CHAPTER I
CHAPTER - I

COUMARIN DERIVATIVES : A BRIEF LITERATURE REVIEW

1.1 Introduction
1.2 Occurrence
1.3 Classification of coumarin derivatives
1.3.1 7-Oxygenated unsubstituted coumarins
1.3.2 7-Oxygenated 3-substituted coumarins
1.3.3 7-Oxygenated 4-substituted coumarins
1.3.4 7-Oxygenated 5-substituted coumarins
1.3.5 7-Oxygenated 6-substituted coumarins
1.3.6 7-Oxygenated 8-substituted coumarins
1.3.7 7-Oxygenated 3,4-disubstituted coumarins
1.3.8 7-Oxygenated 4,5/3,5-disubstituted coumarins
1.3.9 7-Oxygenated 4,6/3,6-disubstituted coumarins
1.3.10 7-Oxygenated 3,8/4,8-disubstituted coumarins
1.3.11 7- Oxygenated 3,4,5/3,5,6/3,5,8-trisubstituted coumarins
1.3.12 7- Oxygenated 5,6,8/3,6,8/4,6,8-trisubstituted coumarins.
1.3.13 Other coumarins
1.4 Aim and nature of work
1.5 References
1.1 Introduction

An oxygen containing heterocyclic compound as represented in Fig I is the parent coumarin molecule where an oxygen containing six membered ring is attached to a benzenoid ring and have oxo group at C₂ position.

\[(I)\]

As can be seen from the structure, a large number of derivatives are possible depending on substituents at 3,4,5,6,7 and 8 positions.

The name coumarin originates¹ from a Caribbean word ‘coumarou’ for the tonka tree whose botanical name is *Coumarouna odorata* Aubl. Coumarin is now the accepted trivial name for the compound whose structure was finally deduced in the later half of 18th century. It also represents a group of naturally occurring lactones containing the fundamental structural unit (I).

The isolation of coumarin was first reported by Vogel² in Munich in 1820. He associated the pleasant odour of the Tonka bean from Guiana with that of clover, *Melilotus officinalis* which gives rise to the characteristic aroma of new-mown hay.

A consequence of the rapid expansion of knowledge concerning naturally occurring coumarins is the appearance of a number of important reviews, notable among which are Spath,³ Reppel,⁴ Dean,⁵ Soine,⁶ Nielsen,⁷ Waterman,⁸ Murray⁹,¹⁰ and Keating.¹¹
Nowadays, coumarins have attracted attention of chemist because, many of them are fluorescent, possess physiological activity in addition to their analytical and biological importance. Some of them are also proven to be useful as disperse dyes in textile industries.

The following is an updated survey of the general properties and applications of coumarin derivatives.

1.2 Occurrence

Coumarin belongs to the group of secondary metabolites which have characteristic colour and odour like many other secondary metabolites but whose role is either not well understood or is in some cases a matter of controversy. All the natural coumarins have been isolated, from botanical sources. Since 1812, when the first coumarin was isolated, more than 800 coumarins have been characterized. Generally coumarins are distributed in all parts of plants. However, fruits are the richest source of coumarins. Fruits of the *Angelica tatianae* contain 2.2% of coumarin compounds\(^\text{12}\) which have been reported to reach 2.5% in unripe fruits of *A. sylvestris*\(^\text{13}\) and 2.59% in ripening fruits of *Archangelica officinalis*.\(^\text{14}\) Generally fruits are followed by roots and then leaves as the sources of coumarins. Coumarins are widespread in the Angiosperms but they are rather rare in Gymnosperms and lower plants. Several other plants like *Apiaceae, Asteraecae, Mimosaceae, Caesalpiniaeae, Clusiaccac, Hypericaceae, Euphorbiaceae, Hippocastanaceae, Oleaceue, Thymelaeaceae, Umbelliferae, Rutaceae* and *Leguminosae* also provide good examples of coumarin containing plants. Other families of smaller size such as *Caryophyllaceae, Euphorbiaceae, Hippocastanaceae, Oleaceae* and *Thymelaeaceae* are also good example of coumarin containing plants.

Regardless of the source, all natural coumarins bear oxygen atom at one or more of the six available nuclear positions, as phenolic ethereal or
glycosidic groups. Most of them are oxygenated at C-7 position and consequently 7-hydroxycoumarin, commonly known as Umbelliferone is often regarded as the parent, both structurally and biogenetically, of the more complex coumarins.

During the later half century there has been a notable reawakening of interest in coumarins. This has led to their discovery in hundreds of plant species and to the elucidation of their structures. In part, progress has stemmed from the development of much improved methods for their isolation combined with a variety of powerful modern techniques for their structural identification. However, much interest has also emanated from the wide range of physiological activity they display and from the characteristic fluorescence of most coumarins on ultraviolet irradiation.

Beside the thousands of naturally occurring coumarins, many synthetic chemists have attempted the synthesis of a variety of new coumarins by placing different substituents on parent structure (I) in order to evaluate it’s fluorescing properties as well as biological activities. In present work, one of such coumarin 7-hydroxy-4-methylcoumarin is modified by coupling it with different azothiazoles and the resulting new coumarin derivatives are characterised and studied for their absorption, fluorescence and biological activities.

1.3 Classification of Coumarin Derivatives

Literature survey clearly indicates that coumarin derivatives are studied mainly based on their optical characteristics. Coumarin by itself is non-fluorescent, but it develops a green fluorescence at a pH > 10 on irradiation with UV light (c.f. Goodwin and Kavanagh15). Amongst various derivatives, those having oxygen or nitrogen at C-7 position are proven to given more
fluorescence and naturally many have attempted their studies. We have classified the available data in following way.

1. 7-Oxygenated unsubstituted coumarins
2. 7-Oxygenated 3-substituted coumarins
3. 7-Oxygenated 4-substituted coumarins
4. 7-Oxygenated 5-substituted coumarins
5. 7-Oxygenated 6-substituted coumarins
6. 7-Oxygenated 8-substituted coumarins
7. 7-Oxygenated 3,4-disubstituted coumarins
8. 7-Oxygenated 4,5/3,5-disubstituted coumarins
9. 7-Oxygenated 4,6/3,6-disubstituted coumarins
10. 7-Oxygenated 3,8/4,8-disubstituted coumarins
11. 7-Oxygenated 3,4,5/3,5,6/3,5,8-trisubstituted coumarins
12. 7-Oxygenated 5,6,8/3,6,8/4,6,8-trisubstituted coumarins
13. Other coumarins

1.3.1 7-Oxygenated Unsubstituted Coumarins

It is a well known fact that most of the natural coumarins bear oxygen atom at one or more of six available nuclear positions. Among these six positions available, C-7 position is found to be more popular and consequently, it is 7-hydroxycoumarin (II) which is commonly known as umbelliferone.
In addition to the extraction of II from natural source, its synthesis is possible using phenol and malic acid.\textsuperscript{16,17} The UV absorption study of 7-hydroxycoumarin (II) shows strong band at \(-217\) nm and 315-330 nm with weak peaks or shoulders at \(240\) nm and \(255\) nm. Consequently, when UV-spectra are recorded in alkaline medium, the absorption intensities of maxima show marked bathochromic shift from \(325\) nm to \(372\) nm.\textsuperscript{18}

The fluorescence behavior of II has been studied in various organic solvents as well as in neutral, acidic and basic aqueous solutions.\textsuperscript{19} It has been revealed that four fluorescent species typically exist in the photo excited state according to solvent conditions. They have been identified as neutral (a), anionic (b), tautomeric (c) and protonated species (d) of the excited molecule.
Telsuo Mariya\textsuperscript{20} has shown that fluorescence of II is quenched due to the presence of Cl\textsuperscript{−} ions. The intensity decrease and life time change in fluorescence from neutral to tautomeric forms of photoexcited states are due to interaction between the protonated molecules generated in excited states and chloride ions.

