

## Synthesis and Characterization of 7,4<sup>1</sup>-Diacyloxy, 3<sup>1</sup>-Methoxy Flavones Derivatives as a Potential SMX Phase Mesogens

Kasi viswanath I.V.<sup>1\*</sup>, Murthy Y L N<sup>2</sup>

<sup>1</sup>Department of Chemistry, K L university, Green fields, Vaddeswaram,  
Guntur, India-522502

<sup>2</sup>Department of Organic Chemistry, Andhra University, Visakhapatnam, India.

\*Corres.author: viswanath\_fed@kluniversity.in  
Fax No : 08645-247249

**Abstract:** We have reported on flavone derivatives as potential mesogens. Few mesogens of flavone derivatives are found in the literature. Flavone esters are exhibited liquid crystalline nature. In present study, a homologous series of 7,4<sup>1</sup>-diacyloxy, 3<sup>1</sup>-methoxy flavones derivatives, was synthesized by condensing 7, 4<sup>1</sup>-dihydroxy, 3<sup>1</sup>-methoxy flavone with six different fatty chain acid chlorides. The lower member of the series does not exhibit liquid crystalline mesophases. The lauryloxy and higher derivatives exhibits only smectic phase. Differential scanning calorimeter studies served the dual purpose of confirming the microscopic transition temperatures, as well as the calculation of enthalpies of various phase transitions.

**Keywords:** Synthesis, flavonoid esters, Liquid crystals, Mesophase.

### Introduction:

Recent years, we have been trying to understand the effect of the Oxygen containing heterocyclic moiety [1, 2] on liquid crystallinity. However, mesogenic mono-oxygen heterocyclic [3-10] has been less exploited. Vora et.al [11] have reported mesogenic polymer containing a coumarin moiety. In the past, Chudgar and shah [12] studied mesogen with a central chalcone linkage, which may serve as precursors to flavones, flavanones, isoflavones and flavanols. Basing last few years research investigations, here we are presented the synthesis and liquid crystalline behavior of 7,4<sup>1</sup>-diacyloxy, 3<sup>1</sup>-methoxy flavones derivatives. In this paper, the synthesis of 7,4<sup>1</sup>-diacyloxy, 3<sup>1</sup>-methoxy flavones derivatives are presented in the following sequence (Scheme I) and characterized by I.R, NMR data and further characterized by liquid crystal properties the results were presented in table 2

### Experimental Details:

#### General synthetic Procedure for 7,4<sup>1</sup>-diacyloxy, 3<sup>1</sup>-methoxy flavones derivatives(a-f):

In our research investigation at the Department of organic chemistry, Andhra university we synthesized, characterized and study the Biological activity of 7,4<sup>1</sup>-dihydroxy, 3<sup>1</sup>-methoxy flavones[13]. 7, 4<sup>1</sup>-dihydroxy, 3<sup>1</sup>-

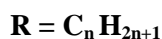
methoxy flavone (1 mole) and long chain fatty Acid chlorides(2 moles) {acid chlorides was prepared by the action of thionyl chloride with Corresponding acid[lauric, myristic, pentadecanoic, Palmitic, hepta decanoic, and stearic acids chloride] and the contents were refluxed for 3 hours. Adding formic acid into the flask until no smell of  $\text{SOCl}_2$  is observed destroyed excess  $\text{SOCl}_2$ . The crude acid chlorides were distilled at reduced pressure and used immediately for esterification} were refluxed in an oil bath at  $110\text{--}120^\circ\text{C}$  for 4 hours and left overnight at room temperature. The solid was filtered and washed thoroughly with 10%  $\text{NaHCO}_3$  solution and water repeatedly and extracted with ethyl acetate. The organic layer was then dried over anhydrous  $\text{MgSO}_4$  and it was evaporated. The product obtained was chromatographed on silica gel and eluted with 99.5: 0.5; Hexane: EtoAc collecting 50 ml fractions.

The ester thus formed was crystallized twice from MeoH- $\text{CHCl}_3$ . TLC confirmed the purity of the compound. This is a low melting solid.

