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Synthesis and mesomorphic properties of new liquid crystalline compounds with β-hydroxy-, β-chloroketone and α,β-unsaturated ketone moieties in the terminal chains

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The syntheses of new liquid crystalline compounds containing β-hydroxy-, β-chloroketone and α,β-unsaturated ketone moieties are described. The key intermediate 1-(4-hydroxyphenyl)-3-hydroxyoctan-1-one was obtained by the hydrogenolysis of the heterocycle in 3-(4-hydroxyphenyl)-5-pentyl-2-isoxazoline. Dehydratation of the intermediate β-hydroxyketone led to 1-(4-hydroxyphenyl)-oct-2-en-1-one. Reaction of 1-(4-hydroxyphenyl)-3-hydroxyoctan-1-one with hydrochloric acid yielded 1-(4-hydroxyphenyl)-3-chlorooctan-1-one. The target liquid crystalline compounds were synthesized by the esterification of these phenols with corresponding acids. The relationships between the moiety type in the terminal chain and the liquid crystalline properties are discussed.

1. Introduction

Recently a new series of liquid crystalline compounds containing the 2-isoxazoline ring have been prepared [1–3]. These substances form various types of smectic and disordered crystal phases (A, B, C, E). It is well documented that the reductive cleavage of 2-isoxazolines can lead to β-hydroxyketones, α,β-unsaturated ketones or β-aminoalcohols [4–6]. The aim of our present work is the application of the 2-isoxazoline ring cleavage reaction as key step in the synthesis of new liquid crystalline compounds. In this paper we report the first results of our investigation in this field and describe the synthesis and mesomorphic properties of new liquid crystalline compounds with β-hydroxy-, β-chloroketone and α,β-unsaturated ketone moieties in the terminal chains. This type of modification of the terminal chain in LC molecules provides the possibility of observing the relationship between the moiety type in the terminal chain and the liquid crystalline properties. Also β-hydroxyketone or α,β-unsaturated ketone functions may be used for the further modification of terminal chains in liquid crystalline molecules, for example by selective fluorination [7, 8]. To our knowledge there is only one report [9] describing the preparation of liquid crystalline compounds with a β-hydroxyketone moiety in the alkyl chains of LC molecules.

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2. Results and discussion

2.1. *Synthesis*

The synthetic route to the new liquid crystalline compounds **7**–**9** is shown in the scheme. The starting material was 4-hydroxybenzaldehyde **1** from which the oxime **2** was obtained by the usual procedure in 71% yield. The reaction of oxime **2** with *N*-chlorosuccinimide and triethylamine led to the corresponding nitrile oxide. 1,3-Dipolar cycloaddition of this nitrile oxide to heptene-1 gave a 70% yield of the corresponding substituted 2-isoxazoline **3**. The most practical method for the cleavage of the 2-isoxazoline ring is hydrogenolysis over Raney nickel in the presence of acids [5]. The hydrogenolysis of the heterocycle over Raney nickel in the presence of boric acid in aqueous methanol in our 2-isoxazoline **3** by the known procedure [4] led to β-hydroxyketone **4** in 76% yield. Dehydratation of the β-hydroxyketone **4** was carried out with perchloric acid in dioxane. The desired α,β-unsaturated ketone **5** was obtained with 65% yield. The β-hydroxyketone **4** was converted in the next stage into the β-chloroketone **6** by reaction with hydrochloric acid in dioxane in 70% yield. The target liquid crystalline compounds **7**–**9** were synthesized in 61–93% yields from the phenols **4**–**6** by esterification with the corresponding acids in the presence of *N,N′*-dicyclohexylcarbodiimide and 4-*N,N*-dimethylaminopyridine. Also we have developed an alternative pathway to the synthesis of compounds **8** containing α,β-unsaturated ketone moieties in the terminal chain. For example, by the use of this route compound **8h** was obtained by the

