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Synthesis and mesomorphism of novel chalconyl esters with a lateral nitro group

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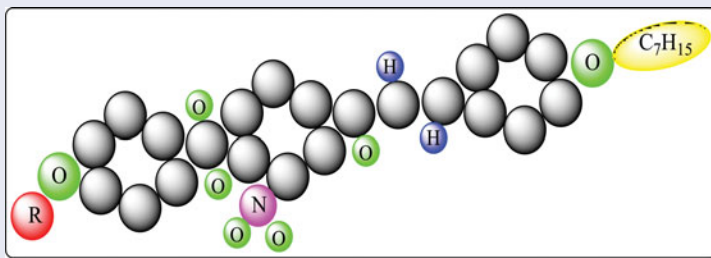
ABSTRACT

A new chalconyl homologous novel series with lateral nitro group: 4-(3-4-(heptyloxy)phenyl) acryloyl-2'-nitro phenyl 4'-alk oxy benzoate have been synthesized and all the members are differed by the terminal chain length C_nH_{2n+1} , where $n = 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18$. Their transition temperatures and mesophase characteristics are studied with the help of polarizing optical microscope (POM). All 13 homolog of series except the C_1 – C_4 are enantiotropically mesogenic. The molecular structures have been confirmed by the analytical techniques of NMR, IR, and elemental analysis.

KEYWORDS



Liquid Crystal; Smectic;
Nematic; Mesophase;
Chalconyl ester

GRAPHICAL ABSTRACT



Introduction

Materials with three phenyl ring and $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{CO}-\text{CH}=\text{CH}-$ central linkage have been synthesized earlier now we attach a lateral nitro group in this structure and study what effect come to the liquid crystal properties. The interest in the study of the liquid crystalline (LC) [1] state of matter has attracted scientists and technologists because of its dual character as to flow like an isotropic liquid and have to behave as rigid crystals. Some LCs like chalconyl esters with lateral nitro group derivatives are thermotropically and biologically active materials which are useful for the manufacture of LC devices or pharmaceutical preparation useful for curing of various physical disorder of human or animal bodies [2–10].

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Present investigation is planned to synthesize novel LC material through homologous series with a view to understand and establish the effects of molecular structure on thermotropic LC properties, with reference to changing the tail group and its flexibility [11–14]. The aims and object in view to study the effect of molecular structure and lateral group on LC properties and LC behavior [15–20] as a result of molecular flexibility keeping molecular rigidity unaltered throughout a series and changing flexibility from series to series for the same homolog at constant rigidity. The novel homologous series contain three phenyl rings and bridged through two central linkage ($-\text{CH}=\text{CH}-\text{COO}$ and $-\text{CO}-\text{CH}=\text{CH}-$) as the rigid core and *n*-alkoxy ($-\text{OR}$), $-\text{OC}_7\text{H}_{15}$ and nitro (NO_2) as flexible units of a molecule.

Experimental

Synthesis

Trans 4-*n*-alkoxy cinnamic acids (A) were prepared by modified method [21,22]. α -3-nitro 4-hydroxy benzoyl β -4'-tetradecyloxy ethylene (B) was prepared by usual established method [23]. Esters were synthesized by a literature method [24]. Thus, the Chalconyl – ester homolog derivatives were decomposed, filtered, washed with solution of sodium bicarbonate and sodium hydroxide followed by water dried and purified till constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage. Alkyl halides, 3-Nitro 4-hydroxybenzaldehyde, 3-hydroxy acetophenone, dicyclohexylcarbodiimide, Dimethyl amino pyridine, DCM, Ethanol, Acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to a series is shown below in Scheme 1.

