filter heated until the carbon is burned off. A blue residue shows the presence of aluminum.

The modification introduced in the test by the authors is that the precipitate produced in the reprecipitation is filtered through a filter paper with a few asbestos fibers at the cone of the filter. Instead of the filter paper, the asbestos fibers which hold the precipitate are burned, hooked in a platinum wire. Blue beads over the asbestos indicate the presence of aluminum.

In this proposed modification, several advantages are obtained. The presence of 0.2 mg. of aluminum is easily detected. The presence of sodium salt with the precipitate does not interfere in the test; thus, complete removal of sodium salt by washing is not necessary. Washing is necessary when a filter is used, for sodium salt will fuse with the filter and lessen the delicacy of the test. The modified test is satisfactory even when the aluminum precipitate is not washed at all. The ignition to produce the blue cobalt aluminate takes a shorter time. A longer ignition does not interfere with the result, as in the case of filter paper, which drops to pieces if ignited too long.

Contribution from the
College of Agriculture
University of the Philippines
Philippine Islands

Elias H. Pañganiban
Florencio A. Soliven

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[Contribution from the Chemical Laboratory, Presidency College]

6-ALDEHYDO-COUMARIN AND DYES DERIVED FROM IT

By Rajendranath Sen and Dukhaharan Chakravarty

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Richard Stoermer and Ed. Oetker[1] first obtained 6-aldehydo-coumarin (melting at 189°) as an intermediate product in the synthesis of coumarin-6-carboxylic acid from 6-acetoxymethylcoumarin, but it was never prepared in quantity and no work appears to have been done with it. In the present case *p*-coumaric aldehyde or 6-aldehydo-coumarin has been prepared in quantity by the application of Reimer and Tiemann's reaction on coumarin (the yield being about 3.5 g. of the aldehyde from 16 g. of coumarin).

The application of Reimer and Tiemann's reaction on coumarin may be expected to lead to the formation of two aldehydes, the aldehyde group occupying the ortho position in one (I) and para position in the other (II) with reference to the lactonic oxygen atom; but it has been possible to isolate only one aldehyde in the pure condition, which is found to be identical with 6-aldehydo-coumarin, melting at 187–189°.

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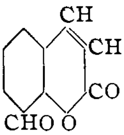
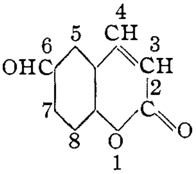
[1] Stoermer and Oetker, *Ber.*, **37**, 192–203 (1904).



I



II

In every preparation it has been found that in addition to the *p*-coumaric aldehyde, which is rather sparingly soluble in alcohol, another by-product is obtained instead of the expected *o*-aldehyde or 8-aldehydo-coumarin, in fairly large yield, which is readily soluble in alcohol but which, on account of its ready transformation into the resinous state, is extremely difficult to purify. After going through a long and laborious process of purification, which necessarily involves much loss of the substance, a small quantity of a solid product has been isolated from this resinous by-product, which softens at 174° with decomposition. It is soluble in alkalies, forming a deep red solution, and the lactonic ring in the substance seems to be rather unstable, as it is broken up when kept for some time in contact with cold sodium bicarbonate solution. It does not respond to the ordinary tests of an aldehyde. It appears to be very probable that the *o*-aldehyde is actually formed and subsequently undergoes some sort of transformation in the presence of the caustic alkali. This substance is still under investigation.

The introduction of an aldehyde group into the benzene nucleus of coumarin seems to affect the stability of the lactonic ring as is shown by the comparatively ready solubility of 6-aldehydo-coumarin in caustic alkalies. The aldehyde also differs from coumarin in the following respects. While coumarin forms a greenish-yellow solution in caustic alkalies, the aldehyde gives a slightly reddish solution. The solubility in water and organic solvents in general is also diminished.

The only derivatives of *p*-coumaric aldehyde prepared by Richard Stoermer and Ed. Oetker[1] were an oxime and a semicarbazone. The aldehyde, prepared by the present method, gives the identical oxime (melting at 223°) and semicarbazone (sintering at 305°) and also a hydrazone with phenylhydrazine (melting at 207°), which was not prepared before. The aldehyde also undergoes benzoin condensation in the usual manner, giving a product which may be called coumaroin. The aldehyde readily responds to Claisen's reaction and dicoumaral[2] acetone ($C_9H_5O_2$-$CH{=}CHCOCH{=}CHC_9H_5O_2$) and coumaral acetophenone ($C_9H_5O_2CH{=}CHCOC_6H_5$) have been obtained by its condensation with acetone and acetophenone, respectively. Dicoumaral acetone is yellow and coumaral acetophenone is colorless; this is probably due to the presence of a larger number of ethylene linkages and C=O groups in the former.