Despite the widespread use of II in biological assays,\textsuperscript{21} it is not fully deprotonated (and therefore not maximally fluorescent) unless the compound is in environment having pH of 10 or higher.\textsuperscript{22} The sensitivity of assays using 7-hydroxycoumarin-based conjugates and enzyme substrates therefore decreases at lower pH, where some or all of assay components are incompatible with basic pH levels. The sensitivity of such assays is especially limited as many enzymes have optimal turnover rates at or below pH 7. Similarly many protein conjugates of II are proven to be unstable or not useful with respect to basic conditions required to obtain maximal fluorescence of the label.\textsuperscript{23} Compound II is used as starting material for synthesis of mannich base and resultant (hydroxycoumarinyl methyl) amino acids were tested for bacterial activities against \textit{Escherichia coli} and \textit{Bacillus subtilis} as well as antifungal activities.\textsuperscript{24,25}

Other 7-oxygenated unsubstituted coumarin derivatives studied are 7-methoxycoumarin (III) and 7-acetoxycoumarin (IV).
Compounds II, III and IV have been shown to photodimerise under 300 to 350 nm UV light to give anti-head to head and anti-head to tail dimers.\textsuperscript{26,27} Moorthy et al.\textsuperscript{28} have shown that such photodimerisation proceeds selectively in solid inclusion complexes with $\beta$- and $\gamma$- cyclodextrins (CD).

The stoichiometries of the complexes have been assigned on the basis of presence or absence of photodimers and from NMR integration ratios of characteristic coumarin and saccharide protons. The relative orientations of substituted coumarins in a complex are inferred from stereochemistry of the photodimers depending upon the substitution pattern of the coumarin molecules and type of CD employed and complexes whose guest-host stoichiometries are 1:1 and 2:2 have been identified. In several instances where dimers are not obtained from irradiation of neat solid coumarins or their solutions but have been obtained from CD complexes.

1.3.2 7-Oxygenated-3- Substituted Coumarins

Several 3-substituted 7-oxygenated coumarins rank among the most efficient photostable laser dyes emitting in the blue-green region of the visible region. Drexhage\textsuperscript{29} and Jones et al.\textsuperscript{30} have shown that lasing range covered by coumarin dyes is appreciably extended when the 3-substituent is heterocyclic moiety.

\[
\text{(V)}
\]

a) $X = S$  \quad b) $X = NH$  \quad c) $X = O$
Elanagdi et al. synthesized the new 3-substituted-7-hydroxy coumarins from β-resorcyaldehyde. Compounds Va, Vb and Vc have been synthesized via condensation of 2,4-dihydroxybenzaldehyde with 3-benzothiazol-2-yl-acetonitrile, 1H-Benzimidazol-2yl-acetonitrile and benzoxazol-2-yl-acetonitrile, respectively. Solutions of these compound in different organic solvents were found to be strongly fluorescent.

![Chemical structure of compound VI](image)

(VI)

a) $\text{Ar} = \text{C}_6\text{H}_5$  
   b) $\text{Ar} = p-\text{Me C}_6\text{H}_4$  
   c) $\text{Ar} = p-\text{Cl C}_6\text{H}_4$

The compounds VI a, VI b, VI c, have been synthesized by condensation of the dihydroxybenzaldehyde with 4-Aryl-2-cyanomethyl-1,3 thiazoles.

![Chemical structure of compound VII](image)

(VII)

a) $\text{R} = \text{Me}$  
   b) $\text{R} = \text{Ph}$  
   c) $\text{R} = p-\text{OMe C}_6\text{H}_4$
Compound VIIa-VIIc were synthesized by reacting dihydroxybenzaldehyde with the appropriate 2-acylamino-5-cyanomethyl, 1,3,4 thiazoles. These newly synthesized compounds show variable antibacterial activity against some Gram positive, Gram negative and acid fast bacteria. The compounds Va, VIa, VIb, VIc and VIIa-VIIc showed significant activity against the acid fast Mycobacterium phlei, probably due to their ability to penetrate the lipid cell-wall.

![Image of compound VIII](attachment:image.png)

(VIII)

a) Ar = ph  
b) p- OMe C₆H₄

3-(5-Aryl-1,3, 4-oxadiazol-2yl)-7-hydroxycoumarin VIIIa and VIIIb have been synthesized by condensing dihydroxybenzaldehyde with ethyl-(5-Aryl- 1,3,4- oxadiazol -2-yl) acetate.

With a view to standardize the parameters which make all the compounds effective in the field of laser, a study of their electronic absorption and emission in different solvents was carried out.

![Image of compound IX](attachment:image.png)

(IX)
7-Hydroxy 3-carbethoxycoumarin (IX) has been synthesized from 2,4 dihydroxybenzaldehyde and diethyl malaonate.\textsuperscript{35}

Nimbdeokar\textsuperscript{36} has studied emission and excitation spectra in different organic solvents. It is observed that compound IX has strong absorption below 300 nm and therefore will probably be a suitable candidate for flash pump laser dye. 7-Hydroxy-3-carbethoxycoumarin shows fluorescence life time closer to natural radiative life time, implying slow rate of intersystem crossing thus giving high quantum yield.

\begin{equation}
\text{(X)}
\end{equation}

\begin{itemize}
  \item[a)] \( R = \text{COOH} \)
  \item[b)] \( R = \text{CN} \)
\end{itemize}

7-Hydroxy - 3-carboxycoumarin (Xa) is synthesized by Lokhande et al.\textsuperscript{37} using the alkaline hydrolysis of 7-hydroxy 3-carbethoxycoumarin and subsequent cyclisation with hydrochloric acid. Chakarvarti\textsuperscript{38,39} reported synthesis of 7-hydroxy-3-cyanocoumarin (Xb) by condensing diethyl ethoxymethyleneacyano acetate [EMCA] with resorcinol in absolute ethanol in presence of sodium ethoxide. Xa and Xb both were buff coloured solids soluble in water and their solutions exhibited blue fluorescence.\textsuperscript{23}

\begin{equation}
\text{XI} \quad \text{XII}
\end{equation}
Compounds XI to XIV are synthesized and well characterized by Nimbdeokar,\textsuperscript{36} using elemental analysis, IR, NMR and mass spectral studies. From their absorption and fluorescence spectra, absorption maxima were found to be at $\sim 202$ nm, 280 nm, and 412 nm with high molar extinction coefficient ($\sim 10^4$ lit mole$^{-1}$ cm$^{-1}$ ) in alkaline ethanolic (93:7) solution. They have also studied absorption and fluorescence behavior in different solvents. Generally, $\lambda_{\text{max}}$ increases with increase in solvent polarity. However, for compounds XI - XIV $\lambda_{\text{max}}$ was found to be higher in ethanol as compared to DMF and DMSO. This was correlated with the existence of specific dye-solvent interaction and presence of more polar mesomeric forms in ethanol. Further increase in $\lambda_{\text{max}}$ emission is suggested to be possible in higher polar solvents like methanol, ethyleneglycol, glycerol and water.
The compound (XV) was synthesized\textsuperscript{31} in order to investigate the effect of introducing an acetoxy group at position 7 of the compound \textit{V} on its fluorescence properties. However, further data regarding the same is lacking.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{XV_diagram.png}
\caption{(XV)

a) $X = S$ b) $X = NH$ c) $X = O$
}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{XVI_diagram.png}
\caption{(XVI)