Characterization

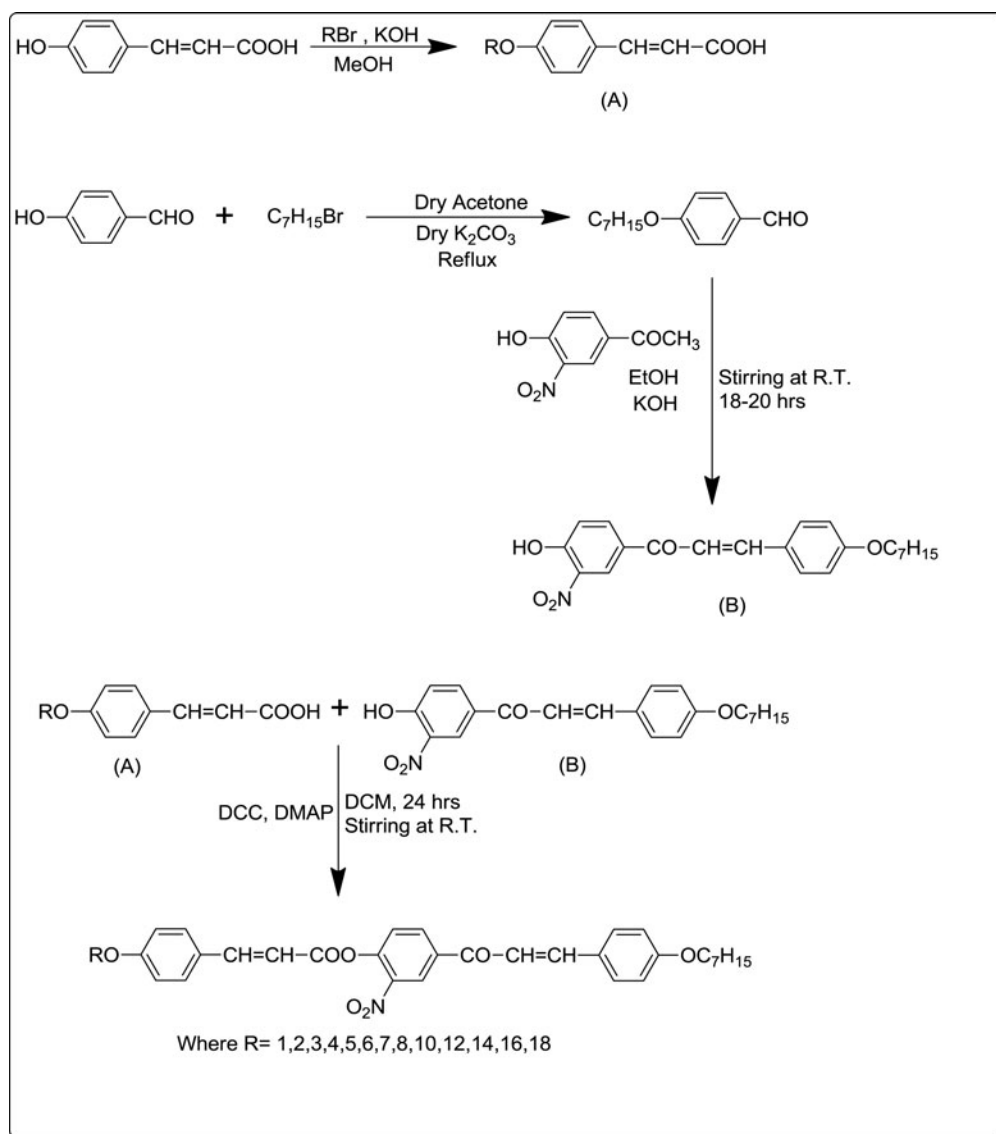
Selected members of the novel homologous series were characterized by Elemental Analysis, infrared spectroscopy, ^1H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ^1H NMR spectra (Table 1) were recorded on Bruker using CDCl_3 as solvent. Microanalysis (Table 2) was performed on a Perkin-Elmer PE2400 CHN analyzer. Transition temperature and LC properties (textures) were determined using an optical polarizing microscopy equipped with a heating stage. Textures of nematic phase are determined by miscibility method.

Analytical data

IR spectra in cm^{-1} for octyloxy & dodecyloxy derivatives

Octyloxy: 721 Polymethylene ($-\text{CH}_2-$)_{*n*} of $-\text{OC}_8\text{H}_{17}$, 831 ($-\text{C}-\text{H}-$ def. m di-substituted), 759 Polymethylene ($-\text{CH}_2-$) of $-\text{OC}_7\text{H}_{15}$, 952 ($-\text{C}-\text{H}-$ def. hydrocarbon), 1112 ($-\text{C}-\text{O}-$) Str, 1165, 1251 and 1379 ($-\text{C}-\text{O}$ str in $-(\text{CH}_2)_n$ chain), 1458 ($-\text{C}-\text{H}-$ def. in CH_2), 1492 (nitro group), 1518 ($-\text{C}=\text{C}-$)str, 1604 ($-\text{C}=\text{O}$ group) 1710 ($-\text{COO}-$ ester group), 2848 and 2922 ($-\text{C}-\text{H}$ str in CH_3).

