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Novel Alternative Heterocyclic Amino Acids Precursors in Phytopigment Like Synthesis and Spectral Characterization

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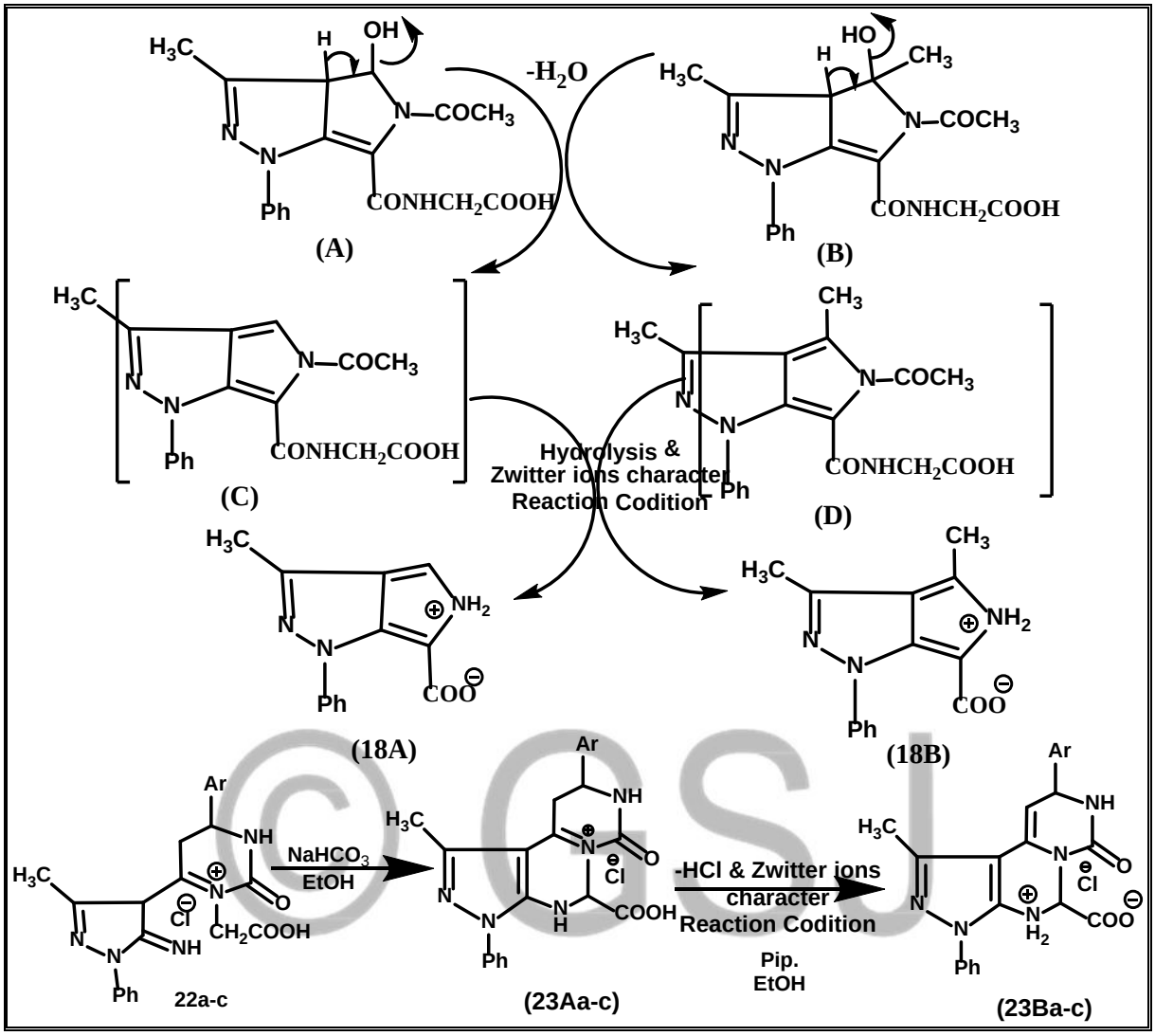
ABSTRACT:

Our approaches to the synthesis of novel heterocyclic phytopigment like incorporating pyrrolo[3,4-c]pyridazin-6-ium-7- carboxylate covering styryl **(19a-c, d),** tri-6[4(1)] methine phytopigments like **(20a-c, d),** pyrazolo[4,3-e] pyrimido[1,6-c] pyrimidin-4-ium-5-carboxylate-4-phytopigment **(24a-e) &** pyrazolo [4,3-e]pyrimido [1,6-c]pyrimidin-4-ium-5-carboxylate-4-[α-Substituted-benzylidene]Styryl-phyto- pigment **(25a-f)** were prepared based on 5-acetyl-4-hydroxy-3-methyl-(3,4-dimethyl)-1-phenyl-1,3a,4,5-tetra[H]pyrrolo[3,4-c]pyrazol-6-carbonyl-glycine **(18a,b)** and pyrazolo[4,3-e]pyrimido[1,6-c]pyrimidin-6-ium-chloride/iodide **(23a-c).** The new synthesized heterocyclic phytopigment like was identified by elemental & spectral analyses. The absorption spectra, solvato-(media)-chromic behaviour of some selected dyes were investigated in 95% Ethanol and pure organic (mixed) solvents, in aqueous universal buffer solutions.

.GRAPHICAL ABSTRACT



Transformation of (18a, b & 22a-c & 23a-c) under Reaction Conditions

Key Words: Heterocyclic phytopigment like, synthesis, spectral, Solvato-(Media)-chromic Behaviour

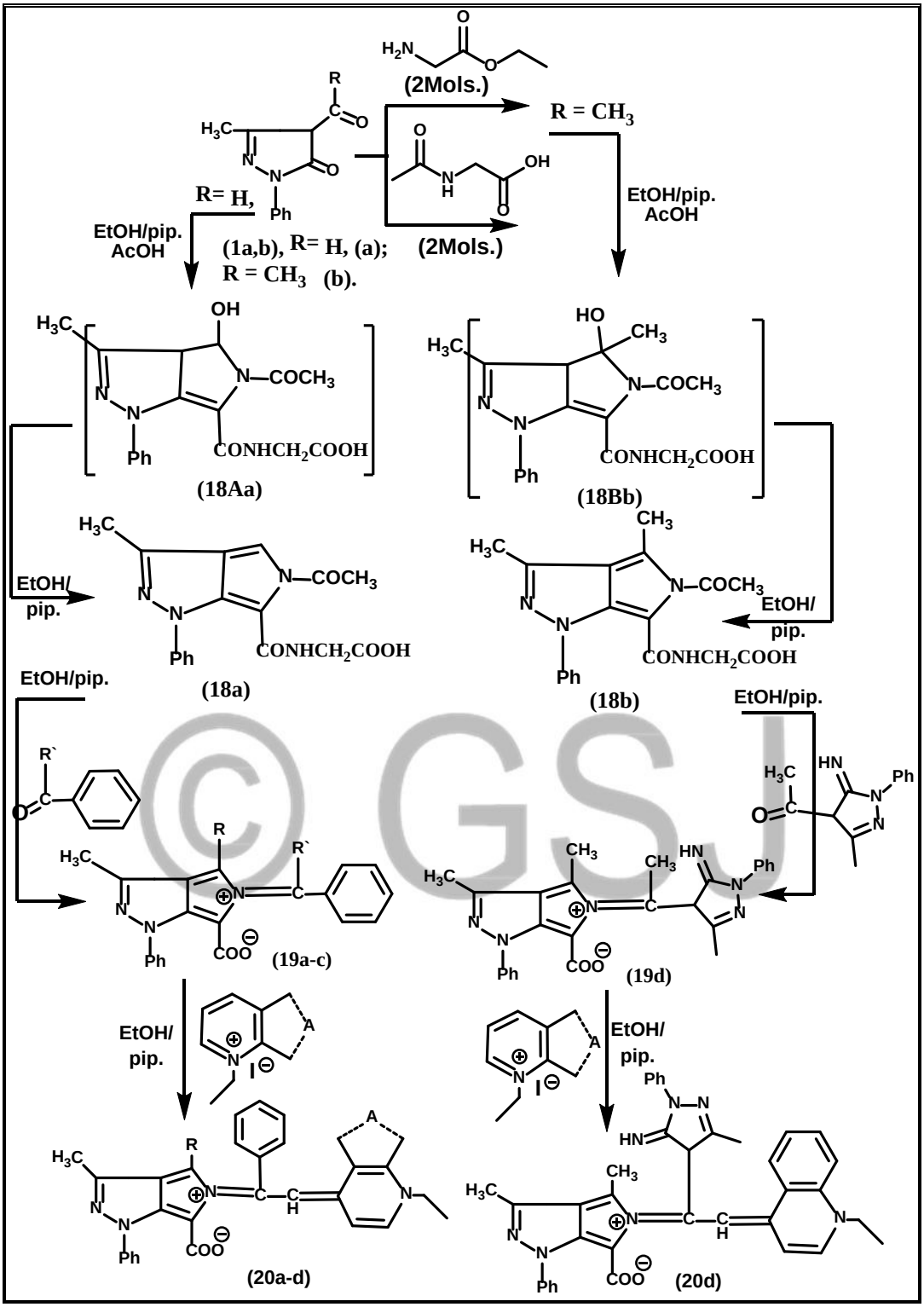
INTRODUCTION

One of the main bottlenecks to the development of multi-property material is to pertain and search of new methodology for direct initial attempts for phytopigment synthesis. It is important to consider synthetic routes for facile and stable heterocyclic reagents and to produce the products in a good yield under the reaction conditions. There are several advantages in using other routes than conventional methods. Deeping the colour and increasing the intensity of spectral bands of such phytopigment like incorporating heterocyclic acid moieties is a criterion of photosensitization effect and play a dominant role in many biochemical systems as heterocyclic acids serve a central role in biology and chemistry being the fundamental constituents of proteins and mediators of nitrogen

metabolism and provide raw material for a large number of biologically important primary and secondary metabolites **[1].** Pyrrolo[3,4-c] pyrazol-6-carbonyl-glycine carboxylic acid phytopigment like moieties have a little and no attention in the literatures The purpose of the present article is to evaluate an improvement of pyrrolo[3,4-c] pyrazol-6-carbonyl-glycine carboxylic acid nuclei & N-bridge head pyrimidine carboxylic acid phytopigment moieties as synthetic precursor's alternative entities to heterocyclic phytopigment like have a little and no attention in the literatures. **[2-4]**

