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Esters derived from 7-decanoyloxychromone-3-carboxylic acid: synthesis and mesomorphic properties

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The synthesis and liquid crystalline properties of a new series of calamitic liquid crystals containing 4-H-benzopyran-4-one (chromone) within the central core is reported. The first homologue in the series display SmA phase (**8a**), the homologues (**8b–e**) exhibit SmA and SmC mesophases and the homologues (**8f–h**) exhibit only a SmC mesophase.

1. Introduction

Many series of liquid crystalline compounds containing heterocyclic groups have been sinsesized because of their interesting properties [1]. Usually 5- or 6-membered heterocycles are involved, and they form part of the core in rod-shape, bent-shape or disc-shape molecules. However, few mesogenic 6-membered heterocycles have been reported.

Some mesogenic compounds containing quinoline [2], flavone [3], isoflavone [4] and coumarin [5] have recently been reported. These structures are asymmetric and have a large dipole moment perpendicular to the molecular axis—two characteristics that influence the mesogenic properties. In this context, it was considered interesting to synthesize a series of chromone derivatives. This paper describes the synthesis and mesomorphic properties of a series of esters that include the heterocycle 4-oxo-4-H-benzopyran (chromone) in the classical calamitic structure.

2. Synthesis

The synthesis of the precursors involved many difficulties (see the scheme). In our first trials a Vilsmeier–Haack type reaction reported to yield the chromone-3-carboxaldehyde derivatives was used [6]; starting with 4-methoxy-2-hydroxyacetophenone and DMF-$POCl_3$ complex, the aldehyde **4** was obtained in a very low yield (<10%). This result has also been reported by other authors [7]. Later, 4-methoxy-2-hydroxyacetophenone was activated forming a complex with boron triflouride **3** to overcome the low yield [8].

The aldehyde **4** was demethylated and acylated. Alkylation with *R*Br in K_2CO_3/acetone yielded (according to the TLC) a mixture of compounds. In order to avoid the demethylation step, formation of boron trifluoride complexes with 2,4-dihydroxyacetophenone and 4-*n*-decyloxy-2-hydroxyacetophenone was attempted; none of them was isolated.

Oxidation of the aldehyde yielded insignificant amounts of the acid under various conditions [9]: *N*-bromosuccinimide in CCl_4 and irradiation with a 150 W lamp for 40 min; sulphuryl chloride in CCl_4 and AIBN; Jones reagent. Finally the acid was obtained in good yield using $NaClO_2$ and amidosulphuric acid [10].

N,*N*-dicyclohexylcarbodiimide was used first, to carry out the esterification reaction. However, no ester was obtained regardless of the condition: i.e. room temperature in dry methylene chloride, the same solvent under reflux, heating the reagents with molecular sieves and withuot solvent, or acid catalysis [11]. Monitoring the reaction by TLC showed that the acid and the imide react easily but the intermediate and 4-*n*-decyloxyphenol does not; neither does 4-methoxy phenol. The reaction was also carried out using dioxane as solvent to allow a higher reaction temperature. In this case the obtained product was fractionated using a silicagel column. The ^{1}H NMR spectrum of one of the isolated fractions showed that 1,4-dioxane and the heterocycle underwent a reaction. Adition to the C-2 is already reported with other nucleophiles [9].

Esterification via the acid chloride was also attempted. It is reported that chromone-3-carboxylic acid is easily decarboxylated by heating in certain solvents [12], consequently the reaction was carried out under what was thought to be mild conditions: stirring the acid with thionyl chloride at room temperature. DMF was used as catalyst and excess $SOCl_2$ was eliminated under reduced pressure. No acyl halide was