Dodecyloxy: 718 Polymethylene ($-\text{CH}_2-$)_{*n*} of $-\text{OC}_{12}\text{H}_{25}$, 815 ($-\text{C}-\text{H}-$ def. m di-substituted), 767 Polymethylene ($-\text{CH}_2-$) of $-\text{OC}_7\text{H}_{15}$, 952 ($-\text{C}-\text{H}-$ def. hydrocarbon), 1110 ($-\text{C}-\text{O}-$) Str, 1377, 1165 and 1254 ($-\text{C}-\text{O}$ str in $-(\text{CH}_2)_n$ chain), 1465 ($-\text{C}-\text{H}-$ def. in CH_2), 1495 (nitro group) 1516 ($-\text{C}=\text{C}-$)str, 1602 ($-\text{C}=\text{O}$ group) 1712 ($-\text{COO}-$ ester group), 2848 and 2920 ($-\text{C}-\text{H}$ str in CH_3).



Scheme 1. Synthetic Route of Series.

***1H*NMR spectra in CDCl₃ in δ ppm for hexyloxy & decyloxy derivative**

Hexyloxy: 0.86(*t*, $-\text{CH}_3$ of $-\text{C}_6\text{H}_{13}$), 1.1–1.5 (*m*, *n*-poly methylene groups of OC_6H_{13}), 1.75(*m*, *n*-poly methylene groups of $-\text{OC}_7\text{H}_{15}$), 3.2–3.4 (*s*, $-\text{OCH}_2-\text{CH}_2-$ of OC_7H_{15}), 4.03 (*s*, $-\text{OCH}_2-\text{CH}_2-$ of $-\text{OC}_6\text{H}_{13}$), 6.8–7.2 (*s*, $-\text{CO}-\text{CH}=\text{CH}$), 8.12 (*s*, *p*-disubstituted phenyl ring).

Table 1. Elemental analysis for heptyloxy, octyloxy, tetradecyloxy, and octadecyloxy derivatives.

Sr. No.	Molecular formula	%Elements found			%Elements theoretical		
		C	H	N	C	H	N
1	$\text{C}_{43}\text{H}_{60}\text{O}_7\text{N}$	73.50	8.54	1.99	73.46	8.51	1.97
2	$\text{C}_{44}\text{H}_{62}\text{O}_7\text{N}$	73.74	8.66	1.95	73.68	8.60	1.92
3	$\text{C}_{50}\text{H}_{74}\text{O}_7\text{N}$	75.00	9.25	1.75	75.03	9.22	1.78
4	$\text{C}_{54}\text{H}_{82}\text{O}_7\text{N}$	75.70	9.57	1.64	75.66	9.53	1.60

Table 2. Texture of nematic phase of C_7 , C_{12} , C_{14} , C_{16} by miscibility method.

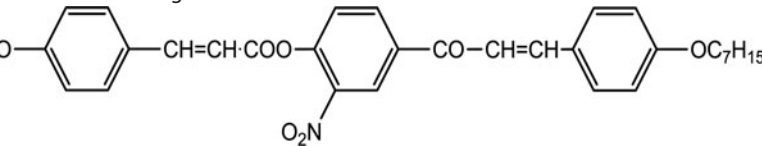
Sr. No.	Homolog	Texture
1	C_8	Threaded
2	C_{10}	Threaded
3	C_{14}	Schlieren
4	C_{16}	Schlieren

Decyloxy: 0.83 (*t*, $-CH_3$ of $-C_{10}H_{25}$), 1.3–1.6 (*m*, *n*-poly methylene groups of $-OC_{10}H_{25}$), 1.77 (*m*, *n*-poly methylene groups of $-OC_7H_{15}$), 3.4–3.6 (*s*, $-OCH_2-CH_2-$ of OC_7H_{15}), 4.12 (*s*, $-OCH_2-CH_2-$ of $OC_{10}H_{21}$), 6.9–7.4 (*s*, $-CO-CH=CH-$), 8.2 (*s*, *p*-disubstituted phenyl ring).