RESULTS AND DISCUSSIONS

4-Formyl(acetyl)-3-methyl-1-phenyl-pyrazolin-5-one **(1a,b) [5-7]** reacted with ethyl glycinate, in bimolecular ratios, in presence of piperidine or acetic acid to afford 5-acetyl-4-hydroxy-3-methyl(3,4-dimethyl)-1-phenyl-1,3a,4,5-tetra[H] pyrrolo [3,4-c] pyrazol-6-carbonyl-glycine **(18a,b).** The later **(18b)** was chemically confirmed by the direct interaction of 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one **(1b)** & acetyl glycine, in bimolar ratios, under acetic acid catalysis to give same melting & mixed melting point of **(18b).** Piperidine catalysis of an ethanolic solution of **(18a,b)** & acetophenone (4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one) achieve 3,5-dimethyl-1-phenyl-4,6-di[H]-1H-pyrrolo[3,4-c]pyridazin-6-ium-7-carboxylat-6-methylene-1-benzylidene-styryl- **(19a-c) &** 3,5-dimethyl-1-phenyl-4,6-di[H]-1H-pyrrolo[3,4-c] pyridazin-6-ium-7-carboxylat-6(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine-4-yl-styryl-phytopigment like **(19d).** The interaction of an ethanolic solution of **(19a-c,d)** & N-ethyl-pyridin(quinolin)-4(1)-ium-ethiodide salts under piperidine catalysis, afforded 3-methyl(3,5-dimethyl)-1-phenyl-4,6-di[H]-1H-pyrrolo[3,4-c]pyridazin-6-ium-7-carboxylate-substituted phenyl-tri-6[4(1)]methine phytopigments like **(20a-c,d), Scheme (1).** On treatment of **(20a-c, d)** with conc. sulphuric acid, no liberated iodine vapor on warming. The strongly acidic form **(**Witter ions character**)** of N-heterocyclic α-carboxylic acid was considered as direct initial attempts for heterocyclic phytopigment like synthesis for their high site reactivity susceptible to be attack either by carbon nucleophiles (electrophiles) in substitution (addition) reactions.



Scheme (1A)

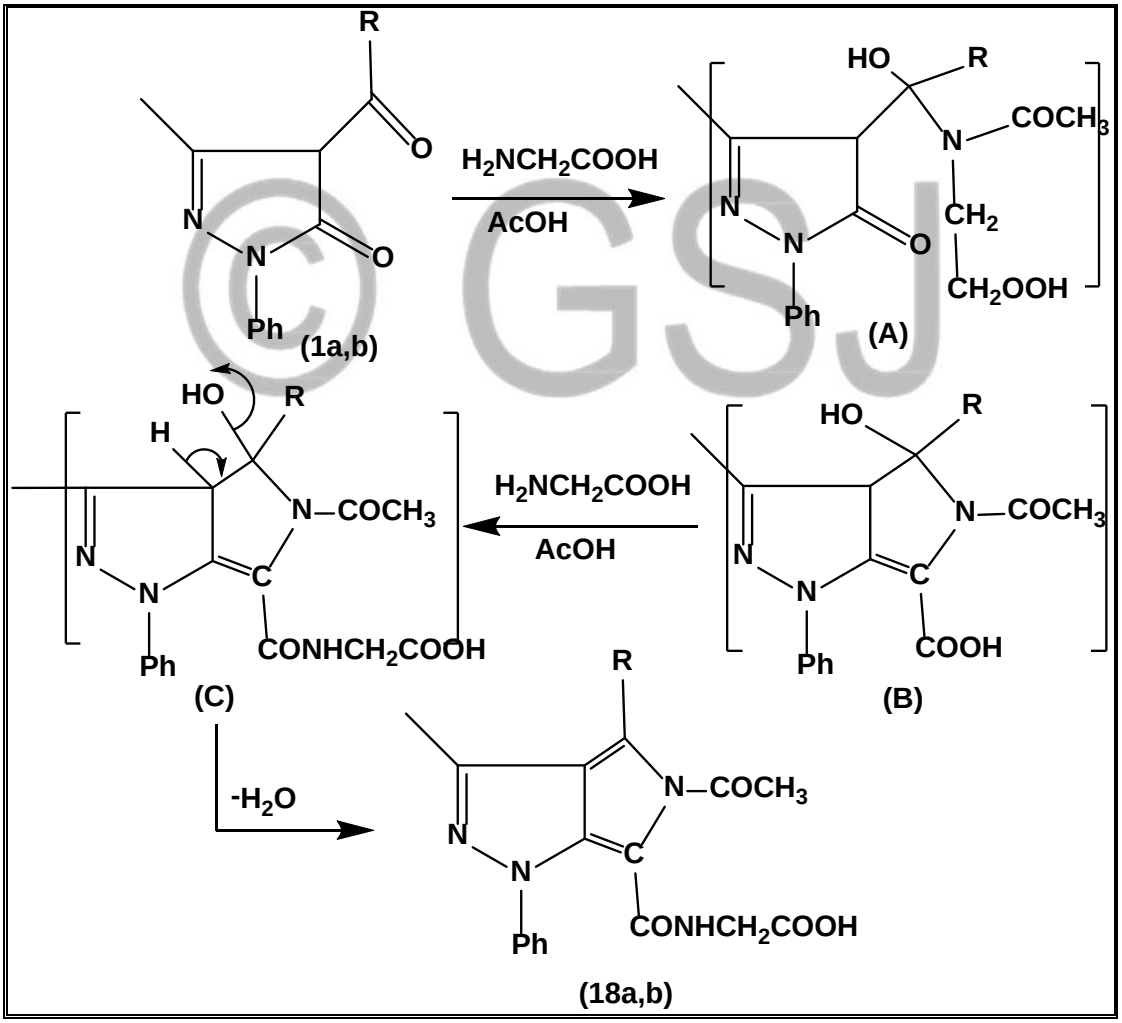
Scheme (1A) Substituents

(19a-d), R=CH_3, R'=H, A=C_6H_5 (a);R=H, R'=CH_3, A=C_6H_5 (b); R=CH_3, R'=CH_3, A=C_6H_5 (c);

(20a-d), R=H, A=C_6H_5, A'=pyridin-4-yl (a);R=H, A=C_6H_5, A'=quinolin-4-yl (b); R=H, A=C_6H_5, A'=quinolin-1-yl (c); R=CH_3, A=C_6H_5, A'=quinolin-4-yl (d);

The structure of (**18a, 19a, 20a)** was characterized & identified by elemental and spectral analysis, Table **(1).** The structure of **(18a & 20a)** was consider most likely and in agreement with molecular formula based on mass spectrum resulted in molecular ion at **m/z**=(358) & base peak at **m/z**= (216) for **(18a) &** M+4 peak at **m/z**= (358) & base peak at m/z=(288) for **(20a) [8].**

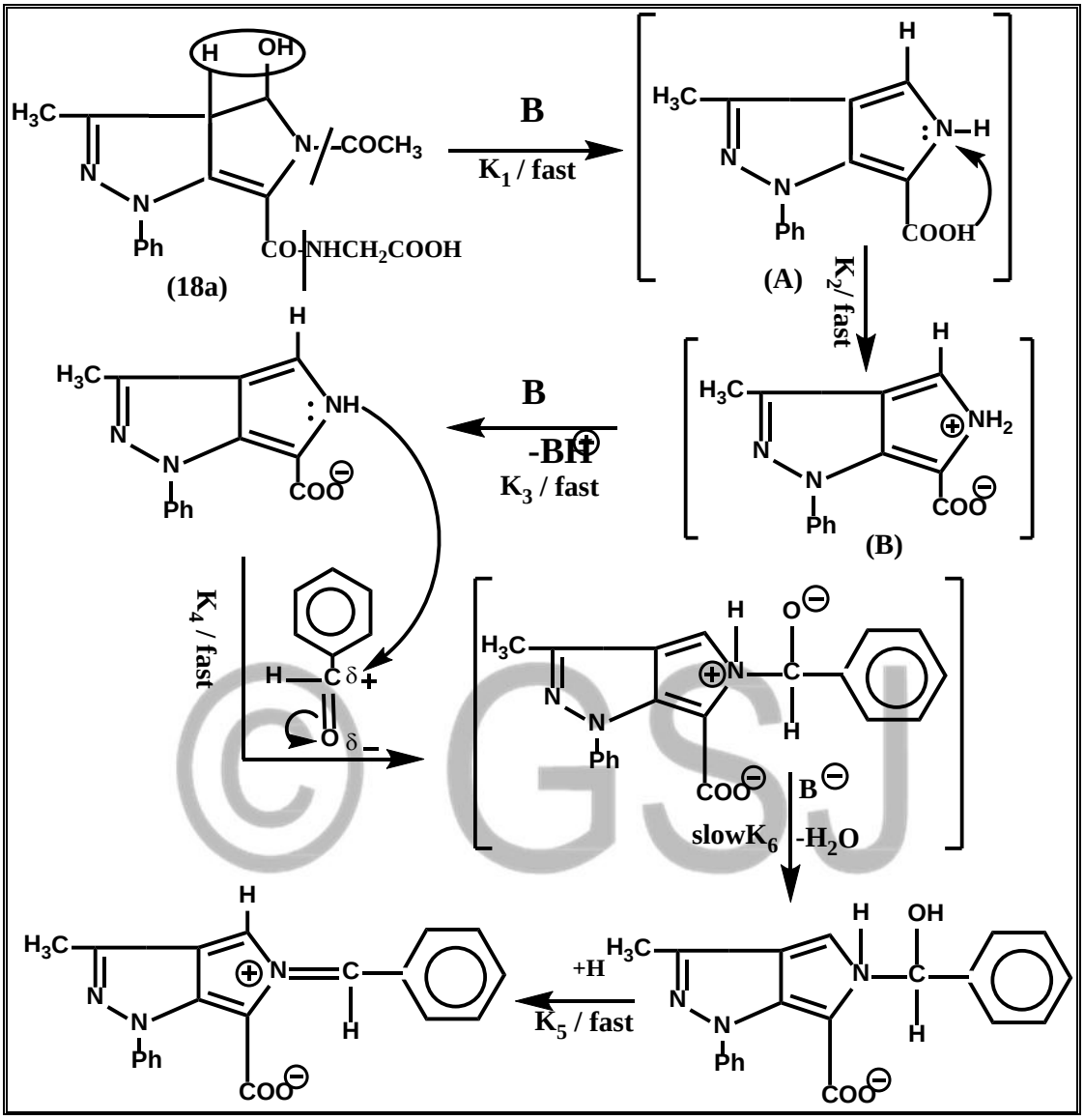
The formation of **(18a,b)** was suggested to proceed via nucleophilic attack of ethyl glycinate under acidic (basic) medium to give an acetyl intermediate **(A)** which easily eliminate water molecule to give an intermediate **(B).**The later intermediate **(B)** reacted with another ethyl glycinate molecule of to give an intermediate **(C).** β-Elimination process was suggested to proceed for the intermediate **(C)** to give desired molecule, 5-acetyl-4-hydroxy-3-methyl (3,4-dimethyl)-1-phenyl-1,3a,4,5-tetra[H]pyrrolo[3,4-c]pyrazol-6-carbonyl-glycine **(18a,b), Equation (1).**