a) $R = \text{NHCOCH}_3$ b) $R = \text{COph}$
}
\end{figure}

Mehendale\textsuperscript{40} has synthesized XVIa and XVIb and studied their fluorescence characteristics. The nitroaldehyde was condensed with phenylacetonitrile in ethanol containing potassium hydroxide to give $\alpha$-phenyl-$\beta$-(2-methoxy-4-nitrophenyl)-acrylonitrile. This acrylonitrile derivative was refluxed in dry benzene with aluminum chloride to give 3-phenyl 7-nitrocoumarin which was reduced to aminocoumarin using iron and dil HCl, and finally acetylated to yield 3-phenyl -7-acetylaminocoumarin (XVIa). Similarly, 3-phenyl 7-methoxycoumarin (XVb) was prepared by condensing 2,4-dimethoxybenzaldehyde with phenylacetonitrile followed by cyclization of the resulting 2-phenyl-$\beta$-(2, dimethoxyphenyl)-acetonitrile by refluxing in
benzene with aluminum chloride under controlled conditions in order to avoid the demethylation of the 7-methoxy group. XVIa and XVIb are shown to give fluorescence maxima at 442 nm and 421 nm respectively in dioxane. Both are also found to be very good optical brighteners for polyester fabrics.

1.3.3 7-Oxygenated 4-Substituted Coumarins

(XVII)

Total fifteen derivatives are reported in this sub-class. The most studied is 7-hydroxy-4-methylcoumarin (XVII). Various procedures have been developed for the synthesis of coumarin from phenol, o-cresol (Rasching method) and salicyaldehyde (Perkin reaction). In these methods non-reusable catalysts such as concentrated sulphuric acid and metal oxides are applied. XVII can be obtained in high yield upon reaction of ethylacetoacetate with 1,3-dihydroxybenzene (resorcinol) with sulphuric acid as condensing agent. Other condensing agents are also used namely phosphorus pentaoxide, trifluoroacetic acid, aluminum chloride, zinc chloride and alcoholic hydrogen chloride solution. In order to reduce the waste problem in all these irreversible catalysts, heterogenous catalysis of the Pachmann reaction by cation exchange resin, by the perfluorinated sulphonic acid and zeolyte has been reported.
Recently, the use of microwaves in the synthesis of XVII has been reported\textsuperscript{54} to reduce considerably the reaction time and to give good yield. The reaction is also carried out on solid support using k-10 mantmorillonite clay under microwave irradiation.\textsuperscript{55} These products were found to be free from impurities such as organic raw materials. Usually they are further purified by repeated crystallization from ethanol. Extensive work\textsuperscript{56-61,22} regarding absorption and fluorescence spectra of XVII have been reported. In many investigations XVII has been employed as a model compound to study the effect of substituents, solvent polarity and different pH on the absorption and fluorescence of various related compounds.

In neutral medium (ethanolic solution), XVII shows an absorption maxima in the range of 322-325 nm. Another maxima are recorded at \(~230\) nm and \(~208\) nm. Since the first maxima being below 300 nm and has very high molar extinction coefficient \((\sim10^4 \text{ lit mole}^{-1} \text{ cm}^{-1})\), this compound is suggested to be suitable as a flash pump laser dye and its optical properties have been well studied.\textsuperscript{58} XVII is known to adopt a number of chemical forms (associated with hydrogen donating and hydrogen accepting capabilities of the dye) depending upon its molecular environment (pH), each of which have different optical spectra. Three of the ground state forms, neutral, anionic and cationic (a, b, & c respectively) absorb at 320 nm, 365 nm and 340 nm, respectively and shown fluorescence at 400, 455 and 420 nm, respectively.

(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d)
The zwitterionic exciplex (d), which exists only in the excited state shows fluorescence at 475-480 nm.\textsuperscript{62-66} The structures of the chemical forms of XVII and their optical properties have been well established. Consequently, it can be tuned to the desired fluorescence by adjusting its molecular environment.

XVII has complex fluorescence behavior upon change in pH. The neutral form is present in neutral and acidic conditions as shown by fluorescence at \(\sim 385\) nm. Under highly acidic condition studied (10\(^{-1}\) M HCl), the zwitterionic form is shown to be present with fluorescence at 480 nm.\textsuperscript{60} Under basic conditions of 10\(^{-3}\) M NaOH and 10\(^{-4}\) M NaOH, fluorescence of neutral form disappears and an ionic form (450 nm) appears.\textsuperscript{65,36}

Effects of solvent polarity on absorption and fluorescence properties of XVII are well studied.\textsuperscript{56,57} As compared to change in pH a change in solvent has a very little influence on the longest wavelength absorbance and fluorescence band maxima [Table No.1], this being \(\sim 3-4\) nm for absorbance and \(\sim 4-10\) nm for fluorescence. These small shifts are explained on the basis that the dipole moment of molecule does not change appreciably on excitation. However, it does indicate that there exists a small difference in the dipole moments in the So and S\(_1\) states. This could arise due to intramolecular charge transfer in the excited state (So\(\rightarrow\)S\(_1\)\(\rightarrow\)S\(_{ICT}\)). The energy of S\(_{ICT}\) would necessarily depend on the extent of charge transfer and the polarity of the surrounding media. The anomalous fluorescence at 450 nm in water and formamide could be due to hydrogen bonding in the formation of exciplexes.

XVII Molecule being highly fluorescent is used as molecular probe and label in biological search and in commercial assays.\textsuperscript{67-71} However, these probes
lack functionality for covalent conjugation and require relatively high pH medium \([\text{pH}=9]\) to achieve maximum fluorescence activities.\(^{72}\) It also acts as starting material for the preparation of insecticide Hymecromone.\(^{54}\) The compound XVII has been widely used in fluorimetric assays of enzyme activity. Assay rely on the action of an enzyme on synthetic fluorogenic substrate, usually an ester or ether of XVII. By choice of the excitation and emission wavelengths so that the fluorescence intensity is much greater than that of the substrate, enzyme activity may be monitored by observing the increase in intensity.\(^{73}\)

A novel fluorinated coumarin is reported by Wei chuan sun et al.\(^{23}\) where \(\text{CH}_3\) group from C-4 position is replaced by \(\text{CF}_3\) group and the resulting compound 7-hydroxy - 4-trifluoromethylcoumarin (XVIII) is studied for it's fluorescence and bleaching properties. It gives absorption maximum shifted by 25 nm at higher side (385 nm) than XVII (at 360 nm). A fluorescence maxima is also shifted by 51nm. However, the absorption intensity as well as fluorescence quantum yield are found to be lower than parent compound i.e. XVII.
Compounds with different substituents viz hydroxy, acetoxy and methoxy group at 7-position and each of these substituent in combination with 4-methyl and 4-phenyl are synthesized i.e. (XXI,XXIV,XIX,XXII, XXV). These compounds have been studied together with XVII by Rathi et al. to compare the effect of substituents and solvents on the fluorescence of coumarins. In water and formamide two of those compounds give anomalous fluorescence (508 nm and 509 nm for XIX, 506 nm and 512 nm for XXV and 450 nm and 454 nm for XXIV) because of strong hydrogen bonding between solvent and solute molecules whereas XXI & XXII do not show anomalous fluorescence as the methoxy group at C-7 position is less amicable to form hydrogen bonds. As seen in Table 1 the normal fluorescence for compounds XIX, XXII and XXV which have a phenyl group in position 4, is weak and even absent in some solvents. It appears that the 4-phenyl group facilitates the process of non-radiative transfer of excitation energy. The phenyl group is linked to the rest of the molecule with comparatively weak bond which impairs its rigidity. When the molecule is excited, a part of the excitation energy may find its way to the phenyl group causing twist out of plane rendering the molecule less fluorescent -or non-fluorescent. However, for XIX and XXV
fluorescence in the longer wavelength region in water and formamide is possible due to hydrogen bonding which has a less stabilizing effect on the excited state. The observed lowering in quantum yield for 4-phenyl derivatives (XIX, XXV) than methyl derivatives (XVII, XXI and XXIV) is indicative of the role of phenyl substituent dissipating the excitation energy.\(^{56-58}\) Antiviral and antimicrobial activities of XXIV have been reported by Parmar et al.\(^{79}\) against some gram positive as well as gram negative bacteria. Fungicidal activity of XXI and XXIV is tested against \(A.\ niger\) and \(H.\ Oryzae\) and found to possess and notable activity.\(^{80,81}\)