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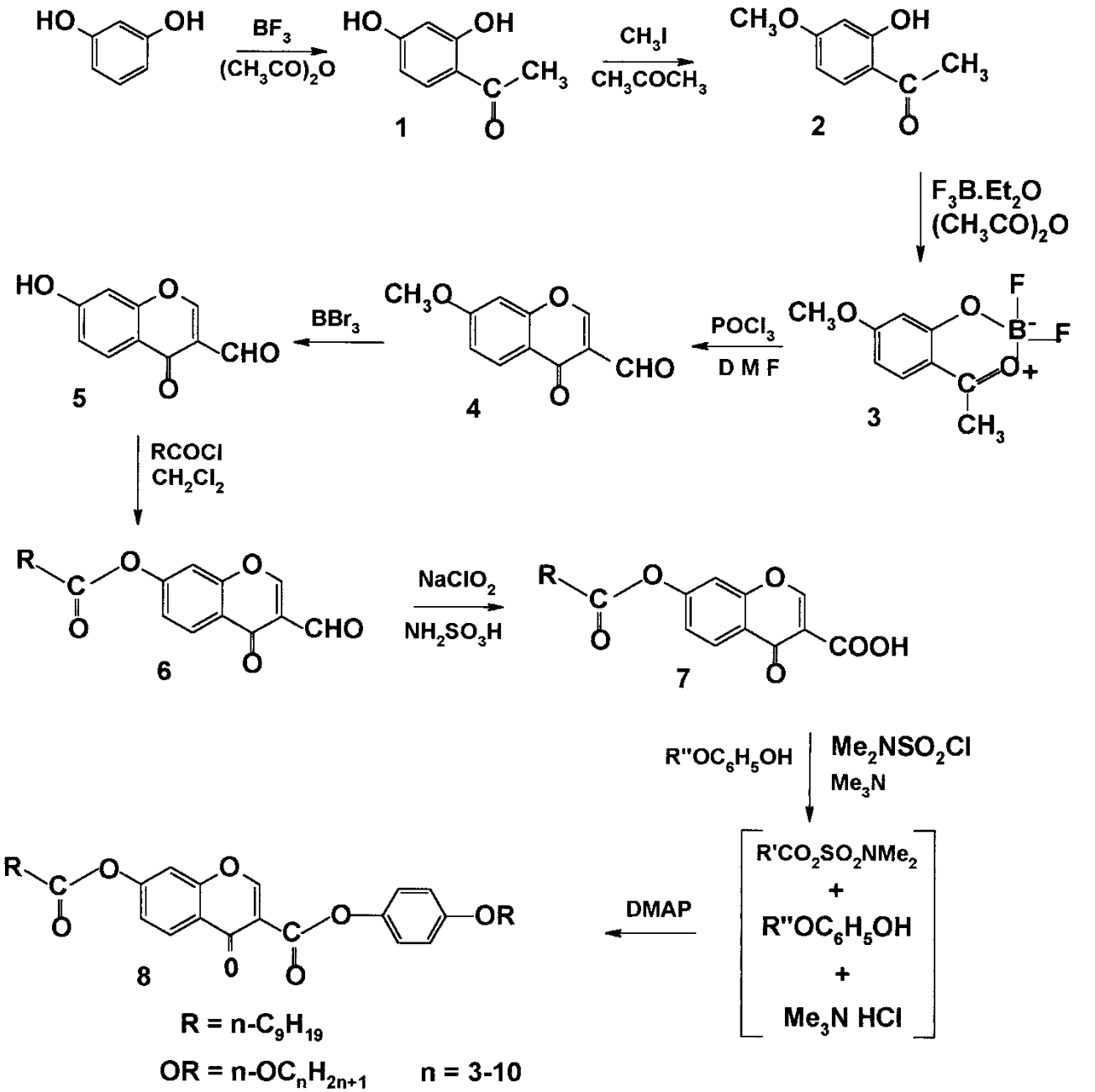


Scheme. Synthesis of compounds **8**.

obtained and the ^{1}H NMR spectrum indicated that chlorine was incorporated at position 2 in the heterocycle. A third method that was also tried without success was the activation of the acid with *N*,*N*′-carbonyldiimidazol [13] and subsequent reaction with 4-*n*-alkoxyphenol.

Esterification was finally successfully achieved using equimolar aumounts of the acid and 4-*n*-alkoxyphenol. The acid was activated with dimethylsulphamoyl chloride (Me_2NSO_2Cl) and trimethylamine, a recently reported procedure [14].

3. Results and discussion

The optical, thermal and thermodynamic data for the esters **8** are gathered in table 1. A graphical representation of the mesomorphic behaviour as a function of the number (n) of carbon atoms in the lateral chain is also presented (see the figure). All the compounds exhibit enantiotropic behaviour. The melting peaks are sharp, melting points decreasing with increasing length of alkoxy side chain. The largest mesomorphic range occurs when $n=10$ (59.8°C). The derivative with $n=3$ shows only a SmA mesophase. The derivatives with

Table 1. Transition temperatures and enthalpies for 4-*n*-alkyloxyphenyl 7-*n*-decanoyloxychromone-2-carboxylates (**8**).

