that only the unassociated lithium alkyls are catalytically active.

If values for m and K are known, the concentration of unassociated RLi present for particular total catalyst concentrations may be calculated.[11] The degree of association of n-butyllithium in benzene solution has been reported to be about 5–7.[10] By choosing a value of $m = 7$ and a value for K such that a critical concentration for association of about 0.02 M resulted, the solid curve drawn in Fig. 4 was calculated. The value for K which gave this close fit with the experimental data was 10.[11] Such a value for the equilibrium constant seems reasonable since it corresponds to $-\Delta F = 15$ kcal./mole which is about the value to be expected for the energy of such an association reaction. Although other values for m and K might give satisfactory agreement with the experimental data, the ones chosen are reasonable and demonstrate the plausibility of this treatment.

The fact that there is no break in the curve in Fig. 1 corresponding to the break observed in Fig. 4 indicates that even associated butyllithium initiates growing polymer chains, although it does not contribute to the rate of polymerization. This requires that the equilibrium (eq. 7) be established rapidly and involve the growing polymer chains, $Bu(M)_xLi$, as well as n-butyllithium. When the lithium alkyl is associated, it is assumed to be in a dormant state; but when it is unassociated it participates in the propagation reaction.

Although it is doubtful that n-butyllithium is ionized to an appreciable extent, the color developed during the polymerization is evidence for the formation of α-alkylbenzyl anions, which are probably present in the hydrocarbon solution as ion pairs. Since there is no apparent change in the dependence of color intensity on catalyst concentration at 0.020 M butyllithium in Fig. 3, association of $Bu(M)_xLi$ does not affect its absorption of light.

From the shape of the rate curves, Fig. 2, it is estimated that $k_p = 5k_i$. Although it might appear that a mechanism of the type proposed involving an initiation step that is slower than propagation would lead to a broad molecular weight distribution, the calculations of Gold[12] indicate that such is not the case. For the case where $k_p/k_i = 10$, the ratio of weight to number average molecular weights is never greater than 1.35 even at very low conversions. For degrees of polymerization of 50 and 500 the calculated ratios are 1.06 and 1.00, respectively.

It has been assumed that m and K are independent of the substituent R in the lithium alkyl. However, the fact that the rate of propagation deviates slightly from a first-order dependence on monomer at high catalyst concentrations (Fig. 2) may be an indication that this assumption is not entirely true. A slight decrease in the value of either m or K as R increases in size would result in the formation of more unassociated lithium alkyl and hence a faster rate. This could happen only for catalyst concentrations in excess of about 0.02 M since at lower concentrations all of the lithium alkyl is already unassociated.

The rate of polymerization is accelerated markedly by the addition of small quantities of ethers, tertiary amines and the like. Tetrahydrofuran is particularly effective in this respect. A later paper will discuss the effect of such substances on the rate of polymerization.

Acknowledgments.—The author is greatly indebted to Messrs. P. D. Wills, H. J. Paxton and P. E. Peters for assistance in the experimental work and to Dr. R. D. Lundberg for many helpful discussions.

(11) A. E. Alexander and P. Johnson, "Colloid Science," Vol. II, Oxford University Press, London, 1949, p. 672.

(12) L. Gold, *J. Chem. Phys.*, **28**, 91 (1958).

SOUTH CHARLESTON, WEST VIRGINIA

[CONTRIBUTION FROM THE GRADUATE DEPARTMENT OF APPLIED SCIENCE, UNIVERSITY OF CINCINNATI]

The Fluorescence of Some Coumarins[1]

BY CHARLES E. WHEELOCK[2]

RECEIVED FEBRUARY 10, 1958

In a study of the effect of constitution on the fluorescence of coumarins, the ultraviolet absorption, fluorescence intensity at various concentrations in alcohol, fluorescence spectra and stability of fluorescence intensity in alkaline solution have been determined. The effect of substituents on intensity of fluorescence and on position of the fluorescence band maximum was noted. Concentration quenching and ultraviolet absorption were found to be related. Structures hindering cleavage of the heterocyclic ring by alkaline solution stabilize fluorescence.

