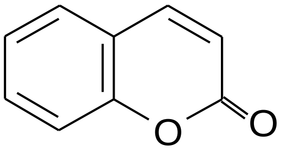
Chapter 1

GENERAL INTRODUCTION

1.1. Synthesis of 7-Hydroxy Coumarins:

Coumarin (I) is the trival name of 2H-benzo [b] pyran-2- one. It is widely distributed in nature, and some of its derivatives are of great importance in chemistry and medicine all natural comanrins; it was found that thirty five of this derivatives are oxygenated at C-7, and consequently 7-hydroxycoumarin known as umbilliferone (2) is often regarded as the parent of more complex coumarins$^{(1)}$.



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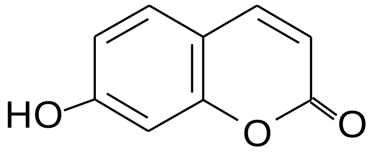

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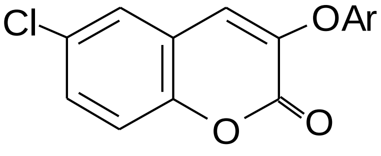
Total synthesis of many natural coumarins have been achieved. The key step in many cases has been the formation of the pyrone ring. In some synthesis a phenol containing the requisite substituents of the natural coumarin has been prepared prior to construction of the pyrone ring. In others, the coumarin nucleus has been prepared first and then modified by steps such as nuclear oxygenation, O- or C-alkylation, and creation of additional rings.

1- Perkin reaction:

This classical method has been reported in almost every text of heterocyclic organic chemistry.

In 1868, perkin$^{(2)}$ prepared coumarin (I) from salicyladehyde by heating with acetic anhydride and anhydrous sodium acetate. Perkin reaction modified by Oglialoro(3), involved the reaction of 5-chlorosalicyladehyde with the sodium salt of phenoxyacetic acids in the presence of acetic anhydride to give coumarin(3).



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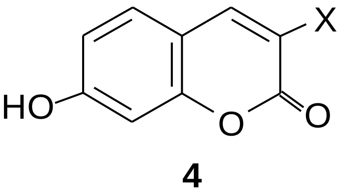
Later, this reaction has been successfully used to synthesized several naturally occurring coumarins (4-9), as well as several 3-substituted. 7-hydroxycoumarins. Thus, the condensation of resorcyladehyde with propionic anhydride and sodium propionate yielded 7-hydroxy-3-methylcoumarin (4a)(10). Similarly, the sodium salts of arylacetic acids, aryloxyacetic acids, arylsulfonylacetic acids, 2- pyridylacetic acid and 2-thienylacetic acid underwant condensation with resorcyaldehyde in acetic anhydride to give the 3-aryl(11-13), 3-aryloxy (14), 3-arylsulfone(15), 3-(2-pyridyl)(16), 3-(2-thienyl)(17)derivatives of 7-hydroxy coumarins (4b, f).



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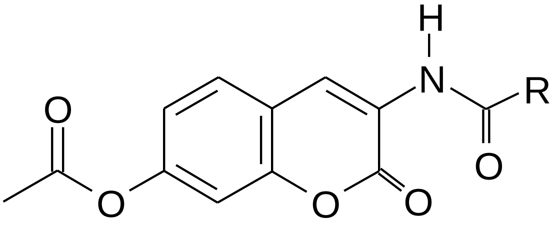
a, x = CH_3
b, x = Ar
c, x= O Ar
d, x = SO_2Ar.
e, x = 2-pyridyl
f, x = 2-thienyl

On parallel lines, the perkin condensation of several amino acids and their derivatives(18-20) was successful. Glycine or its N-benzoyl acetic anhydride/sodium acetate mixture to yield the corresponding 3-acylamino-7-acetoxycoumarin (5), the deacylation of (5) afforded 3-amino-7- hydroxycoumarin (6).



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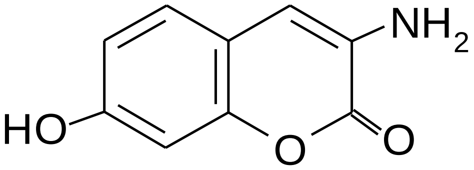

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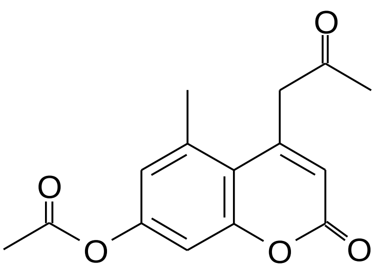
The action of sodium acetate and acetic anhydride on 6-methyl-2,4-dihydroxyacetophenone gave exclusively 7- acetoxy 4-acetomethyl-5- methylcoumarin (7), the acyl groups of which could be hydrolyzed one at a time. Accordingly, treatment of (7) with sulfuric acid gave, (8) which on shaking with sodium hydroxide yielded the deacylated product (9)(21).



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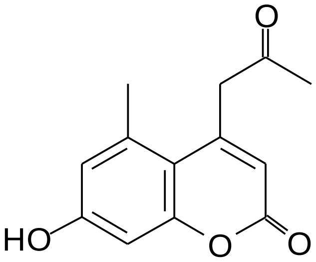

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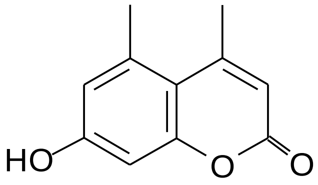

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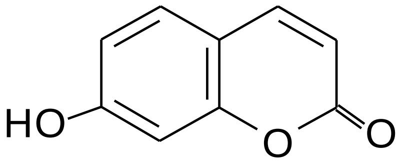
2- Pechmann reaction:

In 1884, Pechmann(22-24) obtained 7-hydroxycoumarin (10) by heating a mixture of resorcinol and malic acid in presence of sulfuric acid.