Equation (1)

The formation of **(20a-c, d)** was suggested to proceed through the oxidative elimination reaction for secondary amino group in **(19a-c, d)** with active hydrogen of N-ethyl-

pyridin(quinolin)-4(1)-ium ethiodide followed by rearrangement with dehydro-halogenated process to give **(20a-c,d).** On treatment of **(20a-c, d)** with conc. sulphuric acid, no liberated iodine vapor on warming. **Equation (2)**

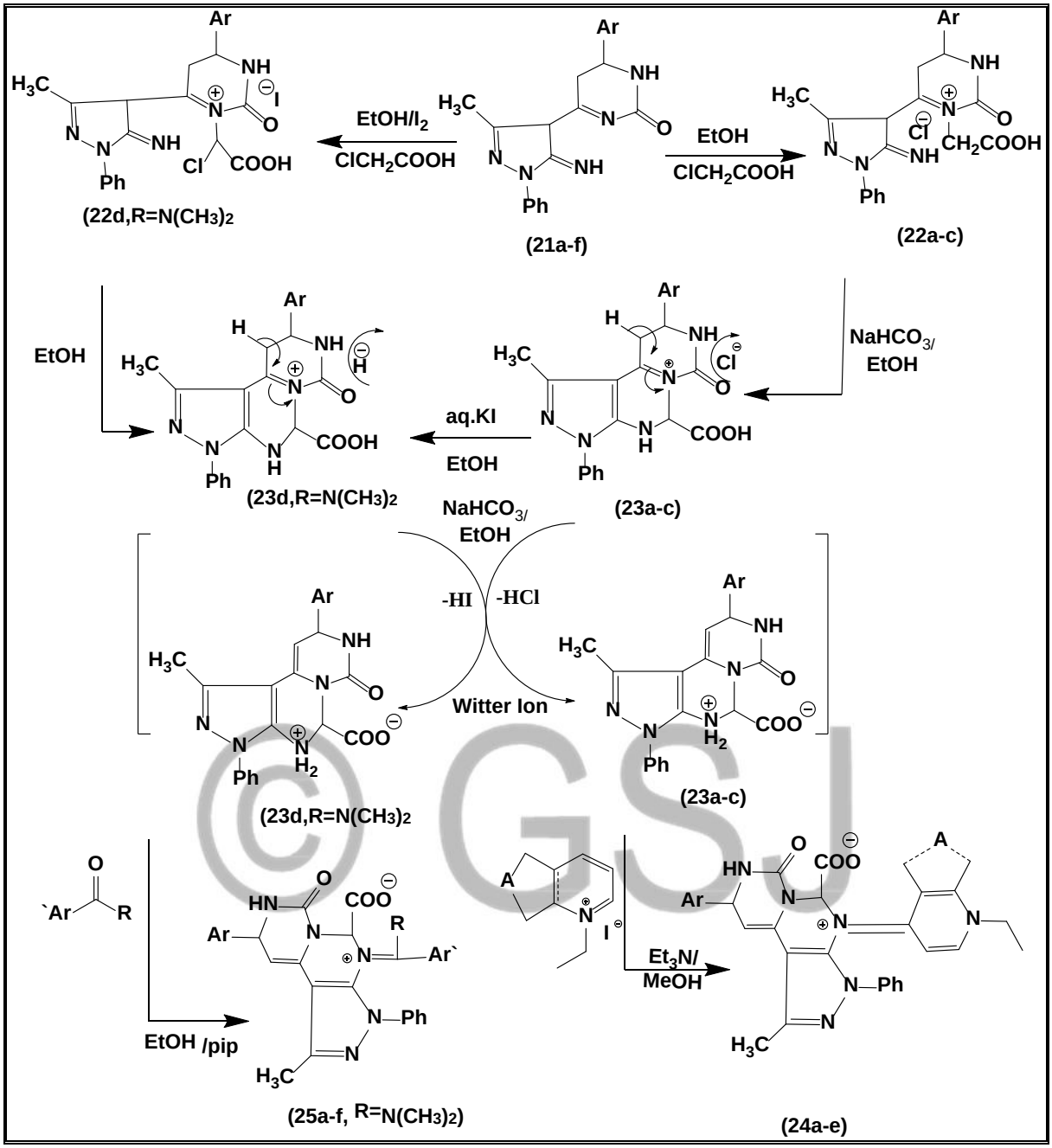


Equation (2)

Our approaches are extended to the synthesis of some novel cyanine phytopigment like. Thus, an ethanolic solution of 6-Arylideno-4-[3-methyl-5-one (imine)-1-phenyl-pyrazol-4-yl]-pyrimidin-2-one **(21d-f) [9-11]** and chloroacetic acid in the presence of sodium bicarbonate achieved 1-(carboxy-methyl)-6-(3-methyl-1-phenyl-4,5-di[H]1H-pyrazol-4-yl-5-imine)-2-oxo-4-substituted-aryl-2,3,4,5-tetra[H]pyrimidin-1-ium **(22a-c) &** 1-(carboxy-chloro- methyl)-4-(4-(dimethyl-amino)phenyl)-6-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imin-4-yl)-2-oxo-2,3,4,5-tetra[H]pyrimidin-1-ium **(22d)** which react with iodine in ethanol to give the key reaction intermediate 5-carboxy-1-methyl-7-oxo-3,diphenyl-9-Substituted- aryl-4,5,7,8, 9,10-hexa[H]3H-pyrazol o[4,3-e] pyrimido [1,6-c]pyrimidin-6-ium chloride **(23a-c).** Route (a)**.** Such compounds was chemically confirmed by direct reaction of ethanolic solution of **(25a-c),**

chloroacetic acid and iodine, in equimolar ratio, to give 5-carboxy-9-(4-(dimethyl amino)phenyl)-1-methyl-7-oxo-3-phenyl-4,5,7,8,9,10-hexa[H]3H-pyrazolo[4,3-e]pyrimido[1,6-c] pyrimidin-6-ium iodide **(23d),** Route (b)**, Scheme (1B).** It was obvious that, 5-carboxy-1-methyl-7-oxo-3,diphenyl-9-substituted-aryl-4,5,7,8,9,10-hexa[H]3H-pyrazolo[4,3-e]pyrimido [1,6-c] pyrimidin-6-ium-chloride **(23a-c)** resulted in iodine vapour on triturating with conc. H_2SO_4 acid warming. Also, when treatment with tri-ethyl amine /MeOH, N-bridgehead heterobicyclic anhydro base moieties is formed, which soluble in conc. sulphuric acid without liberation of iodine vapour on warming? Reaction of (**23a-c)** with N-methyl-pyridin (quinolin)-4(1)-ium ethyl iodide , in equimolar ratio , under piperidine catalysis afforded 1-methyl-7-oxo-3-phenyl-9-substituted-aryl-3,4,5,7,8,9-hexa[H] pyrazolo [4,3-e]pyrimido[1,6-c]pyrimidin-4-ium-5-carboxylate-4-cyanine phytopigment **(24a-e), Scheme (1B).** Meanwhile, 9-(4-(dimethyl-amino)phenyl)-1-methyl-7-oxo-3-phenyl-3,4,5,7,8,9-hexa[H]pyrazolo[4,3-e]pyrimido [1,6-c]pyrimidin-4-ium-5-carboxylate-4-[α-substituted-benzylidene]-styryl-cyanine phytopigment **(25a-f)** were prepared through the reaction of 5-carboxy-1-methyl-7-oxo-3,diphenyl-9-substituted-aryl-4,5,7,8,9,10-hexa[H]3H-pyrazolo[4,3-e]pyrimido [1,6-c]pyrimidin-6-ium-chloride **(23a-c)** with aromatic aldehyde (acetophenone) derivatives, in equimolar ratio, under thermal piperidine catalysis to give 5-arylideno-3-methyl-1-phenyl-pyrazolino-[4,5-d] pyrimidino-[3,4-a]pyrimidine-7-one-8-carboxylic acid-styryl phytopigment like **(22a-f), Scheme (1B).**

The structure of **(22a, 23a, 24a, d, e, 25a, e)** was characterized and identified by elemental analysis IR, 1H-NMR and Mass spectral data **[12-14].Tables (6,7)**