![Chemical Structure](image)

\[(XX)\]

\(a)\ n = 1\quad b)\ n = 4\)

4-(Carboxy alkyl)-7-hydroxycoumarin derivatives, XXa and XXb have been synthesized\(^{82}\) and studied for their absorption as well as fluorescence behavior.\(^{58}\) The results are included in Table 1. These carboxyl alkyl derivatives are also used as precursors for synthesizing 7-hydroxy-8-(N-alkylaminomethyl) coumarin labels.\(^{59}\)

![Chemical Structure](image)

\[(XXIII)\]
7-Acetoxy-4-(bromomethyl)coumarin (XXIII) was studied for its electrochemical reduction by using cyclic voltammetry and controlled potential coulometry. The electrochemical reduction was seen to proceed as an irreversible three step process [-0.58, -1.63 & -2.25 V] of electrochemical transfer before chemical reaction.83

\[
\begin{align*}
\text{(XXVI)} & \quad \text{(XXVII)} & \quad \text{(XXVIII)} \\
X=\text{H} & \quad \text{a) } X=\text{o-C1} & \quad \text{a) } X=\text{o-NO}_2 \\
\quad & \quad \text{b) } X=\text{m-C1} & \quad \text{b) } X=\text{m-NO}_2 \\
\quad & \quad \text{c) } X=\text{p-C1} & \quad \text{c) } X=\text{p-NO}_2 
\end{align*}
\]

Various 7-benzoyl-4-methylcoumarin derivatives XXVI, XXVII and XXVIII are synthesized by benzoylation of XVII with corresponding benzoyl derivatives.36 These compounds are studied for their absorbance and fluorescence properties and compared with XI to XIV coumarin derivatives. The former compound shows higher stoke shifts and lower quantum yield than the latter compounds in both protic as well as aprotic solvents. For XI to XIV fluorescence life time are close to natural radiative life time \((\tau_N=3.96-4.16, \tau_F=3.48-3.49)\) implying slow rate of intersystem crossing, thus giving high quantum yield \((\sim 0.8)\). However for XXVI, XXVII and XXVIII there seems to be noticeable difference in \(\tau_N\) and \(\tau_F\) values \((\tau_N =7.3 \text{ to } 6.94, \tau_F =4.39 \text{ to } 3.96)\) indicating higher rate of intersystem crossing, leading to lower value of quantum yield (0.6).
Few silylated coumarin dyes (XXIX and XXX) with different linkages and degrees of functionality have been synthesized and incorporated in both SiO₂ xerogels and various solvent hosts. The absorption and fluorescence hosts were examined to explore selected structural and environmental effects on the optical properties of these dyes. Silylated dyes are referred to those dye molecules chemically altered to provide alkoxy silane functionality allowing the active molecule to be covalently bonded to the host. Silylated coumarins had little effect on the absorption and fluorescence spectra in neutral solvent environments. The optical spectra are also less influenced by change in pH.

(XXXI)

a) \( R = \text{COC}_6\text{H}_5 \)

b) \( R = \text{CH}_2\text{COOH} \)
7-Hydroxy 4-benzoylcoumarin (XXXIa) and 7-hydroxyacoumarin 4-acetic acid (XXXIb) are synthesized by condensation of resorcinol with corresponding ethylacetoacetate in presence of H_2SO_4. These have been tested for bacterial activities.\textsuperscript{84-88}

1.3.4 7-Oxygenated 5-Substituted Coumarins

1.3.5 7-Oxygenated 6-Substituted Coumarins

1.3.6 7-Oxygenated 8-Substituted Coumarins

Literature survey reveals that few reports on these compounds, mainly on the synthesis are available. Coumarins with substituents at 5, 6, 8 position are found but they are other than 7-oxygenated.\textsuperscript{89-93}

1.3.7 7-Oxygenated 3, 4-Disubstituted Coumarins

\begin{center}
\includegraphics[width=0.5\textwidth]{XXXII.png}
\end{center}

(XXXII)

Resorcinol on condensation with diethyl α- acetoacetic acid in presence of POCl_3 gave 3-(2'-ethoxycarbonyl)methyl-7-hydroxy 4-methylcoumarin (XXXII).\textsuperscript{79} This compound gives uv absorption peaks at 250 nm, 290 nm(sh) and 322 nm in methanol while \textsuperscript{1}H NMR in DMSO-d_6 at 90 MHz gives a singlet at δ 2.32, quadruplet at δ 4.10 and doublet at δ 6.70 ppm due to
protons associated with -CH₂COOCH₂CH₃ groups and C₄-CH₃ protons give signal at δ 3.60 ppm.

Lederer⁹⁴ synthesized one, XXXIII of the two yellow pigments he isolated from the scent gland of the beaver by the Hurtley condensation reaction of resorcinol with 5-hydroxy 2-bromobenzoic acid in the presence of traces of copper (II) sulphate. Further studies regarding its absorption, fluorescence or structure etc is lacking.

a) R₁ = Cl   R₂ = Me
b) R₁ = Ph   R₂ = Me
c) R₁ = C₂H₅ R₂ = Me
d) R₁ = CH₂COOH R₂ = Me
e) R₁ = C₆H₅CO R₂ = Me
f) R₁ = CH₃  R₂ = Me
The compounds XXXIV a-f are synthesized by condensation of resorcinol with corresponding ethylacetoacetate in presence of condensing agent H$_2$SO$_4$.\textsuperscript{95-98}

1.3.8 7- Oxygenated 4,5/3,5- Disubstituted Coumarins

![Chemical Structure of XXXV](image)

(XXXV)

4-Methyl 5,7 dihydroxycoumarin (XXXV) was synthesized by two different ways from dihydroxy phenol and methyl acetoacetate. In first conventional method (thermal heating) the yield was 45% and was enhanced to ~70% using the method of microwave irradiation.\textsuperscript{34} Time of heating the reaction mixture was also reduced tremendously from 20 h to 10 min. by the latter method. The resultant compound was characterized by $^1$H NMR, $^{13}$C NMR, IR and mass spectral data.

![Chemical Structure of XXXVI](image)

(XXXVI)

4-Methyl-5-fluoro-7- hydroxycoumarin (XXXVI) was synthesized by condensation of fluororescorcinol with $\beta$-keto ester \textsuperscript{99} in the presence of
methane sulphonic acid at room temperature. Its photophysical properties were compared with XXII which showed the minor effects on the absorption and fluorescence wavelength. The pK value also lowered (7.8 to 5.9) on fluorination which results in a significant signal enhancement in absorbance and fluorescence wavelength compared to that for (XVII) for applications in biological systems that are conducted at a near neutral pH.

\[
\text{(XXXVII) } R = -C-NH-(CH_2)_n-Si-(OCH_2CH_3)_3, \\
R' = -C-(CH_2)_3-Si-(OCH_2CH_3)_3
\]

\[
\text{(XXXVIII) } R = -(CH_2)_n-Si-(OCH_2CH_3)_3, \\
R' = -(CH_2)_3-Si-(OCH_2CH_3)_3
\]

The silylated coumarin dyes with propyl linkage XXXVII and XXXVIII are studied for their absorption and fluorescence properties. The results are compared with dyes containing urethane linkages (XXIX and XXX). Dyes with propyl linkage were found to be less affected by local environment (pH) than the dyes with urethane linkage. This is explained on the basis of greater electron transfer in urethane linkage than propyl moieties.
The structures of XXVII and XXVIII are not conducive to form the anionic or zwitterionic species as observed in (XXIX and XXX) based on the fact that propyl linkage would not allow electron transfer.