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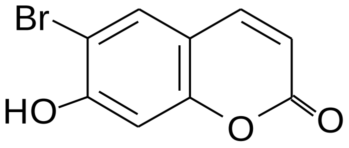
The same procedure was further adopted for the synthesis of 7-hydroxycoumarin derivatives using substituted resorcinols (25-30), 4-bromoresorcinol condensed with malic acid to yield 6-bromo-7-hydroxy coumarin (11) (28), while pyrogallol afforded the dicoumarin, (12)(27), under the same conditions.



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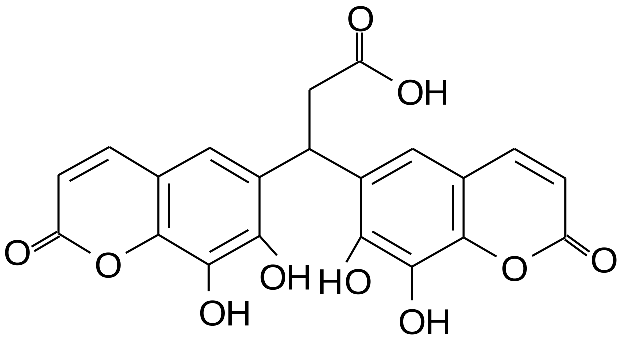

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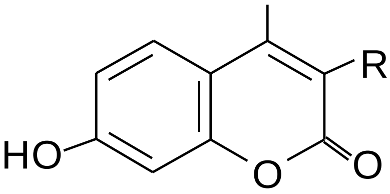
However, this reaction is of limited applicability since only 7-hydroxycoumarins unsubstituted in the pyrone ring are formed.

On the other hand, the pechmann reaction involved the condensation of resorcinol (31-56), and alkylresorcinols(57-68) with β-ketonic esters in the presence of sulfuric acid provided an elegant method for the synthesis of many 7-hydroxycoumarin derivatives, substituted in both the pyrone and benzene rings. Ethyl α-alkylacetoacetates (36, 46), ethyl acetosuccinate(54), ethyl α (α- hydroxy- β, β, β- trichloromethyl) actate(55) and ethyl acetoglutarate(56), condensed with resorcinol to afford the 3-substituted 7-hydroxy-4- methyl coumarins $13_{a\text{-}d}$ respectively.



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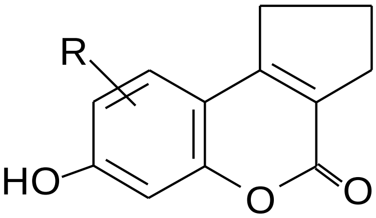
a, R= alkyl
b, R = CH_2COO Et
c, R = CH $(OH)CCl_3$
d, R= CH_2CH_2 COO Et

The formation of 7-hydroxycoumarins from resorcinol and cyclic β-ketonic esters was systematically studied(69-71). It was found that, generally, the cyclic β- ketonic esters behave similarly to the open chain ones, as was evidenced when cyclopentanone-2- carboxylate reacted with resorcinol in presence of sulfuric acid to give the corresponding product 14 (71).



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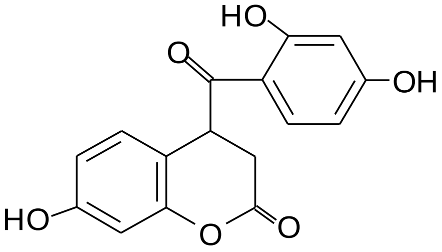
The condensation of resorcinol with several β-substituted acetoacetates with simple alkyl groups to give coumarins was found to be irrespective of the substituent in the ester used. Furthermore, it was found that the presence of electron- attracting groups in the resorcinol molecule exercise an inhibiting effect, to a varying extent; on the power of resorcinol to undergo coumarin condensation, while electron- donating groups do not interfere with this property(72-82).

Beside the two, common condensing agents, sulfuric acid and phosphorus pentoxide, several other have been used to a greater or less extent. 7-hydroxycoumarins were obtained by the condensation of resorcinol with some β-ketonic esters in the presence of dry hydrogen chloride in glacial acetic acid(83), ferric chloride(84), boric anhydride(85), posphorus oxychloride in dry benzene (81), phosphoryl chloride(86), anhydrous aluminium chloride (87,88) and trifluoroacetic acid (89).

The pechmann condensation of resorcinol with maleic anhydride(27) in presence of zinc chloride afforded the 4-substituted dihydro-7-hydroxy coumarin (15).



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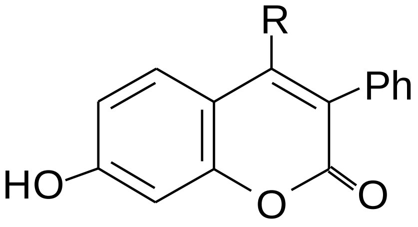
4-Substituted 7-hydroxy-3-phenylcoumarins (16) were obtained by the interaction of resorcinol with α-formyl phenylacetonitrile derivatives in the presence of phosphorus oxychloride or hydrogen chloride(90).



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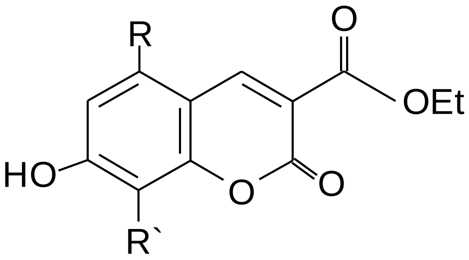
Condensation of diethyl ethoxymethylene malonate with resorcinol(91) and with methyl 2, 6- dihydroxy-4- methoxybenzoate(92) in presence of boron trifluoride yielded the 3-carboethxy-7-hydroxcoumarin derivatives $17_{a,b}$ respectively.