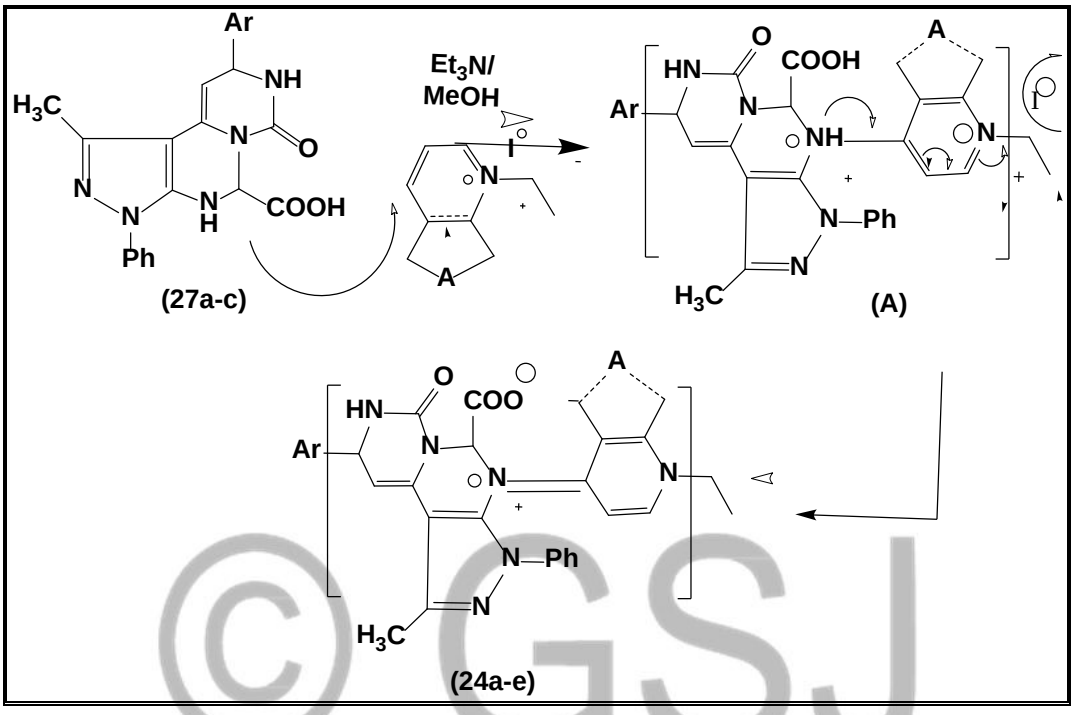
Scheme (1B)

<u>Scheme-(1B) Substituents</u>:

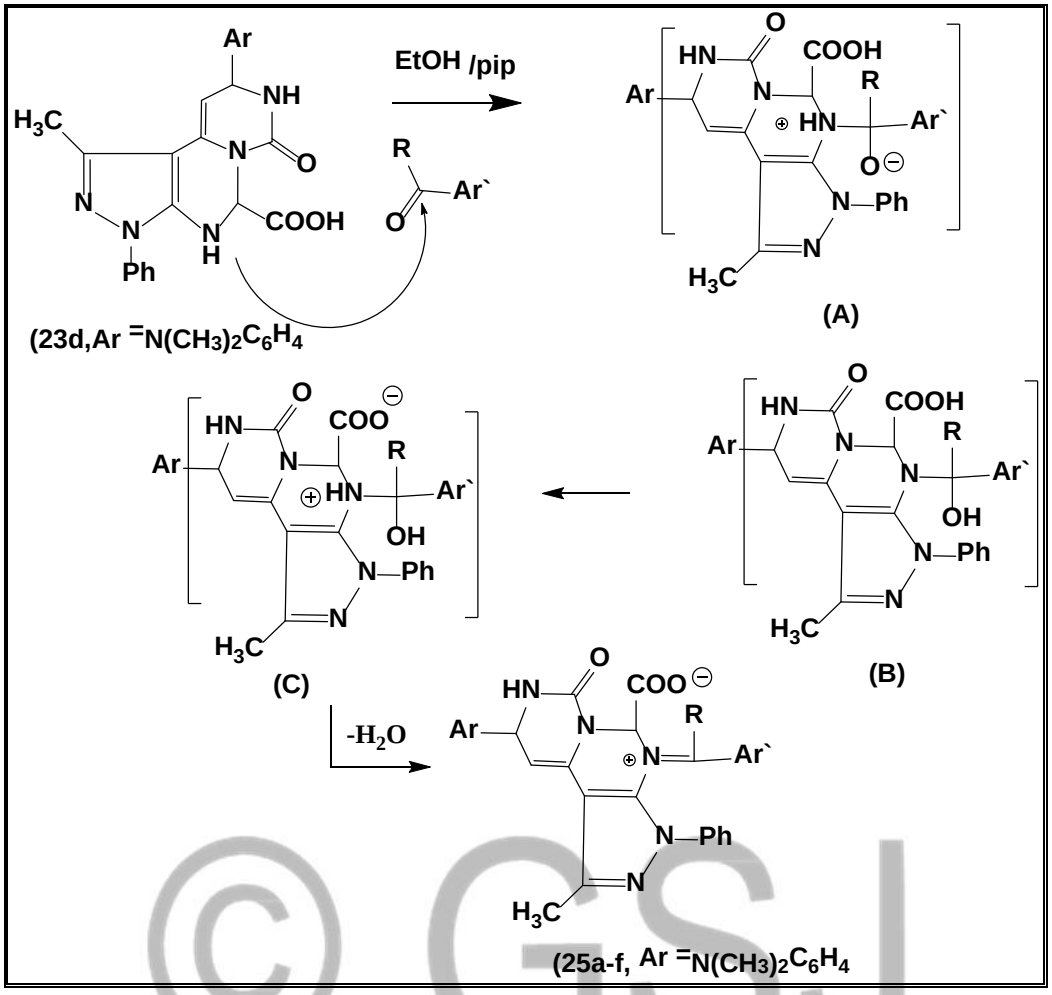
(22,23a-c), Ar=p-$N(CH_3)_2$**a)**; Ar=m-NO_2 **(b)**; R= H **(c), (24a-e):**Ar=p-$N(CH_3)_2C_6H_4$, A=quinolin-4-ium salt **(a)**; Ar= p-$N(CH_3)_2$ C_6H_4, A=quinolin-1-ium salt (**b)** Ar= p-$N(CH_3)_2$, C_6H_4, A=pyridin-4- ium salt **(c)** Ar= m-NO_2 C_6H_4-, A=quinolin-4-ium salt **(d)**; Ar= C_6H_4-, A=quinolin-4-ium salt (**e**). **(25a-f):** Ar (Ar`)=H (**a)** Ar (Ar`)=H**, (**p-$N(CH_3)_2$) **(b**), Ar (Ar`)=H**,(** m-$NO_2$) **(c) ,** Ar (Ar`)=CH_3 **(**H), (**d**); R=CH_3, Ar`= p-$N(CH_3)_2$ **(e)** R=$CH_3$, Ar`= p-OCH_3, **(f)**.

The formation of **(24a-e)** was suggested to proceed via nucleophilic attack of (27a-c) towards quinolin-4-ium ethiodide salt under basic medium to give an intermediate **(A)** which easily eliminate HI molecule flowingly Witter ion to give the desire molecules**, (24a-e),**

Equation (3). The formation of **(25a-f)** was suggested to proceed via nucleophilic attack of (23d) towards aromatic acetophenone derivatives under piperidine catalysis to give an intermediate **(A)** flowingly hydrogen proton transfer to give an intermediate carbinolamine (**B).** The later intermediate undergo Witter ion migration to give an intermediate (**C)** which easily eliminate water molecule to give the desire heterocyclic phyto pigment like **(25a-f), Equation (4)**



Equation (3)



Equation (4)

The absorption spectra of **(19a-e)** in absolute ethanol showed absorption bands batho (hypso) chromically) shifted depending upon the nature of aldehyde aromatic or heterocyclic), substituted of aldehyde and the nature of heterocyclic amines. Thus, the absorption spectra of (**19b)** showed absorption band located at λ_{max}, 530 nm. (**ε_{max}**, 10410 cm^2 mol^{-1}**).** Changing linkage position of methyl group in (**19a)** causes hypsochromic shifted of absorption band in (**19b) Δ λ** = 90 nm. λ_{Max}, 440 nm**. (**ε_{max}, 3700 cm^2 mol^{-1}**)**. On comparison between the absorption spectra of dyes **(19a** & **19c)**, it was obvious that the later dye showed absorption band more hypsochromic shifted by **Δ λ** = 30 nm **$\lambda_{max.}$** 410 nm (**ε_{max}**, **1182** cm^2 mol^{-1}), relative to that band in dye **(19a).** This may be due to electron withdrawing character of H-atom in 5-position. Substituting of benzene moiety in dye **(19b)** by 3-methyl-1-phenyl-pyrazolin-5-imine moiety in dye (**19d)** causes hypsochromic shifted of **Δ λ** = 80 nm. λ_{max}. 450 nm. (**ε_{max}**, 4150 cm^2 $mol^{-1)}$. The hypsochromic shift of absorption band in (**19d)** is due to the presence electron-withdrawing character of heterocyclic ring. The absorption spectra of **(20a-e)** in 95% EtOH showed absorption bands batho (hypso) chromically) shifted depending upon the nature of heterocyclic moieties A, their linkage position and the nature of aldehyde and amine of Schiff's bases. Thus, the absorption