Compound $R=C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
8a ($n=3$)	Cr–SmA	118.8	16.3
	SmA–I	144.4	2.9
8b ($n=4$)	Cr–SmC	123.8	20.0
	SmC–SmA	150[a]	
	SmA–I	161.4	3.5
8c ($n=5$)	Cr–SmC	116.9	22.3
	SmC–SmA	155[a]	
	SmA–I	160.9	4.6
8d ($n=6$)	Cr–SmC	112.7	25.7
	SmC–SmA	157[a]	
	SmA–I	162.4	5.2
8e ($n=7$)	Cr–SmC	112.4	20.4
	SmC–SmA	156[a]	
	SmA–I	161.3	5.0
8f ($n=8$)	Cr–SmC	110.1	22.5
	SmC–I	163.2	6.1
8g ($n=9$)	Cr–SmC	104.7	23.3
	SmC–I	163.3	6.3
8h ($n=10$)	Cr–SmC	101.9	22.1
	SmC–I	161.7	5.8

[a]Polarizing optical microscopy data (second cooling).

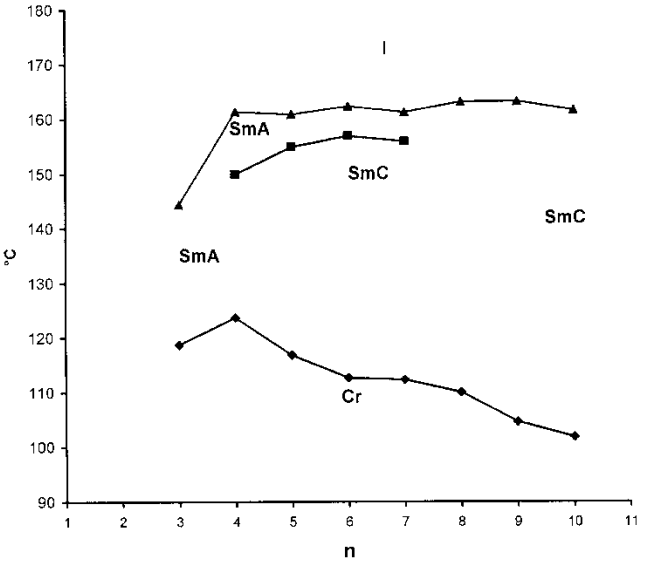


Figure 1. Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for esters **8**.

$n=4$, 5, 6, 7 exhibit SmA and SmC mesophases and the homologues with $n=8$, 9, 10 exhibit only the SmC mesophase. The temperatures of SmC–SmA transitions were determined by polarizing optical microscopy. On cooling a homeotropic SmA texture, the appearance of schlieren texture is observed.

The mesogenic properties of some naphthylcarboxylic esters have been already described [15]; those compounds have a structure similar to that of the compounds described in this paper. An example is presented in table 2. In comparing the transition temperatures for 4-nonyloxyphenyl 6-nonyloxynaphthalen-2-carboxylate and compound **8 g**, it is observed that the mesogenic range is about 5°C wider in the heterocyclic structure. It may also be noted that the series of heterocyclic esters exhibit no nematic mesophase.

The occurrence of a tilted smectic C mesophase opens an interesting possibility for further studies with this type of compound, such as the introduction of a chiral terminal alkyl chain in the calamitic structure in order to obtain chiral mesophases that may exhibit interesting electro-optical properties.

4. Experimental

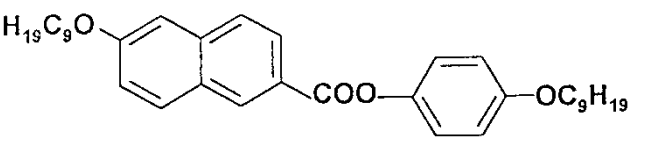
The structures of the new esters compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250 P) and FTIR (Nicolet 550) spectra (table 3). The purity of the products was evaluated by thin layer chromatography and elemental analysis (table 4).

The transition temperatures and enthalpies were determined by differential scanning calorimetry using a Rheometric DSC-V calorimeter with a heating and cooling rate of 5°C min^{-1}; the instrument was calibrated using an indium standard (155.66°C, 28.45 J g^{-1}). The textures of mesophases were studied with a Leitz Ortholux Pol polarizing microscope, equipped with a Mettler FP 52 hot stage.