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a, R= R`= H.
b, R= OMe, R`= COOMe

Likewise, the reaction of resorcinol with unsaturated acid or esters such as cinnamic acid (93), methyl cinnamate(94) phenyl propiolic acid(95), ethyl propiolic ester(96), ethyl acrylate(97) or acrylonitrile(98) in dry hydrogen gas, polyphosric acid or zinc chloride afforded the expected 7-hydroxycoumarins.

PART II

SOLVENT POLARITY PARAMETERS

1.2. Solvent polarity parameters :

Any reaction can’t be separated from the medium in which it takes place. This raised the problem of how to solvent affected the dissolved molecules, and the physical quantities by which this influenced could be described in greater details.

Most investigations were directed towards correlating the equilibrium constants, the rate constants of the reactions, or the spectroscopic absorption position bands with the so-called ‘polarity’ of the solvent.

Attempts were made to express the polarity in terms of the dielectric constant, the dipole moment, the refractive index, or other bulk properties of the solvent.

The polarity of a solvent is determined by its solvation behavior which in turn depends on the action of intermolecular forces between the solvent and the solute.

This review is concerning with the medium effect on UV-VIS spectroscopic results. The electronic absorption spectra are affected by the environment specially polarity of the surrounding solvents, thus the shape, position and even intensity of absorption maxima change as the polarity of the solvent changes.

I- Solute-solvent interactions:

The main interactions between the molecule and the solvent may be classified as:

1- Dipole- dipole interaction where both solute and solvent are polar.

2- Solute permanent dipole-solvent induced dipole interaction.

3- Solvent permanent diple-solute induced dipole interaction.

4- Dispersion interaction between the solute transition dipole and the dipole induced in the solvent.

5- Specific interactions such as hydrogen bonding, CT-complex formation, ………etc.

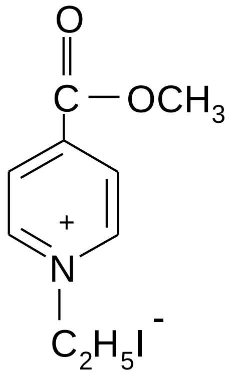
6- Solvent-cage compression effects on the solute where the solute species occupies a volume larger than the site in the solvent quasi-lattice.

ii- Empirical solvent polarity scales:

a- Microscopic solvent polarity parameters:

i- Kosower Z-values (99):

Kosower was the first to set up a comprehensive solvent polarity scale. He found that, the intermolecular charger transfer of 1-alkyl pyridinium iodides exhibited a pronounced negative solvatochromism, and chose 1-ethyl-4-methyoxy carbonyl-pyridinium iodide (18) as a test dye.



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Kosower termed the molecular transition energies E_T (equation (1)) calculated from the position of the absorption maximum (cm^{-1}) “Z-value’.

$$E_T \text{ (K. cal mole}^{-1}\text{)} = 2.859\text{-x } 10^{-3} = Z \qquad \ldots(1)$$

High Z-values correspond to a high transition energy.

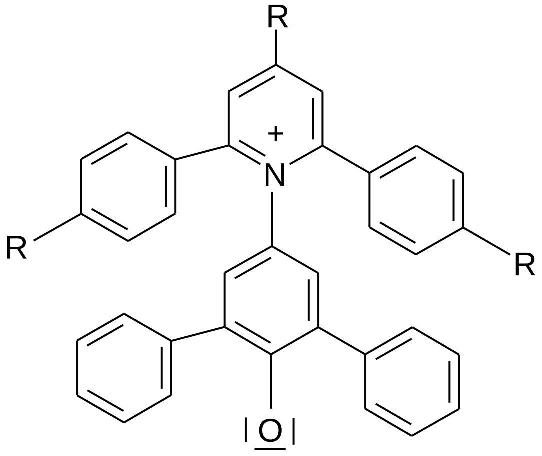
The stronger the stabilizing effect of the solvent on the ion pair in the ground state as compared with that on the less polar exicted state, the lower the wave length of the intermolcular CT-band. The experimental Z-values therefore provide a direct empirical measure of the solvation behavior of the solvent towards (18).

Z- values depend somewhat upon electrolyte concentration and in general, the lower the Z-value, the greater its sensitivity to the electrolyte concentration. Also, it vary with temperature, decreasing with increasing temperature.

Since Z-values reflect the dipole- dipole solute- solvent interactions, it gives poor correlations in non-polar solvents.

(ii) Reichardt – Dimroth's E_T values(100) :

The most comprehensive solvent polarity scale is that determined by Dimroth and Reichardt. The E_T-values calculated from equation (1) for the intramolecular CT-transition of pyridinium-N-phenol betaine (19) used as the test substance provide an excellent characterization of polarity of solvents.



19 a, R = H
b, R = CH_3

E_T- values are sensitive to polar and hydrogen-bonding interaction and also another interactions such as dispersion forces are probably operative. Thus it exhibits a good, generally linear correlation with a large number of solvent sensitive absorption bands.

(b)Recent solvent polarity parameters:

Great attention has recently been paid to the problem of solvent effect on spectral, chemical, and reactivity data by Taft, Kamlet, and co-workers (101-103). The authors consider the total solvent effect tot be composed of three independent contributions- polarity, acidity, and basicity and they introduced corresponding empirical solvent polarity (π), acidity (α) and basicity (β) scales.