maximum of dye **(20b)** [A = quinolin-4-yl ethiodide] showed **$\lambda_{max.}$** 540 nm ($\varepsilon_{max,}$ **12720** cm^2 $mol^{-1)}$. Substitution of [A = pyridin-4-yl-ethiodide] in dye **(20a)** resulted in hypsochromic shift of Δ **$\lambda_{max.}$** 30 nm, λmax. = 510m ($\varepsilon_{max,}$ 6070cm^2 $mol^{-1)}$ for **(20a).** This is due to the more extensive **π**-delocalization & extra conjugation in quinoline ring. Additionally, changing of the linkage position of quinolin-4-yl salt in dye **(20b)** to 1-yl analogue salt in dye **(20c)** causes hypsochromic shifted of **Δ λ** = 10 nm **$\lambda_{max.}$** 530 nm ($\varepsilon_{max,}$ **4900** cm^2 $mol^{-1)}$. This is due to the extended of **π**- delocalization within quinolin-4-yl ethiodide in dye **(20b)** rather than quinolin-1-yl linkage in dye **(20a)**. On comparison between the absorption spectra of dyes **(20b** & **20d)**, it was obvious that the later dye showed absorption band more hypsochromic shift by Δ λ = 90 nm λ_{max}. 450 nm (ε_{max}, 3800 cm^2 mol^{-1}) relative to that band of dye **(20b).** This is due to the presence of methyl group acting as electron donating inductively effected .On comparison between the absorption spectra of dyes **(20b** & **20e)** ,it was obvious that dye **(20e)** showed absorption band more hypsochromic shifted by Δ λ = 20 nm $\lambda_{max.}$ 520 nm ($\varepsilon_{max,}$ 4150 cm^2 mol^{-1}) relative to that band of dye **(20b)**. This is due to the presence of electron-withdrawing character of heterocyclic ring. **Table (5).** The absorption spectra of **(24a-e)** in 95% ethanol consists of different absorption bands, their position and molar extinction coefficient being influenced by the type of heterocyclic quaternary residue **(A)**, nature of aryl substituents **(R),** Thus, the absorption spectra of **(24a)** R=p-N-$(CH_3)_{2,}$ A=quinolin-4-ium-ethiodide) exhibit (λ_{max} 409 nm; ε_{max} 25000 $mol^{-1}cm^2$). Substituting in **(24c)**, R=p-N-$(CH_3)_{2,}$ A=pyridin-4- ium- ethiodide), exhibit (λ_{max} = 406 nm.ε_{max}= 35069 $_{mol}{}^{-1}cm^2$) causes bathochromic shift due to the more extensive π-delocalization or conjugation. Changing the linkage position of quinolin residue from 4-ium in dye **(24a)** (A= quinolin-4- ium ethiodide) to 1- ium in dye **(24b)** (A=quinolin-1-ium ethiodide) resulted in bathochromic shift in absorption band exhibited (λ_{max} 404 nm; ε_{max} 22069 $mol^{-1}cm^2$. On other hand, substituting of R=p-N-$(CH_3)_2$ in **(24a)** to R= m-NO_2in dye **(24d)** resulted in bathochromic shift in absorption band exhibited (λ_{max} 390nm; ε_{max} 34122 $mol^{-1}cm^2$. This is due to the more electron withdrawing character of NO_2 group. Also, substituting of R=p-N-$(CH_3)_2$ in **(24a)** to R= H in dye **(24e)** resulted in bathochromic shift in absorption band exhibited (λ_{max} 470, 495nm; ε_{max} 17990, 17989 $mol^{-1}cm^2$). This is due to the more electron donating character of the N-dimethyl group. Changing R= H in dye **(24a)** to R= m-NO_2 in dye **(24c)** resulted in bathochromic shift in absorption band exhibited (λ_{max} 405nm; ε_{max} 32658mol^{-1} cm^2). This is due to the more electron withdrawing character of the NO_2 group. Thus, the absorption spectra of **(28d)** R=p-N-$(CH_3)_2$, exhibit (λ_{max} 409 nm; ε_{max} 18262$mol^{-1}cm^2$).**Table (7)**. The absorption spectra of **(25a-f)** in 95% ethanol consists of different absorption bands, their position and molar extinction coefficient being influenced by the nature of aryl substituents **(R),** Thus, the absorption spectra of **(25a), R=**H, exhibit (λ_{max} 358,410,470 nm; ε_{max} 33389 $mol^{-1}cm^2$). Substituting of R=H by R=p-N-$(CH_3)_2$ in **(25b)**, exhibit (λ_{max} = 337,399 nm.ε_{max}= 24486 mol^{-}

$^{1}cm^{2}$) causes bathochromic shift. This is due to the more electron donating character of N-dimethyl group. Substituting R=p-N-$(CH_3)_2$ by R=p-NO_2 in **(25e)** exhibit (λ_{max} = 411 nm.ε_{max}= 26027 $_{mol}^{-1}cm^{2}$) causes bathochromic shift this is due to the more electron withdrawing character of NO_2 group. Substituting of (R=H) in dye **(25d)** to **(**R=p-OCH_3) in dye **(25f)** resulted in bathochromic shift in absorption band exhibited (λ_{max} 417nm; ε_{max} 25513 $mol^{-1}cm^{2}$. This is due to the more electron withdrawing character of the NO_2 group. **Table (7)**. In point view of light absorption, it was obvious that most selected cyanine phytopigment like, **(24a, c-e, 25a, c, d, e)** are absorbed the fundamental light absorption (violet-red) as they have got absorption values in the range 350-660 nm **Tables (7) [15].** The absorption spectra of **(20b, 24a,c-e & 25a,c,d,e)** in the wavelength range 250-700 nm, have been studied in different organic solvents (H_2O, DMF, EtOH, acetone, $CHCl_3$, C_6H_6 & CCl_4) **[16]** for (**20b)** (H_2O, DMF, EtOH, MeOH, acetone, CCl_4, $CHCl_3$, and C_6H_6) for **(24a,c-e & 25a,c,d,e) [17]** respectively. This is constructed with the intention to illustrate the solvatochromic behaviour of such dye (λ_{max} and ε_{max}) values of the intramolecular charge transfer bands are given in Table **(2)**. This is constructed with the intention to illustrate the solvatochromic behaviour of the dyes (λ_{max} and ε_{max}) values of the intramolecular charge transfer bands are given in **Tables (2)**. These dyes are showed positive solvatochromism with increased solvent polarity which depend on the structure and type of dye. This indicates that the polar excited states of such cyanine phyto pigments like are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. The absorption spectra of dyes in ethanol are characterized by the presence of one or two essential bands which reflect the presence of intermolecular charge transfer **[17].** This intermolecular charge transfer had arisen from transferring the electron lone pair of nitrogen atoms of the heterocyclic ring system towards positively charged residue along the conjugated chain between both. The relevant data in **Tables (2)** as well as the representing graphs disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, $CHCl_3$, and CCl_4. These shifts can be attributed to the bathochromic shift occurred in DMF relative to ethanol is mainly a result of an increase in solvent polarity due to increasing the dielectric constant of the former**.** The hypsochromic shifts appeared in ethanol relative to $CHCl_3$, and CCl_4 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center**.** It was worth mentioning that the intermolecular hydrogen bonding between $CHCl_3$ molecules and lone pair nitrogen electrons of heterocyclic ring system is

difficult due to the steric hindrance of three bulk chlorines. Moreover, solute solvent interactions in cases of $CHCl_3$, and CCl_4 generated a residual negative charge on heterocyclic ring nitrogen atoms of the system which intern facilitated electronic charge transfer to positively charged center and this explain the bathochromic shifts in these solvents relative to ethanol, **Table (2).** The unexpected hypsochromic shifts in the absorption spectral maxima in water relative to ethanol and its lower extinction coefficients were mainly ascribed to an ease of interactions of water molecules, through intermolecular hydrogen bonding with lone pair of heterocyclic nitrogen electrons ring system, through intermolecular hydrogen bonding, which intern preclude charge transfer from heterocyclic ring system to positively charged residue along the conjugated bridge, **Table (2).** In point view of light absorption, it was obvious that most of the previous selected cyanine phyto pigments like **(24a,c-e & 25a,c,d,e)** are absorbed the fundamental light absorption (violet-red) as they have got absorption values in the range 350-660 nm **Tables (2) [18]**. The selected cyanine phyto pigments like might be suggested to be used as photosensitizers in most polar and non-polar organic solvents in the (violet-red). Thus, It was obvious that dyes **(24a,c)** absorbed green-blue light in EtOH, acetone, benzene, $CHCl_3$, CCl_4 and MeOH λ_{max} = 340-385 nm extended and improved to the absorption of green light in DMF and acetone λ_{max} = 440-495 nm. Dyes **(24a, c-e, 25a,c,d,e)** absorbed green-blue light in EtOH, acetone, benzene, $CHCl_3$, CCl_4 and MeOH λ_{max} = 300-350 nm extended and improved to the absorption of green light in DMF and acetone λ_{max} = 400-480 nm.

Table (1): Characterized Colour of (20b) & Values of λ nm. & Єmol^{-1} cm^{-1} in pure organic solvents

Comp No.	Water	DMF	EtOH	Acetone	$CHCl_3$	C_6H_6	CCl_4	Alcoholic Solution in H_2SO_4	Alcoholic Solution in NaOH
20b	Reddish violet	Reddish violet	Reddish violet	Reddish violet	Red	Red	Red	Yellow	Violet
	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3	$\lambda_{max.}$ Є $_{max.}$ x10^3
	530 (6.62)	560 (9.57)	550 (10.98)	555 (10.22)	545 (6.83)	550 (8.30)	550 (6.49)	-- ---	-- ---

Table (2): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of **(24a, c, d, e, 25a , c, d, e)** in pure organic solvents

Comp No.	Water		DMF		C_6H_6		$CHCl_3$		CCl_4		Acetone		MeOH		EtOH	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
24a	398	20407	396	20287	438	12401	430	12129	404	19652	449	27296	401	21948	409	25000
24c	401	12567	403	18509	425	11247	420	11132	404	12567	427	10530	409	17188	406	35069
24d	385	10386	414	7487	394	6167	393	8348	388	9439	396	9181	398	11620	390	34122
24e	503 476	13942 13036	497 470	11253 12129	506 478	12209 12129	503 476	12794 11646	500 473	7447 7296	495 467	11888 11646	492 467	13036 12009	495 470	17990 17989
25a	407	9712	413 424	35966 33791	434 410	25906 28051	410 437	35966 31767	413 424	35915 32129	416 437	37235 34184	432 407	33549 38383	470 410 358	30861 38504 33398
25c	399	34351	410 437	33519 32543	429	30965	440 416	30850 33864	421	29874	413 437	36533 32658	410	36418	405	32658 -
25d	401	28323	406	23096	414	31616	412	28836	411	12915	404	28202	406	29078	409	18262
25e	398	25634	409	25000	430	20045	420	26419	406	13157	414	26661	409	28685	411	26027

The spectral behaviour of substituted phenyl-tri-6[4(1)]methine phytopigments like **(20b)** in mixed solvents of different polarities is studied & discussed. The study is performed to trace the possibility of the formation of a hydrogen-bonded solvated complex between the solute & solvent molecules. It is also aimed to prove whether the solvent shift in the spectra of such compound in ethanol solutions is due to hydrogen-bonding or to more salvation effect. The complexes which are liable to form in solution are those of compounds capable of forming stable hydrogen bond between solute & solvent. The effect of addition of successively increasing amounts of polar solvents on the absorption spectra of phytopigment like in low & high polarity solvents is discussed including **(20b)** in the mixed solvents, Table **(3)**.

