CHAPTER - I

INTRODUCTION
Untill the middle of 19th century the natural dyes and pigments were mainly used for imparting colour on the natural fibers. With the advent of the first synthesised dye in 1850 by Perkin, in an attempt to prepare quinine, new approach for dye synthesis was made available (1). Since then numerous dyes have been synthesised and with the incorporation of different moieties in the dye synthesis, dyes of varied properties were obtained (1). Hence, the utility of these dyes have been increased and made them applicable in various fields, viz. non-toxic dyes for food colour, thermally stable dyes in plastic industry, as drugs in medical science, as indicators in analytical field and as an optical brightening agent and fluorescent dyes.

With the development of newer technology, the applicability of the organic dyes/colourant increased to a greater extent. In the last few decades the applications have been extended in high technology (2), i.e. for thermal printing colour imparting property of dye, whereas for photocopying and laser printing the photo conduction and electrical charging property is utilised (3). In the electronic field organic dye is employed in device, viz. dye for liquid crystal, solar cells, dyes for nonlinear optics and dyes for microcolour filters etc. Laser is one of the high technology field where fluoresceing property of dye is exploited.

Laser is an abbreviated form of Light Amplification by Stimulated Emission of Radiation. In other words, laser is a light amplifying device by means of which monochromatic radiation of high spectral and geometrical intensity can be obtained.
For a molecule or atom to exhibit the stimulated emission, it must be capable of exciting to one of the higher vibrational level and must have vacant energy level of the lower vibrational level. Laser emission takes place when irradiated radiation interacts with the molecule or atom existing in an excited state, thereby causing the molecule to decay, by emitting a radiation, to lower energy level (3).

Gases like CO\textsubscript{2}, N\textsubscript{2}, He-Ne (mixture), Kr, Ar are gaseous molecule and for excimer (i.e. excited dimers) laser like KrF, KrCl, XeF, XeCl, etc. were being employed as a active medium for laser, which were capable of undergoing fluorescent transition from excited energy level to lower energy level. Some of the metal ion incorporated in the crystal and addition mixture are also good active medium for solid laser. e.g. ruby crystal, Nd - YAG (neodymium-yttrium aluminium garnet), Ga-Al-As (gallium-aluminium-arsenate) etc. (4,5). The main drawback of gas and solid laser is that they emit specific wavelength.

Liquid laser is also called dye laser, because it employs the organic fluorescent dye as an active material in solution. Since, the fluorescent dyes are employed as active medium, the laser radiation is obtained within the fluorescent band of dye employed. The main advantage of dye laser is that they are tunable over the fluorescent band of the dye (i.e. in the range 10-100nm) (6). Since different dye fluoresces at different wavelength, the laser generation from the dye covers the whole spectral region (300-1000 nm i.e. violet, visible and near infrared).
The idea of organic lasers was given by Brock et al (7) and independently by Rautian and Sobel'man (8). They proposed the use of meta-stable triplet-state of the conjugated molecules for laser generation. Morantz et al (9) reported to have achieved the emission by above mentioned method, but Lempicki et al (10) and Smith et al (11) when tried to repeat the same they found that triplet-singlet transition hindered the emission. Although, Stockman et al (12) found that fluorescence phenomenon was advantageous as compared to phosphorescence but they failed to obtain the laser emission from ethanolic solution of perylene.

The stimulated emission was successfully produced in 1963 by Lempicki et al (13) from rare earth chelate complex. But in that the energy absorbed by ligand is transferred to luminophore metal ion which in turn emitted the laser radiation.

In 1966 Sorokin and Lankard obtained first true organic laser action from ethanolic solution of chloro-aluminium phthalocyanine (14) when excited by giant pulse of Ruby laser. Similar visible coherent radiation from a number of organic dyes excited by giant pulse of Ruby laser were reported by Schafer (15), Speath et al (16) and others (17,18) within short span of time. The first tunable laser radiation was obtained by Soffer and Mcfarland (19) in 1967.