7-Hydroxy- 4-methoxy-5-methylcoumarin (XXXIX) was synthesized by condensation of orcinol with ethylcyanoacetate and hydrolysis of the resulting product with dilute hydrochloric acid.\textsuperscript{100}

Phenol is treated with an equimolar amount of malonic acid in the presence of two or three molar equivalent each of uhhydrous zinc chloride and phosphoryl chloride at 60-75 °C. The resulting compound XXXX is known as Siderin\textsuperscript{101} and can also be synthesized using orcinol and formic acid by the same procedure used for XXXIX.\textsuperscript{102,103}
1.3.9 7-Oxygenated 4,6/3,6 Disubstituted Coumarins

![Chemical Structure](image)

(XXXXI)

a) R = hexyl  
b) R = Cl  
c) R = Et

4-Methyl-6-hexyl-7-hydroxy coumarin (XXXXIa), 4-methyl-6-chloro-7-hydroxy coumarin (XXXXIb) and 4-methyl-6-ethyl-7-hydroxy coumarin (XXXXIc) have been extensively studied for their absorption and fluorescence spectral behavior.\(^5\)

Introduction of alkyl groups in the 6-position of 4-methyl-7-hydroxy coumarin (XVII) causes a red shift in the fluorescence to 470 nm, 485 nm, and 490 nm for XVII, XXXXIa and XXXXIb respectively. Introduction of 6-Cl (XXXXIc) increases fluorescence emission but the efficiency is not greatly altered on going from $10^{-4}$N acid to $10^{-4}$N alkali. A large shift in absorption (328.4 nm to 373 nm) and a blue shift in fluorescence (485 nm to 455 nm) are observed for chloro compound. However, the fluorescence does not diminish which is in contrast to Zelinskii's generalization\(^10^4\) that groups having a strong dipole-moment with its +ve end on the benzene nucleus and its -ve end on the terminal atom of the group should diminish fluorescence.
a) \( R = \text{CH}_3 \)  

b) \( R = \text{CF}_3 \)

4-Methyl-6-fluoro-7-hydroxycoumarin (XXXIIa) and 4-fluoromethyl-6-fluoro-7-hydroxycoumarin (XXXIIb) are synthesized using similar procedures to that of XXXV. Introduction of fluorine at C-6 position of XVII does not alter the quantum yield but it is strongly affected by replacement of \(-\text{CH}_3\) group with \(\text{CF}_3\). (0.64 to 0.44).\(^{22}\)

Mattoo\(^{58}\) has reported spectral studies of 4-methyl-6-ethyl-7-acetoxy coumarin (XXXIII). On acetylation of hydroxy group of C-7 position of the XXXXIa, the fluorescence efficiency decreases but spectral distribution is not altered. This may be due to weaker mesomeric effect of acetoxy group compared with that of hydroxy group.
6,7-Diacetoxy-4-methylcoumarin (XXXIVa) and 6,7-diacetoxy-4-phenylcoumarin (XXXIVb) have been synthesized and studied for their fluorescence and absorbance in different organic solvents. The observations are listed in Table 1. The effects of polysubstitution are much more complicated since the overall electron mobility is determined by the combined effects of the substituents. A single fluorescence band in the region 416-425 nm which is fairly broad and its shape indicates that it could be due to overlap of two unresolved bands possibly lying in the normal and anomalous region. The effect of replacing methyl group by phenyl in position C-4 resulted in shifting of $\lambda_a$ & $\lambda_b$ to longer wavelengths. This indicates conjugation effect due to resonance interaction which reduces activation energy and hence shift towards longer wavelength is observed. As the shift is comparatively small (342 nm to 357 nm) it can be attributed to the non-planarity of the molecule caused by steric hinderence of the phenyl substitution.
4-Methyl-7-hydroxy-8-acetylcoumarin (XXXXVA) has been synthesized and studied for its optical properties. On comparison with XVII, the acetyl group considerably reduces the fluorescence efficiency, in spite of an increase in resonance, as is apparent from absorption data. The inhibiting effect of the 8-acetyl group cannot be explained by presuming shift of the fluorescence band to the infra-red region because the fluorescence is observed in the visible region though the efficiency is less. The inhibition can be explained on the basis that movement of the charge from the hydroxyl group to the pyrone (C = O) group is hindered by the presence of an O-acetyl group.

\[
\begin{align*}
\text{(XXXXVVA)} \\
\text{a) } R_1 = \text{C}_6\text{H}_5, R_2 = \text{OH} \\
\text{b) } R_1 = \text{CH}_3, R_2 = \text{OH}
\end{align*}
\]
Condensation products of pyrogallol and corresponding acetoacetate in presence of H₂SO₄ are isolated as 4-substituted 7, 8-dihydroxy coumarins (XXXXVB a and b). However, further studies regarding their optical properties as well as biological activities are seem to be lacking.

\[(\text{XXXXVIB})\]

a) \(R₄ = \text{OC}_₂\text{H}_₅, R = \text{OCH}_₃\)

b) \(R₄ = \text{N(CH₃)}₂\)

c) \(R₃ = \text{Br}, R₅ = \text{Br}, R₆ = \text{OH}\)

d) \(R₃ = \text{CH₃}, R₆ = \text{OH}\)

e) \(R₄ = \text{Cl}\)

Several 3-(7-hydroxy-4-methylcoumarin-8-yl)-5-arylisoaxazoles (XXXXVI) were synthesized by condensation of hydroxylamine hydrochloride with 7-hydroxy-4-methylcoumarin-8-yl chalcones.
The chalcones (XXXXVII a to h) were prepared through the condensation reactions between 8-acetyl-7-hydroxycoumarin and aromatic aldehydes. All these compounds are found to be notably active against a fungi *A. niger* and *H. Oryzae*.80
a) $R_2 = \text{OCH}_3$, $R_3 = \text{Cl}$

b) $R_2 = \text{CH}_3$, $R_3 = \text{NO}_2$

c) $R_3 = \text{NO}_2$

d) $R_2 = \text{Cl}$, $R_3 = \text{NO}_2$

e) $R_2 = \text{NO}_2$, $R_3 = \text{NO}_2$

f) $R_2 = \text{NO}_2$, $R_3 = \text{NO}_2$, $R_5 = \text{Br}$

\[
\begin{align*}
\text{(a)} & \quad \text{R}_2 = \text{OCH}_3, \quad \text{R}_3 = \text{Cl} \\
\text{(b)} & \quad \text{R}_2 = \text{CH}_3, \quad \text{R}_3 = \text{NO}_2 \\
\text{(c)} & \quad \text{R}_3 = \text{NO}_2 \\
\text{(d)} & \quad \text{R}_2 = \text{Cl}, \quad \text{R}_3 = \text{NO}_2 \\
\text{(e)} & \quad \text{R}_2 = \text{NO}_2, \quad \text{R}_3 = \text{NO}_2 \\
\text{(f)} & \quad \text{R}_2 = \text{NO}_2, \quad \text{R}_3 = \text{NO}_2, \quad \text{R}_5 = \text{Br}
\end{align*}
\]
Lokhande and Rangnekar\textsuperscript{34} have studied 3-substituted 8-aryl - 7 hydroxycoumarin (XXXVII to (L)). Condensation of resorcinol with conjugated enol ethers in presence of sodium ethoxide followed by cyclization of the resulting compounds in \textit{situ} with hydrochloric acid afford the 3-substituted 7-hydroxycoumarins which undergo coupling reaction with suitable aryl diazonium salts to yield these compounds. These monoazocoumarin derivatives are highly coloured and when applied as disperse dyes on polyester and polyamide fibers, showed good pick-up and fastness with brilliant yellow to red shades. The exhaustion of the dyes was found to be better in the case of polyamide as compared to polyester fibers.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

