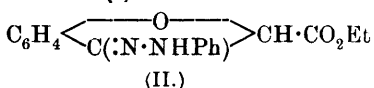
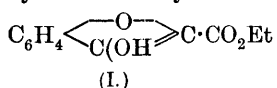


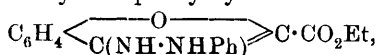
CXCIX.—*Coumaranone Derivatives. Part II. The Constitution of Ethyl Coumaranonecarboxylate.*

By RICHARD WILLIAM MERRIMAN.

SEVERAL distinct observations indicate that ethyl coumaranonecarboxylate normally exists in the enolic form (I) :



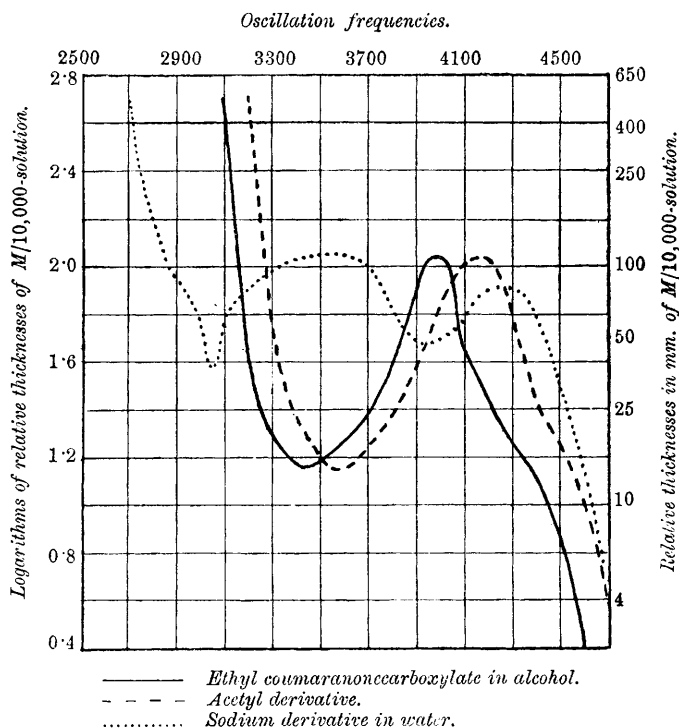
(a) Out of fifty attempts to prepare the phenylhydrazone (II), described in Part I. (T., 1911, **99**, 911), by the interaction of an alcoholic solution of the ester and a solution of phenylhydrazine in 50 per cent. acetic acid, only two were successful. In all the other cases, when air was excluded an isomeric substance with entirely different properties was formed. The phenylhydrazone melts at 126°, and undergoes normal hydrolysis with alkalis and acids, and its behaviour towards light is similar to that of benzaldehydephenylhydrazone. The isomeric substance melts at 142°, is not acted on by light, and is entirely stable towards all kinds of hydrolytic agents. It is probably the phenylhydrazino-derivative,



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produced from the enolic form of ethyl coumaranonecarboxylate. (b) All attempts to prepare the oxime of ethyl coumaranonecarboxylate were unsuccessful. (c) The ester is strongly acidic. On titrating its dilute alcoholic solution with *N*/10-sodium hydroxide, using phenolphthalein as indicator, exactly one equivalent of the alkali was required for neutralisation. (d) It reacts towards magnesium methiodide entirely in the enolic form. (e) Further evidence for the enolic constitution of ethyl coumaranonecarb-

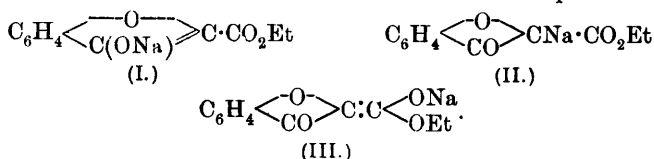
FIG. 1.