In earlier studies, the effect of substituents on the intensity of fluorescence of coumarins was studied by visual observation of solutions in sunlight.[3–5] As the fluorescence intensities of solutions vary irregularly with concentration,[6,7] comparison of coumarins at a single concentration is inadequate. Consequently, the behavior of selected coumarins in solutions of various concentrations as well as the wave lengths of their absorption and emission bands is of interest in further clarification of the effects of structure on the fluorescence of coumarins. As electron attracting groups in the 3-position and electron repelling groups in the 7-

(1) Taken from a thesis submitted by Charles E. Wheelock in partial fulfillment of the requirements for the D.Sc. degree, University of Cincinnati, 1947. This work was sponsored by the Procter and Gamble Co.

(2) The Phillips Petroleum Co., Bartlesville, Okla.

(3) S. Rangaswami and T. R. Seshadri, *Proc. Ind. Acad. Sci.*, **12A**, 375 (1940).

(4) S. Rangaswami, T. R. Seshadri and V. Venkateswarlu, *ibid.*, **13A**, 316 (1941).

(5) V. Balaiah, T. R. Seshadri and V. Venkateswarlu, *ibid.*, **14A**, 68 (1942).

(6) W. West, "Technique of Organic Chemistry," Arnold Weissberger, Ed., Interscience Publishers, Inc., New York 1, N. Y., Vol. I, p. 1439.

(7) Peter Pringsheim and Marcel Vogel, "Luminescence of Liquids and Solids," Interscience Publishers, New York 1, N. Y., 1943, p. 25.

TABLE I: FLUORESCENCE OF COUMARINS IN ALCOHOL (95%)

	Compound	Preparations: Ref.	Preparations: Purif., and m.p. (uncor.)	Fluorescence intensity: At 300 mg./100 ml.[27]	Fluorescence intensity: At max.[27]	Spec. fluor. intensity[28]	Ultraviolet absorption: At maxima λ (mμ)	Ultraviolet absorption: At maxima Spec. ext.	Ultraviolet absorption: Rel. abs. of energy[29]	Fluor. band maxima, Å.
I	4-Methylcoumarin	8	79.0–79.7[a]	0	0	0	270	62.5	11.4	3830
							310	37.7		
II	Coumarin	9		0	0	0	...	...	...	3515
III	5-Hydroxycoumarin	10	226.6–227.2[b]	0	0	0	299	74.5	21.2	...
							249	40.7		
IV	6-Nitrocoumarin	11	186.0–186.6[c]	0	0	0	260	122.8	10.7	...
V	6-Aminocoumarin	11	162.6–163.4[a]	4.5	No max.	...	240	152.0	8.9	...
							280	66.8		
							370	18.2		
VI	7-Hydroxycoumarin	12	229.3–229.8[d]	100.5	186.8 at 15 mg./100 ml.	124.5	325	89.2	23.7	4410
VII	7-Methoxycoumarin	13	116.4–117.2[e]	7.5	No max.	...	320	86.4	26.2	3850
VIII	4-Methyl-6-hydroxycoumarin	14	240.2–241.0[f]	5.6	6 at 18.8 mg./100 ml.	3.2	270	59.7	9.0	4270
							340	25.1		
IX	4-Methyl-6-methoxycoumarin	15	161.0–161.8[g]	6.0	7.2 at 140 mg./100 ml.	0.5	275	58.3	7.8	4180
							342	26.5		
X	4-Methyl-7-hydroxycoumarin	16	184.9–185.7[h]	100	No max.	...	325	89.7	24.9	4420
XI	4-Methyl-7-methoxycoumarin	15	157.4–158.0[i]	5.5	No max.	...	320	78.3	23.8	3920
XII	4-Methyl-7-diethylaminocoumarin		70.1–71.0[j]	109	122 at 9.4 mg./100 ml.	129.8	375	111.3	42.2	4560
							318	17.1		
							278	8.3		
							243	67.3		
XIII	3-Isopropyl-4-methyl-7-hydroxycoumarin	17	208.5–211.0[k]	35.8	50.3 at 75 mg./100 ml.	6.7	323	78.1	20.0	4460
XIV	3-Benzyl-4-methyl-7-hydroxycoumarin	17, 18	221.7–223.0[l]	81.7	99.2 at 84 mg./100 ml.	11.8	326	66.4	13.9	4480
XV	3-Acetyl-7-hydroxycoumarin	5	237.0–237.6[m]	3.3	10.1 at 0.6 mg./100 ml.	168.3	368	58.6	27.1	...
							284	15.7		
							250	25.4		
XVI	4-Methyl-5,7-dihydroxycoumarin	19	271.0–271.5[n]	5.9	7.5 at 9 mg./100 ml.	8.3	320	62.4	20.0	...
							250	27.8		
XVII	4-Methyl-6,7-dihydroxycoumarin	20	271.0–271.5[o]	39.5	No max.	...	348	64.7	22.1	...
							290	28.0		
XVIII	4-Methyl-7-hydroxycarbostyril	21, 22, 23	333.0–336.0[p]	126.8	151 at 80 mg./100 ml.	18.9	338	67.2	15.3	4120
							324	73.5		
							282	22.6		
							256	30.4		
XIX	4-Methyl-7-aminocarbostyril	23, 24	270.4–272.0[m,a]	126	No max.	...	...	...	...	4070
XX	Ethyl 7-hydroxycoumarin-3-carboxylate	25	171.9–172.3[b]	...	...	...	...	...	...	4540
XXI	3-Chloro-4-methyl-7-hydroxycoumarin	26	242.0–242.9[q]	80	101.3 at 18.8 mg./100 ml.	53.9	332	74.4	23.6	4580

