusing at about 50°.

When mixed with alcohol it reacts with evolution of heat, and produces the ether, which is a pale yellow viscid oil heavier than water.

*Methylparoxyphenylacrylamide, C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>(NH<sub>2</sub>).*—The chloride just described when mixed with alcoholic ammonia becomes hot, and deposits crystals. On evaporating off the alcohol and treating the residue with water, a white product is left. This was purified by crystallisation from water, and gave the following numbers on analysis:—



- I. ·2619 of substance gave  
 ·648 of CO<sub>2</sub> and,  
 ·156 of H<sub>2</sub>O.  
 II. ·3265 of substance gave  
 ·808 of CO<sub>2</sub> and  
 ·178 of H<sub>2</sub>O.

	Theory for C <sub>10</sub> H <sub>9</sub> O <sub>2</sub> (NH <sub>2</sub> ).	Experiment.	
		I.	II.
Carbon .....	67·79	67·46	67·47
Hydrogen .....	6·21	6·6	6·1

This amide melts at 186°, and crystallises on cooling. It is deposited in scaly crystals from alcohol, in which it is very soluble. It is not easily soluble in water, and the crystals obtained from this solvent are very small.

*Hydromethylparoxyphenylacrylic Acid or Methylparoxyphenylpropionic Acid.*

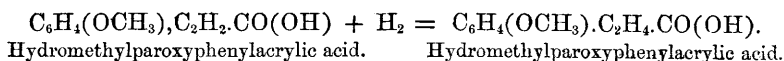
One part of methylparoxyphenylacrylic acid was mixed with fifty parts of water, and sodium amalgam containing two per cent. of sodium, added by degrees, the mixture being constantly agitated. When the acid had dissolved, excess of amalgam was added, and the mixture allowed to stand twenty-four hours. The clear solution was then separated from the mercury and acidified with hydrochloric acid. A copious white crystalline precipitate separated, which after standing for several hours, was thrown on a filter, and washed with cold water. It was then purified, by solution in boiling water, and filtering from a small amount of insoluble impurity. On cooling, the new acid was deposited in feathery crystals.

This product gave on analysis the following numbers:—

- 2746 of substance gave  
 ·669 of CO<sub>2</sub> and  
 ·166 of H<sub>2</sub>O.

	Theory for C <sub>10</sub> H <sub>12</sub> O <sub>3</sub> .	Experiment.	
Carbon .....	66·66	66·44	
Hydrogen .....	6·66	6·73	

This acid melts at 101°. Its formation may be expressed thus—



II. *Methylparoxyphenylcrotonic Acid.*

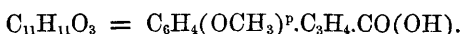
Two parts of anisic aldehyde, three parts of propionic anhydride, and one part of sodium propionate were the proportions used in the prepara-

tion of this acid. The mixture was heated in sealed tubes to about 170—175° for six hours. The product when boiled with water to remove unconverted anisic aldehyde, was left as an oily layer, solidifying on cooling to a crystalline cake. The aqueous solution containing the sodium propionate also deposited the new acid in beautiful thin plates. The crude product after being washed with water was boiled with sodium carbonate, which dissolved most of it, but left a good deal of neutral oily matter. The solution was filtered, but as it was milky, it was found necessary to treat it with ether; it was then boiled and acidified with hydrochloric acid, which caused the new acid to separate as a white precipitate. It was collected, washed, and crystallised from alcohol. On analysis it gave the following numbers:—

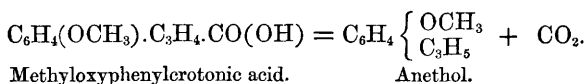
·2865 of substance gave  
 ·719 of CO<sub>2</sub> and  
 ·161 of H<sub>2</sub>O.

	Theory for C <sub>11</sub> H <sub>12</sub> O <sub>2</sub> .	Experiment.
Carbon .....	68·74	68·46
Hydrogen .....	6·24	6·25

This acid is therefore *methylparoxyphenylcrotonic*,



It melts at 154°. When heated to boiling, it decomposes, yielding an oil which has the odour of oil of anise, and when cooled becomes crystalline. There can be scarcely any doubt that it is anethol; it is under examination. The decomposition may be expressed thus:



Methoxyphenylcrotonic acid is moderately soluble in alcohol, and crystallises from it in beautiful transparent rectangular plates.

*Calcium salt.*—On adding calcium chloride to a dilute solution of the sodium salt, a crystalline precipitate forms, which dissolves on boiling, and is deposited on cooling in small white needles.

*Barium salt.*—Prepared in an analogous manner to the calcium salt. It crystallises from its boiling aqueous solution in thin brilliant plates.