(iii) π - Scale of solvent polarity (101):

Seventy solvents are arranged in a π-scale of solvent polarities, so named because it derives from and best correlates solvatochromic effects on P-π^* and π-π^* electronic spectral transition.

Some microscopic solvent polarity parameters were arranged in table (1).

Table (1): Some microscopic solvent polarity parameters.

Solvent	Type of solvent	Z-value	E-value	π-value
Water	HBA-D	94.6	63.1	1.090
Formamide	HBA-D	83.3	56.6	1.118
Ethylene glycol	HBA-D	85.1	56.3	0.932
Methanol	HBA-D	83.6	55.5	0.586
Ethanol	HBA-D	79.6	51.9	0.540
Acetic acid	HBA-D	79.2	51.1	0.664
Benzyl alcohol	Ar- HBA-D	-	50.8	0.984
1-Propanol	HBA-D	78.3	50.7	0.534
1-Butanol	HBA-D	77.7	50.2	0.503
2- Propanol	HBA-D	76.3	48.6	0.505
Nitromethane	HBA-HBD[a]	-	46.3	0.848
Acetonitrile	HBA-HBD$_{a}$	71.3	46.0	0.713
t-Butyl alcohol	HBA-D	71.3	43.9	-
Ethylene chloride	NBA	-	41.9	-
Methylene chloride	NBA	64.2	41.1	0.802
Chloroform	NBA-HBD[a]	63.2	39.1	0.760
Dimethyl sulphoxide	HBA	71.1	45.0	1.000
Sulforlane	HBA	-	44.0	0.997
Dimethyl formammide	HBA	68.5	43.8	0.875
Dimethylacetamide	HBA	-	43.7	0.882
Acetone	HBA	65.7	42.2	0.683
Nitrobenzene	Ar-HBA	-	42.0	1.029
Cyclohexanone	HBA	-	40.8	0.755
Pyridine	Ar-HBA	64.0	40.2	0.867
Ethylacetate	HBA	59.4	38.1	0.545
Bromobenzene	Ar-NHB-HBGA[b]	-	37.5	0.794
Chlorobenzene	Ar-NHB-HBGA[b]	-	37.5	0.709
Tetrahydrofuran	HBA	-	37.4	0.576
Anisole	Ar -HBA	-	-	0.734
Dioxane	HBA	-	36.0	0.553
Diethylether	Ar- NHB-HBA[b]	-	34.6	0.273
Benzene	Ar-NHB-HBA[b]	-	34.5	0.588
Diisopropylether	HBA	-	34.0	0.271
Toluene	Ar-NHB-HBA$_{b}$	-	33.9	0.535
Di-n-butylether	HBA	-	33.4	0.239
Carbon disulphide	NHB	-	32.6	0.514
Carbon tetrachloride	NHB	-	32.5	0.294
Cyclohexane	NHB	-	31.2	0.000
Henxane	NHB	-	30.9	0.081
Tetrachloroethylene	NHB	-	-	0.277

Where :

NHB= non- hydrogen bonding solvent,
HBA= hydrogen bonding acceptor,
HBD= hydrogen bonding doner,
HBA-D= amphiprotic hydrogen bond donor,
Ar= aromatic solvent;

a- Usually act as non-hydrogen bonding solvent, but have shown weak HBD properties with strong HBA indicator solutes.

b- These aromatic solvents are usually weak hydrogen bond acceptor, but sometimes behave as non-hydrogen bonding solvents.

IV- α and β-scales of solvent polarity(102, 103):

Its is a type of solvent parameters which reflects the hydrogen bonding strengths of hydrogen bond donor and acceptor solvents respectively.

Solvatochromic comparison of UV-VIS spectral data is used as a measure of hydrogen- bonding strengths and to construct a β-scale of solvent hydrogen bond acceptor HBA ability (β-HBA Basicity) and the α-scale of solvent hydrogen bond donor HBD ability (α-HBD acidity).

Table (2) shows the β-scale of solvent basicities while table (3) shows the α- scale of solvent HBD acidities.

Table (2): The β-Scale of solvent HBA basicities:

Solvent	β-Value	Solvent	β-value
Anisole	0.247	Methylacetate	0.456
Dimethylsulphoxide	0.247	Ethylacetate	0.481
Ethylchloroacetate	0.363	Diethylether	0.488
Dioxane	0.363	di-n-butylether	0.490
Nitrobenzene	0.393	Butyrolactone	0.479
Benzonitrile	0.409	Acetone	0.499
Dibenzylether	0.410	2-Butanone	0.504
Ethylbenzoate	0.431	Tetrahydropyrane	0.512
Tetrahydrofuran	0.523	Triethylamine	0.686
Cyclohexanone	0.534	Dimethylformamide	0.610
Cyclopentanone	0.537	Dimethylacetamide	0.749
Dimethylbenzylamine	0.595	N-methylpyrrolidone	0.754
Tri-n-butylamine	0.635	Dimethyl sulphoxide	0.752
Pyridine	0.661	Trimethylphosphate	0.797
HBA-Basicities (β-values) of R-OH solvent			
Tert-butyl alcohol	0.95	Phenylethanol	0.64
Iso-propyl alcohol	0.92	Ethylene glycol	0.51
n-Butyl alcohol	0.85	Benzyl alcohol	0.36
Ethanol	0.77	Chloroethanol	0.31
Methanol	0.62	Water	0.14

Table (3): The α-Scale of solvent HBD acidities:

Solvent	α-value	Solvent	α-value
Tert-butyl alcohol	0.436	Benzyl alcohol	0.430
Isopropyl alcohol	0.687	Water	1.017
n-Butyl alcohol	0.710	Acetic acid	0.790
n-Propyl alcohol	0.766	Formamide	0.612
Ethanol	0.850	Chloroform	0.233
Methanol	0.998	Acetonitrile	0.290
Ethylene glycol	0.792		

PART III

FLUORESCENCE EMISSION SPECTROSCOPY

1.3. Fluorescence emission spectroscopy:

Many chemical systems are photoluminescent, that is, they can be excited by electromagnetic radiation and, as consequence, reemit radiation either of the same or longer wavelengths, the two most common manifestations of photoluminescence are fluorescence and phsophorescence which are produced by different mechanisms.