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[2] The radical [$C_9H_5O_2CH{=}$] of 6-aldehydo-coumarin may be called "Coumaral."

Several interesting azo-methine dyes have been obtained by the condensation of 6-aldehydo-coumarin with (1) mono-amines such as *p*-toluidine, β-naphthylamine, *p*-nitraniline and amino-azobenzene, (2) diamines such as benzidine, *o*-, *m*- and *p*-phenylenediamines and (3) such dyes as rosaniline, chrysoidine and safranine, which contain free amino groups. These azo-methine dyes are usually hydrolyzed by warming with dilute acids.

One molecule of a mono-amine ordinarily reacts with one molecule of the aldehyde. One molecule of *o*-, *m*- or *p*-phenylenediamine reacts with two molecules of the aldehyde; but with benzidine and chrysoidine only one molecule of aldehyde condenses, the presence of the free amino groups being proved by diazotization. With rosaniline and safranine the reaction goes normally, one molecule of the former reacting with three molecules of the aldehyde and one molecule of the latter reacting with two molecules of the aldehyde. It is interesting to note that the replacement of the NH_2 groups in *p*-nitraniline, amino-azobenzene and the dyes rosaniline and safranine markedly diminishes the intensity of color, owing perhaps to the elimination of the auxochromic effect of the NH_2 groups. It is curious that although coumaral-chrysoidine, $C_6H_5N{=}NC_6H_3(NH_2){-}N{=}CHC_9H_5O_2$, contains chromophoric groups, $N{=}N$, $CH{=}N$ and the auxochromic group NH_2, yet it produces a much yellower shade on silk and wool than chrysoidine.

By the condensation of the aldehyde with dimethylaniline in the presence of zinc chloride or hydrochloric acid as the condensing agent, tetramethyldiaminodiphenylcoumarylmethane, $C_9H_5O_2CH(C_6H_4N(CH_3)_2)_2$, has been obtained. This leuco-base, on oxidation with lead dioxide in the usual manner, gives a fine deep bluish-green dye (coumaral green), which is of much interest on account of the presence of the lactone ring associated with the basic group $N(CH_3)_2$, the compound being soluble both in acids and alkalies.

Pyronine dyes have been obtained by condensing the aldehyde with diethyl-*m*-aminophenol and also with such hydroxy compounds as resorcinol, hydroquinone and gallic acid in the presence of sulfuric acid (sp. gr. 1.84) at a temperature of 120–130° in the manner described by Sen and Sinha.[3] α- and β-naphthols give colorless, phthalein-like compounds under similar conditions.

It has been noticed, however, in the course of these condensations, that the $C{=}O$ group in the lactone ring of coumarin, which was observed to react in the presence of zinc chloride by Sri Krishna[4] and also by Sen and Guha Sarkar,[5] reacts with the hydroxy compounds in the presence of concd.

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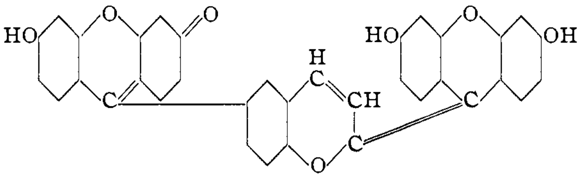
[3] Sen and Sinha, THIS JOURNAL, **45**, 2984 (1923).

[4] Krishna, *J. Chem. Soc.*, **119**, 1420 (1921).

[5] Sen and Sarkar, THIS JOURNAL, **47**, 1079 (1925).

sulfuric acid also in many cases at much lower temperature than when zinc chloride is used as the condensing agent.

Thus resorcinol-coumarein[4] is found to be readily obtained by condensing coumarin with resorcinol in the presence of sulfuric acid (sp. gr. 1.84) at a temperature of 120–130° on the oil-bath. Hence in the condensation of 6-aldehydo-coumarin with the aromatic hydroxy compounds like resorcinol under similar conditions the $C{=}O$ group in the lactone ring as well as the aldehyde group reacts. Therefore the compound with resorcinol is given the structure of tetraresorcinol-coumarein (III).