The theory and instrumentation for laser generation from dyes is well documented by Webb (20) and various improvisation in the instrument has been done as per requirement. The theory is well explained by eigenstate diagram of the typical dye.
TRIPLET STATE

SINGLET STATE

\[ t_n^s = 1 \text{ ps} \]

\[ t = 10 \text{ ns} \]

\[ t = 1 \text{ ns} \]

\[ t = 10 \mu\text{s} \]

FIG. 1: EIGENSTATES OF TYPICAL DYE MOLECULE

--- RADIATIVE TRANSITION

--- NON-RADIATIVE TRANSITION
The energy level diagram shows singlet state $S_0, S_1, S_2,$ etc. and the triplet state $T_1, T_2,$ etc. of a dye, which portrays broad and almost continuous band because of large number of vibrational state of the dye and its interaction with that of solvent molecule. At equilibrium all dye molecules occupies lowest vibrational level of $S_0$. When dye molecule is excited by absorbing a radiation it passes to the first excited singlet state of $S_1$, sometimes it might reach to the $S_2$ (second excited state vibrational level). From $S_2$ and from higher vibrational level of $S_1$ by vibrational relaxation it reaches the lowest vibrational level of $S_1$ in $10^{-11}$ - $10^{-12}$ seconds. Hence, the population of the molecule in other vibrational level will be negligible as compared to ground state vibrational level of $S_1$. From $S_1$, molecule reaches to the higher vibrational level of $S_0$ by spontaneous or stimulated emission of fluorescence photon. The relaxation to lowest vibrational level of $S_0$ via thermal equilibrium occurs in $10^{-11}$ - $10^{-12}$ seconds. For this reason dye molecule always encounter the empty vibrational level in transition from the lowest $S_1$ to $S_0$. Hence, low population of excited state $S_1$, is sufficient for laser process.

Some dye molecule reach the triplet state $T_1$ from the vibrational level of $S_1$ by means of spin forbidden transition, which is also called intersystem crossing. This state is occupied in $10^{-6}$ sec., so for a very short pulse of excitation, this intersystem crossing will not interfere, but for a long excitation pulse and for continuous laser operation the high population can build up in $T_1$, and this molecule further absorb the energy and excite to $T_2$, $T_3$ etc. Since, this T-T absorption band often lies in the same spectral region as that of laser emission, there is a loss of emitted radiation energy due to self absorption. Hence, for the laser generation from the dye, T-T absorption play a major role.
The theory of laser generation from the dyes show that triplet absorption present over the fluorescence band of an organic dye reduce the quantum fluorescent yield of a dye. Pavlopoulos and Hammond (21) gave the theory regarding introduction of the new substituent by auxochromic group in the laser dye and described that “For obtaining new and possibly better laser dye, there are only two main constellation where substitution by auxochromic group will yield a potential laser dye. That is, a compound which has only a small triplet absorption over the fluorescence region. If, in addition the substitution yeilds a compound with a fluorescence quantum yield ($\Phi_f$) close to unity, then in that respect at least a new laser dye will have been synthesised” (21).

Knowing the nature of substituent group and its location and the polarisation characteristic of the singlet-singlet absorption band and triplet-triplet absorption band located near fluorescence region of the chromophore, it is possible to predict the extent of T-T absorption present over the fluorescence band of organic dye (21).

In the initial stage the existing organic fluorescence dyes were examined for laser generation. Warden et al (22) divided the laser dye on the basis of the chromophoric group present in the dyes. i.e. dyes with choromophore were called classical laser dyes and dyes without choromophore were called scintillators.

Laser dyes can be catagorised on the basis of structural moiety present and also the specific class of dyes lase in specific tuning range, although, several factors affect tuning range apart from substitution in the moiety. Solvent and optical pumping also shifts the tuning range of the dye.
The most short wave generation (\( \equiv 310 \text{nm} \)) can be obtained from p-terphenyl and its derivatives (23). The planerisation of these oligophenyl by ortho-linkage with hetero atom or by ethylenic double bond causes bathochromic shift but it increases the photostability of the dye (24).