*Silver salt, C<sub>11</sub>H<sub>11</sub>AgO<sub>3</sub>.*—This is prepared by adding silver nitrate to the sodium salt, filtering off the first portions of the precipitate and then adding an excess of silver nitrate. The salt which comes down as a satiny crystalline precipitate, is slightly soluble in cold water, but

more so in hot water; from the latter it crystallises on cooling in fine needles; it is only slowly acted upon by light. It gave the following numbers on analysis:—

- I. .3800 of substance gave  
     .138 of silver = 36.32 p.c.
- II. .3775 of substance gave  
     .136 of silver = 36.02 p.c.

The above formula requires 36.12 per cent. of silver.

III. *Methylparoxyphenylangelic Acid.*

A mixture of sodium butyrate, anisic aldehyde, and butyric anhydride in the proportions corresponding with those employed in the preparation of the preceding acid, was heated in sealed tubes to 180° for six hours; the product was boiled with water as in the previous cases, and the crude acid, after washing, dissolved in an alkaline carbonate, and filtered from oily impurities. The boiling alkaline solution, when acidified, deposited the new acid as a white precipitate, part of which fused in the hot fluid. It was then crystallised from alcohol four times. In one experiment sodium acetate was used in place of sodium butyrate; the product, however, was not considered to be quite so good, as there appeared to be minute crystals of another acid present; these, however, disappeared on repeated crystallisation. Analysis I. was made with this preparation.

- I. .2832 of substance gave  
     .721 of CO<sub>2</sub> and  
     .168 of H<sub>2</sub>O.
- II. .3165 of substance gave  
     .807 of CO<sub>2</sub> and  
     .188 of H<sub>2</sub>O.

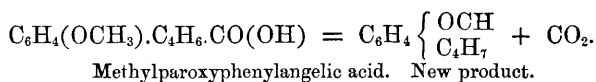
Theory for C <sub>12</sub> H <sub>14</sub> O <sub>3</sub> .		Experiment.	
		I.	II.
Carbon.....	69.9	69.43	69.54
Hydrogen .....	6.79	6.58	6.61

This is therefore *methylparoxyphenylangelic acid*—



It melts at 123—124° to a colourless oil, and on cooling crystallises in a most beautiful manner. It crystallises from alcohol in needles.

If heated until it boils, it decomposes and gives an oil similar in odour to the oil of anise. It is probably another homologue of anethol, and formed thus:



## ACIDS FROM METHYLSALICYLIC ALDEHYDE.

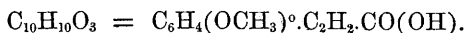
I.  $\beta^*$ .—*Methylorthoxyphenylacrylic Acid.*

Two parts of hydride of methyl salicyl, three of acetic anhydride, and one of sodium acetate, were heated in sealed tubes to about  $180^\circ$  for six hours. The contents of the tubes on cooling consisted of two distinct products, one forming small groups of crystals as fine as pin-heads, the rest being a radiating crystalline mass. On opening the tubes, carbonic anhydride escaped. The solid product was boiled with water in a retort as usual, and the crude acid remaining collected on a filter, washed with water, dissolved in boiling sodium carbonate, and then filtered through a wet filter, the clear solution, on being acidified with hydrochloric acid, deposited the new acid as a nearly white precipitate. It was collected, washed, and finally purified by crystallisation from alcohol. It gave, on analysis, the following numbers:—

I.	·283 of substance gave
	·7005 of $\text{CO}_2$ and
	·141 of $\text{H}_2\text{O}$ .
II.	·2935 of substance gave
	·723 of $\text{CO}_2$ and
	·150 of $\text{H}_2\text{O}$ .

	Theory for $\text{C}_{10}\text{H}_{10}\text{O}_3$ .	Experiment.	
		I.	II.
Carbon . . . . .	67·41	67·50	67·16
Hydrogen . . . . .	5·61	5·57	5·66

This acid is, therefore, *methylorthoxyphenylacrylic* or *methylcoumaric acid*—



It melts at  $182\text{--}183^\circ$ . When heated until it boils, it decomposes, yielding an oil, having an odour very unlike that obtained from the *para*-acid, but somewhat similar to that of coal-tar naphtha.

It is moderately soluble in alcohol, and crystallises from it in small hard prisms.

When fused with potassium hydrate, it first becomes yellow, apparently owing to the formation of coumaric acid, but when further heated, it yields salicylic acid in abundance.

When heated with phosphorus pentachloride it decomposes, yielding a chloride. This, when treated with ammonia, is converted into

\* The reason why this acid is called  $\beta$ -acid will be seen further on in this paper.

methylorthoxyphenylacrylamide, crystallising from alcohol in needles. It fuses at 191—192°.