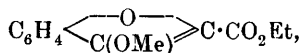
oxylate was obtained by comparing its absorption curve with that of its acetate. The curves are drawn in Fig. 1. The curve of the ester shows a deep band in the ultraviolet with its head at  $1/\lambda$  3440. The absorption curve of the acetyl derivative is parallel to the former curve throughout its length, with a slight shift towards the more refrangible end of the spectrum, the head of the band being at  $1/\lambda$  3560. The constitutions of the ester and its acetyl derivative are evidently identical, so that, assuming the ordinary formula for

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acetyl compounds, the ester exists in the enolic form. Three different constitutions for the sodium derivative are possible:

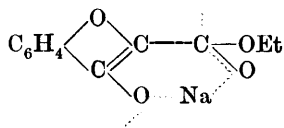


Formula (II) would not account for the intense and characteristic colour of the ferric derivative. Formula (I) receives support from the work of Auwers (*Annalen*, 1912, **393**, 338). By the action of methyl sulphate and aqueous alkali at 0° on ethyl coumaranonecarboxylate, this author obtained the *O*-methyl ether,



its formation being attributed to the action of the ions of the methyl sulphate on the ions of the sodium derivative of the strongly acidic ester.

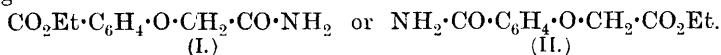
The absorption curve of the sodium derivative, also given in Fig. 1, is entirely different from the other two curves. The solution used was made by dissolving the ester in the exact quantity of dilute aqueous sodium hydroxide required for neutralisation. The general absorption for the large thicknesses of solution is moved towards the visible spectrum in the usual manner. The band present in the absorption curves of the ester and of its acetyl derivative becomes narrower and less persistent, whilst its head is shifted to  $1/\lambda$  3050. A new band of small persistency, with its head at  $1/\lambda$  3930, also appears. A similar difference in the absorption spectra of an acetyl and a sodium derivative has been observed by Hantzsch (*Annalen*, 1912, **393**, 286) in the case of the 2-alkylindandiones. The stable sodium salt of ethyl coumaranonecarboxylate is probably considerably ionised, so that its constitution may be expressed according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the following formula:



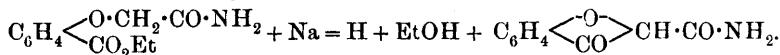
Other coumaranone derivatives react in the enolic form. For instance, Feuerstein and Brass (*Ber.*, 1904, **37**, 817) found that dihydroxycoumaranone,  $\text{C}_6\text{H}_2(\text{OH})_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}(\text{OH}) \end{array} \text{CH}$ , did not form an oxime or a phenylhydrazine.

Attempts to prepare the amide,  $\text{C}_6\text{H}_4\langle\text{O}\rangle\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , by the action of alcoholic ammonia on ethyl coumaranonecarboxylate, always resulted in the formation of the ammonium salt of the ester, as was to be expected from the stability of the ester towards alkalis. The stability of ethyl coumaranonecarboxylate towards boiling alkalis is probably due to the salt formation, as Auwers (*loc. cit.*) found that the *O*- and *C*-alkyl derivatives were readily hydrolysed.

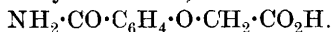
The monoamide of ethyl *o*-carboxyphenoxyacetate, previously described (Part I., T., 1911, **99**, 912), must have one of the following formulæ:



If formula (I) is correct, the monoamide should react with metallic sodium in benzene solution in the same way as ethyl *o*-carboxyphenoxyacetate, with the formation of the amide of coumaranonecarboxylic acid:



On isolating the product from the sodium salt, however, it was found to be a new amic acid with the composition  $\text{C}_9\text{H}_9\text{O}_4\text{N}$ . Therefore the constitution of the monoamide of ethyl *o*-carboxyphenoxyacetate probably corresponds with formula (II), so that the amic acid (*o*-carbamylphenoxyacetic acid) has the formula:



Both the original monoamide and the amic acid gave, on hydrolysis, *o*-carboxyphenoxyacetic acid, which was first prepared by Rössing (*Ber.*, 1884, **17**, 2995). The formation of the amic acid from its ester is interesting, and the method might be capable of general application. The absorption curves of the amic acid and of its ester are given in Fig. 2. They are nearly parallel to each other throughout, and the head of the band is at  $1/\lambda$  3440 in each case. A comparison of these curves with that of ethyl coumaranonecarboxylate, given in the same figure, is not without interest. The three curves are as nearly as possible parallel with each other; the head of each band is at  $1/\lambda$  3440; the three bands are of exactly the same persistence. It seems that the band might be due to the same centre of vibration in each case, the intensity being much increased in the case of ethyl coumaranonecarboxylate owing to the formation of a carbonyl group in place of a carboxyl group. The equal persistence of the three bands is certainly curious, and points to the fact that the persistence of selective absorption bands is not without physical significance (compare Dawson, this vol., p. 1311).