The stilbene and distyryl benzene derivatives generate laser radiation in the violet and near UV range (23,25). Hetero-analogues of the distyryl benzene are also efficient laser generating compound (26,27) which covers 417 - 490 nm range. The important examples are PPO., PyPO, PPD etc. (28,29).

The coumarin dyes which covers the 400 - 600 nm range of the visible spectra are one of the most active laser generating compounds (30). The structural modification of the coumarin dye, by substituting the carbonyl group by phosphorous containing group and oxygen of carbonyl group by imino or dicyanomethylene group, lased in the 600-700 nm (31-33).

The other class of the laser dyes which resembles coumarin are pyrylium and thiopyrilium salts (34,35) which covers 600 - 700 nm and extends upto 800 nm.

The amino xanthanes i.e. rhodamine B1, rhodamine 6H, sulphorhodamine etc are best known and widely known laser generating dyes. It covers 600-750 nm of visible spectrum (14).
The oxazine dyes which are aza-analogues of rhodamines which shows bathochromic shift as compared to rhodamine (36) covers the 700-800 nm.

Polymethine dyes lases in the near IR spectral range (37). However heterocyclic substituted polymethine dye covers ultra-far spectral range. The important examples are pyrylocyanines and thiopyrylocyanines (38-40).

Substitution in coumarin with auxochromic group at 7-position leads to highly fluorescent compounds and are useful as fluorescent dye or as fluorescent brightening agent. Among this, 7-hydroxy and 7-alkoxy coumarin are useful fluorescent brightening agent while 7-amino or substituted amino coumarin are useful as fluorescent dyes.

In the initial stage of dye laser the existing fluorescent dyes and fluorescent brightening agents were checked for laser generation and found that two different class of coumarin i.e. 7-hydroxy and 7-amino and substituted amino coumarin were having better laser generation property. The literature reveals that two different approaches were being taken for obtaining better laser generation from the dye.

1. By studying various parameters which affect the laser emission from the existing coumarin laser dyes.
2. By making substitution in existing coumarin laser dye and by structural modification of existing coumarin laser dyes.
7-dimethylamino-4-methyl coumarin and 7-hydroxy-4-methyl-coumarin are the oldest coumarin dyes which were synthesised by Von-Pechmann in 1899 (41). The other analogous dyes are 7-amino-4-methyl-coumarin and 7-diethylamino-4-methyl-coumarin.

In the review of the literature on the coumarin laser dyes, it is divided on the basis of substitution at 7-position of coumarin i.e.

- 7-amino coumarin,
- 7-diethylamino coumarin,
- 7-hydroxy coumarin.

The brief review on the various modifications made in the coumarin dyes of the above classes is described.

1. 7- Amino Coumarin

In this class 7-amino-4-methyl-coumarin is the most explored dye among the 7-amino coumarin. It was synthesised by Gauthier et al (42) and Atkins et al (43).

![7-amino 4-methyl coumarin](C-120)
Borisevich et al (44) has generated the Laser from 7-amino-4-methyl coumarin dye by taking the 0.1% solution in ethanol, DMF and acetic acid, after pumping it by flash lamp. Telle et al (45) obtained lasing radiation in the range of 427 - 480 nm (λ max- 450nm) with 15% quantum efficiency, when ethanolic solution of the C-120 was pumped by XeCl excimer laser at 308 nm.

Effect of C-314 on the emission characteristics of C-120 was studied by Aristov et al (46) and found that addition of the C-314 to the dye enhanced the fluorescence quantum yield 1.8 folds and it also increased the photostability of the active medium 3-4 times.

The effect of 1,4-diaza bicyclo [2,2,2] octane (DABCO) on the photostability of the C-120 was studied by Kunjappu (47), and found that it stabilize the dye by retarding the degradation of dye due to quenching of the singlet oxygen. Further the effect of different protic and aprotic solvents on the quenching effect of DABCO were studied by Priyadarshini et al (48).

