which may be ascribed to the mass action of the halogen. It should be possible to judge the relative importance of these two factors by a study of derivatives of fluorescein in which bromine is replaced by chlorine or iodine.

The positions of the absorption bands for the neutral and acid solutions of fluorescein and its halogenated derivatives are listed in Table I.

TABLE I

FREQUENCY NUMBERS OF BANDS FOR NEUTRAL AND ACID SOLUTIONS OF HALOGENATED FLUORESCEINS

Fluoresceins				Fluoresceins			
Fluorescein	Dibromo-	Tetrabromo- (eosin)	Tetrachloro-	Fluorescein	Dibromo-	Tetrabromo- (eosin)	Tetrachloro-
Absolute Ethanol as Solvent				Concd. Sulfuric Acid as Solvent			
	1905						
2075	2005	1968	2013	2317	2250	2201	2228
2198	2106	2100	2141	3039	2868	2759	2922
2319	2227	2215	2239	3215	2987	3032	3111
2700	2548	2548	3060	3451	3307		3377
3460		3107	3224		3605		
3533	3472	3371	3441	3906	3755	3605	3868
3604	3580	3492	3610	4005	3857	3738	3957
			3949		4287	4115	

Summary

1. The effects of halogen substitution on the absorption spectra and chemical properties of fluorescein are discussed. Absorption curves and data are presented for dibromo-, tetrabromo- and tetrachlorofluorescein.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALBERTA]

ETHYL- AND HEXYLFLUORESCEIN. THEIR DIBROMO AND MONOMERCURY DERIVATIVES

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A great number of mercury derivatives of phenolphthalein and related compounds has been prepared. Many of these have been reported in the patent literature.[1] White[2] has prepared mercury derivatives of phenolphthalein, *o*-cresolphthalein, fluorescein, dibromofluorescein and phenolsulfonephthalein, containing from one to four atoms of the metal. Very recently Harden[3] has reported salicylsulfonephthalein, its tetrabromo and monomercury derivatives. The latter compound shows marked germicidal power.

[1] Pauly and Traumann, German Patent 201,903 (1909); Fahlberg, List and Co., German Patent, 308,335 (1918); White, U. S. Patent 1,535,003 (1925); 1,549,942 (1925).

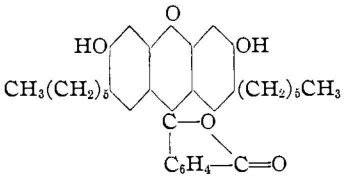
[2] White, THIS JOURNAL, **42**, 2355 (1920).

[3] Harden, *ibid.*, **49**, 3139 (1927).

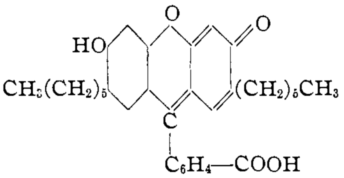
In connection with a study of the mercuration of the alkylresorcinols,[4] the authors have prepared the monomercury and dibromo derivatives of ethyl- and hexylfluorescein. At present work is proceeding on a study of the bactericidal value of the mercury derivatives.

The ethyl- and hexylfluoresceins were prepared by the action of phthalic anhydride on ethyl- and hexylresorcinol,[5] respectively. This was done in a manner similar to Gatterman's[6] preparation of fluorescein, with the exception that the cold melt was extracted with a solution of sodium hydroxide and the dye then precipitated by the addition of hydrochloric acid or acetic acid.

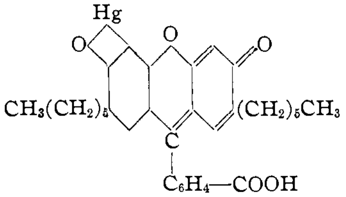
In the preparation of the ethyl- and hexylfluorescein, some observations have been made which are similar to the observations made by Orndorff and Hemmer[7] in connection with fluorescein. When an alkaline solution of ethyl- or hexylfluorescein, as obtained in the original preparation, was treated with acetic acid in the cold, the yellow dye was precipitated. However, when a boiling alkaline solution of either phthalein was treated with concentrated hydrochloric acid, the dye in each case was precipitated as a dark brown amorphous mass. In accordance with the views of Orndorff and Hemmer, a suggested structure for the yellow modification is Formula I, and for the brown modification, Formula II.