*Calcium salt* is obtained as a white precipitate, becoming crystalline on adding calcium chloride to a solution of the sodium salt.

*Barium salt*: similar to the above.

*Copper salt*: a green precipitate.

*Ferric salt*: a pale brown precipitate.

*Silver salt*,  $C_{10}H_9AgO_3$ .—Obtained by adding silver nitrate to a solution of the sodium salt. It is a white precipitate, and gave, on analysis, the following numbers:—

- I. ·301 of substance gave  
·1135 of silver = 37·7 per cent.
- II. ·3145 of substance gave  
·118 of silver = 37·52 per cent.

The above formula requires 37·8 per cent. of silver.

II.—*Methylorthoxyphenylcrotonic Acid.*

Seventeen grams of hydride of methylsalicyl, twenty-four grams of propionic anhydride, and twelve grams of sodium propionate, were heated in sealed tubes to 165° for five or six hours. The product, on cooling, was a pale-brown crystalline mass. On boiling it with water, some unchanged hydride of methylsalicyl volatilised with the steam, leaving in the retort an oily product, which on cooling, gradually solidified. It was washed from saline matter, and then boiled with sodium carbonate. The solution was filtered from a small quantity of neutral oil, boiled, and acidified with hydrochloric acid. The new acid separated as an oil, but on cooling solidified to a crystalline cake. When cold, it was washed, dried, and crystallised from petroleum spirit. This operation yielded thirteen grams of crude acid before crystallisation. It gave the following numbers on analysis:—

- I. ·281 of substance gave  
·705 of  $CO_2$  and  
·157 of  $H_2O$ .
- II. ·2565 of substance gave  
·646 of  $CO_2$  and  
·1445 of  $H_2O$ .

	Theory for $C_{11}H_{12}O_3$ .	Experiment.	
		I.	II.
Carbon . . . . .	68·74	68·42	68·68
Hydrogen . . . . .	6·25	6·20	6·26

This substance is, therefore, *methylorthoxyphenylcrotonic acid*,



It melts at 104—105°. It is very soluble in alcohol and benzol, not very much so in petroleum spirit, but from a boiling solution in this solvent it is deposited on cooling in large leafy crystals arranged in fern-like groups. When heated in a watch-glass, it fuses to a clear oil, and on cooling, crystallises, forming small circular discs, radiating from the centre, and as these increase, they crack with such force as to cause the watch-glass to emit a distinct sound each time. The crystalline mass often shows colours somewhat like those of mother-of-pearl.

*Calcium salt.*—This comes down as a white crystalline precipitate if calcium chloride be added to a solution of the sodium salt. If the solution be very dilute, it crystallises in beautiful groups of satiny needles; it is more soluble in hot than cold water.

*Barium salt, C<sub>22</sub>H<sub>22</sub>BaO<sub>6</sub>.*—On adding barium chloride to a boiling solution of the sodium salt somewhat dilute, this compound on cooling, separates out in needles. It is rather soluble in cold water. The crystals appear to contain water of crystallisation, as they change in appearance on drying over sulphuric acid. A specimen dried at 100° gave the following numbers:—

·134 of substance gave

·060 of BaSO<sub>4</sub> = 26·32 per cent. of barium.

The above formula requires 26·39        "        "

*Silver salt, C<sub>11</sub>H<sub>11</sub>AgO<sub>3</sub>.*—Silver nitrate, added in small quantities to a solution of the sodium salt, gives a white precipitate, which, on stirring, dissolves almost entirely; but excess gives a pure white precipitate, which, during washing, contracts to a small bulk, and apparently becomes crystalline. It is slightly soluble in water. On analysis, the following number was obtained:—

·239 of substance gave

·08625 of silver = 36·08 per cent.

The above formula requires 36·02 per cent. silver.

### III.—*Methylorthoxyphenylangelic Acid.*

A mixture of one part of sodium butyrate, three of butyric anhydride, and two of hydride of methyl salicyl, was heated in sealed tubes to 165° for about seven hours. The resulting product was a viscid liquid, and on opening the tubes, a good deal of carbonic anhydride escaped. After boiling with water as usual, the residue in the retort contained an oil which on standing for some hours partially solidified. It was separated from the aqueous solution of sodium butyrate, and boiled with a solution of sodium carbonate, which dissolved the new acid, but left a considerable quantity of neutral oil, which was removed from it by means of ether.