Further, Kunjappu et al (49) studied the effect of solvent (water, methanol, dioxane) surfactant (sodium dodecylsulphate, cetyl trimethyl ammoniumchloride, Triton X100) and polymeric membrane (Nafion) on the absorption and fluorescence spectra of the dye. The comparison was made for the shift in spectra among the medium.
Kovalenko et al (50) prepared the inclusion complex of the C-120 with β-cyclodextrin and its structure was established by MH2 molecular mechanism. Further, the effect of complex on the spectral, luminescent and laser generation is discussed. Marier et al (51) studied the effect of bifluorophoric system of C-120 with p-terphenyl and naphthalene and found that there was a intramolecular charge transfer among the molecule.

Moreau et al (52) modified the structure of 7-amino-4-methyl coumarin by preparing methyl ester of 7-amino-coumarin 4-aceticacid and obtained spectral and lasing property. Application of these synthesised dye to cellular biochemistry has been discussed.

Chamton et al (53) synthesised water soluble 7-amino coumarin laser dyes by introducing long aliphatic chain containing more than one ethoxy group at 4-position of 7-amino coumarin which lased at 475 nm when pumped by XeCl excimer laser at 308 nm.

2. 7-Diethylamino Coumarin

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\text{7-diethylamino- 4-methyl- Coumarin (C-1)}
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This is an important class among the 7-substituted-amino coumarin, much work has been done in the 7-diethylamino coumarin. Important dyes are having substitution at 3-and/or 4-position. The oldest dye among this class is 7-diethylamino-4-methyl coumarin, which was synthesised by Von-Pechmann by reaction of m-diethylamino phenol and ethyl acetoacetate.

The first laser pulse from this dye was obtained by Capelle et al in 1970 when they pumped the ethanolic solution by N2 laser (54). Borisevich et al (44) obtained the lasing frequency in the band width of 427-453 nm by pumping the 0.1% ethanolic solution with flash lamp. Greeg et al (55) obtained long pulse of laser around 38-69 \( \mu \text{m} \) in 440-490 nm region in the presence of Triplet State Quenching Additive [TSQA] 1:3 di-cycloeloctadiene.

Takahaki et al (56) when used mixed solvent system of ethanol-toluene, found that there was increase in wavelength of stimulated emission by 6 nm. Weber et al (57) studied the effect of temperature on fluorescence decay time from 300°-115°K in basic alcoholic solution i.e. (90% ethanol 10% methanol) using nitrogen pulsed laser at 337 nm and fluorescence quantum yield \( \Phi \leq 0.74 \) was estimated at 300° K.

Sivram et al (58) have studied the effect of solvents on the spectral and gain characteristic of the dye C-1.

Cox and Matise (59) have studied the energy transfer from C-1 donar to C-314 (acceptor) in methanolic solution and found that the laser generation from the mixture was twice efficient as that of laser generation from C-314 alone.
Denisov et al (60) have studied the energy and spectral characteristic at different concentrations with flash lamp pumping.

Morgan et al (61) have obtained the energy conversion efficiency of 7% by pumping the dye with XeF excimer laser at 351nm in ethanol and found it lase in the tuning range of 440 - 478 nm with peak output at $\lambda_{\text{max}}$ 457nm.

Clayton et al (62) studied the effect of organic co-solvent on fluorescence quantum yield of dye C-1 and found that the small amount of organic co-solvent produces dramatic enhancement in fluorescence quantum yield.

The triplet characteristic of the dye in benzene using nano-second pulse radiolysis technique was studied by Priyadarshini et al (63) and the energy transfer from coumarin triplet to various acceptor such as trans-stilbene, pyrene etc. Further, they also studied triplet-triplet and singlet-singlet energy transfer with trans-stilbene. Triplet-Triplet studies done by pulse radiolysis technique (64) and they found that energy transfer takes place through exchange mechanism. In order to stabilize the dye, Priyadarshini et al (48) studied the effect of [DABCO] 1-4, diazabicyclo [2,2,2] octane in protic and aprotic solvent and found that quenching was efficient in aprotic solvent as compared to protic solvent.