Measurements of fluorescent intensity, permits the quantitative determination of many inorganic and organic species in trace amounts; many useful fluorometric methods exist, particularly for biological systems (104).

(i) Fluorescence and phosphorescence processes:

Luminescence is one of the oldest analytical techniques and its theory is well documented in the literature, photoluminescence describes the luminescence process where excitation is achieved by the interaction of the molecules with photons of electromagnetic radiation.

It involves the two major processes of fluorescence and phosphorescence which were confused until 1944 (105).

The initial step in a photoluminescence process is the absorption of a photon in a time period of about 10^{-15} seconds. Prior to the absorption of radiation, an aromatic organic molecule in solution is usually in its ground electronic state S_o.

When a molecule absorbs light it is said to become excited and the electrons in the molecule are promoted to a high electronic orbital in which there are no unpaired electrons.

Electronic excitation produces molecules with additional vibrational as well as electronic energy. The excess vibrational energy is rapidly lost in about 10^{-12} seconds and the molecule returns to the lowest excited metastable sate S_1.

When the electron returns to the vibrational levels of the ground state from the lowest vibrational level of the first excited singlet state the energy released may be dissipated in one of several ways. It may be emitted as light, via a process known as fluorescence or radiationless transitions may occur, i.e. where no fluorescence is observed. These radiationless transition may involve conversion into rotational, vibrational or kinetic energy i.e. heat or chemical energy.

Photodecomposition may also take place before the electron reaches the lowest vibrational level of the first excited state thus the transition from the excited state to the ground stage may occur by a number of routes other than fluorescence emission see Fig. (1)

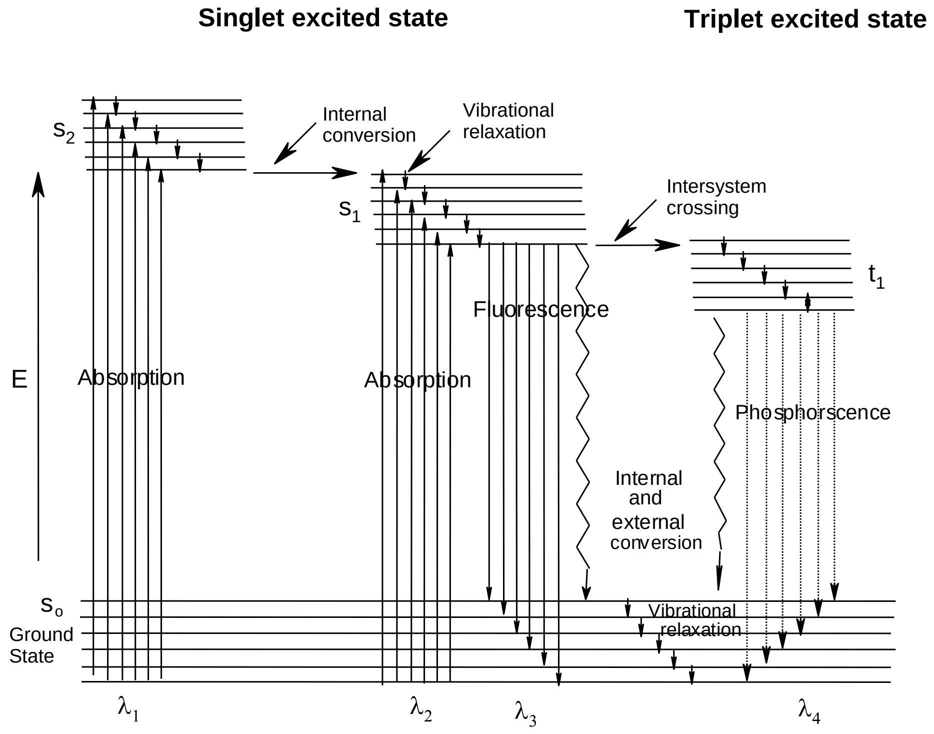


Fig. (1): Partial energy diagram for a photoluminescent system.

Thus molecules that have chromophores and hence can absorb light, will have the potential to exhibit fluorescence, but not all absorbing compounds are fluorescence because of possible radiationless transition(106).

A molecule in an excited state is a highly energetic species with a very short lifetime. Fluorescence usually occurs from the lowest vibrational level of the first excited state and the mean lifetime is about 10^{-8} seconds.

Since some energy is lost in the short period between the excitation and the emission the observed emission spectral band is at a longer wavelength than to observed absorption band. This differences in wavelength is called the ‘Stoke’s shift’ Fluorescence involves emission originating and terminating in states of the same multiplicity normally singlet states in which the electrons in the molecules have antiparallel spins.

Radiationless transitions between energy levels of the same multiplicity are referred to as internal conversions. Radiationless transitions occurring between energy levels of different multiplicities are referred to as intersystem crossing.

In a triplet state (T) the electrons occupy an orbital with a parallel spin. The transition to the triplet state is of low probability or ‘forbidden’, but does occurs if there is good orbital mixing and a suitable overlap between the excited electronic singlet state and the vibrational levels of the triplet state.