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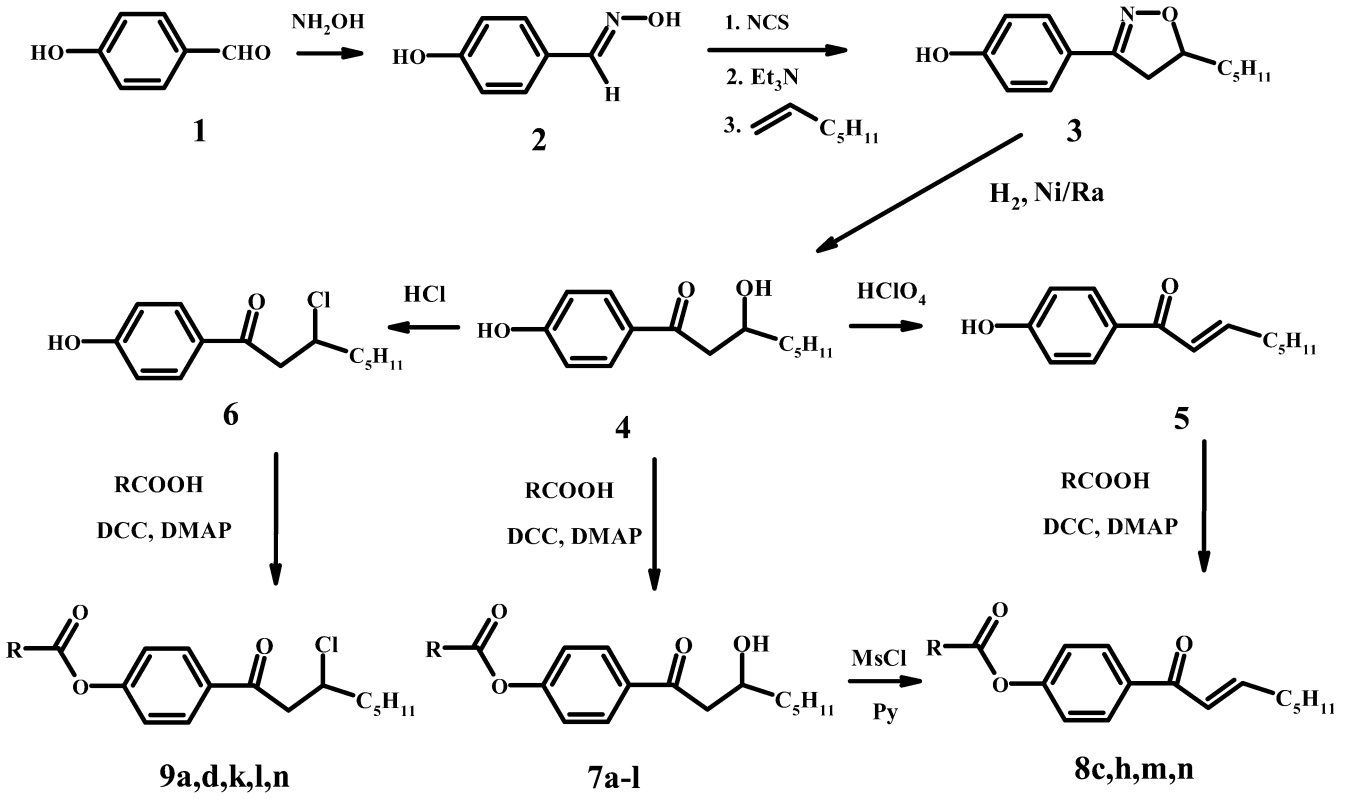


Scheme. The letters a,b,c... correspond to identical acid fragments.

dehydratation ester **7h** with methanesulphonyl chloride in pyridine in 59% yield.

The structures of the compounds prepared **3**–**9** were confirmed by IR, UV and ^{1}H NMR spectroscopy. The formation of the heterocycle by 1,3-dipolar cycloaddition was established by the presence of the multiplets of 4-CH_2 and 5-CH protons in the ^{1}H NMR spectrum of compound **3** at δ 2.90, 3.32 and 4.54–4.74 ppm. The reductive cleavage of the 2-isoxazoline ring in the next stage was evidenced by the presence of C=O group absorption at 1664 cm^{-1} in the IR spectrum of the compound **4**. The hydroxyketone moiety in compound **4** was characterized by the multiplets of 2-CH_2 and 3-CH protons at δ 2.95, 3.11 and 4.16–4.25 ppm, in the ^{1}H NMR spectrum. The intens bands at 1662 and 1620 cm^{-1} in the IR spectrum of the α,β-unsaturated ketone **5** corresponds to the stretching vibrations of conjugated carbonyl group and double bond respectively. The vinyl protons 2-CH and 3-CH in compound **5** are associated with two multiplets at δ 6.82–6.98 7.05 ppm, respectively, with vicinal coupling constant J=15 Hz in the ^{1}H NMR spectrum. There are some characteristic differences between the ^{1}H NMR spectra of β-hydroxyketone **4** and β-chloroketone **6**. For example the signals of 2-CH_2 and 3-CH protons have different chemical shifts.