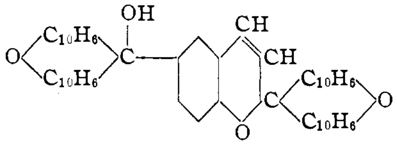


III

Silk and wool are dyed bright orange shades by the potassium salt of this compound.

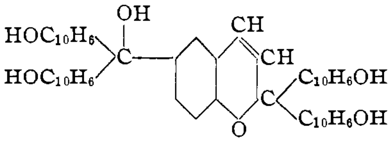
The condensation products with hydroquinone and resorcinol can be very readily brominated in an alcoholic medium; the former giving a tetrabromo and the latter a hexabromo derivative; silk and wool are dyed dark brown shades by the former and beautiful dark red shades by the latter.

α- and β-naphthol condense with the aldehyde, giving rise to phthalein-like bodies. The β-naphthol compound is completely insoluble in alkali and the analytical result corresponds to the following formula (tetranaphthol-coumarein): (IV)



IV

but in the case of α-naphthol, two different compounds are obtained;[5] one (IV) insoluble in caustic alkali (ortho condensation) and the other (V) soluble in caustic alkalies with a deep green color (para condensation)



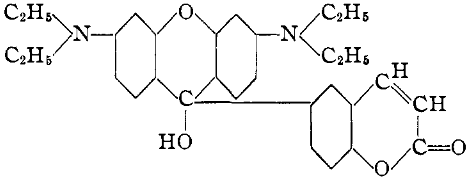
V

but the second product has not been obtained in a sufficiently pure condition for analysis.

The condensation product of 6-aldehydo-coumarin and gallic acid is, as expected, tetragallic acid coumarein, which is a polygenetic dye, wool being dyed a dark brown shade on chrome mordant, a reddish-brown shade on aluminum mordant and a dark olive shade on iron mordant.

Qualitative experiments show that the compound with *o*-cresotinic acid also exhibits polygenetic character, wool being dyed a pink shade on aluminum mordant and a light blue shade on chromium mordant.

The condensation product of the aldehyde with diethyl-*m*-aminophenol, which may be called coumaral-rhodamine (VI) is a fine bluish-violet dye, soluble both in acids and alkalies. It is interesting to note that unlike the other hydroxy compounds already mentioned, only 2 moles of diethyl-*m*-aminophenol condense with 1 mole of the aldehyde; the C=O group of coumarin itself failing to react with diethyl-*m*-aminophenol under these conditions.



VI

A comparative study of the colors of coumaral green and coumaral rhodamine and the analogous compounds from benzaldehyde is interesting. Thus while malachite green and benzaldehyde-rhodamine (rosamine) produce green and bluish-red shades, respectively, on silk and wool, the analogous compounds with 6-aldehydo-coumarin produce beautiful bluish-green and bluish-violet shades. The latter compounds differ from the former in the presence of an additional lactonic ring, which is perhaps responsible for this marked change in color.

Experimental

Preparation of 6-Aldehydo-Coumarin.—Sixteen grams of coumarin is dissolved with 27 g. of caustic soda in 40 cc. of water and heated on the boiling water-bath with a reflux condenser for eight to nine hours with frequent addition of chloroform (20 cc. in all), keeping the temperature at 80° initially for three hours. The deep red solution is heated on the water-bath to drive away the excess of chloroform and when cooled is filtered and acidified with concentrated hydrochloric acid. A liquid separates out which solidifies on keeping.

The precipitate is filtered off, washed with water and extracted with a mixture of alcohol and ether (8:1) after slight warming. The insoluble white residue is filtered off rapidly at the pump and washed with alcohol. This is the 6-aldehydo-coumarin. It is finally crystallized from 80% alcohol; yield about 3.5 g.; a white, needle-shaped crystalline solid, slightly soluble in cold water and in cold alcohol, moderately soluble in cold benzene and practically insoluble in ether, readily soluble in chloroform, acetone and glacial acetic acid, m. p. 187–189°.