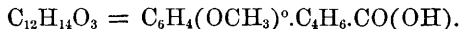
The alkaline solution was boiled and acidified with hydrochloric acid: the acid then separated as an oil, but solidified on cooling. It was collected, washed, and again dissolved in sodium carbonate, using about the calculated quantity necessary to form the sodium salt, and converted into the calcium salt by the addition of calcium chloride. This salt came down in a plastic state, adhering to the sides of the vessel, but on cooling, the liquid was filled with small crystals, which appeared as fine needles.

The calcium salt was collected and washed several times with cold water, and then decomposed with hydrochloric acid. The acid thus obtained was twice crystallised from alcohol, from which it separated in hard needles, about three-quarters of an inch in length. It gave the following numbers on analysis:—

·255 of substance gave  
 ·6515 of CO<sub>2</sub> and  
 ·157 of H<sub>2</sub>O.

	Experiment.	
Theory for C <sub>12</sub> H <sub>14</sub> O <sub>3</sub> .	I.	II.
Carbon .....	69·90	69·67
Hydrogen .....	6·79	6·83

This is therefore *methylorthoxyphenylangelic acid*—



It fuses at about 105°, is very soluble in alcohol, but much less so in petroleum spirit.

*Acids obtained from Coumarin.*

As all the aromatic aldehydes experimented on, with the exception of the hydride of salicyl, yield an acid when treated with acetic anhydride and an acetate, there could be no doubt that the formation of coumarin is preceded by that of an acid. This acid would, of course, be an ortho-oxy-compound, and would, therefore, readily split up into water and an anhydride, which would be coumarin. This agrees with the views of the constitution of that substance proposed by Fittig (*Chem. News*, xix, 73).

But coumarin, when treated with potassium hydrate, yields two compounds of the same composition. The first, which was examined by R. Williamson (*Journ. Chem. Soc.*, xxviii, 852), is obtained by simply boiling coumarin with an aqueous solution of the alkali; the second is produced in the same manner, but employing a higher temperature.

The first compound, when decomposed with an acid, yields coumarin; the second, ordinary coumaric acid.

Now it appeared doubtful which of these two alkaline compounds represented the acid of which coumarin is the anhydride, because it was possible that this acid might be so unstable as to split up into coumarin and water as soon as it was liberated; and, on the other hand, that coumaric acid, on account of the high temperature at which it is produced, might be an alteration-product, and not the true acid.

R. Williamson's metallic derivatives must have the constitution  $C_6H_4(OR) \cdot C_2H_2 \cdot CO(OR)$ , which is the same as that of a coumarate, unless they be regarded as molecular compounds, which I think is untenable.

If this constitution be correct, it is evident that these substances, by treatment with methylic iodide, might be expected to yield the compound,  $C_6H_4(OMe) \cdot C_2H_2 \cdot CO(OMe)$ .

This should be the methylic derivative of an acid already described in this paper, namely, methylorthoxyphenyl acrylic, and by treatment with potassium hydrate should be decomposed into its potassium-salt.

Experiments were made in this direction with the following results:—

A quantity of an alcoholic solution of the compound obtained by boiling coumarin with sodium hydrate was treated with iodide of methyl in a sealed tube and heated to  $100^\circ$  for about three hours. On opening the tube, the reaction was found to be complete. The alcohol was distilled off and water added: this caused an oil to separate in quantity.

On distilling this oil it was found to boil at  $278$ — $280^\circ$ , very little coming over on either side of this temperature. It was analysed, and gave the following numbers:—

I.	·2588 of substance gave
	·6495 of $CO_2$ and
	·142 of $H_2O$ .
II.	·273 of substance gave
	·6882 of $CO_2$ and
	·1565 of $H_2O$ .

	Theory for $C_{11}H_{12}O_3$ .	Experiment.	
		I.	II.
Carbon .....	68·75	68·44	68·71
Hydrogen .....	6·25	6·09	6·37

This substance has therefore the composition of the methylic derivative of methylorthoxyphenylacrylic acid, and may be written thus,  $C_6H_4(OCH_3) \cdot C_2H_2 \cdot CO(OCH_3)$ , and is formed from the sodium compound simply by the substitution of that metal by methyl. It is the



methyl ether of an acid I propose to call *α-methylorthoxyphenylacrylic acid*.

A portion of this ether, before it had been distilled, was boiled with alcoholic potassium hydrate, which decomposed it, and after adding water and boiling off the alcohol, hydrochloric acid was added in excess; this caused an oily substance to separate, which crystallised very beautifully on cooling.