2.2. *Mesomorphic properties*

The phase transition temperatures of the compounds synthesized **7**–**9** are summarized in table 1. Most of β-hydroxyketones **7** are mesomorphic. Only four members of this series are not mesomorphic (**7a**,**j**–**l**). Compound **7b** forms only a monotropic smectic A phase. Two-ring 4-alkoxybenzoates **7c**–**h** have high melting points (about 100°C) and exhibit smectic C and A phases. Incrensing the alkoxy chain length in esters **7c**–**f** leads to an increase of the temperature range of the smectic C phase. However the temperature ranges of the smectic A phase in compounds **7c**–**f** are similar (1–2.5°C).

Further increase alkoxy in chain length in esters **7g**,**h** leads to a decrease of the temperature range of the smectic C phase but an increase in that of the smectic A phase in compound **7h** (5.5°C). Ester **7i** forms only the smectic A phase in a 20°C interval.

The influence of the hydroxy group in the β-position to the carbonyl on the mesomorphic behaviour may be determined by comparing esters **7c**–**f**,**h** with **10c**–**f**,**h** in which the β-hydroxy group is absent (see table 2). The

Table 1. Transition temperatures (°C) of esters **7**–**9**.

Compound	*R*	Cr		SmC		SmA		I
7a	4-C_3H_7O–C_6H_4	•	126–126.5	—	—	—	—	•
7b	4-C_4H_9O–C_6H_4	•	118.5	—	—	•	(112)	•
7c	4-$C_5H_{11}O$–C_6H_4	•	108	•	118.5	•	119.5	•
7d	4-$C_6H_{13}O$–C_6H_4	•	106	•	122.5	•	124.5	•
7e	4-$C_7H_{15}O$–C_6H_4	•	103	•	124	•	126	•
7f	4-$C_8H_{17}O$–C_6H_4	•	98	•	128.5	•	130	•
7g	4-$C_9H_{19}O$–C_6H_4	•	107	•	126.5	•	127.5	•
7h	4-$C_{12}H_{25}O$–C_6H_4	•	108	•	124	•	129.5	•
7i	4-$C_{16}H_{33}O$–C_6H_4	•	104	—	—	•	124	•
7j	4-C_6H_{13}–C_6H_4	•	104–104.5	—	—	—	—	•
7k	4-F–C_6H_4	•	129–130	—	—	—	—	•
7 l	4-CN–C_6H_4	•	123–124	—	—	—	—	•
8c	4-$C_5H_{11}O$–C_6H_4	•	90.5–91	—	—	—	—	•
8h	4-$C_{12}H_{25}O$–C_6H_4	•	107–107.5	—	—	—	—	•
8m	4′-$C_{10}H_{21}O$–C_6H_4– C_6H_4	•	125	•	205.5	—	—	•
8n	4′-C_5H_{11}–C_6H_{10}–C_6H_{10}	•	98	•	183	•	191	•
9a	4-C_3H_7O–C_6H_4	•	85	—	—	•	(77)	•
9d	4-$C_6H_{13}O$–C_6H_4	•	86	• (SmB)	92.5	•	94	•
9k	4-F–C_6H_4	•	93–94	—	—	—	—	•
9 l	4-CN–C_6H_4	•	95–96	—	—	—	—	•
9n	4-C_5H_{11}–C_6H_{10}–C_6H_{10}	•	156	•	171	•	174 **N** 179[a]	•

[a]With decomposition.

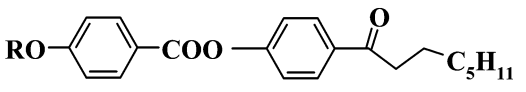
temperature ranges in compounds **7d**–**f**,**h** are similar or wider than those in compounds **10d**–**f**,**h**. The temperature of the Cr–Sm transition in compounds **7c**,**d** is higher than that in **10c**,**d** by 19 and 11°C, respectively. However the temperatures of the Cr–Sm transition in compounds **7e**,**f**,**h** are rather similar (about 1–2°C) to those of the esters **10e**,**f**,**h**. Also the introduction of the hydroxy group in the β-position to the carbonyl group changes the smectic phase type. Compounds **10d**–**f**,**h** form the smectic A phase only. In the case of β-hydroxyketones **7** the more ordered smectic C phase is dominant (except compound **7i** with a very long $C_{16}H_{25}O$-chain).