[a] Recrystallization from water. [b] Recrystallization from dilute alcohol. [c] Recrystallization from benzene. [d] Recrystallization from alcohol with charcoaling. [e] Recrystallized twice from dilute alcohol and distilled 151–154° at 1 mm. [f] Recrystallized from dilute alcohol with charcoaling. [g] Fraction distilling at 174–184° at 1 mm. recrystallized from alcohol. [h] Recrystallized three times from alcohol with charcoaling. [i] Fraction distilling at 195–196° at 3 mm. recrystallized from alcohol. [j] Distilled 240–243° at 6.5 mm. [k] Recrystallized several times from alcohol. Precipitation from dilute NaOH with CO_2 and recrystallization from dilute alcohol raised m.p. to 223.8–225.0°. [l] Recrystallized from alcohol twice. Precipitation from dilute NaOH with powdered Dry Ice followed by two recrystallizations from alcohol with charcoaling raised m.p. to 226.3–227.0°. [m] Recrystallized from alcohol. [n] Recrystallized twice from acetic acid. Precipitated with CO_2 from dilute NaOH and recrystallized from acetic acid–water, m.p. 284–285° dec. [o] Precipitated from an aq. soln. of the borate with sulfuric acid. [p] Pptd. from dil. NaOH with Dry Ice and recryst. from dil. EtOH. [q] Recryst. five times from dilute alcohol with charcoaling.

position have been shown to enhance the fluorescence intensity of coumarins,[3-5] these are well represented in the series selected for study (Table I).

Fluorescence Spectra in Alcohol.—Coumarin (II, Table I), 4-methylcoumarin (I), 7-methoxycoumarin (VII) and 4-methyl-7-methoxycoumarin (XI) have fluorescence band maxima falling in the ultraviolet region. In addition, two weakly fluorescent coumarins, 4-methyl-6-hydroxycoumarin (VIII) and 4-methyl-6-methoxycoumarin (IX), have fluorescence band maxima just within the visible region of the spectrum. Thus previous studies of the effect of structure on the fluorescence of coumarins may have omitted significant compounds.

Comparison of coumarin (II), 7-hydroxycoumarin (VI) and 7-methoxycoumarin (VII) with 4-methylcoumarin (I), 4-methyl-7-hydroxycoumarin (X) and 4-methyl-7-methoxycoumarin (XI) shows that the 4-methyl group shifts the fluorescence band to longer wave lengths. Similarly, 7-hydroxycoumarin (VI), 7-methoxycoumarin (VII), 4-methyl-6-hydroxycoumarin (VIII), 4-methyl-6-methoxycoumarin (IX), 4-methyl-7-hydroxycoumarin (X), 4-methyl-7-methoxycoumarin (XI) and 4-methyl-7-diethylaminocoumarin (XII) compared with coumarin (II) or 4-methylcoumarin (I) show a 6-hydroxy-, 6-methoxy-, 7-hydroxy-, 7-methoxy- or 7-diethylamino-group to move the fluorescence band to longer wave lengths. Comparison of ethyl 7-hydroxycoumarin-3-carboxylate (XX) and 3-chloro-4-methyl-7-hydroxycoumarin (XXI) with 7-hydroxycoumarin (VI) and 4-methyl-7-hydroxycoumarin (X) shows that a 3-chloro- or a 3-carbethoxy- group shifts the fluorescence band to longer wave lengths. Apparently, electron repelling groups in the 4-, 6- or 7-position or electron attracting groups in the 3-position cause a shift of fluorescence band to longer wave lengths. When the substituent occupies the 7-position of 4-methylcoumarin, the shift of fluorescence band to longer wave lengths is greatest with the diethylamino group, less with the hydroxyl group and least with the methoxy group; this also applies to substituents in the 6-position as shown by 4-methyl-6-hydroxycoumarin (VIII) and 4-methyl-6-methoxycoumarin (IX). Both the 3-isopropyl (XIII) and the 3-benzyl group (XIV) have a small effect. The heterocyclic atom has some effect as the fluorescence band maximum occurs at a shorter wave length for 4-methyl-7-hydroxycarbostyril (XVIII) than for 4-methyl-7-hydroxycoumarin (X).