This acid was also prepared in a different manner. A quantity of the compound obtained by boiling coumarin with sodium hydrate was dissolved in alcohol and mixed with only enough methyl iodide to combine with *half* the sodium: the mixture was heated in a sealed tube to 150° for five or six hours: the resulting product was a pale-coloured fluid. The alcohol was distilled off, and on cooling a syrupy mass was obtained, and on dissolving it in water only a trace of oily product was found to be present; this was removed with ether. The clear aqueous solution was boiled and acidified with hydrochloric acid; the new acid then separated as an oil, but solidified to a crystalline mass on cooling.

It was not found practicable to purify it by crystallisation from alcohol, but after trying various solvents, ordinary acetic acid (about 50 p.c.) was found to answer the purpose. After crystallisation from this acid, it gave on analysis the following numbers:—

	·2458 of substance gave	
	·608 of CO <sub>2</sub> and	
	·1245 of H <sub>2</sub> O.	
Theory for C <sub>10</sub> H <sub>10</sub> O <sub>3</sub> .		Experiment.
Carbon .....	67·41	67·45
Hydrogen .....	5·61	5·62

This compound then has exactly the composition of methylorthoxyphenylacrylic acid, and when fused with potassium hydrate also yields salicylic acid, but in other respects it is entirely different. It melts at 88—89°, the other at 182—183°, and is very much more soluble in alcohol, &c. This is why I have called it *α-methylorthoxyphenylacrylic acid*.

This new acid is moderately soluble in ordinary acetic acid, and separates from it, on cooling, in beautiful glistening crystals, which generally lose their lustre on drying.

*Sodium salt*.—Obtained by boiling this acid with the theoretical quantity of sodium carbonate. It is excessively soluble in water, and dries up to a gummy mass.

*Copper salt*: bright yellowish-green precipitate.

*Ferric salt*: pale brown precipitate.

*Silver salt*, C<sub>10</sub>H<sub>9</sub>AgO<sub>3</sub>.—This comes down as a white crystalline precipitate on adding silver nitrate to the sodium salt. The filtrate from

this deposits a small quantity of salt, on standing, as a white powder, which when seen under the microscope is composed of distinct crystals. It gave on analysis the following numbers:—

- I. .4118 of substance gave  
 .1558 of silver = 37·83 p.c.  
 II. .5102 of substance gave  
 .1927 of silver = 37·76 p.c.

The above formula requires 37·8 p.c.

*Action of Heat on some of the above Coumarin Derivatives.*

These substances are modified in a remarkable manner when heated. If a mixture of an alcoholic solution of the compound obtained by boiling coumarin with sodium hydrate be mixed with methylic iodide in about theoretical quantities, and heated in a sealed tube to 150°, instead of 100°, the product after removal of the alcohol, &c., is an oil as in the other case; but when decomposed with alcoholic potassium hydrate, yields the salt of an acid which fuses only at a high temperature.

Moreover if the oil produced by heating the sealed tubes to only 100° C. (and which produces a very fusible acid,  $\alpha$ -methylorthoxyphenylacrylic acid), be heated alone in a sealed tube to 150—165° for a few hours, and then decomposed with alcoholic potassium hydrate, it yields the same difficultly fusible acid. On examining the oil which was purified by distillation and used for analysis (p. 418), it was found to give on decomposition a mixture of the fusible and difficultly fusible acids; therefore by the influence of heat alone this substance is changed.

This difficultly fusible acid was purified by crystallisation from alcohol and submitted to analysis.

- I. .261 of substance gave  
 .6465 of CO<sub>2</sub> and  
 .132 of H<sub>2</sub>O.  
 II. .205 of substance gave  
 .506 of CO<sub>2</sub> and  
 .105 of H<sub>2</sub>O.

		Experiment.	
		I.	II.
Theory for C <sub>10</sub> H <sub>10</sub> O <sub>3</sub> .			
Carbon . . . . .	67·41	67·54	67·31
Hydrogen . . . . .	5·61	5·61	5·68

It has therefore the same composition as the easily fusible one, but its melting point is 182—183°. It is in fact identical with the acid obtained by treating the hydride of methylsalicyl with acetic anhydride and sodium acetate, and called in this paper  $\beta$ -methylorthoxyphenylacrylic or methylcoumaric acid.

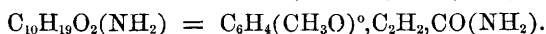
The easily fusible or  $\alpha$ -acid on being heated to its boiling-point, and then purified by crystallisation, was found to be changed, and converted into the  $\beta$ -acid fusing at  $183^{\circ}$ .

