[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Influence of Chemical Constitution upon Visible Color and other Tinctorial Properties in the Case of Certain Structurally Related Methoxychalcones and Methoxybenzalcoumaranones[1]

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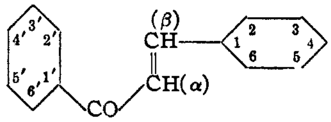
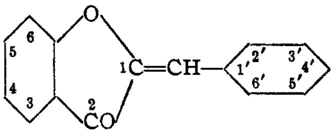
The purpose of this investigation was the comparison of certain amino derivatives containing the complex chromophore —COCH=CH— as part of a straight chain, with analogously constituted amines in which this same chromophore was present as part of a closed chain, in order to ascertain the effect of ring closure upon the visible color and other tinctorial properties of the compounds examined.

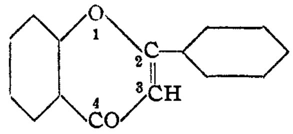
The most interesting substances for such a study were the chalcone (I), β-benzalcoumaranone (II) and flavone (III) types, since derivatives of (I) and (III) occur in nature as the coloring matters of plants and flowers, and some find use as commercial dyes.



Chalcone (I)



β-Benzalcoumaranone (1-benzal-2(1)-benzofuranone) (II)



Flavone (III)

Although the benzalcoumaranones (II), the oxygen analogs of the indogenides, do not occur in nature so far as we are aware, they often possess darker colors (orange to red) than the corresponding yellow flavones, as well as dyeing properties.

Because the naturally occurring flavones and chalcones are mostly hydroxyl derivatives, such derivatives have been studied extensively. Similar compounds, in which the auxochrome is an amino instead of a hydroxyl group, however, have been the subject of but few researches.[3]

The compounds discussed in the present paper are the 2',3',4'-trimethoxychalcones and the 5,6-dimethoxybenzalcoumaranones, the synthesis of which is recorded in our previous paper[4] in this field.

Acknowledgment.—To Professor Hal T. Beans of the Laboratories of Analytical Chemistry, of Columbia University, we are under obligations for much valued assistance and advice.

In Table I are given the colors of some of these pure compounds; while in Table II are recorded the colors of the solutions when certain of them are dissolved in concentrated sulfuric acid.

Absorption Spectra

Absorption spectra were photographed and curves plotted for the following compounds: (a) 2',3',4'-trimethoxy-3-aminochalcone (V), (b) 2',3',4'-trimethoxy-4-aminochalcone (V), (c) 5,6-dimethoxy-3'-aminobenzalcoumaranone (X), (d) 5,6-dimethoxy-4'-aminobenzalcoumaranone (X). The products used were first examined spectroscopically for metallic impurities, and traces of the following were detected: in (a)—Na and Sn, in (b)—Na, Ca and Mg, in (c)—Na, Ca and Sn, in (d)—Na and Sn. That these traces of impurities were inconsequential was proved by adding very much larger quantities of salts of these metals to the alcoholic solutions of the compounds being studied. No change in color or in other properties could be detected.

The experiments were carried out by dissolving the compound in a 95% ethyl alcohol which had been freed from aldehydes, etc., by careful treatment with silver nitrate, caustic alkali and distillation, appropriate concentrations being used for the different portions of the spectrum. The source of light was a condensed spark (15,000 volts) between tungsten electrodes. Eastman Panchromatic plates served for the visible region and process plates for the ultraviolet. A Hilger Sectorphotometer was employed, in conjunction with a Hilger E1 Spectrograph, which gave a dispersion of 20 in. from 2400 to 8000 Å.