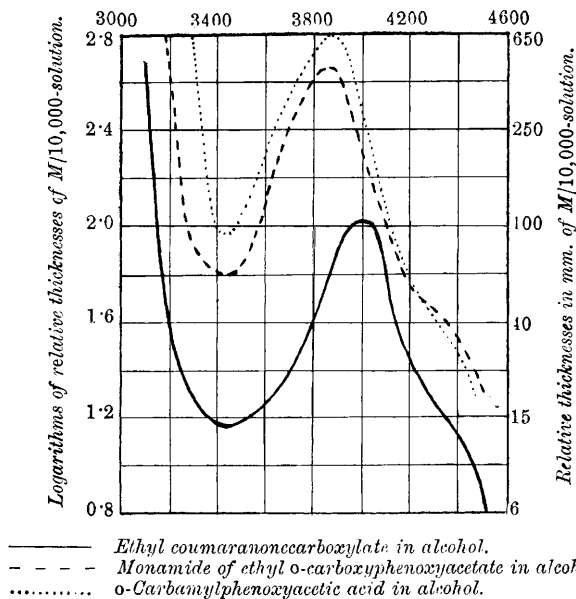
## EXPERIMENTAL.

*Ethyl Phenylhydrazinocoumaranonecarboxylate,*

This substance was obtained during most of the attempts to prepare the phenylhydrazone of ethyl coumaranonecarboxylate.

Phenylhydrazine (1 mol.) dissolved in 50 per cent. acetic acid was mixed with an alcoholic solution of ethyl coumaranonecarboxylate (1 mol.) contained in a tightly-stoppered flask filled with

FIG. 2.

*Oscillation frequencies.*

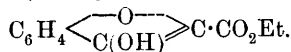
hydrogen. In the course of two days yellow crystals separated, which, when recrystallised by dissolving in acetone and adding light petroleum, were obtained in yellow leaflets melting at  $142^\circ$ .

This substance is insoluble in alkalis or acids, and is not hydrolysed by them even on boiling for a long time:

0.1086 gave 0.2744  $\text{CO}_2$  and 0.0525  $\text{H}_2\text{O}$ .  $\text{C}=68.9$ ;  $\text{H}=5.4$ .

0.2057 „ 16.8 c.c.  $\text{N}_2$  (moist) at  $14^\circ$  and 763 mm.  $\text{N}=9.7$ .

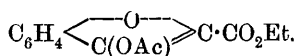
$\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_2$  requires  $\text{C}=68.9$ ;  $\text{H}=5.4$ ;  $\text{N}=9.5$  per cent.

*Titration of Ethyl Coumaranonecarboxylate,*

The strongly acidic character of this ester was proved by titrating its solution in dilute alcohol with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0.2376 gram neutralised 11.6 c.c. *N*/10-NaOH. Equivalent weight = 205.

$\text{C}_{11}\text{H}_{10}\text{O}_4$  requires equivalent weight = 206.

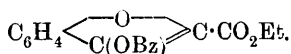
*Ethyl Acetocoumaranonecarboxylate,*

Ethyl coumaranonecarboxylate (3 grams) was heated with acetic anhydride (10 grams) and fused sodium acetate (3 grams) for two hours. The hot mixture was poured into hot alcohol to remove the excess of acetic anhydride. The acetyl compound, after crystallisation from dilute alcohol, separated, like the parent ester, as an emulsion, which changed into long, white needles, melting at 77°:

0.1937 gave 0.4463  $\text{CO}_2$  and 0.0861  $\text{H}_2\text{O}$ . C = 62.9; H = 4.95.

$\text{C}_{13}\text{H}_{12}\text{O}_5$  requires C = 63.0; H = 4.85 per cent.

This acetyl derivative is stable towards cold alkalis.

*Ethyl Benzocoumaranonecarboxylate,*

Ethyl coumaranonecarboxylate was boiled for three hours with sodium benzoate and benzoyl chloride, the product being worked up in the usual way. *Ethyl benzocoumaranonecarboxylate* crystallises from light petroleum in glistening, white needles, melting at 123°, and is readily soluble in the usual organic solvents:

0.1011 gave 0.2580  $\text{CO}_2$  and 0.0410  $\text{H}_2\text{O}$ . C = 69.5; H = 4.5.