It has been seen that the methylic derivative of the  $\alpha$ -acid is converted by heat into that of the  $\beta$ -acid. Neither of these compounds are acted upon by alcoholic ammonia at  $100^{\circ}$ , and of course if the temperature be raised above  $150^{\circ}$ , the reaction virtually takes place on the  $\beta$ -compounds. On heating a mixture of either of these substances to  $200^{\circ}$  for 10 or 14 hours, with alcoholic ammonia, the product on cooling deposits crystals: these were collected, recrystallised, and submitted to analysis. The following results were obtained:

- I. ·282 of substance gave  
 ·697 of  $\text{CO}_2$  and  
 ·159 of  $\text{H}_2\text{O}$ .  
 II. ·2745 of substance gave  
 ·6795 of  $\text{CO}_2$  and  
 ·157 of  $\text{H}_2\text{O}$ .

	Experiment.	
Theory for $\text{C}_{10}\text{H}_9\text{O}_2(\text{NH}_2)$ .	I.	II.
Carbon .....	67·41	67·5
Hydrogen .....	6·25	6·35

This substance is therefore  $\beta$ -methylorthoxyphenylacrylamide.



It is moderately soluble in alcohol, from which it crystallises in beautiful white needles. It melts at  $191$ — $192^{\circ}$ .

*Action of Pentachloride of Phosphorus on  $\alpha$ -Methylorthoxyphenylacrylic Acid.*

When this acid is mixed with phosphorus pentachloride, chemical action sets in with energy, and the mixture becomes fluid, hydrochloric acid being abundantly given off. The product, when treated with ammonia, yields an amide insoluble in water. This, when crystallised from alcohol, was found to be  $\beta$ -methylorthoxyphenylacrylamide. The aqueous filtrate from the preparation of this amide on being acidified with hydrochloric acid gave a white precipitate of an acid, which was purified by crystallisation from alcohol. It gave the following numbers:—

·2415 of substance gave  
 ·594 of  $\text{CO}_2$  and  
 ·121 of  $\text{H}_2\text{O}$ .

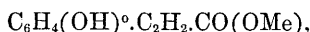
	Experiment.	
Theory for $\text{C}_{10}\text{H}_{10}\text{O}_3$ .		
Carbon .....	67·44	67·08
Hydrogen .....	5·61	5·56

This acid fuses at about 183°, and is therefore  $\beta$ -methylorthoxyphenylacrylic acid.

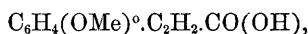
An analogous experiment was made in which carbon disulphide was mixed with the phosphorus pentachloride and the acid, to keep the temperature low, but the result was the same.

We therefore see that heat and also powerful chemical action convert the  $\alpha$ - into the  $\beta$ -compounds.

But why are these substances isomeric and not identical? Of course it is evident that two acids having their composition might exist thus :



which is orthoxyphenylacrylate of methyl, or in other words, a coumarate of methyl, and



methylorthoxyphenylacrylic acid, or methylcoumaric acid.

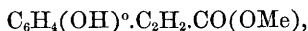
Both of these compounds would form metallic derivatives, and at first sight this might be thought to be an explanation of the difficulty, but I think it is not consistent with experiment.

As already stated, if the methylic ether of the  $\alpha$ -acid which is produced at low temperatures, and of course yields the  $\alpha$ -acid when treated with alcoholic potassium hydrate, &c., be heated to 150°, it is changed into the  $\beta$ -methylic ether and yields the  $\beta$ -acid.

The methylic ether of the  $\alpha$ -acid has all the hydrogens of its hydroxyls replaced by methyl, so that the effect of heat cannot cause any change of position to take place in this respect, and there is no ground for supposing that the alkali in one case should remove the methyl from the phenolic position, and in the other from the CO(OH) group, experiment always showing that the phenolic is the more difficult to influence of the two.

Again, when the alkaline compound of coumarin obtained by boiling coumarin with caustic alkali is treated with enough methylic iodide to remove half the metal, a salt of the  $\alpha$ -acid is produced. In mixed compounds, I believe that the metal replacing phenolic hydrogen, is much more readily acted upon, than that replacing hydrogen in the CO(OH) group.

If the  $\alpha$ -acid were the methyl ether of orthoxyphenylacrylic acid,



we should expect it to give with phosphorus pentachloride methylic chloride and the chloride of orthoxyphenylacryl; in fact, to behave like oil of gaultheria under similar circumstances; but instead of this,

it is converted into the chloride of the  $\beta$ -acid, yielding, with ammonia, the amide.

These acids being both derived from coumarin, which is an ortho-compound, are necessarily ortho-acids, which is also seen by their yielding salicylic acid when fused with potassium hydrate; and if coumarin be the anhydride of coumaric acid, it is difficult to understand that there can be any difference of structure in the group which represents the radicle of these acids, viz. :—



so that it appears probable that we must seek for an explanation of their isomerism from other sources than that of position.

