XXXV.—*Action of Cinnamic and Salicylic Aldehydes on Malonic Acid.*

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A MIXTURE of equal parts of cinnamic aldehyde and malonic acid with half its weight of glacial acetic acid was heated at 100° for six hours; the crystalline product, after being collected and washed successively with glacial acetic acid, water, and chloroform, presented the appearance of yellow needles. On analysis—

0.3639 gram gave 0.8829 gram CO ₂ and 0.1446 H ₂ O.			
= H.....	4.41 per cent.	Theory.....	4.59
C.....	66.16	„	66.05

It is therefore phenylbutindicarboxylic acid,

It melts at 208° with effervescence, carbon dioxide being evolved. The residue had no constant melting point, but if a larger quantity was heated at 210° till it ceased to give off carbon dioxide, and the product crystallised from benzene, pure cinnamerylacrylic acid, melting at 165° (Perkin, *Chem. Soc. J.*, **31**, 403), is obtained; the cinnamerylacrylic acid is partially decomposed by heating above 200°.

Phenylbutindicarboxylic acid, unlike benzalmalonic acid, can be boiled with water, without decomposition.

I now tried salicylaldehyde, with the view of ascertaining the influence of a hydroxyl-group in the ortho-position.

A mixture of salicylaldehyde, malonic acid, and glacial acetic acid, on being heated for some time at 100° and allowed to cool, became semi-solid from the formation of crystals. These were drained from acetic acid and recrystallised from hot water, when white needles, melting at 187° without effervescence, were obtained.

On analysis—

I.	0.4347 gram gave 1.0056 gram CO ₂ and 0.1288 gram H ₂ O.
II.	0.3667 „ 0.8489 „ 0.1091 „
III.	0.3521 „ 0.8131 „ 0.1016 „

corresponding to—

	I.	II.	III.	Theory. C ₁₀ H ₆ O ₄ .
C.....	63.09	63.13	62.97	63.15
H.....	3.29	3.30	3.21	3.16

The substance treated with dilute ammonia dissolved, and the solution gave a white precipitate with silver nitrate, of which on analysis—

0.6045 gram gave 0.2211 gram Ag,	
corresponding to 36.57.	Theory for C ₁₀ H ₅ O ₄ Ag.... 36.36.

The *barium salt* was obtained as a white precipitate on adding barium chloride to the same solution.

0.7117 gram dried at 130° gave 0.3229 gram BaSO ₄ .	
= 26.67 per cent. Ba.	Theory (C ₁₀ H ₅ O ₄) ₂ Ba .. 26.60.

This acid is therefore a monobasic acid of the composition

and may be called coumarincarboxylic acid. It is not decomposed by boiling with water, or on melting, but on heating it in a distilling flask above its melting point it evolves carbon dioxide, and at 290° a substance distils over and solidifies in the receiver. When recrystallised, this melts at 67° , and its solution in sodium hydrate gives the characteristic reactions of coumarin with metallic salts. The thermometer then rises rapidly above the boiling point of mercury, and a small quantity of the unchanged coumarincarboxylic acid distils over. An attempt to produce a bibasic hydroxy-acid corresponding to coumaric acid, by heating coumarincarboxylic acid with sodium ethylate, according to Fittig and Ebert's method (*Annalen*, **226**, 351), led to no result.

I am at present occupied with the production of benzalmalonic acid containing some negative element, such as chlorine, in the ortho-position, and hope soon to have the honour of laying my results before the Society.