Kalmykova et al (65) studied the photolysis of the dye C-1 via dye - dye interaction in the range of $10^{-3}$ to $10^{-1}$M and have also identified the photodestruction product of dye. Further they studied the steady state photo irradiation of the oxygen containing alcoholic solution of dye (66) and found that it leads to oligomer formation which absorbed in the same region as that of the dye.
Priyadarshini et al studied triplet-triplet energy transfer between biphenyl - C-1 and C-1 -thionine in benzene and nafion polymeric membrane (67).

Kunjappu et al (49) studied the effect of solvents, surfactant and polymeric membrane on the C-1 and found that the maximum shift was obtained in aqueous surfactant media.

The modification was done in the 7-diethylamino 4-methyl coumarin by Mohr et al (68). They found that the methyl group at C4 of this dye undergoes photo-oxidation to form -COOH, which absorbs at the same wavelength and it leads to the loss of laser energy of the dye. The photochemical stability of this dye was increased successfully by replacement of methyl group by trifluoromethyl group (69), to give 7-diethylamino-4-trifluoromethyl-coumarin which lase in the blue green region (481 nm) pumped continuously by high intensity pulse (70).

Various studies are being done on this dye. Medge et al (71) obtained laser generation at 480 nm in dioxane using 40 picosecond pulse from N₂ laser at 347 nm. When the C-153 was pumped by KrF excimer laser at 248 nm it lased in the range of 340 - 580 nm (72). The energy conversion efficiency study
of C-153 at 351 nm from XeF excimer laser was done and higher band width around 460-525 nm with peak output at 485 nm with 18% energy conversion efficiency was obtained (61).

The triplet characteristic of the dyes C-153 in benzene using nanosecond pulse radiolysis technique was obtained and energy transfer from coumarin triplet to various acceptor viz. trans-stilbene and pyrene was studied by Priyadarshini et al (63). The triplet and singlet energy transfer with trans-stilbene was studied by Priyadarshini et al (64) and found that triplet-triplet energy transfer takes place through exchange mechanism.

The effect of solvent, surfactant and nafion polymeric membrane on the absorption and fluorescent spectra of this dye was studied and observed that the maximum red shift was obtained in dioxane as compare to water (49).

In order to extend the lasing frequency of the 7-diethylamino coumarin dyes to the longer wavelength the substitution at 3-position is done and are found to lase in green region (73). Substitution at 3-position of 7-diethylamino coumarin by heterocyclic moiety such as benzothiazole, benzimidazole and 1-methyl-benzimidazole shifts the lasing frequency to longer wavelength.

The important dyes of this class are:

1. 3-[2-benzthiazolyl]-7-diethylamino coumarin (C-6)
2. 3-[2-benzimidazolyl]-7-diethylamino coumarin (C-7)
3. 3-[2-(1-Methyl) benzimidazolyl]-7-diethylamino coumarin (C-30)
Taylor et al (72) obtained the lasing radiation in the range of 507 - 529 nm when pumped the ethanolic solution of the dye C-6 by He - N₂ charge transfer laser operating at 427.8 nm. Johnson et al (75) studied the laser emission in mixed solvent system with the Argon laser pumping system and found the peak output 35% at 575nm with tuning range of 510 - 545 nm.

The absolute fluorescence quantum yield was obtained for C-6 using photo acoustic spectroscopy by Zhang et al (73) and it was found to be 0.82.

The comparative fluorescence study of rigidised coumarin laser dye C-6 with series of solvent was made by Mottaleb et al (77) and this experimental data were further augmented by theoretical quantum chemical SCF-CI-MO calculation. They have also correlated the fluorescence with viscosity and temperature.
(2) 3-[2-benzimidazolyl]-7-diethylamino-coumarin (C-7) and 3-[2-(1-methyl) benzimidazolyl]-7-diethylamino coumarin (C-30)

The other dyes of this class are 3-(2-benzimidazolyl)-7-diethylamino coumarin [C-7] and 3-[2-(1-methyl)-benzimidazolyl]-7-diethylamino coumarin [C-30] which were studied to some extent. The literature for these dye is also reviewed.