4.1. *2,4-Dihydroxyacetophenone (**1**)*

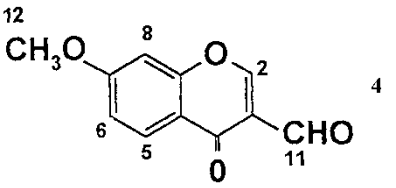
This compound was synthesized according to the method described in [16]. The product was purified by column chromatography on silica using hexane/ethyl acetate 9/2. M.p.144–145°C (lit [16] 144–145°C); yield 50%.

Table 2. Transition temperatures of 4-*n*-nonyloxyphenyl 6-*n*-nonyloxynaphthalen-2-carboxylate [15].



Transition	Temperature/°C
Cr–SmC	89.4
SmC–SmA	115.5
SmA–N	125.7
N–I	128.4

Table 3. Chemical shift data (δ/ppm) for ^{1}H NMR (in $CDCl_3$) and ^{13}C NMR (in DMSO) of the compounds **4**, **5**, **6**, **7**, **8** $n=10$; and IR absorption data.



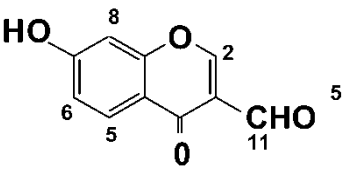
^{1}H NMR

2	5	6	8	11	12
8.91(s)	8.12 (d) $J_{56}=8.8$	7.22 (dd) $J_{65}=8.8$ $J_{6.8}=2.4$	7.31(d) $J_{86}=2.4$	10.21(s)	3.89 (s)

^{13}C NMR

2	3	4	5	6	7	8	9	10	11	12
163.0	118.1	174.1	126.7	115.6	164.5	101.6	157.4	119.8	188.5	56.3

IR (KBr) cm^{-1}: 3082 (H–C–); 2857 (H–C–O); 1658 (C–O aldehyde); 1616 (C–O ketone).



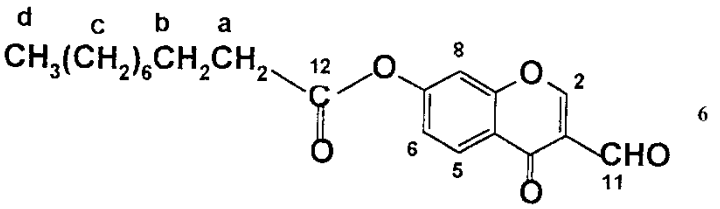
^{1}H NMR

2	5	6	8	OH	11
8.87(s)	8.06 (d) $J_{56}=8.7$	8.89 (dd) $J_{65}=8.7$ $J_{6.8}=2.2$	7.10 (d) $J_{86}=2.2$	11.16 (s)	10.20 (s)

^{13}C NMR

2	3	4	5	6	7	8	9	10	11
162.6	117.5i	174.2	127.1	116.0	163.5	103.1	157.4	119.7i	188.6

IR (KBr) cm^{-1}: 3281 (O–H); 3086 (H–C–); 2850 (H–C–O); 1698 (C–O aldehyde); 1618 (C–O ketone); 1510 (C–C).



^{1}H NMR

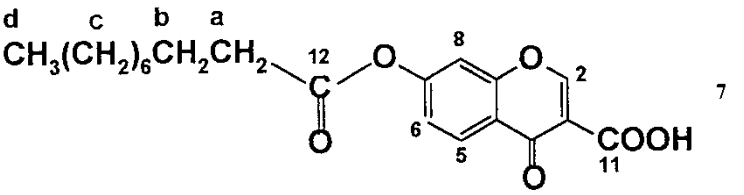
2	5	6	8	11	a	b	c	d
8.51(s)	8.30 (d) $J_{56}=8.7$	7.24 (dd) $J_{65}=8.7$ $J_{68}=1.7$	7.36 (d) $J_{86}=1.7$	10.37 (s)	2.61(t) $J_{ab}=7.4$	1.6–1.9 (m)	1–1.5 (m)	0.86 (t)

Table 3. (*Continued*).