Result and discussion

Novel series of chalconyl derivatives with lateral nitro group have been synthesized by condensation of *trans* 4-*n*-alkoxy cinnamic acids and α -3-nitro 4-hydroxy benzoyl β -4'-tetradecyloxy ethylene (m.p. : 69°C and yield : 64.54%). Series consist of thirteen (C_1 – C_{18}) homologs of which C_1 – C_4 homologs are nonliquid crystals and C_5 homolog is enantiotropically nematogenic without exhibition of smectic property and C_6 – C_{18} homologs are enantiotropically nematogenic and smectogenic. Transition and melting temperatures (Table 3) were determined through an optical polarizing microscopy (POM) equipped with a heating stage and were plotted versus the number of carbon atoms present in *n*-alkyl chain R of left –OR group. Transition curves, Cr-N/I and N-I were drawn by linking like or related transition points as depicted in a phase diagram (Fig. 1) showing phase behaviors of series. Cr-Sm/N transition curve follow zigzag path of rising and falling with overall descending tendency and behaved in normal manner. N-I transition curve initially descended from C_5 to C_8 through C_6 homolog and then ascended to C_{10} homolog through C_8 and finally descended up to last C_{18} homolog with exhibition of odd-even effect. Sm-N transition curve showing descending

Table 3. Transition temperature of homologous series.

Homologous series : 

Transition temperatures in °C				
Sr.no	R = <i>n</i> -alkyl group	Smectic	Nematic	Isotropic
1	C_1	—	—	240
2	C_2	—	—	236
3	C_3	—	—	238
4	C_4	—	—	224
5	C_5	—	188	227
6	C_6	166	182	216
7	C_7	155	169	197
8	C_8	156	167	128
9	C_{10}	153	164	135
10	C_{12}	138	159	132
11	C_{14}	147	162	137
12	C_{16}	144	158	115
13	C_{18}	121	134	119

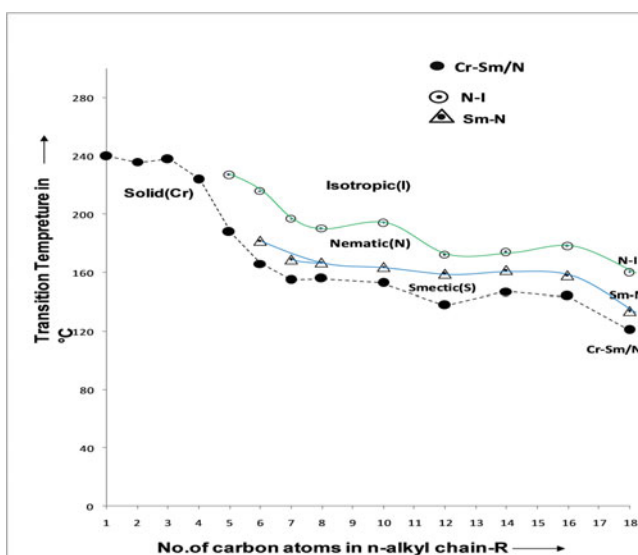
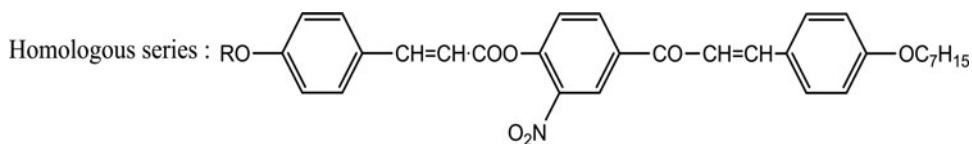


Figure 1. Phase behavior of series.

tendency from C₅ homolog up to C₁₈ homolog. Thus, it behaves in normal manner. Odd-even effect is observed between C₆ to nearby C₉ homologs and then it disappears from and beyond C₉ homolog for higher homologs of longer *n*-alkyl chain 'R' of -OR group. N-I transition curve of odd members occupy lower position than even members. Textures of nematic phase are threaded or schlieren and smectic phase textures are smectic-A type are confirmed by polarizing optical microscope (POM) equipped with heating stage. Analytical, spectral, and thermometric data supported the molecular structures of homologs. LC properties from homolog to homolog in the same series varied keeping right terminal and geometrical shape unchanged throughout the series, except number of changing number of methylene unit or units.