From the formation of the  $\alpha$ -acid there can be no doubt that the metallic compounds of coumarin examined by R. Williamson are salts of an unstable acid, isomeric with coumaric acid.

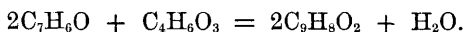
I hope to investigate this subject more fully, and to make analogous experiments with the homologues of coumarin.

Appended is a table showing some of the differences of properties between the methyl-para and  $\alpha$ - and  $\beta$ -methylorthoxyphenylacrylic acids.

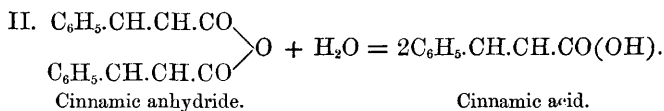
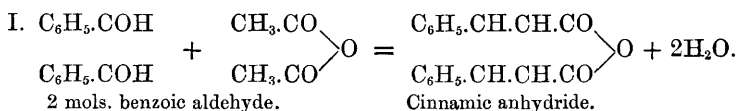
	I. Methylparoxy- phenylacrylic acid.	II. $\beta$ -Methylorthoxy- phenylacrylic acid.	III. $\alpha$ -Methylorthoxy- phenylacrylic acid.
Fusing points . . . .	171°C.	182—183°C.	88—89° C.
Colour of ferric salt.	Brown precipitate.	Pale-brown precipitate.	Pale-brown precipitate.
„ copper „	Pale bluish-green precipitate.	Green precipitate, yellower and darker than I.	A bright yellowish-green precipitate, darker than I and II.
1 p.c. solution of sodium salt, with CaCl <sub>2</sub> and BaCl <sub>2</sub> }	A crystalline white precipitate.	—	—
2½ p.c. solution of sodium salt, with CaCl <sub>2</sub> and BaCl <sub>2</sub> }	Ditto . . . . .	A white precipitate.	—
	A 2½ p.c. solution of this sodium salt deposits a large quantity of the salt on cooling in white satiny crystalline masses.	A 2½ p.c. solution of the sodium salt remains clear on cooling; the salt is only deposited on concentration, when it separates in crystals.	The sodium salt is excessively soluble in water, and, when evaporated, dries up to a gummy mass.

The formation of the acids from the aromatic aldehydes by the use of an anhydride and a metallic salt is not easy to understand. I will take the formation of cinnamic acid as a typical case.

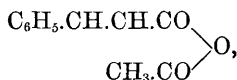
This acid has already been obtained from benzoic aldehyde by the action of acetyl chloride, by Bertagnini, and also by heating a mixture of this aldehyde and acetic acid in the presence of hydrochloric acid or a small quantity of zinc chloride, by Hugo Schiff; and there is no doubt that there is a certain amount of analogy between these reactions and the one under consideration, the remarkable part of the latter being the absolute necessity of the presence of a metallic salt. If the reaction succeeded without this it could be easily accounted for thus—



this reaction taking place in two phases, thus—

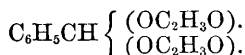


Of course if we suppose that only half the above quantity of benzoic aldehyde takes part in the reaction, instead of getting cinnamic anhydride we should get acetocinnamic anhydride—



which afterwards would decompose with the water produced in the reaction into acetic and cinnamic acid.

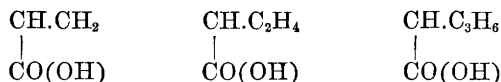
But we know that benzoic aldehyde does not act in this manner when heated with acetic anhydride, but yields only the diacetate of benzylene—



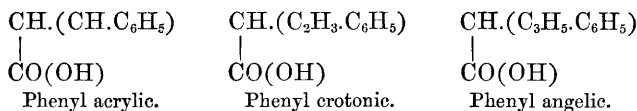
It is possible that the formation of this substance precedes that of the acid, and I am about to make experiments in this direction; but if this be the case, it is difficult to understand why sodium acetate, or any analogous salt, should cause this compound to decompose into acetic and cinnamic acids: all we know is that the product of the reaction contains, when cold, an acid cinnamate.

I have not obtained any satisfactory results by the use of valeric anhydride and a valerianate on the aromatic anhydrides, but the formation of valeric coumarin would make it appear probable that new substances may be produced in this manner.