Any of the vibrational levels of the triplet state may be involved, but by radiationless vibrational relaxation and internal conversion, the lowest vibrational level T_1, is quickly attained. The molecule returns directly to the ground state, S_o, by emitting the excess energy. This is observed as phsophorescence.

Phosphorescence thus is a radiative emission originating from and terminating in different multiplicities. It has a longer lifetime, T_p, of about 10^{-4} seconds to 10 seconds and because of this radiative long lifetime, it is prone to quenching at room temperature due to competitive deactivation processes.

Phsophorescence is, therefore, usually studied at 77k, in rigid glass solvent media, on thin layer plates or other rigid support (107).

Phosphorescence emission is of lower energy than fluorescence emission. It is therefore possible, at 77k, to obtain a total luminescence spectrum, in which the intensities and emission wavelengths of fluorescence and phsophorescence can be simultaneously measured.

(ii) Determination of quantum yield:

The quantum yield, or quantum efficiency, for a fluorescent process is simply that ratio of the molecules that fluoresce to the total number of excited molecules.

From a consideration of figure (1), the fluorescent quantum yield ϕ_f for a compound must be determined by the relative rates for the processes by which the lowest excited singlet state is deactivated namely, fluorescence, intersystem crossing, external and internal conversion, predissociation, and dissociation. We may express these relationship the equation (108).

$$\phi_f = \frac{K_f}{K_f + K_i + K_{ec} + K_{ic} + K_{pd} + K_d} \qquad \ldots(2)$$

where the K terms are the respective rate constants for the several processes enumerated above. The magnitude of K_f, K_{pd}, and K_d are mainly dependent upon chemical structure, the remaining constants are strongly influenced by environment and a somewhat lesser extent by structure.

The recent method(109) for measuring quantum yields are the comparative methods which are based on fact that, if two substance 1 and 2 are studied in the same apparatus, and using the same incident light intensity, the integrated areas under their corrected fluorescence spectra (S_1 and S_2) are simply related as follows:

$$\frac{S_2}{S_1} = \frac{\phi_2}{\phi_1} x \frac{A_2}{A_1} \cdots \qquad \ldots(3)$$

where ϕ value are quantum yields, and A values absorbances at the respective excitation wavelength. The application of this method, has been thoroughly discussed else where (110).

As corrected spectra are becoming more readily available, this method is likely to remain the most popular approach to quantum yield determinations.

However, it requires a series of suitable standard materials of it is to be used over a range of wavelength (See Table 4).

Table (4): Fluorescence Quantum yield standards in various emissionr ranges.

Region	Compound	Solvent	ϕ
270- 300 nm	Benzene	Cyclohexane	0.05 ± 0.002
300-380 nm	Tryptophan	H_2O (pH 7.2)	0.14±0.02
300-400 nm	Naphthalene	Cyclohexane	0.23±0.02
360-480 nm	Athracene	Ethanol	0.27±0.03
400-500 nm	9, 10-DPA	Cyclohexane	0.90±0.02
400-600 nm	Quinin Bisulfate	1N H_2SO_4	0.546

PART IV

LUMINESCENCE PROPERTIES OF 7-SUBSTITUTED COUMARIN

1.4. Luminescence properties of 7-substituted coumarin:

(a) 7-Hydroxycoumarin as active media of lasers:

A group of widely used laser dyes emitting in the blue-green region of the spectrum were derived from coumarin by various substitutions some members of this group ranks among the most efficient laser dyes yet known (111). Extensive investigations (112). Were carried out in order to correlate the emission characteristics with chemical structures and it was found that the introduction of a hydroxyl groups in position –7 of the coumarin molecule greatly enhanced fluorescence and lasing properties.

(b) Photochemical properties of 7-hydroxycoumarins :

The presence of a hydroxyl group in position-7 of coumarin generates a chromophore characterized by the conjugation of the push-pull substituents. Substitution of the dye chromophore with additional groups can either elevate or depress the excited state dipole moment.

The effect of substitution in position –4 was illustrated by the investigation carried out by Loboda et. al.,(112) they compared the electronic spectra of 7-hydroxy coumarin and its protonated, anionic and tautomeric forms with those for 7-hydroxy-4-(trifluoromethyl) coumarin and 7-hydroxy-4-methylcoumarin.

For a better understanding of the photochemical properties of 7-hydroxy coumarins a feature to be highlighted, is the role of solvent, pH of the medium, temperature and concentration of the dye.

(i) Effect of solvent(113-118):

The response of fluorescence emission yield and lifetime to changes in solvent polarity is a sensitive function of coumarin substitution pattern. Most important are substituent influence which result in a large excited state dipole moments (for the fluorescence state), in restriction of rotatory motion of the substituent at position-7-, and the delocalisation of excitation energy away from the coumarin moiety. For dyes displaying sharp reduction in emission yield and lifetime with increased solvent polarity, protic media and particularly water are most effective in inhibiting fluorescence (112).

Jones et. al.,1980 (119) reported that for a series of alcohol solvents, the greater the tendency of H-bond to dye –correlates with a red, shift of fluorescence. This smooth dependence is consistent with the relative stabilization (lower relative energy) that must occur for the zwitterionic excited state. This finding extend to a longer set of solvents including those not capable of H-bonding.

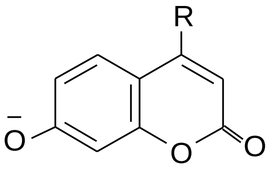
Muthuramu (120) and others(121-123) studied the solvent effect on fluorescence emission of a number of 7-alkoxycoumarins and 7-alkoxy-4-methylcoumarins. The fluorescence emission maximum was found to be slightly dependent on the solvent polarity, and it was gradually shifted only by small amount to longer wavelength when the solvent was changed from benzene to water. On the other hand, the relative fluorescence intensity measured in a series of protic and aprotic solvent was found to be solvent dependent, and these coumarin derivatives exhibit intense fluorescence in water and are weakly fluorescent in aprotic solvents.