(LI)

\begin{itemize}
\item [a)] \( R = H \)
\item [b)] \( R = Cl \)
\item [c)] \( R = Br \)
\item [d)] \( R = I \)
\item [e)] \( R = NO_2 \)
\item [f)] \( R = CH_3 \)
\item [g)] \( R = OCl_3 \)
\item [h)] \( R = COOH \)
\item [i)] \( R_1 = COOH \)
\item [j)] \( R = OH \)
\item [k)] \( R_1 = OH \)
\item [l)] \( R = SO_3H \)
\item [m)] \( R = N(CH_3)_2 \)
\end{itemize}
Y. M. Issa et al\textsuperscript{109} have synthesized (LI) compounds and proton ligand stability constant of these compounds and their metal complexes with Ce\textsuperscript{III}, Th\textsuperscript{IV} and UO\textsuperscript{III} ions have been determined pH metrically in 60% (V/V) ethanol: water mixture at 25 °C and at $\mu = 0.1$. The order of stability constants was found to be Th\textsuperscript{IV} > Ce\textsuperscript{III} > UO\textsuperscript{II}. 1:1 and 1:2 (M:L) complexes are formed as evidenced by conductometric studies. The complex have been isolated in solid state and characterized on the basis of elemental and thermal analysis and IR and $^1$H NMR spectral data.

\begin{itemize}
  \item [a)] $R_1, R_2 = -(\text{CH}_2)_2 -O-(\text{CH}_2)_2$-
  \item [b)] $R_1, R_2 = -(\text{CH}_2)_5$-
  \item [c)] $R_1, R_2 = -(\text{CH}_2)_4$-
  \item [d)] $R_1, R_2 = -C_2\text{H}_5$-
  \item [e)] $R_1 = \text{benzyl}, R_2 = \text{H}$
\end{itemize}
Adamecyzk et al. synthesized five new 7-hydroxy 8-(N alkyl amino methyl coumarin [LII a- e] which were prepared from 4-(4-carboxybutyl)-7-hydroxy coumarin (XX), in yield 28-48%. As compared to XVII, substitutions at the 8-position of coumarin nucleus with a functionality such as an aminomethyl group that can form strong hydrogen bond with phenolic hydroxy group lowered the pK of the phenolic group and exhibited higher emission intensity over a broader pH range.

1.3.11 7-Oxgenated 3,4,5/3,5,6/3,5,8-Trisubstituted Coumarins

![Coumarin structure diagram]

(LIII)

a) R1 = Cl, R2 = CH3, R3 = OH
b) R1 = CH3, R2 = CH3, R3 = OH
c) R1 = C2H5, R2 = CH3, R3 = OH
d) R1 = C6H5, R2 = CH3, R3 = OH

Compounds (LIII a-d) are synthesized by condensation of phloroglucinol with corresponding esters in presence of H2SO4 as condensing reagent and characterised by IR, NMR and elemental analysis.110-111
Another derivative of this class has also been reported. 3-(2'-Ethoxycarbonyl)methyl-5,7-dimethoxy-4-methylcoumarin (LIV) is synthesized by the condensation of phloroglucinol with diethyl α-acetosuccinate in the presence of POCl₃ and methylation of the resultant product. Compound LIV shows two absorption bands in UV region at 250 nm and 320 nm in methanol. It is further characterised by using ¹H NMR, ¹³C NMR and mass spectroscopy.

1.3.12 7-Oxygenated 5,6,8 / 3,6,8 / 4,6,8 Trisubstituted Coumarins.

(LV) \( R₁ = H, \quad R₂ = CH₃ \)

(LVI) \( R₁ = COOC₂H₅, \quad R₂ = H \)

(LVII) \( R₁ = COOH, \quad R₂ = H \)

(LVIII) \( R₁ = H, \quad R₂ = CF₃ \)
6,8-Difluoro-7-hydroxy-4-methylcoumarin (LV), 3-carboethoxy-6,8-difluoro-7-hydroxycoumarin (LVI), 3-carboxy-6,8-difluoro-7-hydroxycoumarin (LVII) and 3-trifluoromethyl-6,8-difluoro-7-hydroxy coumarin (LVIII) are reported as fluorescent dyes. Their absorbance and fluorescence parameters are compared with the parent coumarin derivative XVII. For compound LV & LVIII absorption maxima, fluorescence maxima and $\varepsilon_{\text{max}}$ values remained almost unaltered. However, $pK$ values are found to be lowered. In case of LVI & LVII absorption maxima are shifted to higher side (~ 360 nm to 400 nm) while fluorescence remain unchanged. Molar extinction coefficient values are also enhanced to $30 \times 10^3$ from $17 \times 10^3$ moles liter$^{-1}$ cm$^{-1}$. $pK$ values are reduced to almost half (7.5 to 7.8). Both these compounds are suggested to have the most desirable photophysical properties. Their lower $pK$, increased resistance to photobleaching and higher quantum yields make them superior dyes for use as probe molecules in biological systems.

\[(\text{LIX}) \quad R = \text{Acetyl}\]

\[(\text{LX}) \quad R = \text{Cinnamoyl}\]

\[(\text{LXI}) \quad R = 8-(p-OCH_3) \text{Cinnamoyl}\]
8-Substituted-4-methyl-6-ethyl-7-hydroxycoumarin derivatives are compared for their spectral properties by changing the substitution at C-8 position from acetyl (LIX) to cinamoyl (LX) to 8-(p-OCH₃)-cinnamoyl (LXI). Out of these three, LIX shows fluorescence maxima at 465 nm while the latter two show no fluorescence. On recalling discussion regarding XXXXIV, complete inhibition of fluorescence is expected as we pass from acetyl to cinamoyl to p-methoxy cinnamoyl group at 8-position.

![Chemical structures](image)

(LXII) $R_1 = \text{C}_6\text{H}_5$, $R_2 = \text{OCOCH}_3$

(LXIII) $R_1 = \text{CH}_3$, $R_2 = \text{COOC}_6\text{H}_5$

(LXIV) $R_1 = \text{CH}_3$, $R_2 = \text{OH}$

Condensation of 4-ethyl-2-acetylresorcinol with ethyl benzoyl acetate and ethyl acetoacetate gives compounds 4-phenyl-6-ethyl-8-acetoxy-7-hydroxycoumarin (4-methyl-6-ethyl-8-benzoyl-7-hydroxycoumarin, 7,8-dihydro-4-methylcoumarin (LXII & LXIII) and compound (LXIV) was obtained by condensation of the 4-ethyl pyrogallol with ethyl acetoacetate. However, further studies regarding their optical properties as well as biological activities have not so far been reported.
Issa et al.\textsuperscript{116} have synthesized some new mono azo dyes (LXV) derived from 6, 7 dihydroxycoumarin and their electronic spectra have been investigated in organic solvents of varying polarities. The spectra in ethanol, display mainly five bands which are assigned to their appropriate electronic transitions. The effects of substituents on absorption spectra have been investigated. The important IR bands and \textsuperscript{1}H NMR signals are assigned and discussed in relation to molecular structure. The presences of intramolecular hydrogen bonding and quinone – hydrazone tautomerism within molecules have been demonstrated from IR spectra. The biological activities of the azo compounds
towards some filamentous microscopic fungi, yeasts and bacteria have also been studied.