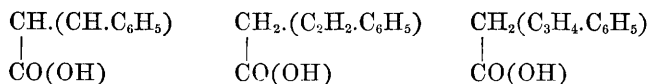
The acids described in this paper have been named as belonging to the ordinary acrylic series; those obtained by the use of acetic anhydride are certainly such, but it is doubtful if those produced with other anhydrides are strictly so. Acrylic, crotonic, and angelic acids are usually written—



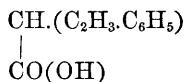
therefore the phenylated acids should be—



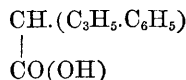
instead of which they are—



if we assume, as is most likely to be the case, that the oxygen of the aldehyde removes two atoms of hydrogen from the methyl of the propionic or butyric anhydrides, and does not attack in any way the  $\text{CH}_2$  in union with the  $\text{CO(OH)}$ . Fittig and Bieber (*Jahresb.* 1869, p. 584) write their phenylangelic acid thus:  $\text{C}_6\text{H}_5.\text{CH.CH.CH}_2.\text{CH}_2.\text{CO(OH)}$ , which is the same as the above; but so long as acetic anhydride is employed true acrylic acids will of course be obtained. Thus the aldehyde of  $\alpha$ -toluic acid (phenylacetic) should yield with acetic anhydride a true phenyl crotonic acid—

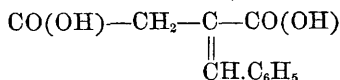


and the aldehyde of phenylpropionic acid a true phenylangelic acid—

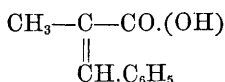


In the experiments in which I employed succinic anhydride and a succinate with benzoic aldehyde (the reaction does not take place without the succinate), the oxygen of the aldehyde must have combined with the hydrogen of one of the  $\text{CH}_2$  groups in the anhydride (unless

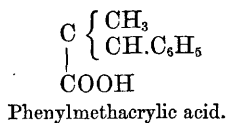
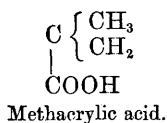
it removed one of hydrogen from each, which is not probable), and therefore at first produced a dibasic acid, constituted thus—



which, when giving up carbonic anhydride, would yield—



This acid would thus be phenylmethacrylic or isophenylcrotonic acid—



The acids obtained with cinnamic aldehyde belong to the  $\text{C}_n\text{H}_{2n} - \text{CO(OH)}$  series, of which phenylpropionic acid was previously the only representative.

The following is a list of the acids described in this paper, those in italics being previously known:—

*Acids from Benzoic Aldehyde.*

<i>Phenylacrylic or cinnamic</i> .....	$\text{C}_9\text{H}_8\text{O}_2$
<i>Phenylcrotonic</i> .....	$\text{C}_{10}\text{H}_{10}\text{O}_2$
<i>Isophenylcrotonic</i> .....	$\text{C}_{10}\text{H}_{10}\text{O}_2$
<i>Phenylangelic</i> .....	$\text{C}_{11}\text{H}_{12}\text{O}_2$

*Acids from Cuminic Aldehyde.*

<i>Cumenylacrylic or isopropylcinnamic</i> ..	$\text{C}_{12}\text{H}_{14}\text{O}_2$
<i>Hydrocumenylacrylic</i> .....	$\text{C}_{12}\text{H}_{16}\text{O}_2$
<i>Hydrocumenylcrotonic</i> .....	$\text{C}_{13}\text{H}_{16}\text{O}_2$
<i>Hydrocumenylangelic</i> .....	$\text{C}_{14}\text{H}_{18}\text{O}_2$

*Acids from Anisic Aldehyde.*

<i>Methylparoxyphenylacrylic</i> .....	$\text{C}_{10}\text{H}_{10}\text{O}_3$
<i>Hydromethylparoxyphenylacrylic</i> .....	$\text{C}_{10}\text{H}_{12}\text{O}_3$
<i>Methylparoxyphenylcrotonic</i> .....	$\text{C}_{11}\text{H}_{12}\text{O}_3$
<i>Methylparoxyphenylangelic</i> .....	$\text{C}_{12}\text{H}_{10}\text{O}_3$

*Acids from Methylsalicylic Aldehyde and Coumarin.*

$\alpha$ -Methylorthoxyphenylacrylic .....	$\text{C}_{10}\text{H}_{10}\text{O}_3$
$\beta$ -Methylorthoxyphenylacrylic.....	$\text{C}_{10}\text{H}_{10}\text{O}_3$
<i>Methylorthoxyphenylcrotonic</i> .....	$\text{C}_{11}\text{H}_{12}\text{O}_3$
<i>Methylorthoxyphenylangelic</i> .....	$\text{C}_{12}\text{H}_{14}\text{O}_3$



*Acids from Cinnamic Aldehyde.*

Cinnamethylacrylic .....	$C_{11}H_{10}O_2$
Hydrocinnamethylacrylic .....	$C_{11}H_{12}O_2$
Cinnamethylcrotonic .....	$C_{12}H_{12}O_2$
Cinnamethylangelic .....	$C_{13}H_{14}O_2$

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