(ii) Effect of pH:

The numerous applications of fluorescence properties of 7-hydroxycoumarins, has led to much interest in the description of the fluorescence of these molecules in solution over a wide range of pH(124-138).

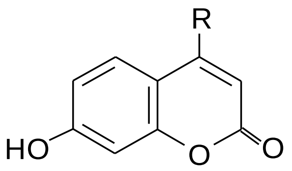
Fink and Koehler in 1970(128) studied the fluorescence of 7-hydroxycoumarin in the pH range 1.2 to 11.2, they found an intense blue fluorescence band which was pH independent for all pH values greater than 2.2, while at pH values between 1.2 and 2.2 the latter emission was red shifted and decreased in intensity. These authors assigned this phenomenon to a rapid excited state acid-base equilibrium which takes place during the lifetime of the singlet excited state.

More investigations of the fluorescence and absorption spectra of 7-hydroxycoumarins in ethanol and water at various pH values, led to the assignments of structures which appear successively on going from basic to acidic aqueous media. These are, the basic anion (A^-), the neutral species (N), the tautomer (T) and the cation (C^+) (129,130).



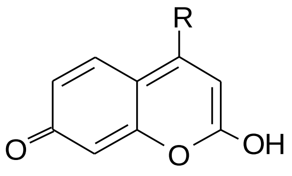
A$^-$

,

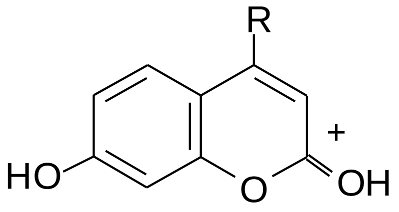


N

,



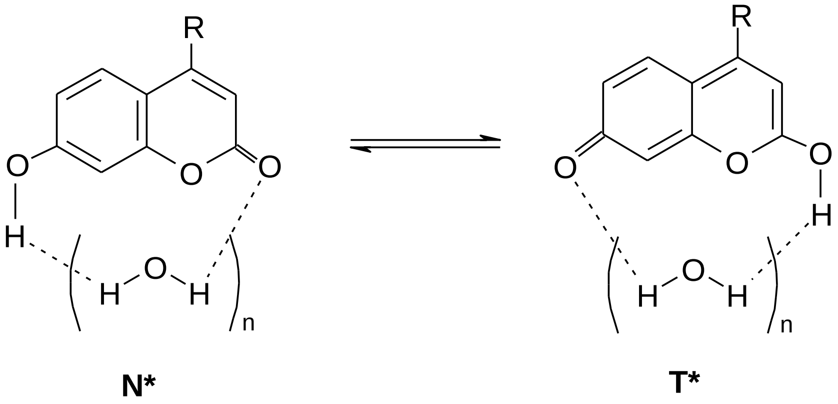
T



C^+

Moriya (131-133) made an extensive study of the fluorescence spectra of 7-hydroxycoumarin and its 4-methyl derivative in aqueous solution and in organic solvents over a wide range of pH. The spectra in aqueous solutions showed four emission peaks which are related to each of the four species of the excited singlet state, i.e., two neutral tautomers (N^*, T^*), an anion (A^{-*}) and a cation (C^{+*}). The fluorescence intensity from each excited species changed with pH. It is emphasized that, an excited cation (C^{+*}) and an excited anion (A^{-*}) are only formed in strongly acidic solutions and in basic solution, respectively (131, 132).

Tautomerization in aqueous solution in mainly caused by the transfer of a proton between two active sites in the on molecule. Such an intramolecular proton transfer of the coumarins is promoted by water molecules with a hydrogen bond surrounding the excited molecule (132). However, former studies (134-136), did not reveal the coexistence of the T^* band with N^* and A^{-*}.



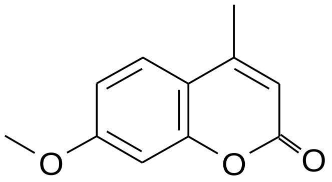
The emission characteristics of 7-hydroxy-4-methylcoumarin were investigated by studying the intensity fluorescence spectra and the laser-pumped gain spectra for various solvents and pumping powers, A total of five different forms were found to excite, each of which can be isolated in a proper solvent. Of the five species, on e is the neutral molecule, two other results from ground state reactions, while two are produced by excited-state reactions and do not have a stable ground state. By proper adjustment of the solvent a number of combinations of the five forms can coexist and lose together, giving rise to a variety of gain spectra and allowing the possibility of 'tailoring' a desired gain curve over most of the visible spectrum. Comparison of the gain and fluorescence spectra indicates the presence of triplet or excited state losses in some of the forms yields. Comparative values of emission parameters reveals an acidity –dependent quenching of one of the excited-state species (137, 138).

Early studies (139,140) mentioned that, 7-hydroxycoumarin is photolabile at high pH. However, Fink and Koehler(128) identified an intense green fluorescence band at 500 nm, which developed with time when 7-hydroxycoumarin was irradiated in highly alkaline solutions. They assigned this band to 2, 4-dihydroxy cinnamic acid as a photolysis products of the parent dye.

(iii) Effect of temperature:

Increase in the temperature of the dye solution results in population of the higher vibrational levels of the ground state with more and more transitions taking place from these levels to higher vibrational sub-levels of the first excited state. Thus the absorption spectrum broadens and any vibrational fine structure is lost. By contrast, cooling of the solution can enhance the vibrational characteristic of both the absorption and fluorescence spectra (141).