^{13}C NMR

2	3	4	5	6	7	8	9	10	11	12
160.6	120.4 i	175.2	127.5	120.8	156.6	111.6	155.5	122.8	188.4	171.2

Alkyl chains = 34.3 ($\underline{CH_2}$C–O); 31.8; 29.4; 29.2; 29.0; 24.7; 22.6; 14.1
IR (KBr) cm^{-1}: 2853 (H–C–O); 1772 (C–O ester), 1706 (C–O aldehyde), 1639 (C–O ketone); 1613 (C–C); 1215 (C–O).



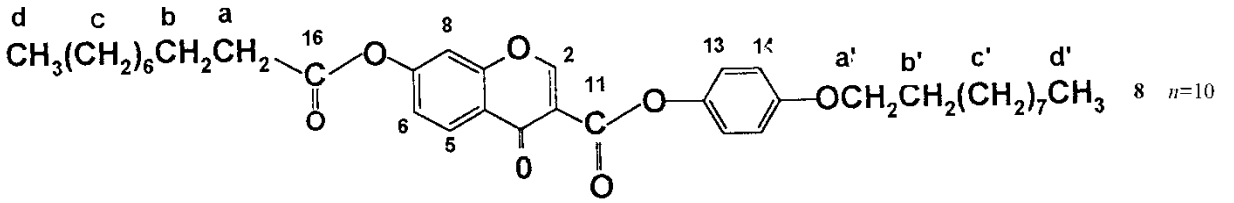
^{1}H NMR

2	5	6	8	11	a	b	c	d
8.91(s)	8.26 (d) $J_{56}=8.8$	7.26 (dd) $J_{65}=8.8$ $J_{68}=2.0$	7.42 (d) $J_{86}=2.0$	13.1(s)	2.56 (t) $J_{ab}=7.4$	1.1–1.4 (m)	1.6–1.8 (m)	0.86 (t)

^{13}C NMR

2	3	4	5	6	7	8	9	10	11	12
163.8	112.8[a]	178.4	127.3	121.5	157.0[a]	111.5	156.3[a]	120.2[a]	163.7	170.9

Alkyl chains = 34.1 ($\underline{CH_2}$CO); 31.7; 29.2; 28.8; 24.5; 22.5; 13.9.
IR(KBr) cm^{-1}: 3422 (O–H); 3079 (H–C), 1764 (C–O ester), 1619 (C–O ketone); 1570 (C–C); 1221 (C–O).



^{1}H NMR

2	5	6	8	13–13′	14–14′	a	a′	b+b′	c+c′	d+d′
8.75 (s)	8.25 (d) $J_{56}=8.7$	7.15 (dd) $J_{65}=8.8$ $J_{68}=2.1$	7.29 (d) $J_{86}=2.1$	7.05 (d) $J=9.0$	6.83 (d) $J=9.1$	2.54t $J_{ab}=7.5$	3.87t	1.6–1.8 (m)	1.2–1.5 (m)	0.81t

^{13}C NMR

2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
163	116i	172	128	121	157[a]	111	155[a]	123[a]	162	144	122	115	156[a]	171

Alkyl chains = 68.4 ($\underline{CH_2}$–O); 34.6 (CH_2COO); 31.9; 31.8; 29.6; 29.4; 29.3; 29.2; 29.0; 26.0 24.7; 22.7; 14.1.
IR (KBr) cm^{-1}: 3087 (H–C–); 1752 (C–O ester aliph–arom.); 1657 (C–O ester arom–arom); 1621 (C–O ketone); 1509 (C–C).

[a]Not assigned.

Table 4. Elemental analysis of 4-*n*-alkyloxyphenyl 7-*n*-decanoyloxychromone-2-carboxylates (**8**).

Empirical formula $R=-OC_nH_{2n+1}$	C/%		H/%	
	Calculated	Found	Calculated	Found
$n=3$, $C_{29}H_{34}O_7$	70.44	70.79	6.88	6.48
$n=4$, $C_{30}H_{36}O_7$	70.87	70.63	7.09	7.39
$n=5$, $C_{31}H_{38}O_7$	71.26	71.37	7.28	7.58
$n=6$, $C_{32}H_{40}O_7$	71.64	71.53	7.46	7.56
$n=7$, $C_{33}H_{42}O_7$	72.00	71.65	7.64	7.87
$n=8$, $C_{34}H_{44}O_7$	72.34	72.17	7.80	8.13
$n=9$, $C_{35}H_{46}O_7$	72.66	72.46	7.96	8.05
$n=10$, $C_{36}H_{48}O_7$	72.97	73.22	8.11	8.46

4.2. *4-Methoxy-2-hydroxyacetophenone (**2**)*

This was prepared according to a reported method ([17], but with some changes in the work-up. The mixture was heated for 8 h and then filtered. The solvents (acetone and ether) were removed and the residue purified by recrystallization from methanol. M.p.49–50°C (lit [17] 49–50°C); yield 86%.