\[
\begin{align*}
\text{(C}_2\text{H}_5\text{)}_2\text{N} & \quad \text{R=} \text{H} \quad \text{(C-7)}, \quad \text{R=} \text{CH}_3 \quad \text{(C-30)} \\
\end{align*}
\]

Ethanolic solution of C-30 when pumped by He-N\(_2\) charge transfer laser at 427.8 nm lased in the tuning range of 482-507 nm (74) and laser action in the tuning range of 499-557 nm was obtained when the C-7 pumped by He-Strontium recombination laser at 430.5 nm (78). Richardson et al (79) studied the fluorescence life-time in different solvents at different concentration and discussed effect of various solvents. Medge et al (71) obtained laser radiation at 510 nm from ethanolic solution of C-30 by absorption of the lowest singlet state from N\(_2\) laser pulse of 40 pico-second at 347 nm. Johnson et al (75) obtained peak power output of 38% at 518 nm by pumping C-30 in mixed solvent by Argon laser.
Role of C-7 as sensitizer in the bifluorophoric system of Rhodamine110 - C-7 was studied by Geng et al (80) and found that under coaxial pumping of the bifluorophoric system the laser output of Rhodamine increased by 130%.

The laser emission at 515 nm with 15% efficiency was obtained from C-30 when the dye doped in epoxy polymer pumped by CdS and Ze-Se Multi component laser (81).

In the 7-amino and 7-substituted amino coumarin, it was found that there was a loss of emission energy due to the rotation of free nitrogen atom about its axis. In order to eliminate the loss of emission radiation the nitrogen was fixed / rigidised by ring closure with phenyl ring by Drexhage et al (82). Various rigidised amino coumarin laser dyes with hydrogenated phenyl ring and other substituents on amino group like ethyl, methyl etc. (43,73) and other (83) have been synthesised. The rigidised quinoilino amino coumarin with substitution at 4-position by methyl [C-102] and trifluoromethyl group [C-153] are important dyes of this class and substitution at 3-position by ethyl carboxylate [C-314] and carboxylic acid also shows good photo-stability and quantum efficiency.

The C-102 and C-153 dyes have been studied extensively because of the better photostability.
C-102 laser dye in ethanol lased in the region 453-510 nm when pumped by He-N$_2$ charge transfer laser operating at 427.8 nm (74). The fluorescence lifetime for C-102 and C-153 were studied by Richardson et al (79) in different solvent at different concentration and found that decrease in the polarity of solvent increases the fluorescent lifetime of dye.

Telle et al (45) obtained the energy conversion efficiency for C-102 and C-153 dye around 180% and 8.4% in the tuning range of 456-503 nm and 513-588 nm respectively, when the ethanolic solution was pumped by XeCl excimer laser at 308 nm. When C-102 pumped by argon laser of 5.8 W power lased in the tuning range of 460-520 nm with peak output of 10% at 477 nm (75).

The photo-acoustic study of C-102 at 25°C and 35°C was done by Ram and Prakash (84).

The fluorescence lifetime was obtained for the C-102 (85) and was found to be 4.3 ns, which was the longest among the free amino-coumarin and substituted-amino-coumarin laser dyes due to the rigidity of nitrogen atom.

The triplet-triplet and singlet-singlet energy transfer process between trans-stilbene and C-102 and trans-stilbene and C-153 has been studied by Priyadarshini et al (64).

Inamdar et al (86) studied the fluorescence and laser emission from C-102 - Acridine orange mixture and found that acridine itself does not lase when
pumped by \(N_2\) laser but in the presence of C-102, it lase efficiently via singlet-singlet energy transfer. Kunjappu et al (52) studied the effect of solvent (water, ethanol, p-dioxane) surfactants (sodium dodecylsulfate, tricetyl ammonium chloride, triton X100) and polymeric membrane (nafion) on the absorption and fluorescence spectra of C-102 and C-153 and found that the maximum red shift was observed in aqueous surfactant medium and blue shift was observed in p-dioxane as compared with water.