Fluorescence Intensity in Alcohol.—As shown in Fig. 1, solutions of coumarins behave differently on dilution. For example, with 4-methyl-7-hydroxycoumarin (X), the fluorescence intensity of the alcohol solution decreases as concentration decreases. Others, like 3-chloro-4-methyl-7-hydroxycoumarin (XXI), show a maximum at a relatively high concentration in contrast to 3-acetyl-7-hydroxycoumarin (XV), which has a maximum fluorescence intensity at a low concentration. Certain other coumarins retain approximately the same fluorescence intensity over a wide range of concentrations; examples are 4-methyl-7-diethylaminocoumarin (XII) and 4-methyl-6,7-dihydroxycoumarin (XVII). These varying concentration effects make quantitative comparisons difficult.

In general, the qualitative comparison of the gross effects of structure on the fluorescence intensity (Table I) supports earlier observations.[3-5] However, in contrast to the observation of Rangaswami and Seshadri,[3] comparison (Fig. 2) of 7-hydroxycoumarin (VI) and 7-methoxycoumarin (VII) with 4-methyl-7-hydroxycoumarin (X) and 4-methyl-7-methoxycoumarin (XI) shows a 4-methyl substituent to diminish fluorescence intensity. As noted before [3-5] an electron repelling group in the 7-position of 4-methylcoumarin increases fluorescence intensity; the diethylamino group (XII) is most effective (Fig. 2), the hydroxyl group (X) is less effective and the methoxyl group (XI) is least effective of the three. In contrast, the unsubstituted 4-methylcoumarin (I) has no visible fluorescence. Since both 4-methyl-7-hydroxycarbostyril (XVIII, Fig. 3) and 4-methyl-7-aminocarbostyril (XIX) are more strongly fluorescent than 4-methyl-7-hydroxycoumarin (X), replacement of the heterocyclic oxygen by a less electronegative nitrogen increases the fluorescence intensity.

In Fig. 4 is plotted the absorbance *versus* concentration for several coumarins. These obey Beer's law.

The maxima of fluorescence intensities found with solutions of some coumarins (Fig. 1, Table I) are caused by concentration quenching and provide an interesting comparison. If the specific fluorescence intensity[28] is plotted against the relative absorption of energy[29] of the coumarin solution, the points for comparable pure derivatives of 4-methylcoumarin fit a curve (Fig. 5); a different curve for coumarin derivatives is indicated. These indicate a relationship between concentration quenching and energy absorption. Since 4-methyl-

(8) F. Peters and H. Simonis, *Ber.*, **41**, 831 (1908).

(9) Coumarin was used as received from Eastman Organic Chemicals.

(10) H. Shah and R. Shah, *J. Chem. Soc.*, **141**, 1832 (1938).

(11) G. Morgan and F. Micklethwait, *ibid.*, **85**, 1233 (1940).

(12) H. von Pechmann, *Ber.*, **17**, 932 (1884).

(13) B. H. Dey, R. H. R. Rao and T. R. Seshadri, *J. Ind. Chem. Soc.*, **11**, 743-749 (1934).

(14) W. Borsche, *Ber.*, **40**, 2732 (1907).

(15) G. Desai and C. Mavani, *Proc. Ind. Acad. Sci.*, **15A**, 1 (1942).

(16) H. von Pechmann and G. Duisberg, *Ber.*, **16**, 2122 (1883).

(17) C. E. Wheelock and W. B. Reynolds, U. S. Patent 2,673,186 (to the Procter and Gamble Co.), March 23, 1954.

(18) S. Jacobson and B. Ghosh, *J. Chem. Soc.*, **107**, 428 (1915).

