

# UNITED STATES PATENT OFFICE

2,647,133

## ALLYL DERIVATIVES OF COUMARIN

Robert Sidney Long, Bound Brook, N. J., and  
Carleton Alfred Sears, Stamford, Conn., as-  
signors to American Cyanamid Company, New  
York, N. Y., a corporation of Maine

No Drawing. Application June 10, 1952,  
Serial No. 292,726

5 Claims. (Cl. 260—343.2)

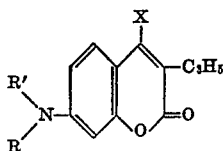
1

The present invention relates to a new class of compounds which are useful for the whitening of wool and silk and synthetic fibers, such as nylon and cellulose acetate.

These fibers generally have a slight yellow cast and, as the material becomes older, the yellow hue develops further and is not removed by laundering or dry cleaning. This same yellowing is characteristic of cellulosic fibers, and numerous products have been recommended recently for the optical bleaching of such materials. These optical bleaching agents function by absorbing ultraviolet light and re-emitting it in the form of visual light of such a wave length or hue that it neutralizes the yellow cast and gives a pure white fabric. The products which have been used for cellulosic fibers have been largely derivatives of diaminostilbenedisulfonic acid and benzidine sulfone disulfonic acid.

Such products are of little value for the whitening of wool, silk, and synthetic fibers, since they have little or no affinity for such fibers under neutral or weakly acidic conditions, such as prevail in application with detergents. There has been, therefore, a great need for products of modified structure which will have the desired property of absorbing ultraviolet light and converting it to visual light of the proper wave length and, in addition, the property of having affinity for the above-mentioned fibers under neutral or weakly acidic conditions. One product which has been recommended for this purpose is 4-methyl-7-diethylaminocoumarin. This compound has the desired effect when used in sufficient amounts, but tends to give the fiber a pink cast, which is not desirable. This is particularly true in the case of cellulose acetate.

The products of this invention are represented by the general formula shown below:



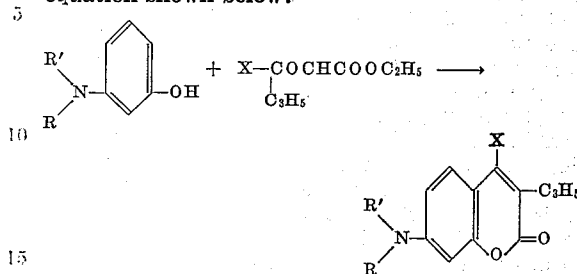
in which R, R' and X are lower alkyl radicals and C<sub>2</sub>H<sub>5</sub> is either a propen-1-yl or a propen-2-yl (allyl) group.

As indicated above, the products are characterized, in general, by a surprisingly increased fluorescence intensity and by the fact that they do not impart an undesirable pink hue to the fibers to which they are applied.

Compounds of this type may be prepared by

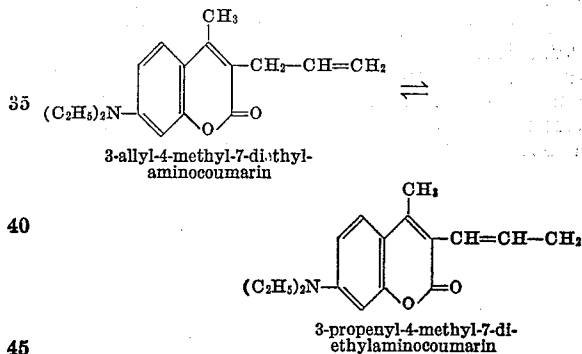
2

the condensation of a metadialkylaminophenol with an alpha-substituted beta-keto ester. This preparation may be represented by the general equation shown below:



Thus, it is apparent that variation of X groups will lead to a variation of the substituents in the 4-position of the coumarin nucleus. For example, ethyl  $\alpha$ -allyl-acetoacetate in which X is methyl will lead to a 3-propenyl-4-methylcoumarin. By varying X, the substituent in the 4-position can be changed. Thus, ethyl  $\alpha$ -allylvaleroacetate will produce a 3-propenyl-4-butylcoumarin.