The fluorescent spectra as a function of pressure was studied by Kutty et al (87) and the large frequency shift with the pressure towards red end was observed.

The effect of inclusion complex of the dye with \(\beta\) - cyclodextrin on the fluorescence life time and the fluorescence quenching by \(\text{KIO}_3\) has been studied by time resolved fluorescence spectroscopy (88).

The C-314 is also important dye of this class, although not much work has been reported on this dye.

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\begin{align*}
\text{C-314} &
\end{align*}
\]

The influence of luminescing admixture of C-314 with C-120 on the operating efficiency of laser is studied by Aristov et al (46) and it was observed that the fluorescence quantum yield increased 1.8 times and the photostablity
was increased 3 to 4 times. The effect of Ce(III) ion complexation on fluorescence is studied by Ismail (89). The conversion efficiency of this dye was increased 3 to 10 times by introduction of triplet quenchers in the dye solution and it lased at 510 nm (90).

7 - Hydroxy coumarin

It is the other important class of coumarin laser dye. It was obtained naturally from tonka beans and possessed blue fluorescence. It is also called umbelliferone. The highyl explored dye from this class in 4-methyl umbelliferone (4MU) or 4-methyl 7-hydroxy coumarin.

![4-methyl 7-hydroxy coumarin](image)

Snavely et al (91) obtained first laser emission in 1967 from 4MU at 454 nm when aqueous solution was excited by flash lamp. In 1969 Dzyubenko et al (92) obtained the energy characteristic in ethanol and found that the results were compatible with solid lasers. In the same period Capelle et al (54) obtained laser pulse by pumping with N₂ laser. Snavely et al (93), when excited the aqueous solution of dye (9pH) by flash lamp, lased at 454 nm with tuning range of 420-520 nm.
Diene, Shank and Trozzolo (94) gave evidence for the broad tuning range, which was due to multiple excited state complex (Multiplex). This was supported by time dependent stimulated fluorescence from acidified fluorescence.

Fawcett (95) obtained 100 KW peak output power at 450 nm when aqueous solution pumped by Ruby and Nd Q-switched laser at 346.5 nm.

Shank et al (96) obtained tunable laser from acidic, basic and neutral solution in near UV to yellow spectral region. Borisevich et al (97) obtained lasing frequency from various protic solvents in the band width 7-14 nm.

Bergman et al (98) obtained broad band tunable laser with high efficiency in the region 460 - 560 nm with 2nd harmonic Ruby laser.

In 1970 Shank et al (99) used an 10 mole% electron acceptor (naphthalene, anthracene, pyrene, biphenyl etc) and obtained a broad band laser output of 176 nm in the range of 391-567 nm from 5 X 10^{-3} M acidic solution of the 4-MU. Further, the emission characteristic were investigated in different solvent and with different excitation pump power and each of the five different excited state complex were isolated in proper solvent (100).

Weber et al (57) measured the fluorescence decay time as a function of temperature (300°-1150K) in basic alcoholic solution of dye using nitrogen pulse laser at 337 nm and the estimated quantum yield was < 1 at 300° K.
When the basic ethanolic solution of the 4-MU was excited by 40 pico-second pulse from nitrogen laser at 347 nm it lased at 450 nm (71).

The spectral and emission characteristic of the 4-MU in various solvents is studied by Takahashi et al (101) and the lasing was observed in the range of 435-510 nm when pumped by N₂ laser at 337.1 nm. Further, the energy transfer process was observed with the Rhodamine.

Denisov et al (102) studied the effect of temperature on lasing properties and observed that with the increase in temperature the quantum efficiency decreases due to triplet-triplet absorption. The effect of acidity on the fluorescence was studied spectrofluorimetrically by Ponomarev et al (103) and the fluorescence quenching was observed due to protropic conversion.

The other substituents apart from 4-methyl-7-hydroxy coumarin are substitution at 3-position of 7-hydroxy coumarin by phenyl, carbethoxy, cyano, methoxy, benzothiazole etc. were carried out by Wolfbies et al (104), which gave water soluble laser dye emitting in the range 440-525 nm when pumped by frequency tripled Nd⁺³ laser.