Giri(142) illustrated the effect of temperature on fluorescence spectra of a number of 7-alkoxycoumarin derivatives. The fluorescence emission spectra of compounds in aqueous solution as well as in benzene solution were studied at different temperatures. It was observed that, the fluorescence intensity decreased with increase of temperature for the coumarin derivatives (20-22) but remained constant in the case of (23). It seems that intermolecular quenching by the substituent groups plays an important role in the deactivation process, which depends upon the position and the nature of the substituent groups that could twist about the connecting bonds, leading to a non planar nonfluorescent state of the molecule.



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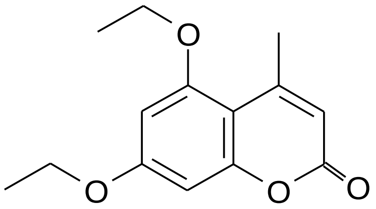

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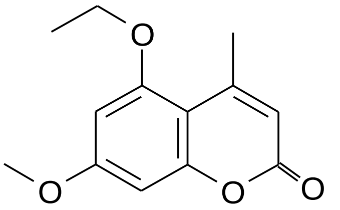

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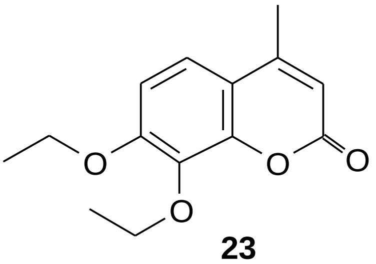

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Peters et al., (143) on investigating the temperature dependence of the peak power of a Haensch-type dye laser, reported the absence of a noticeable temperature, dependence of the peak power of 7-hydroxy-4-methylcoumarin in methanol.

Kumbhakar et al.(144,145) and Roy et al.(146) showed that, the effect of temperature on the decay and salvation of some coumarin dyes.

(iv) Effect of concentration:

It has long been known that, organic dyes in aqueous solution have a tendency to form dimers and higher aggregates which make themselves known through a distinctly different absorption spectrum. The dimers usually have a strong absorption band at short wavelengths than the monomers and often an additional weaker band at the long wavelength side of the monomer band. Furthermore, they are generally only weakly fluorescent on not at all (147-149). It has been suggested that hydrogen bonding between the dye molecules (150, 151) may be responsible among other factors for the dimerization.

In organic solvents, there is usually a strong interaction between excited molecules and those in the ground state and this shows up at high concentrations. Although the fluorescence of the majority of organic compounds is quenched at high concentrations by this mechanism, it has been found that with some other compounds a new fluorescence band appears when the concentration is increased. This new band is due to dimers that exist only in the excited state i.e., excimers (152-154).

An investigation of the fluorescence spectra and quantum yield of some 3-substituted 7-alkoxycoumarins in different solvents showed that, the fluorescence characteristic depend on the solvent nature and concentration. An increase of concentration in non polar, as well as enhancement of solvent polarity cause a red shift of fluorescence spectra and a decrease in the quantum yield. The specific features of fluorescence characteristics of 3.7-disubstituted coumarin compounds are supposed to be closely related to formation of associations in non polar solvents and to additional polarization of molecules in polar solvents (155).

(v) Fluorescence quenching;

The interception of dye triplet states by a ‘quenching’ agent has been viewed both as a benefit in terms of depletion of unwanted triplets and as a source of potentially harmful photoproducts.

The best known of the triplet quenchers is molecular oxygen(156) which present at concentrations of 10^{-3}- 10^{-4} M in dye solutions that are exposed to air.

Marling et. al.,(157) demonstrated that, the lasing output for coumarin dye lasers is dramatically reduced on removal of oxygen from ethanol solutions.

On the other hand, Fletcher and Cowerkers(158) showed that removal of oxygen results enhanced efficiency. This reversal was found in for circumstances in which short-wavelength (flashlamp) pump light is filtered. The suggestion was that excitation at shorter wavelengths results in population of upper singlet states opening up additional intersystem crossing pathways and an elevated role for oxygen quenching.

Sharma et al.(159), Giri (160) and Rusalov et al. (161) showed that, the quenching of some coumarin dyes by halide ions, or interamolecular fluorescence quenching.

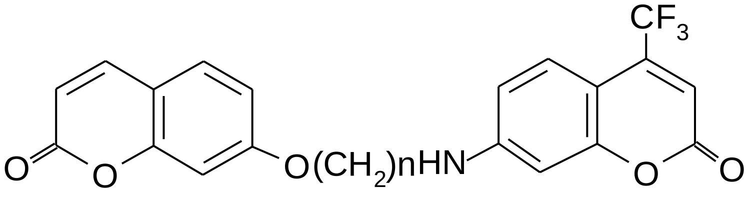
(vi) Energy transfer in linked dye systems;

Peterson and Snavely (162) suggested that dye laser efficiency could be enhanced by the use of mixtures of dyes. Benefits to accrue to such a system is enhancement of what may be a poor absorptivity at pump wavelength by the primary (active) dye by the secondary (booster) dye. In addition an efficient means of disposal of excess energy for dye mixture may be render photodegradation paths less important.

Mugnier and Colleagues(163) studied the linked coumarins systems 24. These structures deploy a higher- energy coumarinyl ether (donor) moiety fused with a lower energy (acceptor) fluorinated aminocoumarin component. Variations in the link to which dye components are attached (n= 3, 4, 8 or 12) also provide a range of average distances for inspection (random chromophore orientation).

Due to the very favorable overlap of donor emission and acceptor absorption, high energy transfer efficiencies are observed with small variations with temperature, and a slight fall-off with the value of (n) in some solvents.

High photochemical stability was also noted for the linked coumarin structures(164).



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