

XXIX.—*On some new Bromine Derivatives of Coumarin.*

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

IN my endeavours to get a clearer insight into the constitution of coumarin, I have lately been studying the action of bromine upon it, and although my results do not at present throw much fresh light upon the subject, still I have thought it as well to bring a short account of my experiments before the Society.

Bromine combines readily with coumarin, without evolution of hydrobromic acid in appreciable quantities; the product, however, varies according to the manner in which the experiment is performed. I have not as yet investigated all the products of this reaction, but have obtained the following results.

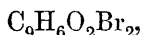
On adding about fourteen parts of powdered coumarin to sixteen parts of bromine, disulphide of carbon being previously added to both bodies, the resulting solution when allowed to evaporate spontaneously leaves a crystalline residue.

This can be freed from secondary products, first, by washing with a little cold alcohol, and then crystallising from the same solvent. This latter operation should be conducted as quickly as possible, and with the use of but little heat.

The analysis of specimens of the product dried in vacuo gave the following numbers:—

I.	·7873	grm. of substance gave
	·9685	„ AgBr.
II.	·3910	„ substance gave
	·5051	„ CO ₂ , and
	·0759	„ H ₂ O.
III.	·3645	„ substance gave
	·4784	„ CO ₂ , and
	·0701	„ H ₂ O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show—

	Theory.		Experiment.		
			I.	II.	III.
C ₉	108	35·29	—	35·23	35·79
H ₆	6	1·96	—	2·16	2·14
O ₂	32	10·46	—	—	—
Br ₂	160	52·29	52·35	—	—
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	306	100·00			

This body is, therefore, formed by the direct union of bromine and coumarin. I propose to call it *dibromide of coumarin*.

Dibromide of coumarin fuses at about 100° C., with partial decomposition, and when further heated gives off bromine vapour. It is easily soluble in alcohol, and crystallises from it in transparent oblique prisms. When boiled with alcohol it quickly decomposes; the same thing takes place when its alcoholic solution is exposed to light, the bromine apparently acting upon the solvent, leaving coumarin in solution. It is also soluble in ether and disulphide of carbon.

When a mixture of bromine and coumarin, in the proportion of two parts of the former to one of the latter, both being previously mixed with disulphide of carbon, is heated in a sealed tube to about 140° C. for a few hours, most of the bromine disappears, but not all, the liquid being still of an orange-red colour. On cooling, the resulting product crystallises, generally showing two kinds of crystals, and on opening the tube large quantities of hydrobromic acid are given off.

The contents of the tube, after the disulphide of carbon has been allowed to evaporate, dissolve in boiling alcohol, and the solution on cooling deposits a quantity of crystals. These, when purified by three or four recrystallisations from alcohol, gave the following numbers on analysis. The substance was dried at 100° C.—

I.	·3356	gram. of substance gave
	·4178	„ AgBr.
II.	·2855	„ substance gave
	·3751	„ CO ₂ , and
	·0371	„ H ₂ O.

III.	·3152	gram. of substance gave
	·4093	„ CO ₂ and
	·0409	„ H ₂ O.
IV.	·3292	„ substance gave
	·4319	„ CO ₂ and
	·0445	„ H ₂ O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

	Theory.		Experiment.			
			I.	II.	III.	IV.
C ₉ ..	108	35·53	—	35·83	35·41	35·78
H ₄ ..	4	1·31	—	1·44	1·44	1·50
Br ₂ ..	160	52·63	52·97	—	—	—
O ₂ ..	32	10·53	—	—	—	—
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	304	100·00				

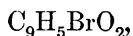
This substance is, therefore, coumarin with two of hydrogen replaced by bromine, and may be called *dibromocoumarin*.

Dibromocoumarin fuses at 174° C., and distils nearly unchanged. It dissolves easily in boiling alcohol, and crystallises from this solvent in small needles.

The mother-liquors from dibromocoumarin contain more or less of a second substance, which may be obtained by evaporating off part of the spirit, and recrystallising the product, which separates out several times. This body is not easily obtained in quantity. On analysis it gave the following results:—

I.	·1905	gram. of substance gave
	·1579	„ AgBr.
II.	·2548	„ substance gave
	·4506	„ Co ₂ and
	·0504	„ H ₂ O.
III.	·2271	„ substance gave
	·3975	„ Co ₂ and
	·0471	„ H ₂ O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

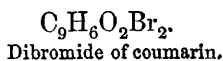
	Theory.		Experiment.		
			I.	II.	III.
C ₉	108	48·00	—	48·23	47·74
H ₅	5	2·22	—	2·20	2·30
Br	80	35·56	35·27	—	—
O ₂	32	14·22	—	—	—
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	225	100·00			

This body is therefore coumarin with one of hydrogen replaced by bromine, or *bromocoumarin*.

Bromocoumarin melts at 110° C. It is more easily soluble in spirit than dibromocoumarin. It crystallises in transparent prisms, which are often beautifully curved.

When heated with potassic hydrate, both bromo- and dibromocoumarin dissolve, forming a yellowish solution, and on boiling for a short time, crystalline products are obtained. These consist of the potassium salts of new acids, which may perhaps be brominated coumaric acids. These are at present under examination.

It may be worth remarking that the dibromide of coumarin possesses the same composition as mellilotic anhydride with two of hydrogen replaced by bromine, thus:—



I do not think, however, that they will be found to be identical.