The alcoholic solution, which remains after the separation of the aldehyde, is evaporated to drive away the alcohol and ether, when a pasty semi-solid substance remains. This is then washed with benzene and ether in order to remove coumarin and a certain portion of the tarry matter produced. The residue is again dissolved in alcohol and gradually poured with constant stirring into water acidified with hydrochloric acid. After repeated treatment in this manner (at least ten or twelve times), a product is isolated which is a pale yellow solid and decomposes at 174–175°, the decomposed product melting at 205–207°. It is sparingly soluble in cold water, ether and benzene, fairly soluble in chloroform and readily soluble in alcohol, acetone and glacial acetic acid.

Anal. Calcd. for $C_{10}H_6O_3$: C, 68.96; H, 3.44. Found: C, 68.8, 68.7; H, 3.9, 3.8.

Coumaral-phenylhydrazone.—The hydrazone is prepared in glacial acetic acid medium; yellow, microcrystalline substance, moderately soluble in alcohol, readily soluble in acetone and glacial acetic acid; m. p. 205–207°.

Anal. Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.6. Found: N, 10.67, 10.8.

Coumaroin.—Coumaroin is prepared in the usual manner like benzoin and crystallized from water; microcrystalline, reddish-yellow substance, moderately soluble in water and alcohol. It reduces Fehling's solution and softens at 178–180°.

Anal. Calcd. for $C_{20}H_{12}O_6$: C, 68.96; H, 3.44. Found: C, 69.1, 68.8; H, 3.7, 3.9.

Dicoumaral-acetone.—Two grams of 6-aldehydo-coumarin is dissolved in 2 g. of caustic soda in 10 cc. of water and warmed with 5 cc. of acetone on the water-bath at 70–80° for two to three hours with a reflux condenser. The solution is then cooled and filtered and the filtrate acidified with dilute acetic acid. The yellow precipitate thus obtained is thoroughly washed with water and crystallized from absolute alcohol, giving yellow, needle-shaped crystals, insoluble in water and moderately soluble in alcohol and acetone; m. p. 159°.

Anal. Calcd. for $C_{23}H_{16}O_5$: C, 74.6; H, 3.78. Found: C, 74.2, 74.3; H, 4.1, 4.

Coumaral-acetophenone.—The method of preparation is the same as with acetone; colorless micro crystals from absolute alcohol, insoluble in water and fairly soluble in alcohol; m. p. above 250°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.26; H, 4.34. Found: C, 77.9, 77.7; H, 4.6, 4.7.

Dyes Derived from 6-Aldehydo-coumarin. Azo-methine Dyes

Coumaral-*p*-toluidine.—The preparation of coumaral-toluidine is typical: 2 g. of 6-aldehydo-coumarin (dissolved in boiling alcohol) and 2 g. of *p*-toluidine (dissolved in glacial acetic acid) are boiled on the water-bath with a reflux condenser for four to five hours. The alcohol is then evaporated on the water-bath, when needle-shaped crystals of the compound separate. These are filtered off, washed with water acidified with hydrochloric acid and finally crystallized from a mixture of absolute alcohol and glacial acetic acid (6:1); yellow, needle-shaped crystals, insoluble in water, sparingly soluble in alcohol, readily soluble in glacial acetic acid; m. p. 145–147°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: N, 5.3. Found: N, 5.45, 5.3.

Other azo-methine dyes prepared are listed in Table I.

Triphenylmethane Dyes

Tetramethyldiaminodiphenylcoumarylmethane.—Two grams of 6-aldehydo-coumarin and 10 cc. of dimethylaniline are heated on the boiling water-bath for thirty hours with an air condenser with frequent additions of concentrated hydrochloric acid (10 cc. in all). The solution is then made alkaline with caustic soda, distilled in steam, filtered and acidified with hydrochloric acid. The green solution is filtered and ammonia is added to the filtrate, when a greenish-white precipitate is obtained. The precipitate is filtered off, washed with water, and finally crystallized from acetone; yield, 90% of