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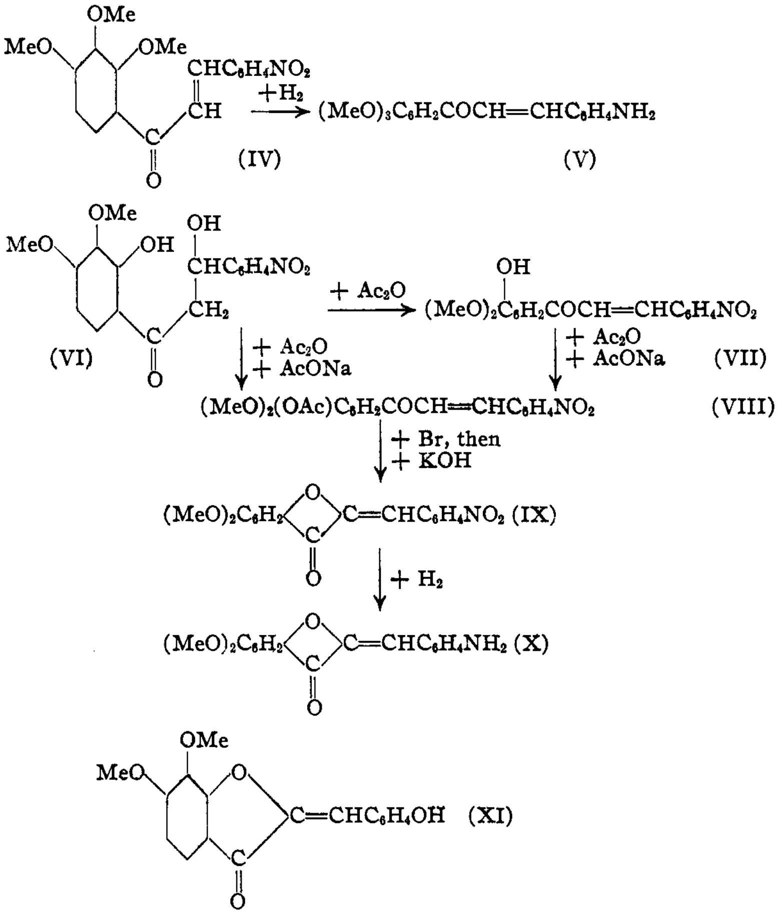
[1] Presented at the Washington Meeting of the American Chemical Society, March 27, 1933, before the Division of Dye Chemistry. Based in part upon the Dissertation submitted by Donald Price, 1929, in partial fulfilment of the requirements for the Ph.D. degree at Columbia University, and to which the reader is referred for further details.

[2] Du Pont Fellow at Columbia University, 1928–1929.

[3] (a) Rupe and Porai-Koschitz, *Z. Farb.-Ind.*, **5**, 318 (1906); (b) Bogert and Marcus, THIS JOURNAL, **41**, 83 (1919); (c) Pfeiffer, *J. prakt. Chem.*, [2] **109**, 50 (1925).

[4] Price and Bogert, THIS JOURNAL, **56**, 2442 (1934).

FLOW SHEET



In the curves shown in Fig. 1, the molecular absorption coefficient β_m is plotted against wave length, according to the formula $\beta_m = M/cd \log 1/T$.

An examination of these curves will show for the p-aminochalcone (b) considerable absorption in the ultraviolet, with a maximum at 3890 Å., and a curve which approaches fairly closely to that of the p-aminobenzalcoumaranone (d). The latter shows a distinct and well-defined band in the visible region at 4450 Å., which gradually tapers off into the ultraviolet, giving broad general absorption with a distinct minimum at about 2950 Å.

The m-aminochalcone (a) shows very little absorption in the visible region, but only one definite band in the ultraviolet, with a maximum at 3130 Å. The m-aminobenzalcoumaranone (c), like the corresponding chalcone, exhibits but slight absorption in the visible field, with well-defined maxima in the ultraviolet at 3090 and 2540 Å.

It will be observed that the absorption spectrum of the 3′-aminobenzalcoumaranone appears somewhat anomalous, in that the form of its curve differs from that of its 4′-isomer. This anomaly does not appear in the curves for the corresponding m- and p-aminochalcones. The determination of these spectra was therefore repeated with new apparatus and great care, but the results were the same.

TABLE I

COLOR OF SOLIDS

Formula	Name	Ortho	Meta	Para
IV	Nitrochalcone $[(MeO)_3]$	Pale yellow	Pale yellow	Yellow
V	Aminochalcone $[(MeO)_3]$	?	Bright green-yellow	Deep golden-yellow
VI	Nitrochalcone aldol $[(MeO)_2HO]$	Colorless	Very faint yellow	Very faint yellow
VII	Nitrochalcone $[(MeO)_2HO]$	Yellow	Yellow	Bright orange-red
VIII	Acetoxynitrochalcone $[(MeO)_2AcO]$	Pale yellow	Pale yellow	Pale yellow
IX	Nitrobenzalcoumaranone	Brilliant canary yellow	Pale yellow	Brilliant orange
X	Aminobenzalcoumaranone	Bright orange-red	Pale lemon-yellow	Bright orange-red
XI	Hydroxybenzalcoumaranone[5]	Bright orange-yellow	Pale yellow	Lemon-yellow

TABLE II

COLOR OF SOLUTION IN CONCENTRATED H_2SO_4

Formula	Name	Ortho	Meta	Para
IX	Nitrobenzalcoumaranone	Red	Pale orange-red	Red
X	Aminobenzalcoumaranone	Red	Yellow	Red
XI	Hydroxybenzalcoumaranone[5]	Red with yellow tinge	Orange-red	(Not in lit.)