(19) H. von Pechmann and J. Cohen, *Ber.*, **17**, 2189 (1884).

(20) E. B. Vliet, "Organic Syntheses," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 360.

(21) H. von Pechmann, *Ber.*, **32**, 3687 (1899).

(22) H. von Pechmann and O. Schwartz, *ibid.*, **32**, 3700 (1899).

(23) C. E. Wheelock, U. S. Patent 2,616,855 (to the Procter and Gamble Co.), Nov. 4, 1952.

(24) E. Besthorn and H. Byvanck, *Ber.*, **31**, 798 (1898).

(25) H. von Pechmann and E. Graeger, *ibid.*, **34**, 385 (1901).

(26) H. von Pechmann and E. Hanke, *ibid.*, **34**, 357 (1901).

(27) Fluorescence intensity = average reading for coumarin solution/average reading for a solution of 4-methyl-7-hydroxycoumarin (300 mg. per 100 ml. of alcohol) × 100%.

(28) Specific fluorescence intensity = fluorescence intensity at maximum/concentration at maximum (mg./100 ml.) × 10.

(29) Relative absorption of energy $\alpha \sum_{\nu} I(\nu)K(\nu)$, where ν = frequency of line, I = relative intensity of line, and k = specific extinction of the coumarin at that frequency.

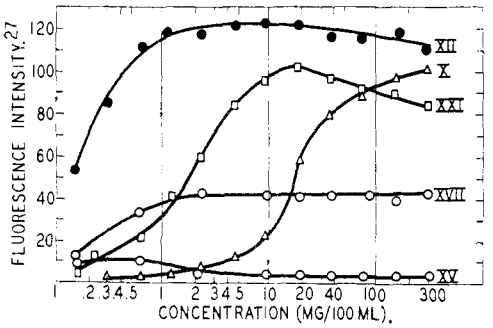

Fig. 1.—Effect of concentration on fluorescence intensity.

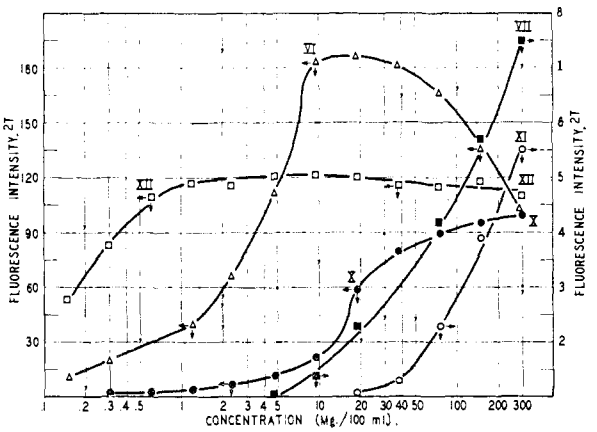

Fig. 2.—Effect of substituents on the fluorescence intensity of coumarins (scale shown by arrows).

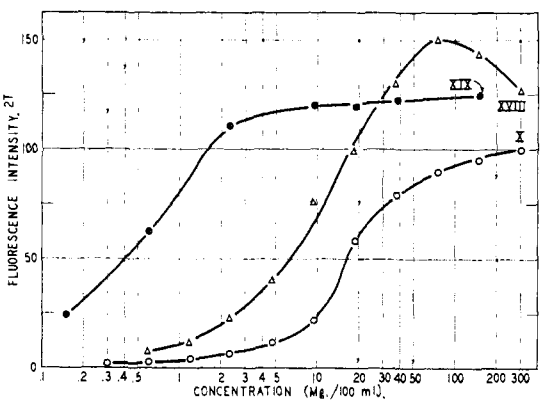

Fig. 3.—Fluorescence intensity of carbostyrils.

coumarins are different from coumarins in concentration quenching and a variety of 5-, 6- or 7-substituted 4-methylcoumarins, as well as a 4-methyl-7-hydroxycarbostyril (XVIII) fit the lower curve (Fig. 5), the 4-position or the Δ^3-double bond is significantly involved in the quenching process.

Stability of Fluorescence Intensity in Ethanolic Potassium Hydroxide.—The fluorescence intensities of 7-hydroxycoumarin (VI), 4-methyl-7-hydroxycoumarin (X) and 4-methyl-7-diethylamino (XII) diminish very rapidly in alkaline solution. As the fluorescence intensity of the 7-hydroxy compounds was initially enhanced, a degradation of the molecule is indicated. In alkaline solution, 7-hydroxycoumarin is degraded to *trans*-2,4-dihydroxycinnamic acid and resorcinol.[30] Similarly, 4-methyl-7-hydroxycoumarin has been degraded to resorcinol[16] and *trans*-2,4-dihydroxy-β-methylcinnamic acid.[31] Consequently, the behavior of 3-substituted coumarins and carbostyrils is of interest.