The absorption spectra of substituted phenyl-tri-6[4(1)]methine phytopigments like **(20b, $1x10^{-4}$)** in Et-OH containing varying amounts in increasing proportion of water added give an increase in the dielectric constant of the medium & leads to an increase in the solute solvent hydrogen bonding. This n-electron of the oxygen atom causes a blue shift of the CT band. Thus, on plotting the absorbance at λ_{max} nm versus the mole fraction of Et-OH & water solvents reveals that the absorbance increases sharply as the mole fraction of Et-OH increases up certain limit & then decreases accompanied with red shift in λ_{max}. On plotting the energy against the mole fraction of H_2O, a broken line with three segments is obtained. From this plotting, the energies in pure water are 55 $k.cal.mole^{-1}$, the orientation & hydrogen bond energies are 0.54, 1.5 k $cal.mol^{-1}$, the stability constant of the molecular complex which formed between solute & EtOH molecules is calculated from the molarities of EtOH & the log k_f **(k_f = 1.27)** and the number of solvent molecules **(n)** of EtOH equal to one **–**ΔG = 691.91 k. cal. mol^{-1} and the values of **k_f, ΔG** and **n** indicate that a 1:1 complex is formed for **(20b),** Table **(3)**.

Table (3) Commutative data of (20b) in Mixed Solvent (EtOH-H_2O)

Comp. No.	Solvent Mixed System	Excitation energy K. cal. mol^{-1} Pure Solvents		Orientation energy K. cal. mol^{-1}	H-bond energy K. cal. mol^{-1}	Total energy K. cal. mol^{-1}	n	Log K_f	K_f	(±)ΔG K. cal. mol^{-1}
20b	**Et-OH-H_2O**	52 EtOH	55 H_2O	0.524	1.5	2.024	1	0.1034	1.27	-691.91

Styryl & Methine phyto pigments like **(19, 20)a-c, d** are highly colour (orange to reddish violet), easily soluble in polar organic solvents and on triturating with concentrated sulphuric acid exhibiting no iodine vapor liberation on warming, they easily soluble in polar organic solvents and exhibited permanent coloured in basic media which reversibly discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution in order to ensure optimal pH in the application of such dyes as photosensitizers and determine their pKa values too. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity, **[15]**, Table **(1)***.* Phytopigment like **(24a, c, e & 25a,c,d,e)** gives a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution in order to ensure optimal pH in the application of such dyes as photosensitizers and determine their pKa values too. The effectiveness of compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity **[15].**

Styryl & Methine phyto pigments like **(19, (20) a-c, d** & **24a, c, e & 25a, c, d, e)** are highly colour (orange to reddish violet), easily soluble in polar organic solvents and on triturating with concentrated sulphuric acid exhibiting no iodine vapor liberation on warming, they easily soluble in polar organic solvents and exhibited permanent coloured in basic media which reversibly discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution in order to ensure optimal pH in the application of such dyes as photosensitizers and determine their pKa values too. The effectiveness of compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity **[15],**Table **(1)***.* Such dyes undergo a hypsochromic colour change due to protonation of pyridin [quinolin]-4(1)-ium] salts In such cases the intramolecular charge transfer (CT) between heterocyclic donor nitrogen and heterocyclic acceptor nitrogen atoms of heterocyclic amino acids does not occur, and long wave length CT band disappears. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated, Table **(4)**. On plotting

the absorbance at settled wave number versus pH values, S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to left corresponded to the acidic form of an indicator, while the upper portion to right corresponded to the basic form. Since the pKa value was defined as the pH value for which one half of the indicator (dye) is in basic form and the other half in an acidic form. This point, (pKa value), was determined by the intersection of the S-curve with horizontal line midway between the left and right segments **[15].** The pKa values and spectral characteristics of the protonated forms of dyes are collected in Table **(4).** The spectral behaviour of **(20b & 24a, c, e & 25a, c, d, e)** in 95% ethanol and/or in aqueous universal buffer solution showed that these compounds absorbed the blue light λ_{max} = 340-385 nm and the near violet light extended to the green light λ_{max} = 440-495 nm. In acid (pH ≥ 2.09) medium these dyes undergo a hypsochromic colour change due to the protonation of the (quinolin-2/ pyridin-(4)-ium salts and Aryl Substituents. A new short wave length band is observed, which could be assigned to a localized **π–π*** transition. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated. Several methods had been adopted for spectrophotometric estimation of dissociation constants of weak acids; the variation of absorbance at settled wavelength could be utilized. Thus, on plotting the absorbance at settled wave number versus pH values, S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to the left corresponded to an acidic form of the indicator, while the upper portion to the right corresponded to basic form. Since pKa value was defined as pH value for which one half of an indicator dye is in basic form and the other half in the acidic form pKa value was determined by the intersection of the S-curve with horizontal line midway between the left & right segments pK_a values and spectral characteristics of protonated forms of dyes are collected in **Table (4).** The absorption spectra of an ethanolic solution of substituted phenyl-tri-6[4(1)]methine phytopigments like **(20b & 24a, c, e & 25a,c,d,e)** in aqueous universal buffer solution of different values of pH **(1.98-12.12)** show regular changes with increasing the pH of the medium especially in n- $\pi\acute{\sigma}^*$ and CT bands. The absorption spectra of substituted phenyl-tri-6[4(1)]methine phytopigments like **(20b)** in 95% EtOH showed absorption of blue-green light λ_{max}= 550 nm showed that these compounds absorbed blue light λ_{max} = 340-385 nm and near violet light extended to the green light λ_{max} = 440-495 nm. In acid medium (pH ≥ 2.09), The pK_a values were obtained using the standard procedure **[19]**, Meanwhile, their absorption spectra in universal buffer solution reveals absorption of blue light λ_{max}= 450 nm at pH ≥ 1.99 extended to green-red light, the absorption spectra at λ_{max}= 570 nm (pH ≥ 6.07), resulted in hypso chromically shifted if compared with those

obvious in ethanol, **Table (4).** The absorption spectra at (pH ≥ 1.99) medium dye **(20b)** undergo a hypochromic colour change due to the protonation of the heterocyclic nitrogen atom. In such cases the intramolecular charge transfer (CT) between the heterocyclic donor nitrogen and the heterocyclic amino acid nitrogen atom acceptor atom does not occur, and the long wave length CT band disappears. A new short wave length is observed, which could be assigned to a localized π^*-π^* transition. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated, pK_a values and spectral characteristics of the protonated forms of dye **(20b)** is pK_a value=3.8 & 9, Table **(2)**. pK_a values and spectral characteristics of the protonated forms of phytopigment like **(24a,c e)** is pK_a value=6.9,8.38 for **(24a)** at λ 450nm & 7.0 for **(24c)** at λ 440nm & 7.10, 10.38 for **(24e)** at λ 510nm and. pK_a values and spectral characteristics of the protonated forms of phytopigment like **(25a,c,d,e)** is pK_a value=6.9,8.38 for **(25a)** at λ 430nm & 6.9,8.38 for **(25c)** at λ 410 nm,7.0 for **(25d)** at λ 440nm & 4.1,7.0 for **(25e)** at λ 430nm. Thus, it was suggested that such phytopigment likes **(20b & 24a, c, e & 25a, c, d, e)** are more sensitive as photosensitizer in both acidic & basic medium. This may be due to the presence of N-methyl pyridin (quinolin)-4(1)-yl linkage and aryl substituents in compound causing the high planarity of the phytopigment molecule, Table **(2)**.

Table (4): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of (20b, 24a, c, e, 25a, c, d, e) in Aqueous Universal Buffer Solution.

Comp No.	Universal buffer							pKa
	2.09	4.10	6.09	7	8.36	10.38	11.98	
	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	
20b	550 (10.98)	430 (2.06)	450 (2.289)	430 (1.970)	440 (2.044)	485 (2.844)	500 (2.840)	3.8 9
24a	361 (6.5)	444 (9.32)	412 (7.91)	401 (12.83)	398 (10.87)	346 (14.22)	340 (12.52)	6.9, 8.38
24c	353 (6.69)	345 (11.89)	348 (8.78)	401 (7.160)	398 (18.150)	404 (15.540)	406 (20.570)	7.0
24e	233 (38.81)	250 (39.11)	503 (5.47) 473 (5.72)	500 (6.27) 473 (6.44)	506 (9.79) 473 (10.35)	476 (7.19)	484 (12.861)	7.10 10.38

Comp No.	Universal buffer							pKa
	2.09	4.10	6.09	7	8.36	10.38	11.98	
	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	λ_{max} (ε_{max}) x10^3	
25a	358 (29.1) 375 (2738)	356 (26.13) 413 (25.52)	402 (28.08)	344 (21.79)	405 (31.01)	410 (39.13)	407 (39.31) 364 (32.38)	6.9 8.38
25c	358 (33.13) 383 (29.56)	407 (37.63) 424 (34.05)	397 (20.63)	399 (25.52)	405 (26.33)	410 (29.04)	407 (32.15) 364 (25.01)	6.9 8.38
25d	347 (13.21)	425 (10.94) 353 (113)	409 (30.1) 350 (28.36)	401 (14.59)	348 (26.59)	401 (24.66)	396 (15.24) 358 (1.346)	7.0
25e	355 (23.76)	409 (2.29)	401 (19.04)	396 (20.48)	348 (28.93)	412 (32.15) 358 (28.99)	436 (31.35) 361 (28.83)	4.1 7.0

EXPERIMENTAL

The chemicals employed in the present work were of highest purity available (A.R. reagents) from BDH. They were used without further purification. The organic solvents used ethanol, acetone & dimethylformamide (DMF) were spectroquality. All melting points are uncorrected. Elemental analysis were carried out at the Micro analytical centre. IR spectra & mass spertra were determined with Perkin Elmer Infrared 127B (cairo-University). & on a Hp Ms 6988 spectrophotometer.The visible spectra was recorded on UV-Visible recording spectrophotometer UV-240. 4-Acetyl (formyl)–3–methyl-1-phenyl pyrazol–5–one (imine) was carried out according to **[5-7),** 4-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine-4-yl)-6-substituted aryl-5,6-di[H]pyrimidin-2(1H)-one **(21a-f)** was carried out according to prospective reference **[9].**

Synthesis of N-acetyl-3-methyl-1-phenyl-pyrrolo[3,4-d] pyrazole-2-carboxamido acetic acid (18a,b):Route (A)