1.3.13 Other Coumarins

Beside I to LXV, there are several other coumarin derivatives which have been reported. But we have included only those studied for their optical properties and structural resemblance to that of XVII as well as coumarin derivatives having simpler common substituents or those without long chain substituents at other positions.

It is well-known that for designing a good laser dye from coumarin, it is essential to have a donor substituent preferably bearing oxygen or nitrogen at C-7 position.

\[
\begin{align*}
\text{(LXVI)} \\
\begin{array}{c}
\text{H}_2\text{N} \\
\text{O} \\
\text{R} \\
\text{O} \\
\end{array}
\end{align*}
\]

(a) \( R = \text{CH}_3 \)  \hspace{1cm} (b) \( R = \text{CF}_3 \)

\textit{m-} Amino phenol on condensation with acetoacetic ester yielded 7-amino-4-amino 4-methyl coumarin (LXVIa)\textsuperscript{117} which belongs to an important group of laser dyes in the blue – green spectral region.\textsuperscript{118, 119}
a) \( R_1 = \text{CF}_3, \ R_2 = -(\text{CH}_3)_2\text{N} \)

b) \( R = \text{CF}_3 \)

a) \( R = \text{CH}_3 \)

b) \( R = \text{CF}_3 \)
It is well known that the first excited singlet-singlet state $S_1$ of these molecules has a high dipole moment resulting from the electron donor nature of the amino group and the electron acceptor nature of the carbonyl group. The $S_1$ charge transfer character grows with increasing the alkylation degree of the amino group (LXVII to LXXII)$^{120,121}$ resulting in an increased stabilization of the excited state.$^{122,118,123}$ The high dipole moment of $S_1$ state leads to very large stoke shifts strongly dependent on the solvent polarity which correlate$^{123}$ with the solvent polarity parameter $\alpha$ $^{124}$ or the hydrogen bonding parameter, $\alpha$ $^{125}$ making 7-aminocoumarins popular probe molecules in time dependent fluorescence stoke shift (TDFSS) measurements.$^{126-142}$ Detailed parameters for all amino coumarins (LXVII to LXXII) are listed in Table 1.

\[
\begin{align*}
\text{(LXXIV)} \\
a) & \quad R = H \\
b) & \quad R = \text{COCH}_3 \\
c) & \quad R = \text{COph}
\end{align*}
\]

\[
\begin{align*}
\text{(LXXIII)} \\
a) & \quad R = H \\
b) & \quad R = \text{phenyl} \\
c) & \quad R = p-\text{chlorophenyl} \\
d) & \quad R = p-\text{methoxyphenyl}
\end{align*}
\]
Some 3-aryl-7-substituted aminocoumarins LXXIII, LXXIV and LXXV show intense blue fluorescence and good light fastness and hence constitute an important group of optical brighteners for synthetic fibers i.e. polyamide and polyesters. 40

Giri et al. 57 studied the absorption and fluorescence emission of substituted coumarins in different solvents. It is observed that substitution alters both the absorption and fluorescence emission maxima. These shifts are discussed in terms of the change in mobility of \( \pi \)-electrons mainly determined by the nature and position of substituent in parent compound.

In LXXVI fluorescence maxima was observed at \( \sim 385 \) nm. The absorption and normal fluorescence maxima shifted to longer wavelengths as group at position -7 is changed as discussed earlier for compound XVII and XVI (i.e. \( \text{CH}_3 \rightarrow \text{OCH}_3 \rightarrow \text{OH} \)). Compound XVII and XVI containing non-bonding electron on oxygen contribute towards the increase of \( \pi \)-electrons on
benzene ring but in the case of compound LXXVI, substituent -CH$_3$ does not produce any such change in the electron mobility.

\[
\begin{align*}
\text{(LXXVII)} \\
&\text{a) } R_1 = \text{OH}, \quad R_2 = \text{H} \\
&\text{b) } R_2 = \text{OH}, \quad R_1 = \text{H} \\
&\text{c) } R_1 = \text{COOCH}_3, \quad R_2 = \text{H} \\
&\text{d) } R_2 = \text{COOCH}_3, \quad R_1 = \text{H}
\end{align*}
\]

The presence and position of the hydroxy group is a deciding factor in the fluorescent property of coumarins. Strongest fluorescence is observed in compound XVII which may emits strong blue fluorescence but in case of compounds LXXVIIa and LXXVIIb, the spectral distribution of the emission also differ. According to Balaiah$^{143}$ for 5-OH coumarins the fluorescence shifts to infra-red, due to “deeper” absorption. However, this view has been contradicted by Mattoo$^{58}$ who ascribe the efficiency of 6-OH coumarin to the inability of hydroxy groups to produce additional resonance. The 5-OH coumarin has still lower efficiency. Introduction of alkyl group at position 5 or 6 (LXXVIIc) and (LXXVIIId) reveal bathochromic shift.$^{58}$

\[
\begin{align*}
\text{(LXXVIII)}
\end{align*}
\]
Elnagdi et al. have synthesized dicoumarins (LXXVIII) by condensation of β-resorcylaldehyde with ethyl(5-cyanomethyl 1,3,4-oxidizol-zyl) acetate in 2:1 molar ratio in ethanol in presence of pipyridine as a catalyst. These dicoumarins show intensive anticoagulant activity and are used in thrombolism.

\[
\text{LXXIX) a) } R=\text{OMe} \\
\text{b) } R=\text{NEt}_2
\]

\[
\text{(LXXX) a) } R=\text{OMe} \\
\text{b) } R=\text{NEt}_2
\]

\[
\text{(LXXXI) R = } -p-(\text{OEt})_2
\]

\[
\text{(LXXXII) R}_1 = \text{COOEt}
\]
Heterocyclic analogs of coumarin are phosphanocoumarins studied by Chen et al.\textsuperscript{145} In this class, lactone oxygen is replaced by a hetero atom, phosphorous. In same incidences a hetero atom is found to be nitrogen\textsuperscript{146} or sulphur.\textsuperscript{147} Phosphanocoumarin derivatives contain electron-withdrawing phosphoryl ester function at C-3 position of coumarin nucleus (LXXIX). Other derivatives reported are (LXXX to LXXXIII), out of these five, only hetero substituted coumarins having quantum yield of fluorescence comparable to that of corresponding laser coumarin dye (LXXXIII) are the julolydyl derivatives (LXXXII) and (LXXXI). Their stoke shifts are consistently larger which could favour an increase in lasing efficiency because of the decrease in overlap between absorption and emission spectra.

![Chemical Structure](image)

(LXXXIV)

a) \(R=0\text{-}OC_2H_5\), \(R_1=m\text{-}Cl\)  
b) \(R=0\text{-}OC_2H_5\), \(R_1=m\text{-}CH_3\)

c) \(R=0\text{-}OC_2H_5\), \(R_1=0\text{-}OCH_3\)  
d) \(R=p\text{-}Br\), \(R_1=H\)

e) \(R=p\text{-}Br\), \(R_1=m\text{-}CH_3\)  
f) \(R=p\text{-}Br\), \(R_1=m\text{-}OCH_3\)

g) \(R=p\text{-}Br\), \(R_1=p\text{-}Cl\)  
h) \(R=p\text{-}Br\), \(R_1=p\text{-}OCH_3\)

Compounds bearing azo groups and azocoumarins exhibit various biological activities. Jolly et al.\textsuperscript{148} have synthesized 6-(O-alkyphenyl azo) coumarin 3-carboxyanilide (LXXXIV) by condensation of malonic acid with
5-(O-ethoxyphenyl) azo salicyaldehyde. Compound LXXXIVa was evaluated for antifungal activity by agar-plate food poisoning technique in 500 and 1000 ppm concentration and were found to be feebly active against *Alternaria alternata*, *Rhizopus arrizus* and *Aspergillus niger*. The compounds LXXXIVb-e were tested for antibacterial activity against *S.aureus* and *E. coli* using cup-plate technique and the percent control is found in the range 15-30%. Compounds LXXXIVc-h were evaluated for *in vitro* HIV activity which involves susceptible human host cell and the percent control on the infected plate was found in the range 8.26%.