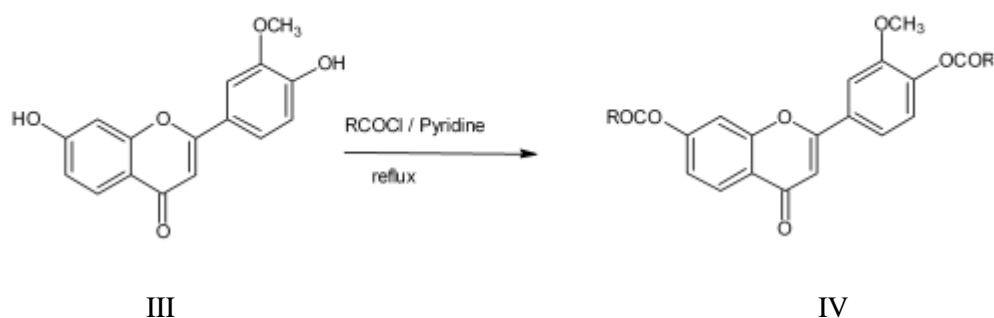


I

II



a ; n = 11 b ; n = 13 c ; n = 14 d ; n = 15 e ; n = 16 f ; n = 17



a ; n = 11 b ; n = 13 c ; n = 14 d ; n = 15 e ; n = 16 f ; n = 17

## Results and Discussions:

**Compound a:** low melting colour less solid, IR (KBr): 2917,2849,,1705, 1464,1412,  $^1\text{H}$  NMR( $\text{CDCl}_3$ ): 0.82(t,6H,2x $\text{CH}_3$ ), 1.2-1.4(s,36H,18x $\text{CH}_2$ ), 2.3-2.4(t, 4H, 2x $\text{OCOCH}_2$ ), 3.9(s,3H,- $\text{OCH}_3$ ), 7.0(s,1H,Olefinic). 7.4(m, aromatic protons)

**Compound b:** low melting colour less solid, IR (KBr): 2917, 2849, 1698, 1594, 1464, 1408, 1218,  $^1\text{HNMR}$  ( $\text{CDCl}_3$ ):0.8(t,6H,2x $\text{CH}_3$ ), 1.2-1.4(s,44H, 22x $\text{CH}_2$ ), 2.3-2.4 (t,4H,2x $\text{OCOCH}_2$ ), 3.9(s,3H,- $\text{OCH}_3$ ), 7.0(s,1H, Olefinic), 7.4(m, aromatic protons)

**Compound c:** low melting colour less solid IR (KBr): 2918,2850,1695,1464,1408,1296,

$^1\text{HNMR}$ ( $\text{CDCl}_3$ ):0.9(t,6H,2x $\text{CH}_3$ )1.2-1.4(s,48H,24x $\text{CH}_2$ ).2.4(t,4H,2x $\text{OCOCH}_2$ ),3.9(s,3H,- $\text{OCH}_3$ ),6.8(s,1H, Olefinic), 7.3(m, aromatic protons)

**Compound d:** low melting colour less solid IR (KBr): 2915,2845,1695,1458,1410,1218,

$^1\text{H NMR}(\text{CDCl}_3)$ : 0.9(t, 6H, 2xCH<sub>3</sub>), 1.2-1.4(s, 56H, 28xCH<sub>2</sub>), 2.4(t, 4H, 2xOCOCH<sub>2</sub>), 3.9(s, 3H, OCH<sub>3</sub>), 6.9(s, 1H, Olefinic), 7.3(m, aromatic protons)

**Compound e:** low melting colour less solid, IR (KBr): 2919, 2852, 1698, 1462, 1413, 1216,  $^1\text{H NMR}(\text{CDCl}_3)$ : 0.9(t, 6H, 2xCH<sub>3</sub>), 1.2-1.4 (s, 56H, 28xCH<sub>2</sub>), 2.4(t, 4H, 2 x OCOCH<sub>2</sub>), 3.9(s, 3H, OCH<sub>3</sub>), 6.9(s, 1H, Olefinic), 7.3(m, aromatic protons)

**Compound f:** IR (KBr): low melting colour less solid, 2917, 2849, 1698, 1594, 1464, 1408, 1218,  $^1\text{H NMR}(\text{CDCl}_3)$ : 0.8(t, 6H, 2x CH<sub>3</sub>), 1.2-1.4(s, 60H, 30xCH<sub>2</sub>) 2.4-2.6(t, 4H, 2xOCOCH<sub>2</sub>), 3.9(s, 3H, -OCH<sub>3</sub>), 6.9 (s, 1H, Olefinic), 7.3(m, aromatic protons)