If objection be raised to the comparison of a

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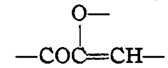
[5] Felix and Friedländer, *Monatsh.*, 31, 67 (1910).

trimethoxy chalcone with a dimethoxy coumaranone, it may be pointed out that the coumaranone is likewise a tri-ether, in that its oxygen bridge is also intrinsically an ether union. From this point of view, the effect of linking one of the phenolic oxygens of the benzene nucleus with a group of considerably greater molecular weight than methyl, ignoring other factors, might be expected to be bathochromic. It will be noted also that the —COCH=CH— chromophore of the chalcone (V) becomes



$\text{—CO}\overset{\text{O—}}{\overset{|}{\text{C}}}\text{=CH—}$

in the coumaranone (X).

An examination of the foregoing tables and curves brings out the following facts.

In so far as superficial observation of visible color is concerned, the hypsochromic influence of the saturation of the ethylenic linkage in the —COCH=CH— group of the nitrochalcones (VII) is evident in the change from the rich yellow (*o*- and *m*-) or bright orange-red (*p*-) chalcones (VII) to the colorless (*o*-) or pale yellowish aldols (VI). It is noteworthy that acetylation of the free phenolic hydroxyl of these same nitrochalcones (VII) is also of hypsochromic influence, the effect being greatest in the para series (VIII).

In the trimethoxynitrochalcones (IV), the replacement of the nitro by the amino groups (V) deepens the shade but slightly, whereas the change is more noticeable in comparing the corresponding (*o*- and *p*-) benzalcoumaranones (IX and X). So far as the hydroxyl derivatives[5] are concerned (XI), their colors more nearly resemble those of the nitro (IX) than of the amino (X) derivatives. In relative depth of shade of their *o*-, *m*- and *p*-isomers, the amino (X) and hydroxy (XI) coumaranones differ in some respects. In both groups, the meta isomers are lightest in color. In the hydroxy derivatives, the ortho isomer is much darker than the para; whereas in the amino derivatives, these two isomers are indistinguishable in color.

As to the influence of ring closure upon color, the *p*-nitrobenzalcoumaranone (IX) is deeper in color than the *p*-nitrochalcone (IV), while in the meta series cyclization seems to be without effect.

In the case of the amino derivatives (V and X), which were the ones of greatest interest, an examination of the absorption spectra curves discloses immediately that, in the para series, cyclization has been accompanied by a considerable deepening in color. For the chalcone, the absorption band lies mostly within the ultraviolet region, while for the coumaranone it has been shifted into the visible portion of the spectrum. What little difference there is in the meta series, however, appears to be in the opposite direction.

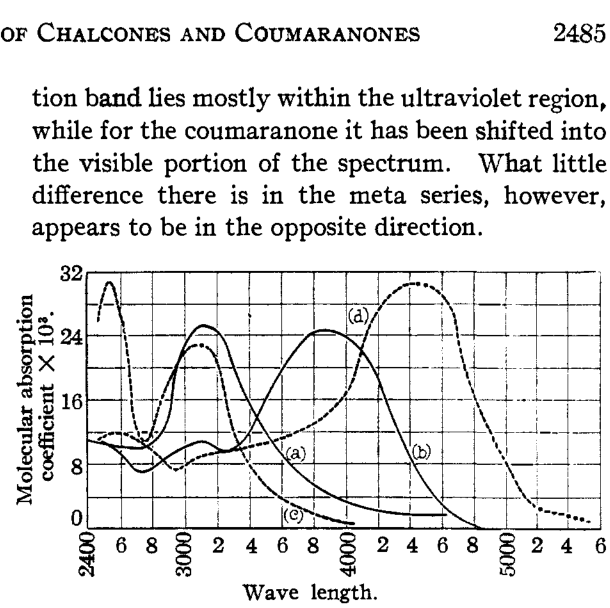


Fig. 1 —(a) 2′,3′,4′-Trimethoxy-3-aminochalcone, (b) 2′,3′,4′-trimethoxy-4-aminochalcone, (c) 5,6-dimethoxy-3′-aminobenzalcoumaranone, (d) 5,6-dimethoxy-4′-aminobenzalcoumaranone.

It is interesting to find that the influence of the position (*m*- or *p*-) of the amino group in the benzal nucleus upon the location of the absorption band, is in the same direction for the coumaranones as for the chalcones, and that the shift in the location of the band is much greater for the former than for the latter. This would suggest that the position of the auxochrome has a more potent influence upon color in the coumaranone than in the chalcone group and this finds some support in the literature, for Felix and Friedländer[5] have reported, in the case of the hydroxybenzalcoumaranones (XI), that the meta isomer is lighter in color than the ortho or para.

Von Kostanecki and Tambor,[6] who prepared all six possible isomeric monohydroxychalcones, carrying the OH on one or the other benzene nucleus, found that, when the OH was on the benzene nucleus attached to the β-carbon, the *m*-isomer was colorless, but the *o*- and *p*- yellow, the ortho having the deeper shade.