6-Methyl-2-phenyl-2,3,4,5-tetra[H]pyridazin-3-oxo-4-carbaldehyde **(1a,** 0.01 mol) or 4-acetyl-5-methyl-2-phenyl-2,4-di[H]-3H-pyrazol-5-one **(1b**, 0.01 mol**)** & ethyl glycinate (0.02 mol) were dissolved in ethanol (30 ml) to which piperidine was added. The reaction mixture was refluxed for about 3-5 h filtered hot, concentrated, cooled and acidified with acetic acid.The products after dilution with water were collected & recrystalised from aqueous ethanol to give

an intermediate open structure, then the product was fused with piperidine followed by Et-OH extraction for one hour. The products were collected and recrystalised to give desired heterocyclic amino acids **(18a,b),** Table **(5).**

Route (B):

3-Methyl-1-phenyl pyrazolin-5-one **(**0.01 mol) & N-acetyl(formyl) glycine (0.02 mol**)** were fused for 5 minutes & then refluxed with acetic acid for one hour, concentrated, diluted with water,collected & recrystalised from acetic acid to give the same products obtained in Route (A)**,** Table **(1).** IR (ν^{KBr} cm^{-1}) of (**18a)** showed general absorption peaks at 1721 cm^{-1} (υ C=O, COOH), 754 cm^{-1} (υ mono subs. Ar.), **Bellamy, L. J. (1962).** The structure of **(18a)** was consider most likely & in agreement with molecular formula based on mass spectrum resulted in molecular ion at **m/z**=(358) & base peak at **m/z**= (216), **[8].**

Synthesis of 3-methyl-1-phenyl pyrrolo[3,4-d] pyrazole Schiff bases (19a-d)

N-Acetyl-3-methyl-1-phenyl pyrrolo[3,4-d]pyrazol-2-carboxamidoacetic acid (18a,b, 0.01 mol), benzaldehyde, acetophenone & 4-acetyl-3-methyl-1-phenyl pyrazolin-5-imine (0.01 mol) were dissolved in EtOH (30 ml) to which piperidine was added. The reaction mixture was refluxed for about 6-8 hrs., filtered hot, concentrated, cooled & acidfied with acetic acid.The products after dilution with water were collected & recrystalised from aqueous ethanol,Table **(1)**. IR (ν^{KBr} cm^{-1}) of 18a 2370 cm^{-1} (υ C=N), 1718 cm^{-1} (υ C=O, COOH), 754 cm^{-1} (υ mono subs. Ar.) **[12].** Table **(5).**

Synthesis of 3-Methyl-1-phenyl pyrrolo[3,4-d] pyrazoline phyto cyanine dye like (20a-e):

3-Methyl-1-phenyl pyrrolo[3,4-d] pyrazole Schiff bases **(19a-d,** 0.01 mol) & N-methyl-pyridin (quinolin)-4(1)-ium ethiodide (0.01 mol) were dissolved in ethanol (30 ml) and piperidine (3-5 drops) was added. The reaction mixtures were refluxed for about 7-9 hrs, filtered hot, concentrated, cooled & acidified with acetic acid. The precipetated solids after dilution with water were collected & crystallized from aqueous ethanol to give **(20a-e).**Table **(5).** IR (ν^{KBr} cm^{-1}) of (**20a),** 3057 (υ N-heterocyclic quaternary salt), 1704 (υ connected chromophoric group) in addition to the general absorption bands cited before in **(18a), [12].** The structure of **(20a)** was consider most likely & in agreement with molecular formula based on mass spectrum resulted in M+4 peak at **m/z**= (358), and base peak at m/z=(288), 89 & base peak (m/z =134) **25d.**m/z =388, and base peak at m/z =148 **[8]**

Table (5): Characterization data of **(18a,b, 19a-d & 20a-e):**

Comp No.	Nature of Products			Mol.Formula (Mol. wt)	% Calcd. (Found)			Absorption Spectra In absolute Et-OH	
	M.P. ^0C	Yield %	Colour		C	H	N	λ_{max} (nm)	ε_{max} ($cm^2 mol^{-1}$) ,$1x10^{-3}$
18a	155	78	orang	$C_{17}H_{17}N_4O_5$ (358)	65.02 (64.73)	4.62 (4.56)	17.25 (17.43)	440	2.004
18b	78	48	orange	$C_{18}H_{17}N_4O_4$ (356)	66.1 (65.88)	4.96 (5.1)	17.01 (16.47)	390	0.625
19a	116	43	Yelow orange	$C_{21}H_{17}N_3O_2$ (343)	73.47 (73.12)	5.0 (5.16)	12.25 (12.48)	410	0.1182
19b	109	76	red	$C_{21}H_{17}N_3O_2$ (343)	73.47 (73.01)	5.0 (5.23)	12.25 (12.35)	530	10.410
19c	127	51	orange	$C_{22}H_{19}N_3O_2$ (357)	73.95 (74.05)	5.32 (5.51)	11.76 (11.25)	440	3.700
19d	163	47	red	$C_{25}H_{21}N_6O_2$ (437)	68.65 (68.23)	4.81 (4.78)	19.22 (18.96)	450	4.150
20a	115	40	Red	$C_{27}H_{22}N_4O_2$ (434)	74.65 (75.04)	5.07 (5.19)	12.9 (13.31)	510	6.070
20b	167	42	Red violet	$C_{31}H_{24}N_4O_2$ (484)	76.86 (77.21)	4.96 (5.33)	11.57 (12.04)	540	12.720
20c	118	38	Red violet	$C_{31}H_{24}N_4O_2$ (484)	76.86 (76.45)	4.96 (5.21)	11.57 (12.06)	530	4.900
20d	290	39	Brown red	$C_{32}H_{26}N_4O_2$ (498)	77.11 (74.86)	5.22 (5.13)	11.25 (10.98)	450	3.800
20e	131	35	Brown	$C_{35}H_{28}N_7O_2$ (578)	72.66 (73.15)	4.84 (5.08)	16.96 (17.24)	520	4.150

Synthesis of 1-(carboxymethyl)-6-(3-methyl-1-phenyl-4,5-di[H]1H-pyrazol-4-yl-5-imine)-2-oxo-4-Substituted-Aryl-2,3,4,5-tetra[H]pyrimidin-1-ium (22a-c) & 1-(carboxychloromethyl)-4-(4-(dimethylamino)phenyl)-6-(5-imino-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-2-oxo-2,3,4,5-tetrahydropyrimidin-1-ium (22d)

An ethanolic solution of **(21a-c,** 0.01mol) and chloroacetic acid (0.01mol)) in the presence of sodium bicarbonate (saturated solution) was refluxed for 8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated product after dilution with water was separated, filtrated, crystallized from ethanol, and afforded **(22a-c), Table (6).**

Synthesis of 5-Carboxy-1-methyl-7-oxo-3,diphenyl-9-Substituted Aryl-4,5, 7, 8,9,10-hexa[H]3H-pyrazolo[4,3-e]pyrimido[1,6-c]pyrimidin-6-ium chloride (23a-c) & 5-carboxy-9-(4-(dimethylamino)phenyl)-1-methyl-7-oxo-3-phenyl-4,5,7,8, 9,10-hexa[H]3H-pyrazolo[4,3-e]pyrimido[1,6-c]pyrimidin-6-ium iodide (23d), Route (A):

An ethanolic solution of **(21a-c**) and chloroacetic acid (0.01mol)) in the presence of sodium bicarbonate (saturated solution) was refluxed for 8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated product after dilution with water was separated, filtrated, crystallized from ethanol, and afforded **(23a-c), Table (6).**

Route (B):

A mixture of **(21a-c**), iodine and chloroacetic acid (0.01 mol) were refluxed in ethanol for 5 hr., filtered hot, concentrated, cooled. The precipetated solids were collected, washed with ethanol and crystallized from aqueous ethanol to give **(27d), Table (5).** IR (ν^{KBr} cm^{-1}), (23a) 1497 **cm^{-1}** (C=N), 1592 **cm^{-1}** (C=C), 1708 **cm^{-1}** (C=O), 3400 **cm^{-1}** (OH) **[12],** ^{1}H-NMR (CD_3OD, 250 MHz), (22a , 23a) δppm 1.19-1.29 (s, CH_3, of pyrazol), δppm 3.1(s,3H,CH_3 of Aromatic aldehyde), δppm 3.86-5.55 (s, 1H, pyrimidine nucleus), δppm 6.4 (s,1H,OH), δppm 7.25-7.90 (m, 13H, Ar +Het + =CH + NH) **[13,14]**,m/z M^+ [Base peak] 26a molecular ion [M-58]$^+$ peaks at m/z =388,(base peak m/z =175), m/z M^+ [Base peak] **23a** molecular ion [M-58-(I)] peaks m/z =387(base peak m/z =77) **[8]**

Table (6): **Characterization Data of (23a-c):**

Comp. No.	Nature of Products			Mol.Formula (Mol.wt)	Calcd. (Found)%		
	M.P. °C	Yield %	Colour		C	H	N
22a	245	47	Reddish brown	$C_{24}H_{26}N_6O_3$ (446)	64.57 (64.59)	5.83 (5.87)	18.83 (18.86)
22b	185	64	Yellow	$C_{22}H_{20}N_6O_5$ (448)	58.93 (58.98)	4.46 (4.49)	18.75 (18.77)
22c	240	58	Violet	$C_{22}H_{21}N_5O_3$ (403)	65.51 (65.55)	5.21 (5.26)	17.37 (17.38)
23a	140	53	Deep red	$C_{24}H_{25}N_6O_3I$ (572)	50.35 (50.38)	4.37 (4.39)	14.69 (14.67)
23b	160	38	Pal brown	$C_{22}H_{19}N_6O_5I$ (574)	45.99 (45.97)	3.31 (3.36)	14.63 (14.67)
23c	120	43	Pal yellow	$C_{22}H_{20}N_5O_3I$ (529)	49.91 (49.95)	3.78 (3.79)	13.23 (13.26)

Synthesis of 1-methyl-7-oxo-3-phenyl-9-Substituted Aryl-3,4,5,7,8,9-hexa[H] pyrazolo[4,3-e]pyrimido[1,6-c] pyrimidin-4-ium-5-carboxylate-4-phytopigment (24a-e),

An ethanolic solution of **(23a-c**) and pyridin (quinolin)-4(1)-ium ethiodide (0.01mol) in the presence of few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol**,** Table **(7)**. IR (ν^{KBr} cm^{-1}) **(24a, d, e)** 1497 **cm^{-1}** (C=N), 1592 cm^{-1}