The other 3 substituted 7-hydroxy coumarin derivatives which were checked for emission are 3-acetyl, 3-carbethoxy, 3-cyano 7-hydroxy coumarin by Takakusa et al (102) and found that the alkaline solution of 3-cyano 7-hydroxy coumarin lased at longer wavelength as compared to ethanolic solution.
Few substitution on the hydroxy group of the 7-hydroxy coumarin were also been checked for laser generation viz. acetyl derivative of 7-hydroxy coumarin (106), 7-Methoxy coumarin derivatives (103,107), 7-ethoxy coumarin derivatives (107) and 7-butoxy coumarin (108) etc. and these dyes lased in visible region.

**Aim & Scope**

The review of the literature on the 7-hydroxy coumarin and 7-amino and substituted amino coumarin, reveals that lot of work has been done in the area of 7-substituted amino coumarin as compared to 7-hydroxy coumarin for improving the lasing property of the dye. Apart from the dyes for laser, the 7-amino and substituted amino coumarin are widely utilized as fluorescent dyes. Hence, this class is being explored and modified to greater extent as compared to 7-hydroxy coumarin. Although, 7-hydroxy coumarin derivatives are having good fluorescing property and hence, are good optical brightening agents, not much modification has been reported in the 7-hydroxy-coumarin derivative as a dye for laser. Further, 7-hydroxy coumarin laser dyes lase efficiently from an alkaline aqueous or alcoholic solution with a broad tuning range (~100nm). Since, the 7-hydroxy coumarin derivative laser generation can be obtained from aqueous solution of the dye. The loss of the lasing energy is due to change in refractive index of the solvent with rise in the temperature. Further, the introduction of the heterocyclic ring system in the 3-position of the 7-amino and substituted coumarin shifts the emission to the longer wavelength.

With this view it is desirable to synthesis a new series of 3-substituted 7-hydroxy coumarin and study their lasing properties to have the better laser dyes.
Present Investigation.

The two series of substitution has been made at the 3-position of the coumarin and 7-hydroxy coumarin to have the series of new compounds. These have been synthesised and their fluorescence and laser properties have been studied.

The present thesis describes the synthesis and properties of 3-[2-substituted-hydrazino-5-thiazolyl]-7-hydroxy coumarin and N-aryl-coumarin-3-hydroxamic acids. The 3-[2-substituted-hydrazino-5-thiazolyl]-7-hydroxy coumarins are synthesised by reacting 3-(ω-bromoacetyl)-7-hydroxy-coumarin and substituted thio-semicarbazide in 1:1 DMF ethanol. The N-aryl coumarin-3-hydroxamic acids are synthesised by reacting N-aryl hydroxylamine with coumarin-3-carbonyl chloride at low temperature in diethyl ether containing aqueous suspension of sodium bicarbonate. These compounds are characterised by mp, elemental analysis, uv, ir, nmr, and mass spectra.

The thermodynamic ionisation constants of newly synthesised 7-hydroxy coumarin derivative and N-aryl coumarin-3 hydroxamic acids in 70% (v/v) dioxane- water media at 25° and 35° ± 0.1° C are determined by pH titration technique. The correction for the non-aqueous media has been done. The average pKₘ values are accurate to ± 0.03. The ΔG°, ΔH° and ΔS° values are calculated.
Fluorescence characteristics of five 3- substituted -7-hydroxy-coumarin dyes have been investigated. The effect of solvent on the fluorescence of these dyes is examined. The lasing performance, relative output, stability and lasing wavelength for these dyes are reported.

Five new N-aryl-coumarin-3-hydroxamic acids have been systematically investigated and applied to N₂ laser-pumped dye lasers. All the compounds show laser action between 5400-6000 Å spectral range.

The method for the determination of hue and the brightness of the synthesised coumarin derivatives as compared to standard by means of reflectance measurement is described. Their L, a*, b* values as well as the colour difference values from standard ΔL, Δa*, Δb*, ΔH were ascertained.
References


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