We are aware of the possibility that the double bond in the allyl group may shift under the reaction conditions to conjugate with the double bonds in the coumarin nucleus. Such a rearrangement is illustrated below for the reaction product from ethyl  $\alpha$ -allyl-acetoacetate and metadiethylaminophenol:



Since either of these products might be expected from the reaction and the actual product is in fact probably a mixture, both products fall within our invention. We have therefore referred to the substituent C<sub>2</sub>H<sub>5</sub> as a propenyl group, by which is meant either of propen-2-yl (allyl) group or the propen-1-yl group.

The alkyl groups attached to the amino nitrogen atom may contain from one to 18 carbon atoms, but we have discovered that the higher

3

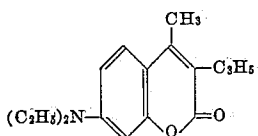
molecular weight alkyl groups diminish somewhat the fluorescent activity and therefore prefer starting material such that the total number of carbon atoms in the dialkylamino group does not exceed six. In the claims, those alkyl radicals containing not more than six carbon atoms are defined as "lower alkyl radicals." Useful starting materials are metadimethylaminophenol, metadiethylaminophenol, meta - (N - ethyl - N - methylamino) - phenol, and metadipropylaminophenol.

It is an advantage of the present invention that these varied condensations do not require special conditions but proceed smoothly under the influence of an acid catalyst, such as zinc chloride. This would have been quite impossible to predict, since it is generally believed that the condensation proceeds through the enol form of the beta-keto ester and since it is well known that the presence of an alpha substituent in a beta-keto ester inhibits this enolization.

The very striking degree of fluorescence and the desirable shade of fluorescence exhibited by these compounds when they are applied to fibers such as wool, silk, nylon, and cellulose acetate does not admit of complete explanation in the present state of the art, since theories of fluorescence are still somewhat incomplete. It was completely unpredictable that this particular combination of 3,4-disubstitution in the coumarin ring with a dialkylamino group present in the benzene ring should prove so strikingly effective. It is particularly noteworthy that even close chemical relatives which differ only in that they do not contain the substituent in the 3-position are appreciably weaker in their fluorescence.

The present invention is further illustrated by the following examples. Parts are by weight unless otherwise specified.

*Example*



A mixture of 41.5 parts of m-diethylaminophenol, 63.8 parts of ethyl  $\alpha$ -allylacetate, and 17 parts of anhydrous zinc chloride was heated overnight at 100-110° C. The product was then steam stripped, washed with dilute sodium hydroxide, taken up in dilute hydrochloric acid, and made alkaline with caustic. The product can be converted to its sulfate by dissolving in acetone and adding sulfuric acid. The sulfate so obtained melts at 192-194° C.

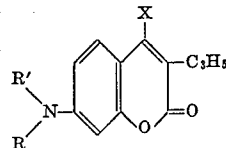
4

When applied to wool from an acid bath, this product shows about 40% greater fluorescence than the corresponding compound unsubstituted in the 3-position. It also has a strong whitening action on acetate, whereas 4-methyl-7-diethylaminocoumarin gives acetate fiber an undesirable pink hue.

Substitution of m-diethylaminophenol for m-diethylaminophenol gives the expected 3-propenyl - 4 - methyl - 7 - dimethylaminocoumarin. This compound has a similar strong whitening action on wool, silk, and acetate fibers.

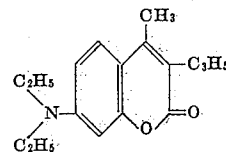
We claim:

1. Compounds having the formula:

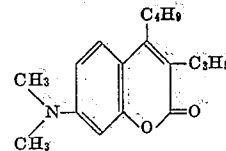


in which R, R' and X are lower alkyl radicals.

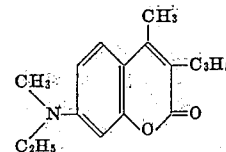
2. A compound having the formula:



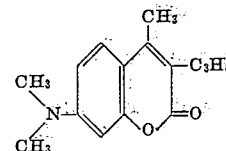
3. A compound having the formula:



4. A compound having the formula:



5. A compound having the formula:



ROBERT SIDNEY LONG,  
CARLETON ALFRED SEARS.

No references cited.