TABLE IA

AZO-METHINE DYES FROM 6-ALDEHYDO-COUMARIN

No.	Coumaral-	Formula	Prepared in alcohol +	M. p., °C.	Analyses, N, % Calcd.	Found	
1	-β-Naphthylamine	$C_{20}H_{13}O_2N$	HCl[a]	173	4.7	4.99	4.8
2	-*p*-Nitraniline	$C_{16}H_{10}O_4N_2$	HCl[a]	<250	9.5	9.99	9.9
3	-Amino-azobenzene	$C_{22}H_{15}O_2N_3$	HCl[a]	169	11.9	12.05	12.2
4	Di-()-*p*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HAc	<250	6.66	6.5	6.6
5	Di-()-*m*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HAc	<250	6.66	6.45	6.5
6	Di-()-*o*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HCl	<250	6.66	7.1	7.0
7	-Benzidine	$C_{22}H_{16}O_2N_2$	HCl	<250	8.2	7.8	7.7
8	Tri-()-rosaniline	$C_{50}H_{33}O_7N_3$	NaAc[b]	142	5.33	4.95	4.9
9	Di-()-safranine	$C_{40}H_{28}O_5N_4$	HCl	...	8.7	8.29	8.4
10	-Chrysoidine	$C_{22}H_{16}O_2N_4$	HAc	210–212	15.2	15.68	15.6

[a] On water-bath.

[b] Rosaniline hydrochloride used.

TABLE IB

PROPERTIES OF AZO-METHINE DYES FROM 6-ALDEHYDO-COUMARIN

No.	Color	Crystal form	Cryst. solvent	Sol. in	Color on silk and wool
1	Pale yellow	Micro	Alc. + acetone (4:1)	...	...
2	Yellow	...	...	Alc.[a] (sp.)	...
3	Red-yellow	Needles	Alc. + HAc (4:1)	...	Yellow
4	Brown	...	...	...	Gray-yellow
5	Brown	Micro	Boiling alc.	...	Red-yellow
6	Yellow	...	...	Alc.[a]	...
7	Yellow	Needles	Boiling alc.	...	Pale yellow
8	Red-violet	Powder	...	$CHCl_3$	Pink
9	Red-violet	Needles	Boiling alc.	...	Bright pink
10	Orange	Powder	...	$CHCl_3$[a, b]	Yellow

[a] Insoluble in ether.

[b] Insoluble in benzene and carbon tetrachloride.

the theoretical; colorless, needle-shaped crystals, insoluble in water, sparingly soluble in alcohol, moderately soluble in acetone, soluble in hot caustic alkalies and also in acids; m. p. 220°.

Anal. Calcd. for $C_{26}H_{26}O_2N_2$: N, 7. Found: N, 7.2, 7.1.

Tetramethyldiaminodiphenylcoumarylcarbinol (Coumaral Green).—The leuco-base is oxidized with lead dioxide in the usual manner. The hydrochloride is a deep bluish-green substance, producing a bluish-green shade on silk, wool and tannined cotton.

Pyronine Dyes

Tetraresorcinol-coumarein (III).—The preparation of this compound is typical. A mixture of 1 mole (2 g.) of dried 6-aldehydo-coumarin, 4 moles (5 g.) of dried resorcinol and 2 cc. of concentrated sulfuric acid (sp. gr. 1.84) is heated on an oil-bath for four to five hours at 120–130° with an air condenser. Copious evolution of sulfur dioxide takes place, as detected by its pungent odor and the development of a blue color on starch-iodate paper. The product is washed with water, dissolved in caustic soda solution and the original compound is precipitated with dilute hydrochloric acid. It is then dissolved in alcohol and the alcoholic solution is poured into water till a turbidity is produced. The solution is then filtered and the filtrate allowed to stand overnight with more water. The precipitate thus obtained is dried at 110° in an air oven. Pyronine dyes prepared, together with their derivatives, are listed in Table II.

TABLE IIA

PYRONINE DYES FROM COUMARIN

Prepared by condensing one mole of coumarin with four moles of combining compound in the presence of sulfuric acid (sp. gr. 1.84) at 120–130°

No.	-Coumarin	Formula	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	Tetraresorcinol-(III)	$C_{34}H_{20}O_7$	80[a]	75.55	75.5 75.44	3.7	3.9 3.93
2	Tripotassium salt	$C_{34}H_{17}O_7K_3$	..	K, calcd., 17.9		Found, 18.26	
3	Hexabromo deriv.	$C_{34}H_{14}O_7Br_6$	..	Br, calcd. 47.3		Found, 46.9	
4	Tetrahydroquinone	$C_{34}H_{22}O_8$	75	73.12	72.76 72.9	3.94	4.1 4.2
5	Tetrapotassium salt	$C_{34}H_{18}O_8K_4$	..	K, calcd., 22		Found, 22.5	
6	Tetrabromo deriv.	$C_{34}H_{18}O_8Br_4$	..	Br, calcd., 36.6		Found, 36.2	
7	Tetra-β-naphthol-(IV)	$C_{50}H_{30}O_4$	60	86.45	85.9	4.32	4.6
8	Tetra-α-naphthol-(IV)	$C_{50}H_{30}O_4$	40	86.45	86.1 86.3	4.32	4.4 4.2
9	Tetragallic acid-	$C_{38}H_{20}O_{19}$	70	58.46	58.3 58.34	2.56	2.8 2.7
10	Coumaral-rhodamine (VI)[b]	$C_{30}H_{32}O_4N_2$	75	N, calcd., 5.8.		Found, 5.7 5.4	

[a] Four to five hours.