Zwayer and Von Kostanecki[7] regard the complex chromophore —COCH=CH— as composed of the two simple chromophores —CO— and —CH=CH— and hence classify as follows all compounds containing this complex: (1) both chromophores cyclostatic (hydroxyflavones); (2) both chromophores streptostatic (hydroxychalcones); (3) CO cyclostatic, C=C streptostatic (oxindogenides and benzalcoumaranones); (4)

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(6) Von Kostanecki and Tambor, *Ber.*, **32**, 1925 (1899).

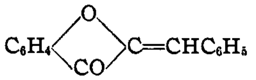
(7) Zwayer and Von Kostanecki, *ibid.*, **41**, 1335 (1908).

C=C cyclostatic, CO streptostatic (hydroxy-1-benzoylcoumaranones).

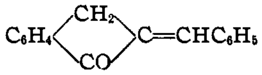
The hydroxyflavones (1) resemble the simple ketones. They are yellow and give colorless alkyl and acyl derivatives. Their solutions in concentrated sulfuric acid are yellow and often exhibit fluorescence. The hydroxychalcones are reddish-yellow and their alkyl and acyl derivatives usually yellow. In concentrated sulfuric acid, their solutions are red or reddish-yellow, without fluorescence.

These investigators[7] state, further, that hydroxy derivatives of Class (3), the class to which the benzalcoumaranones belong, resemble closely the hydroxy derivatives of Class (2). In support of this assertion, they cite the work of Klobski and Von Kostanecki,[8] who compared hydroxyoxindogenides of several types with hydroxychalcones and came to the conclusion that dyestuffs derived from the following chromogens

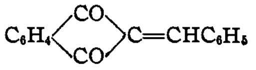
(XII) $C_6H_5COCH=CHC_6H_5$

(XIII) 

$C_6H_4\langle{}^{O}_{CO}\rangle C=CHC_6H_5$

(XIV)  and

$C_6H_4\langle{}^{CH_2}_{CO}\rangle C=CHC_6H_5$

(XV) 

$C_6H_4\langle{}^{CO}_{CO}\rangle C=CHC_6H_5$

owe their character to the streptostatic chromophore C=C, and that it makes no difference whether the CO is streptostatic or cyclostatic.

As we have already pointed out above, this conclusion of Klobski and Von Kostanecki is not in agreement with our results in the study of the amino derivatives of the chalcones and benzalcoumaranones, as is obvious from the absorption spectra curves. The position of the absorption band shows clearly that the color of the *p*-aminobenzalcoumaranone (X), in which the CO chromophore is cyclostatic, is much deeper than that of the *p*-aminochalcone (V), in which it is streptostatic.

Dye Tests

In attempting to carry out these tests in the ordinary manner, difficulties were encountered in the very slight solubility of our compounds in water and in the fact that the usual addenda (*e. g.*, soap solution, Glauber's salt, etc.) tended to precipitate them. Satisfactory results were finally secured by suspending the requisite weight of dye (1% the weight of the fabric) in water, heating the suspension on a salt-bath and adding sufficient acetic acid to bring all into solution. The fabric was then entered and the heating continued until no more dye was taken up.

The cotton dyeings, made on material mordanted with tannic acid and fixed with tartar emetic, were all disappointing, even when used in double strength (*i. e.*, 2% the weight of the fabric).

In the meta series, both aminochalcone (V) and aminobenzalcoumaranone (X) were devoid of tinctorial properties.

The results of the silk and wool dyeings were as follows: **2',3',4'-trimethoxy-4-aminochalcone** (V), greenish-yellow; **5,6-dimethoxy-2'-aminobenzalcoumaranone** (X), orange-yellow; **5,6-dimethoxy-4'-aminobenzalcoumaranone** (X), golden-yellow.

These limited experiments permit comparison only in the *p*-amino series, and there the results are in agreement with those of the absorption spectra, *viz.*, that the cyclic compound possesses a deeper color than its acyclic analog.

Summary

1. The influence of chemical constitution upon color and other tinctorial properties has been studied in the case of certain methoxylated nitro-, amino- and hydroxy-chalcones and benzalcoumaranones.

2. Absorption spectra have been photographed and curves plotted for the 2',3',4'-trimethoxy-3- and 4-aminochalcones and for the 5,6-dimethoxy-3'- and 4'-aminobenzalcoumaranones.

3. The curve for the dimethoxy-3'-aminobenzalcoumaranone appears to be abnormal in that its form differs somewhat from that of its 4'-amino isomer.

4. In comparing these spectra, cyclization in the *p*-aminobenzal series quite clearly has a bathochromic effect, whereas for the meta isomers no such effect is in evidence.

5. The position of the auxochrome amino group seems to have a much greater effect upon the color of the benzalcoumaranones than of the analogous chalcones.

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[8] Klobski and Von Kostanecki, *Ber.*, **31**, 725 (1898).