The exhibition or inexistence of mesomorphic property by a substance depends upon its suitable or unsuitable magnitudes of anisotropic forces of intermolecular end-to-end and lateral forces as a consequence of favorable or unfavorable molecular rigidity and flexibility. The molecular rigidity remains unaltered throughout the series from homolog to homolog in the same series; but, its molecular flexibility alters from homolog to homolog in the same series due to changing number of methylene unit or units present in *n*-alkyl chain bonded to first phenyl ring through oxygen atom. The combined effect of molecular rigidity and flexibility of suitable magnitude induces mesomorphism in a substance to disalign the molecules and resist exposed thermal vibrations on molecules under microscopic examination under floating condition on the surface. The failure of exhibition by C₁-C₄ homologs is attributed to their inability to resist exposed thermal vibrations due to unsuitable magnitudes of intermolecular end-to-end and lateral attractions which abruptly breaks crystal lattices and smoothly transform crystalline state to isotropic state without passing through LC state, due to low dispersion forces and low magnitudes of dipole-dipole and electronic interactions between

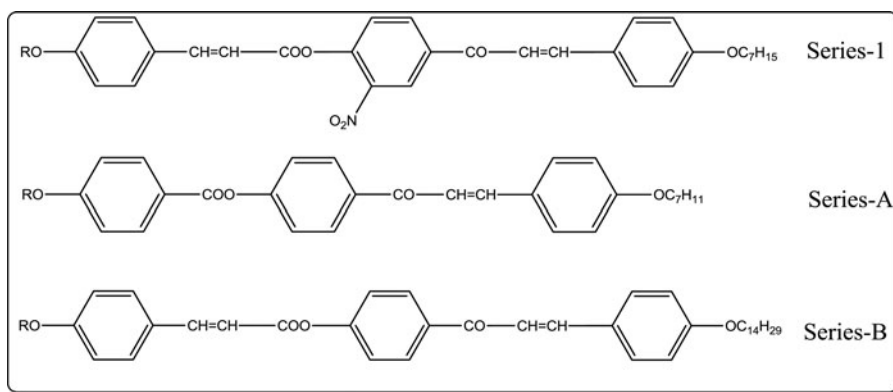


Figure 2. Structurally similar series.

instantaneous dipole produced by spontaneous oscillations of electron clouds of the molecules leading to high crystallizing tendency. Thus, molecules of nonmesomorphs randomly oriented in all possible directions with high order of disorder or uncontrolled movement. Such molecules do not acquire monotropic LC state on cooling the isotropic mass. Thus, any sort of mesomorphism either smectic or nematic is absent for C_1 – C_4 homologs. The commencement of enantiotropic nematic mesophase formation from C_7 homolog and enantiotropic smectic mesophase from C_6 to C_{18} homolog is attributed to disalignment of molecules at an angle ninety or less than ninety degree which resisted exposed thermal vibrations by suitable magnitudes of end to end attractions, acquiring statistically parallel orientational order of molecular arrangement under floating condition during microscopic examination for definite range of temperature according to molecular permanent dipole moment, aromaticity, molecular rigidity, flexibility, polarity, and polarizability. Thus, variations in mesomorphic properties of a present novel series are compared with the structurally similar other known homologous series as shown below in Fig. 2.

Homologous series 1 and A are identical with respect to three phenyl rings, two central bridge linking middle. But they differ with respect to central phenyl ring series 1 have one lateral nitro group and differ by right-handed end group $-\text{OC}_7\text{H}_{15}$ and $-\text{OC}_{14}\text{H}_{29}$ for series 1 and B, respectively. Homologous series 1 and B are identical with respect to three phenyl rings and right handed end group $-\text{OC}_7\text{H}_{15}$ but differ with respect to central phenyl ring series 1 have one lateral nitro group and central linkage $-\text{CH}=\text{CH}-\text{COO}-$, $-\text{CO}-\text{CH}=\text{CH}-$ and $-\text{COO}$, $-\text{CO}-\text{CH}=\text{CH}-$ for series 1 and B, respectively. However, combine effect of molecular rigidity plus flexibility vary for the same homolog from series to series and from homolog to homolog in the same series. Following Table 4 represents some thermometric behaviors of presently investigated novel chalconyl homologous series 1 and the series A [25] and B [26] chosen for comparative study.