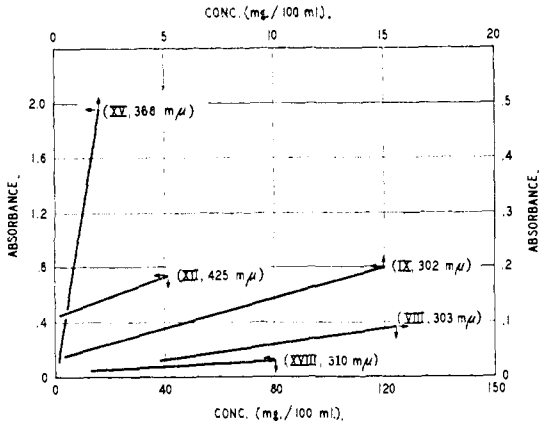

Fig. 4.—Effect of concentration on ultraviolet absorption of coumarins (scale shown by arrows).

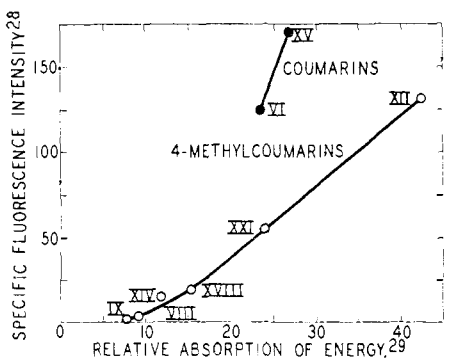

Fig. 5.—Effect of energy absorption on specific fluorescence intensity.

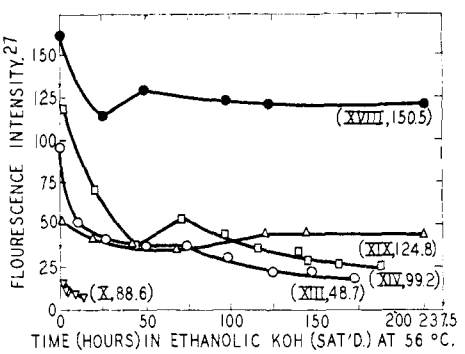

Fig. 6.—Stability of fluorescence in alkaline solution.

As shown by Fig. 6, the fluorescence of carbostyrils and coumarins substituted in the 3-position with an alkyl or an aralkyl radical is very persistent in alkaline solution. All the curves show a discontinuity between 25 and 125 hr. In view of the complexity of the degradation and concentration quenching, this behavior is credible. In the case of 4-methyl-7-aminocarbostyril (XIX) and 4-methyl-7-hydroxycarbostyril (XVIII), the fluores-

(30) F. Tiemann and C. Reimer, *Ber.*, **12**, 994 (1879).
(31) K. Fries and W. Bolk, *Ann.*, **379**, 105 (1910).

cence intensity declines at first but later remains constant at a high level; the values for fluorescence intensity in neutral alcohol are given in the parentheses. While the fluorescence intensity of 3-benzyl-4-methyl-7-hydroxycoumarin (XIV) and 3 - isopropyl - 4 - methyl - 7 - hydroxycoumarin (XIII) decreases both early and late during exposure to warm alkaline solution. The above behavior is consistent with the following speculation: in all four cases opening of the heterocyclic ring occurs much more slowly than for 4-methyl-7-hydroxycoumarin (X). The salts of *cis*-cinnamic acids derived from the carbostyrils are fluorescent and stabilized by hydrogen bonding with the amino group formerly part of the heterocyclic ring; hence fluorescence intensity remains constant at some high level. The salts of *cis*-cinnamic acids derived from the 3-substituted coumarins are fluorescent and gradually isomerize to the corresponding *trans*-cinnamic acid salts but much more slowly than the salt of *cis*-2,4-dihydroxy-β-methylcinnamic acid. Consequently the fluorescence intensity of the 3-substituted coumarin derivatives diminishes both early and late during exposure to alkaline solution.