4.3. *2,2-Difluoro-7-methoxy-4-methylbenzo[e]1,3,2 dioxaborin (**3**)*

This compound was synthesized according to the method described in [8]. M.p. 166–170°C (lit [8] 170°C); yield 85%.

4.4. *7-Methoxychromone-3-carboxaldehyde (**4**)*

Prepared according to the method described in [8], the product was purified by column chromatography on silica using hexane/ethyl acetate 9/1. M.p.187–190°C (lit [8] 188°C); yield of crude product 80%. Column chromatography was used in the first preparation in order to obtain good spectra. In the preparations that followed the crude product was used without further purification.

4.5. *7-Hydroxychromone-3-carboxaldehyde (**5**)*

To a mixture of 5.1 g (25 mmol) of compound **4** and 40 ml of dry dichloromethane, 9.43 ml (100 mmol) of boron tribromide in 10 ml of dichloromethane was added dropwise. The mixture was cooled in ice during the adition, then allowed to warm to room temperature and then heated at reflux for 24 h. Yield of crude product 90%; m.p. 265–270°C (lit [7] 268–271°C). This crude product was used in the next step without further purification.

4.6. *7-Decanoyloxychromone-3-carboxaldehyde (**6**)*

To a mixture of 5 g (26.3 mmol) of crude compound **5** in 50 ml of dichloromethane and 4.1 ml (29.3 mmol) of triethylamine, was added dropwise 6 ml (29.3 mmol) of decanoyl chloride. The mixture was stirred for 6 h at room temperature, then the solvent was removed and the residue purified by column chromatography on silica using hexane/ethyl acetate 8/2. M.p. 93–94°C; yield 50%. Elemental analysis: found C 70.10, H 7.09; calc. for $C_{20}H_{24}O_5$ C 69.76, H 6.98%.

4.7. *7-Decanoyloxychromone-3-carboxylic acid (**7**)*

This compound was synthesized using the conditions described for 7-subtituted chromone-3-carboxylic acid [10]. To a stirred mixture of 0.5 g (1.45 mmol) of compound **6** in 20 ml of dichloromethane, was added 0.5 g (5.15 mmol) of amidosulphuric acid in 10 ml of water. The mixture was cooled to 10°C, then an aqueous solution of 0.3 g (3.32 mmol) of sodium chlorite was slowly added, the temperature was kept at 10–20°C; this temperature was maintained for a further 1.5 h.

The reaction mixture was then poured into an ice–water mixture and extracted twice with dichloromethane; the organic phase was washed several times with water and the solvent was evaporated without drying the organic phase. The residue was purified by recrystallization from *n*-hexane. M.p. 78–80°C; yield 90%. Elemental analysis: found C 66.32, H 7.01; calc. for $C_{20}H_{24}O_6$ C 66.67, H 6.66%.

4.8. *4-n-Alkyloxyphenyl 7-decanoyloxychromone-3-carboxylate (**8**)*

These compounds were obtained following the procedure described in [17] with some variations in the work-up. To a magnetically stirred mixture of 0.3 g (0.83 mmol) of compound **7** in 15 ml of dry MeCN containing 0.239 g (2.50 mmol) of dry $Me_3N.HCl$ at 0–5°C, was added dropwise 0.18 ml (1.69 mmol) of Me_2NSO_2Cl and then 0.35 ml (2.50 mmol) of Et_3N. After 10 min a solution of 0.83 mmol of 4-*n*-alkyloxyphenol in 5 ml of MeCN containing 6.94 mg (0.083 mmol) of DMAP was added. The mixture was stirred at 0–5°C for 3 h and then poured into ice–water and refrigerated overnight. The solid product was filtered off, washed several times with water and purified by recrystallization from ethanol; yield 50–60%.

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