- Homologous series 1 under comparative study are nematogenic and smectogenic, but series A and B are nematogenic with absence of smectogenic property.
- The mesogenic property commences from C_5 (series1), C_5 (series A), and C_6 (series B) homolog.
- Thermal stability for nematic of series B and series A are less than series 1.
- The total mesophase length ranges from minimum to maximum in increasing order from series A to series B to series 1.
- Thermal resistivity is poor for all the series under comparison except series 1.

Table 4. Relative thermal stability in °C.

Series→	1	A	B
smectic-isotropic Or smectic-nematic Commencement of Smectic phase (C ₅ –C ₁₈) C ₅ —	180.6		
Nematic-Isotropic Commencement of Nematic phase (C ₅ –C ₁₈) C ₅	199.5		
(C ₅ –C ₁₈) C ₅	102.0		
(C ₅ –C ₁₈) C ₅	99.75		
(C ₆ –C ₁₈) C ₆			
Total upper and lower mesophase length range in °C C _i –C _j C ₁₄ C ₆	27–50		
	14–32		
C ₁₂ C ₁₀ C ₁₆			
	19–34		
C ₆ C ₈			

From above Table 4 it is clear that

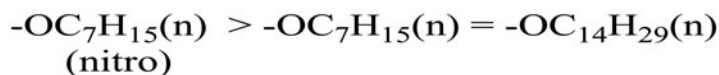
Homologous series 1 and B are almost identical except the difference of seven methylene units at the tail-end groups at right side of the molecules and one lateral nitro group at central ring. Homologous series 1 and A are also almost identical but differ only with the central linkage –COO and –CH=CH–COO and one lateral nitro group at central ring. Because of one nitro group in series 1 its thermal stability is very higher than the series A and B because nitro group increase the polarity of the homologous series and also series 1 shows nematogenic and smectogenic property, but series A and B do not show smectogenic property and only shows nematogenic property because of absence of nitro group they have less polarity. Enthalpy values (ΔH) associated differs from homolog to homolog in the same series and for the same homolog from series to series which plays role in the thermometric behavior of series to series and the homolog to homolog. Thus, facilitation and stabilization of nematic mesophase is more favored in case of series 1 as compared to series A and B. Thus, commencement of nematic mesophase, mesophase length range, and the magnitudes of thermal stability show positive or negative variations in mesogenic behaviors, from series to series for the same homolog and homolog to homolog in the same series.

Conclusions

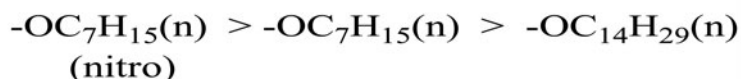
- Present novel chalconyl ester series is nematogenic, smectogenic, and high-ordered melting type whose isotropic temperature vary between 160°C and 240°C.
- Group efficiency order derived for nematic on the basis of
 - (i) Thermal stability
 - (ii) Commencement of mesophase and

(iii) Mesophase length range are as under

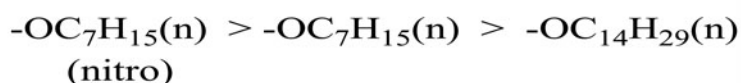
(i) Smectic



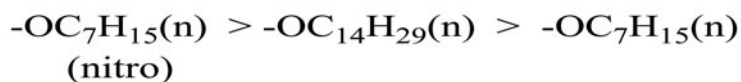
Nematic



(ii) Nematic



(iii) Nematic



- Molecular structure plays an important role in mesogenic behavior with reference to changing tail-end group and lateral group.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Novel homolog of chalconyl ester derivatives with lateral nitro group may be useful in the study of their biological activity lyotropically as antimalarial, anticancer, antibacterial compounds.
- Ester group of present novel investigation may be useful for the agricultural production for the growth of quality and healthy fruits and flowers, potato, and potato-like material as well as chalconyl group being biologically active and antibacterial and antifungal may reduce the consumption of pesticides and insecticides.
- Present study supported early views and raised reliability and credibility to the conclusions drawn earlier.

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