$\text{C}_{18}\text{H}_{14}\text{O}_5$  requires C = 69.7; H = 4.5 per cent.

*Action of Alcoholic Ammonia on Ethyl Coumaranonecarboxylate.*

The ester was not attacked when boiled with alcoholic ammonia for fifteen minutes, but the *ammonium* derivative was prepared by passing ammonia into an ethereal solution of the ester. It was analysed by boiling with sodium hydroxide and collecting the ammonia in standard acid:

0.1740 neutralised 7.5 c.c. *N*/10- $\text{H}_2\text{SO}_4$ .  $\text{NH}_4 = 7.8$ .

$\text{C}_{11}\text{H}_9\text{O}_4(\text{NH}_4)$  requires  $\text{NH}_4 = 8.1$  per cent.

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The ammonium derivative slowly loses ammonia in the presence of water or on remaining for a long time in moist air.

*Action of Grignard's Reagent on Ethyl Coumaranonecarboxylate.*

The Grignard reagent, prepared by dissolving 2.4 grams of magnesium in 8 grams of methyl iodide mixed with dry ether, was slowly added to ethyl coumaranonecarboxylate (10.3 grams), dissolved in dry ether. A vigorous reaction took place, and a solid separated. The cooled mixture was treated with dilute sulphuric acid, the ethereal layer separated, and repeatedly extracted with sodium hydroxide. The alkaline extracts, when acidified, gave 10 grams of unchanged ester, showing that the ester had reacted entirely in the enolic form.

*Action of Sodium on the Monoamide of Ethyl o-Carboxyphenoxyacetate.*

The monoamide (8 grams) was dissolved in dry benzene, and the solution added to sodium (0.84 gram) suspended in dry benzene, when a vigorous reaction took place, with evolution of gas. The reaction was completed by boiling under reflux for three hours, only a trace of ammonia being evolved during the experiment.

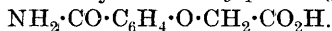
The solid sodium compound which separated was dissolved in much water, the solution separated from benzene, and acidified with hydrochloric acid, when a white solid was precipitated. This was only moderately soluble in the usual organic solvents; when crystallised from alcohol it formed white needles melting at 221°. For analysis it was dried at 100°:

0.1110 gave 0.2262 CO<sub>2</sub> and 0.0454 H<sub>2</sub>O. C=55.6; H=4.6.

0.1835 „ 11.3 c.c. N<sub>2</sub> (moist) at 17° and 763 mm. N=7.3.

C<sub>9</sub>H<sub>9</sub>O<sub>4</sub>N requires C=55.5; H=4.6; N=7.2 per cent.

The substance is evidently *o-carbamylphenoxyacetic acid*,



Its alcoholic solution was titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0.2100 required 10.8 c.c. *N*/10-NaOH. Equivalent weight=194.4.

C<sub>9</sub>H<sub>9</sub>O<sub>4</sub>N requires equivalent weight=195.

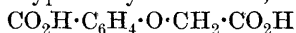
*o-Carbamylphenoxyacetic acid* crystallises from acetone in very light masses having the appearance of cotton-wool, and from glacial acetic acid in clusters of small needles. It is soluble in aqueous alkalis, and is precipitated unchanged on acidifying the solutions. On adding phenylhydrazine to an alcoholic solution of the acid, heat was evolved, and a salt separated in colourless needles, which melted at 177°. This salt was decomposed by cold sodium hydro-

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oxide solution with the liberation of phenylhydrazine. On acidifying the alkaline solution, the original acid, melting at  $221^{\circ}$ , was deposited.

*Hydrolysis of o-Carbamylphenoxyacetic Acid.*

The acid was dissolved in 10 per cent. sodium hydroxide, and the solution heated on the water-bath until ammonia ceased to be evolved. On acidifying the product, white needles slowly separated. The substance melted at  $192^{\circ}$ , and its other properties corresponded with those of *o*-carboxyphenoxyacetic acid,



(Rössing, *Ber.*, 1884, **17**, 2995).

The same acid was formed by hydrolysing the monoamide of ethyl *o*-carboxyphenoxyacetate. The specimen prepared in this way also melted at  $192^{\circ}$ , and a mixture of the two melted at the same temperature

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