Experimental Section

Fluorescence Spectra.—A Cenco Grating Spectrograph was used to obtain fluorescence spectra where possible. As reference the spectrum of the exciting lamp (Mazda B-H-4 lamp, 1 min. exposure) and that of a sodium vapor lamp (15 min. exposure) were taken on each film.

The fluorescence exposures were made as follows: a solution of the fluorescent compound (300 mg./100 ml.) in pure alcohol was placed against the widened slit of the spectrograph in a dark room. A Mazda B-H-4 lamp equipped with an aluminum reflector was placed as close as possible to the fluorescent solution without allowing direct or reflected light to enter the slit. Since the spectrograph is designed so that the wave length of a line is linearly related to its distance on the film from a point of reference, the maximum of the fluorescence band was easily estimated in each case by use of a scale constructed and used with the aid of the reference spectra.

Fluorescence Intensities.—The fluorescence intensities of solutions of coumarins were determined in a fluorometer of simple design.[32] A fresh solution (20 ml.) of 3-benzyl-4-methyl-7-hydroxycoumarin (300 mg. per 100 ml. of 95% ethanol) in a 4 cm. by 2 cm. by 5 cm. rectangular cell was used as standard and alternately measured in the instrument with a solution (20 ml.) of a coumarin in a cell of identical dimensions. The standard cell was sealed under nitrogen and four or more pairs of readings were averaged to minimize fluctuations in line voltage. The fluorescence intensity[27] was calculated from these readings. As an example of the stability of the standard samples, a cell which stood for 192 hr. changed from 81.7 to 79.8% in fluorescence intensity.[27] The reproducibility of the determinations is illustrated in Table II by data from two determinations, made three months apart, on 3-benzyl-4-methyl-7-hydroxycoumarin.

TABLE II

CONCENTRATION (MG./100 ML.)	FLUORESCENCE INTENSITY[27] No. 1	No. 2
150	96.3	94.5
75	98.9	97.5
18.8	75.3	77.9

Ultraviolet Absorptions.—The ultraviolet absorptions of coumarins in 95% ethanol were determined using a Beckman Spectrophotometer. Since a Mazda B-H-4 lamp was used in the fluorometer to excite fluorescence, its photographed ultraviolet spectrum and tables[33] were used to determine an approximation of the energy absorbed[29] by each coumarin.

Stability of Fluorescence in Alkaline Solution.—Alcohol which had been refluxed over potassium hydroxide was distilled under nitrogen into a flask containing aldehyde-free alcohol washed potassium hydroxide pellets.

A portion (100 ml.) of this solution, saturated at room temperature, was heated under nitrogen to a temperature of 56° in a bath. A portion (30 ml.) of fluorescent substance (300 mg. per 100 ml.) in aldehyde-free alcohol was added to the alkaline solution. The mixture was stirred with a nitrogen stream and a sample (9 ml.) removed, placed in a glass cell under nitrogen and diluted with aldehyde-free alcohol (10 ml.). All solutions were protected with nitrogen to prevent precipitation of potassium carbonate. The fluorescence intensity was obtained in the usual manner by alternation in the fluorometer of sample and standard. The change of fluorescence intensity of a fluorescent compound in alkaline solution could be followed. 4-Methyl-7-diethylaminocoumarin[34] has been mentioned in the patent literature. As no details of preparation were given, our preparation is reported. Distilled *m*-diethylaminophenol (20 g.), acetoacetic ester (22 g.), zinc chloride (10 g.) and absolute ethanol (40 g.) were refluxed for 30 hr. The reaction mixture was poured into water (400 ml.) containing a few drops of sulfuric acid. The separated oil crystallized after several days and was filtered, dried and vacuum distilled. The fraction boiling at 240–243° at 6.5 mm. was taken as product; it melted at 70.1–71.0°. The product could exist as a supercooled liquid for long periods.

Acknowledgment.—Gratitude is expressed to Mr. Reuben Lambert of the Procter and Gamble Co. and Mr. Robert Holmes for assistance, respectively, with ultraviolet absorption measurements and fluorescence determinations and to Dr. Wm. B. Reynolds, now of the Phillips Petroleum Company, for counsel.

(32) C. E. Wheelock, *J. Chem. Ed.*, **27**, 9 (1950).

(33) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. V, McGraw-Hill Book Co., New York, N. Y., p. 298.

(34) John Miglarese, U. S. Patent 2,334,348 (to the National Marking Machine Co.), November 16, 1944.

BARTLESVILLE, OKLAHOMA