I. Yellow hexylfluorescein (lactoid)



II. Brown hexylfluorescein (*p*-quinoid)



III. Anhydromonomercurihexylfluorescein

The dibromo compounds were prepared in the usual way by the addition of a slight excess over the required two moles of bromine to a suspension or solution of one mole of the phthalein in glacial acetic acid. The mono-

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[4] Sandin, THIS JOURNAL, **51**, 479 (1929).

[5] The ethylresorcinol used was prepared according to Johnson and Hodge, *ibid.*, **35**, 1014 (1913). The hexylresorcinol was prepared according to Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

[6] Gatterman, "The Practical Methods of Organic Chemistry," Macmillan Co., New York, **1921**, p. 357.

[7] Orndorff and Hemmer, THIS JOURNAL, **49**, 1272 (1927).

mercury compounds were formed by the addition of a solution of one mole of mercuric acetate in hot alcohol and acetic acid to one mole of the dye dissolved in hot alcohol. A suggested structure for the monomercury compounds is shown by Formula III.

The results of the experiments are collected in the following tables.

TABLE I

PROPERTIES AND ANALYSES OF VARIOUS MODIFICATIONS OF ETHYL- AND HEXYLFLUORESCEIN

Color of powder	Obtained by	Analyses, found, % C		H	
	Ethylfluorescein, $C_{24}H_{20}O_5$. Calcd.: C, 74.22; H, 5.15				
Dark brown	Adding HCl to hot NaOH soln.	73.98		5.02	
Yellow	Adding AcOH to cold NaOH soln.	73.93		5.21	
Dark brown	Boiling with HCl	73.94	73.85	5.03	5.07
Brown[a]	Slow evap. of alc. soln.	73.93		5.02	
	Hexylfluorescein, $C_{32}H_{36}O_5$. Calcd.: C, 76.80; H, 7.20				
Brown	HCl to boiling NaOH soln.	76.41		7.12	
Yellow	AcOH to cold NaOH soln.	76.73		7.15	

[a] On pulverizing; crystals with greenish-purple surface color.

TABLE II

PROPERTIES AND ANALYSES OF THE DIBROMO DERIVATIVES OF ETHYL- AND HEXYLFLUORESCEIN

Dibromo-( )-fluorescein	Formula	Color of powder	M. p., °C.	Br, Analyses, % Calcd.	Found	
Ethyl	$C_{24}H_{18}O_5Br_2$	Reddish-brown	Does not melt at 300°	29.27	29.03	29.10
Hexyl	$C_{32}H_{34}O_5Br_2$	Reddish-brown	180–181°	24.29	24.04	24.09

TABLE III

PROPERTIES AND ANALYSES OF THE MONOMERCURY DERIVATIVES OF ETHYL- AND HEXYLFLUORESCEIN

Anhydromonomercuri-( )-fluorescein	Formula	Color of powder	Calcd., % Hg	Calcd., % Acetic acid	Found, % Hg			Found, % Acetic acid
Ethyl	$C_{24}H_{18}O_5Hg$	Red	34.19	0	33.60	34.09	33.90	0
Hexyl	$C_{32}H_{34}O_5Hg$	Red-brown	28.71	0	28.27	28.44	28.34	0

Summary

1. The preparation of ethyl- and hexylfluorescein and their dibromo and monomercury derivatives has been described.

2. Ethyl- and hexylfluorescein each exists in two isomeric forms, a yellow and a brown. The formula of the two isomeric ethylfluoresceins is $C_{24}H_{20}O_5$, and of the two isomeric hexylfluoresceins is $C_{32}H_{36}O_5$. The yellow form is prepared by adding acetic acid to a cold alkaline solution of the dye, and according to Orndorff and Hemmer is given the lactoid structure. The brown modification is obtained by adding hydrochloric acid to a boiling alkaline solution of the dye. It is given the *p*-quinoid structure.

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