[b] Prepared by same procedure from coumarin and two moles of diethyl-*m*-aminophenol.

TABLE IIB

PROPERTIES OF PYRONINE DYES

No.	Color of powder	Color on silk and wool	Remarks
1	Red	Bright orange	Red-green fluores, alk. or alc. solns. Softens, 225°
2	...	...	...
3	Deep red	Deep red	...
4	Red-violet	Chocolate	Sol. in alc. and acetone. Insol. ether and $CHCl_3$
5	...	...	...
6	Yellow	Dark brown	...
7	Almost none	...	Sol. alc., $CHCl_3$, C_6H_6. Insol. acetone, boiling caustic alk.
8	Almost none[a]	...	Sol. $CHCl_3$. Insol. ether, acetone, boiling caustic alk.
9	Black	Polygenetic on mordanted wool: chrome, dark brown; aluminum, red-brown; iron, dark olive	
10	Blue-violet[b]	Blue-violet[c]	Sol. $CHCl_3$. Insol. CCl_4, CS_2

[a] Micro-crystals from boiling alcohol.

[b] Purified by dissolving in acetic acid and precipitating with ammonia, finally recrystallizing from alcohol.

[c] Acetate used; softens at 140°, m. p. 155°.

Summary

1. 6-Aldehydo-coumarin or *p*-coumaric aldehyde, melting at 189°, has been prepared by the application of Reimer and Tiemann's reaction on coumarin; it gives a hydrazone, an oxime and a semicarbazone, responds to Claisen's reaction and undergoes benzoin condensation in the usual manner.
2. Interesting azo-methine dyes have been obtained by the condensation of 6-aldehydo-coumarin with (1) mono-amines such as *p*-toluidine, β-naphthylamine, *p*-nitraniline and amino-azobenzene; (2) diamines such as benzidine, *o*-, *m*- and *p*-phenylenediamines; (3) dyes such as rosaniline, safranine and chrysoidine which contain free NH_2 groups.
3. Beautiful triphenylmethane dyes have been obtained by condensing the aldehyde with dimethylaniline and *o*-cresotinic acid.
4. Pyronine dyes have been obtained by condensing the aldehyde with diethyl-*m*-aminophenol and also with such hydroxy compounds as resorcinol, hydroquinone and gallic acid in the presence of sulfuric acid. The $C{=}O$ group in the lactone ring as well as the aldehyde group reacts in these condensations except in the case of diethyl-*m*-aminophenol.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

EFFECTS OF LIGHT UPON NITRATE ASSIMILATION IN WHEAT[1]

BY W. E. TOTTINGHAM AND HENRY LOWSMA

RECEIVED FEBRUARY 2, 1928 PUBLISHED SEPTEMBER 5, 1928

In a previous article[1a] on temperature effects in the metabolism of wheat the senior writer stressed the need of determining the adequacy of spectral balance when the illumination is wholly from an artificial source. The present paper deals with the assimilation of nitrate by young wheat plants, as affected by differences in spectral distribution and total intensity of light. As grown in our climatic chambers under water cells, the Marquis variety of spring wheat, which we have employed solely, requires between 1200 and 2000 foot candles of illumination at about 18° in a twelve-hour day, from Mazda C electric lamps. This estimate is based upon the maximum yield of dry matter. It is not clear, however, that this is the most significant index of optimal illumination, as will appear in a test to be presented presently. In this case more nitrate was assimilated, but at the expense of tissue production, when the Mazda lamps were supplemented by the visible and long ultraviolet rays from a carbon arc.

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[1] Published with permission of the Director of the Wisconsin Agricultural Experiment Station.

[1a] W. E. Tottingham, *Plant Physiol.*, **1**, 307 (1926).