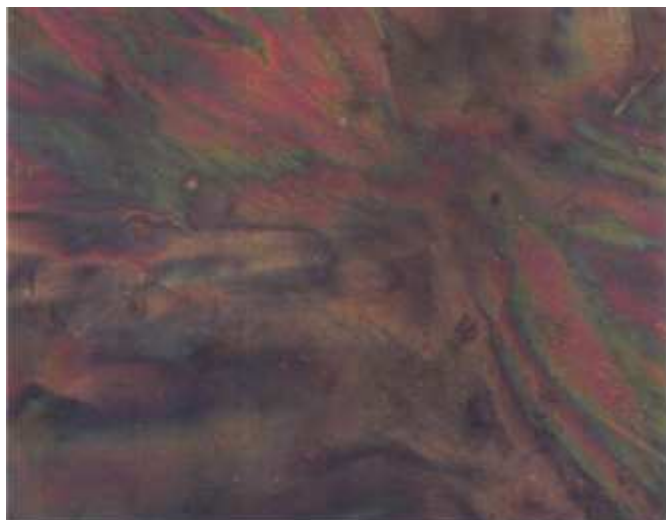
Based on the spectral data the structure of the compounds was confirmed as 7<sup>1</sup>, 4<sup>1</sup> - acyloxy 3<sup>1</sup>- methoxy flavone derivatives. The transition temperatures of the compounds are compiled in table 1. A few transitions were obtained by DSC with a view to confirm the observation under the microscope. The compounds (a-f) were studied for differential scanning calorimetric data at heating rate 2<sup>0</sup> C/ min. The phase transition temperatures and enthalpy changes ( $\Delta\text{H}$ ) were recorded. To check reproducibility, the experiments were repeated.

**Table 1: Phase transitions temperatures (mesophase region) and heat of transition ( $\Delta\text{H}$ ) of the compounds a-f:**

S.No	Compound No.	Temperature in <sup>0</sup> C crystal to mesophase	$\Delta\text{H}$ J/g
1.	a	Not observed	Not observed
2.	b	47.5-63.6	176.9
3.	c	49.3-53.5	166.4
4.	d	50.5-58.2	153.7
5.	e	51.2-60.6	148.9
6.	f	57.5-61.6	138.3

In order to confirm the mesophase compound (a-f) were studied further by employing polarizing microscope at the rate of 2<sup>0</sup>C/min. The observed textures were photographed during mesophase and the textures were recorded for the synthesized compounds c & e were presented in the figures.1 & 2.

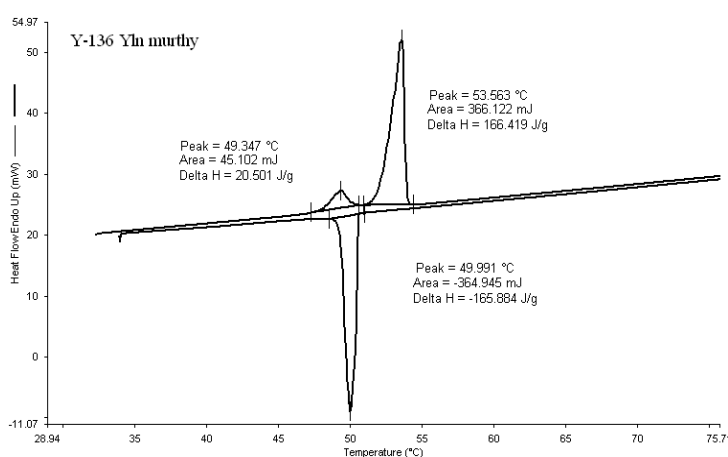
The  $^1\text{H NMR}$  data of compounds (a-f) were given in table 1. DSC thermographic data, i.e. phase transition temperature, enthalpy changes ( $\Delta\text{H}$ ) for the above esters (a-f) were recorded & presented in table 2. The DSC thermogram of compound c was presented in Fig.3.



**Fig 1: Texture photographed on cooling the meso phase of 7,4<sup>1</sup>-dipentadecanoyloxy,3<sup>1</sup>-methoxy flavones**



**Fig 2 :** Texture photographed on cooling the meso phase of 7,4<sup>1</sup>-dihetadecanoyloxy,3<sup>1</sup>-methoxyflavones



**Fig. 3:** DSC Themogram of 7,4<sup>1</sup>-dipentadecanoyloxy 3<sup>1</sup>-methoxy flavone

### Conclusions:

The transition temperatures increases with increasing number of carbon atoms in the acyloxy chain showing Smectic(SmX) meso phase. The present series exhibits mesomorphism of high thermal stabilities as compared to series of other comparable flavonoid esters. The odd and even members of this series seem to show a different trend with increasing spacer length.

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