![Chemical Structure](LXXXVA)

a) $R_1 = \text{CH}_3$

b) $R_1 = \text{CH}_3, R_6 = \text{OCH}_3$

c) $R_1 = \text{CH}_3, R_4 = \text{Cl}$

d) $R_1 = \text{CH}_3, R_6 = \text{NO}_2$

e) $R_1 = R_4 = \text{NO}_2$

f) $R_1 = \text{CH}_3, R_4 = R_6 = \text{Br}$

g) $R_1 = \text{C}_6\text{H}_5, R_4 = \text{Cl}$

h) $R_1 = \text{C}_6\text{H}_5, R_6 = \text{OCH}_3$
Rajeshwar Rao and Padmanabha have synthesized a number of thiazoyl and benzoxazinyl coumarins \( \text{LXXXVA} \) and \( \text{LXXXVB} \) and tested for their antibacterial activities. Coumarin bearing one or more phenolic groups and containing pyridyl moiety at 3-position are spasomolytic and uricosuric agents. Further, thiazoles \(^{151}\) and benzoxazines \(^{152}\) possess an array of biological activities. They envisaged that incorporation of these heterosystems in a coumarin nucleus may impart enhanced biological activity to the resulting compounds.

A convenient one pot synthesis of 3-\((\text{substituted sulphanilamido})\) \(6\)-bromo/6-Chloro 1-benzopyran \(-\) 2\(\text{(II)}\) ones has been achieved by condensing
the corresponding salicyaldehyde with Na-salt of substituted p-acetamidobenzene sulphonyl glycine in presence of acetic unhydride and hydrolysing the product\textsuperscript{153}. The screening was carried \textit{in vitro} against highly virulent H\textsubscript{37} R\textsubscript{v} stains of mycobacterium tuberculosis var hominis using Youman liquid method.\textsuperscript{154}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{LXXXVII.png}
\caption{LXXXVII}
\end{figure}

\begin{align*}
\text{a) } R_1 &= H, \quad R_2 = \text{CH}_3, \quad R_3 = H, \quad R_4 = \text{Br} \\
\text{b) } R_1 &= H, \quad R_2 = H, \quad R_3 = \text{Br}, \quad R_4 = \text{H} \\
\text{c) } R_1 &= H, \quad R_2 = \text{OH}, \quad R_3 = H, \quad R_4 = \text{Br} \\
\text{d) } R_1 &= \text{CN}, \quad R_2 = \text{CH}_3, \quad R_3 = H, \quad R_4 = \text{Br}
\end{align*}

Subha Rao et al.\textsuperscript{155} have synthesized 6-and 7-halo coumarins by direct condensation procedures. In tests using fish, the compound 7-bromo -4-methylcoumarin (LXXXVIIa) is most active among the compounds tested. The corresponding 6-Bromo compound has less toxicity. The introduction of a hydroxyl group at 4-position of 7-halo coumarins or a cyano group at 3-position of 7-halo 4-methylcoumarins does not seems to improve the toxicity but on the other hand to have a retarding effect.
1.4 Aim and Nature of Work

The literature survey reveals that, the use of coumarin dyes have found many applications in the field of laser technology. Many coumarin derivatives have been used as lasing medium. They are found to be capable of yielding high peak powers in short pulses and which further enables shifting of lasing wavelength by making slight changes in the composition of the dye or by making suitable changes in the solvent medium. A good laser dye should possess a strong absorption with high molar extinction coefficient and high quantum yield of fluorescence. Some azo substituted coumarin derivatives are also reported as good disperse dyes for polyester fibers.

It is known that coumarin derivatives and thiazoles posses an array of biological activities. The incorporation of thiazole system in coumarin nucleus may impact an enhanced biological activity of resulting compound.

In view of potential interesting dyeing properties and biological activities, it was considered worthwhile to attempt synthesis of some new thiazolyl azocoumarin derivatives.

In first step, substituted 2-aminothiazoles have been synthesized using known procedures. These aminothiazoles then diazotised to obtain dizonium salt solution and finally been coupled to a well known coumarin derivative viz 7-hydroxy-4-methylcoumarin. The resulting compounds were first characterised using elemental analysis, infrared, $^1$H NMR and powder X-ray diffraction spectral studies in order to evaluate their structural features.
These compounds were expected to contain a azo chromophore in addition to a lactone ring of 7-hydroxycoumarin and hence should have very good dying properties. Their optical properties have been studied in different solvents as well as in different chemical environments i.e. pH.

Fluorescence properties of these compounds have been also studied in different solvent and at different pH. Attempts were made to calculate quantum yield of fluorescence in favourable cases.

The effect of azo-thiazole substituents in parent molecule i.e. 7-hydroxy-4-methylcoumarin have been studied to examine the changes in optical properties due to substitution.

Finally antifungal and antibacterial activities of these compounds have been studied against available fungi and microorganisms by using cup plate method. The details of all above are given in the succeeding chapters.
Table No. 1  Electronic spectral data and fluorescence spectral data of reported compounds.

<table>
<thead>
<tr>
<th>Comp. No</th>
<th>7ml 10⁻⁴N NaOH + 93 ml EtOH</th>
<th>3ml B.A. + 97 ml EtOH</th>
<th>7ml 10⁻⁴N NaOH + 93 ml DMSO</th>
<th>3ml B.A.+ 97 ml DMSO</th>
<th>7ml10⁻⁴ N NaOH +93 ml DMSO</th>
<th>5 ml B.A. +97 ml DMSO</th>
<th>5 ml B.A. +95 ml CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>412nm</td>
<td>202nm</td>
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* ε_max values in [lit mole⁻¹ cm⁻¹]

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ε<sub>max</sub> in lit mole⁻¹ cm⁻¹

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\( \varepsilon_{\max} \) values in \ liter mole\(^{-1}\) cm\(^{-1}\)

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</tr>
<tr>
<td>L XXXII</td>
<td>41.00</td>
<td>420</td>
<td>478</td>
<td>--</td>
<td>62</td>
</tr>
<tr>
<td>L XXXIII</td>
<td>47.00</td>
<td>436</td>
<td>480</td>
<td>--</td>
<td>68</td>
</tr>
<tr>
<td>L XIXa</td>
<td>380</td>
<td>450</td>
<td>--</td>
<td>--</td>
<td>0.92</td>
</tr>
<tr>
<td>L XIX b</td>
<td>406</td>
<td>522</td>
<td>--</td>
<td>--</td>
<td>0.85</td>
</tr>
<tr>
<td>L XIX c</td>
<td>378</td>
<td>458</td>
<td>--</td>
<td>--</td>
<td>1.00</td>
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<tr>
<td>L XIX d</td>
<td>413</td>
<td>522</td>
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<td>--</td>
<td>0.75</td>
</tr>
</tbody>
</table>

$s_{\text{max}}$ values in moles liter$^{-1}$ cm$^{-1}$

Contd..
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