(C=C), 1708 **cm^{-1}** (C=O), 2923 **cm^{-1}**, 1344-1360 **cm^{-1}** (NO_2 aromatic) **[12]** ^{1}H-NMR (CD_3OD, 250 MHz), (24a, d, e), δppm 1.19-1.29 (s, CH_3, pyrazol), δppm 3.1(s,3H,CH_3 Aromatic aldehyde), δppm 3.86-5.55 (s, 1H, pyrimidine), δppm 2.8 (s, 3H, CH_3 Ethyl), 3.05s, 3H, CH_2N), δppm 7.25-7.90 (m, 13H, Ar +Het + =CH + NH), δppm 3.1 s, 3H, CH_3 of Aromatic aldehyde or acetophenone **[13,14]**

Synthesis of 9-(4-(dimethylamino)phenyl)-1-methyl-7-oxo-3-phenyl-3,4,5,7,8,9-hexa[H]pyrazolo[4,3-e]pyrimido[1,6-c]pyrimidin-4-ium-5-carboxylate-4-[α-Substituted-benzylidene]Styryl-phytopigment (25a-f),

A mixture of **(23a-c**) and aromatic aldehyde derivatives (0.01mol) were fused in presence of few drops of piperidine (3-5 drops) for 10 minutes. The reaction mixture was extracted with ethanol, filtered hot , concentrated, cooled and acidified with acetic acid. The precipitated solids after dilution with cooled water were collected and crystallized from the proper solvent to give **(25a-d),** Table **(7)**. A Mixture of **(23a-c**) and acetophenone derivatives (0.01mol) were dissolved in ethanol (30 ml) and piperidine (3-5 drops) was added. The reaction mixture was refluxed in a water bath 4 hr., filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and crystallized from aqueous ethanol to give the intermediate **(25a-d)**. The results data are summarized in Table **(5)**. IR (ν^{KBr} cm^{-1}) of (25a, e) 1497 cm^{-1} (C=N), 1592 cm^{-1} (C=C), 1708 cm^{-1} (C=O), 2923 cm^{-1}, 1344-1360 cm^{-1} (NO_2 aromatic) **[12].** ^{1}H-NMR (CD_3OD, 250 MHz), **(25a, e)**, δppm 1.19-1.29 (s, CH_3, pyrazol), δppm 3.1(s, 3H, CH3 Aromatic aldehyde), δppm 3.86-5.55 (s, 1H, pyrimidine), δppm 2.8 (s, 3H, CH_3 Ethyl), δppm 3.05 (3H, CH_2N), δppm 7.25-7.90 (m, 13H, Ar +Het + =CH + NH), δppm 3.1 s, 3H, CH_3 of Aromatic aldehyde or acetophenone **[13, 14]**

Table (7): Characterization data of (24a-e, 25a-c).

Comp. No.	Nature of Products			Mol.Formula (Mol. wt)	% Calcd. (Found)			Absorption Spectra In absolute Et-OH	
	M.P. °C	Yield %	Colour		C	H	N	λ_{max} (nm)	ε_{max} ($cm^2 mol^{-1}$) $1x10^{-3}$
24a	160	61	Reddish brown	$C_{34}H_{32}N_7O_3I$ (713)	57.22 (57.24)	4.49 (4.47)	13.74 (13.78)	409	25.00
24b	250	57	Yellowish brown	$C_{35}H_{34}N_7O_3I$ (727)	57.77 (57.79)	4.68 (4.66)	13.48 (13.46)	404	22.069
24c	260	48	Pal brown	$C_{30}H_{30}N_7O_3I$ (663)	54.30 (54.35)	4.52 (4.54)	14.78 (14.79)	406	35.069

24d	130	41	red	$C_{32}H_{26}N_7O_5I$ (715)	53.71 (53.75)	3.64 (3.68)	13.71 (13.75)	390	34.122
24e	185	38	Yellow	$C_{32}H_{27}N_6O_3I$ (670)	57.31 (57.36)	4.03 (4.07)	12.54 (12.53)	495 470	17.99 17.989
25a	240	42	Yellowish brown	$C_{31}H_{29}N_6O_3I$ (660)	56.36 (56.39)	4.39 (4.41)	12.73 (12.77)	470 410 358	30.861 38.504 33.398
25b	265	58	Red	$C_{33}H_{34}N_7O_3I$ (703)	56.33 (56.36)	4.84 (4.87)	13.94 (13.96)	337 399	24.486 24.486
25c	247	39	Deep red	$C_{31}H_{28}N_7O_5I$ (705)	52.77 (52.78)	3.97 (3.99)	13.90 (13.95)	405 -	32.658 -

Solvatochromic and acid base properties:

The organic solvents were used of spectroscopic grade which purified according to the recommended methods **[20]**. The electronic absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1cm cell. The stock solution of the dye was of the order 10^{-3} mol-dm^{-3}. Solutions of low molarities used in spectral measurements were obtained by accurate dilution.

Preparation of dyes solution:

1-For studying the effect of pure solvents in the UV and visible range:An accurate volume of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentration. The spectra were recorded immediately after mixing in order to eliminate as possible the effect of time.2- For studying the spectral behaviour in mixed solvents in the visible region: An accurate volume of the stock solution (10^{-3} mol-dm^{-3} in ethanol) of the dyes were placed in10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent. 3-For studying the spectral behaviour in aqueous universal buffer solutions: An accurate volume of the stock solution was added to 5ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked before spectral measurements. 4-For studying the kinetics measurements Stock solutions (1×10^{-3} mol-dm^{-3}), of each of the reagents were prepared by dissolving the accurate weight of the recrystallized solid compound in the required volume of ethanol. Solutions of low molarity were prepared by appropriate dilution of the stock solutions.

Preparation of universal buffer solutions:

A modified buffer series derived in accordance with **[21]** was prepared for use in the present investigation. The constituents are as follows: **(a)** A solution of 0.4 mol-dm^{-3} of each of phosphoric and acetic acid was prepared by accurate dilution of A. R. concentrated stock.

(b) A solution of 0.4 mol-dm^{-3} of boric acid was obtaind by dissolving the appropriate weight of the recrystallized acid in redistilled water. **(c)** A stock acid mixture was prepared by mixing equal volumes of three acids in large bottle. The total molarity of the acid was thus maintained at 0.4 mol-dm^{-3}. A series of buffer solutions with pH values ranging from (1.98-12.12) was prepared as recommended by **[21].** This was done by mixing 150 ml of the acid mixtures in a 250 ml measuring flask with the appropriat volumes of 1.0 mol-dm^{-3} NaOH and completed to the mark with redistilled water. This modification was performed in order to keep the ionic strength constant at all pH's mixed with different proportions of organic solvents used. The pH's of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to ± 0.005 pH units, at 25 ^{0}C.

REFERENCES AND NOTES

[1] Muhammad Z. H., Muhammad A. & Saed, U. R. Journal of the Chinese Chemical Society, (2001), *48*, 45-48.

[2] Khalil, Z. H.; Yanni, A. S. J. Indian Chem. Soc., (1981), LVIII, 494-497

[3] Sedov, Kino-U. A., Bespalova, G. V., Garanzha, V. and Kulikova, Lik. Khim. Farm. Zh. (1976),10 (1) 66-70

[4] Inagaki, Y. K., Kobayashi, T. and Kuho, T.; Jpn Kokai Tokkyo KOHO Jp 04, 13, 373. 17 Jan. (1992), Appl. 90/116, 444, 01 May, (1990), 16pp.

[5] El-Deen, N, S. Ph.D Thesis, (2004), Aswan Faculty of Science, Aswan University.

[6] Abd El Latif, F. M.; Maghraby, A. S. & Koraiem, A. I. M., *Jour. Chem. Soc. Pak.* (1993), *Vol. 15, (1),*

[7] Mohanty, S. K.; Sridhar, R.; Sy. Pad. Manava, S.; Sundarr, Ra. O. and Mittra, A. S., Indian *J. Chem.,* (1977), *15b, 1146-1147*

[8] Porter, Q. N. and Baldas, J.*; "Mass Spectrometry of Heterocyclic Compounds "*Wiely*, New York* (1971).

[9] Sammour, A.; selim, M. I. B.; Nour El, M. M.; and Abd El-Halim, M.; U.A.R.J.Chem. (1970), 13 (I), 7-24

[10]El-Maghraby, M. A.,Koraiem, A. I. M.,Abd el-Latif, F. M. E.;J. Chem. Tech. Biotechnol, (1985), 35A,63-72,

[11]Koraiem, A. I. M.; Khalil, Z. H.; and Abu El-Hamd, R. M.;J. Chem. Tech. Biotechnol, (1986),36,473-79

[12] Bellamy, L. J.; *The infrared spectra of complex molecules*, London; Methuen, (1962).

[13] Sheinman, F., *Nuclar magnetic resonance of complex Molecules, vol.1.*
Sodin, (1972),12, 1619

[14] Batterham, T. J.;"*^{1}HNMR spectra of simple heterocycles"* Wiley New York, (1973). New York, (1973).

[15]Mahmoud, M. R.; Khalil, Z. H. and Issa, R. M., Acta. Chim.Acad. Sci. Hung, (1975), 87(2), 121-5,

[16] Weast, R.C. and Astl, M. J. ;(1980-1981), CRC handbook of chemistry and physics, 61 st. Edn. (CRC press, Inc.) 56

[17] Eissa, Fayez M. , M.Sc. Thesis, Aswan Faculty of Science, South Valley University (2001) 122.

[18] Kotzolv, N. S., Zhikareva, O. O. and Batische, S. A.; Kim. Geterotski Sodin, (1972).12, 1619

[19] Mitewa, M.; Mateeva, N.; Antonov, L. & Deligeorier, T. (1995), *Dyes Pigments, 27(3), 219-25,*

[20] Reddick, J. A. & Banger, W. B.; (1970); Techniques of Chemistry Organic Solvents (1969), a Weiss Berger, Ed), 3rd. Ed N. Y. Wiley 11, and Organikum 1 Th. Ed., Berlin: DVW

[21] Britton, H. T. S.; *Hydrogen Ions*, 4 th., P. 313 Chapman and Hall, London (1952)