In contrast to the liquid crystalline esters **7c**,**h** compounds with an α,β-unsaturated ketone moiety **8c**,**h** are not mesomorphic. The esters **8c**,**h** have melting points similar to those of the saturated esters **10c**,**h**; however, the latter compounds form a smectic phase. It follows that the introduction of a double bond to the alkanone terminal chain leads to disappearance of the mesophase in the case of compounds **8c**,**h**. This may be caused by conformational changes that are typical for an α,β-enone group. Increasing the length of the rigid central part in compounds **8m**,**n** leads to the stabilization of the smectic mesophase in a wide temperature range (see table 1).

As can be seen from table 1, compounds with a β-chloroketone moiety exhibit a smectic phase like the corresponding β-hydroxyketones **7**. Ester **9a** forms a monotropic smectic A phase. Increasing the alkoxy chain length leads to an increase in the temperature range of smectic phases in ester **9d**. Compounds **9k**,**l** with polar substituents (F and CN) are not mesomorphic and thus similar to esters **7k**,**l**. The three-ring compound **9n** with a β-chloroketone moiety exhibits smectic C and A phases and a narrow range nematic phase.

Replacement of the β-hydroxyketone unit by β-chloroketone or enone moieties in the liquid crystalline molecules leads to a decrease of the temperature interval or the disappearance of the mesophase in the case of 4-alkoxy-benzoates synthesized. This may be explained by a decrease of polar intermolecular interactions. In the case of β-hydroxyketones an additional stabilization of the mesophase is the result

Table 2. Transition temperatures (°C) of 4-alkoxybenzoates of 1-(4-hydroxyphenyl)-octan-1-one **10c**–**f**,**h** [10].



Compound	*R*	Cr		*SmA*		I
10c	C_5H_{11}	•	89	• (*SmX*)	113	•
10d	C_6H_{13}	•	*Cr*$_2$ 86.1 *Cr*$_1$ 94.9	•	119.5	•
10e	C_7H_{15}	•	102.6	•	119.6	•
10f	C_8H_{17}	•	99.7	•	121.3	•
10h	$C_{12}H_{25}$	•	107.6	•	119.5	•

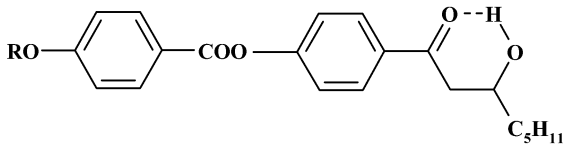


Figure 1. Formation of intramolecular hydrogen bond in β-hydroxyketones **7a**–**h**.

of the formation of a quasi-ring by intramolecular hydrogen bonding (see the figure).

If we compare compounds **7c** and **7g** with the analogous 2-isoxazoline derivatives **11c** and **11g**, it is clear that the cleavage of the heterocycle changes the mesomorphism considerably (see table 3). Three-ring compounds **11c** and **11g** have higher melting points than **7c** and **7g**. Ester **11c** forms a nematic phase in a 13.5°C range. Also the replacement of the 2-isoxazoline ring on the β-hydroxyketone moiety leads to a decrease of the smectic C and A ranges in compounds **7c** and **7g**.

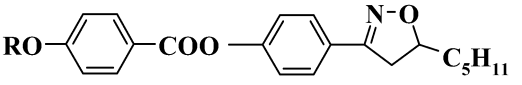
3. Experimental

Confirmation of the structures of all intermediates and final products was obtained using UV (Specord M40, solutions in methanol), IR (Specord IR75, solutions in chloroform) and ^{1}H NMR (Bruker Avance 400, 400 MHz, solutions in deuterochloroform, internal standard hexamethyldisiloxane, δ 0.05 ppm) spectroscopy. Reaction progress and product purity were checked using TLC on Kieselgel 60 F_{254} (Merck). Phase transition temperatures were measured using a heating stage in conjugation with a polarizing microscope. Phase identification was made by comparison of the observed textures with those reported in the literature [11].

3.1. *3-(4-Hydroxyphenyl)-5-pentyl-2-isoxazoline (**3**)*

Gas from the head space of a concentrated hydrochloric acid reagent bottle was collected in a syringe and then bubbled into a solution of 4-hydroxybenzaldehyde oxime **2** (1.6 g, 11.7 mmol) in dimethylformamide (50 ml). *N*-Chlorosuccinimide (1.7 g, 12.7 mmol) was added to the reaction mixture in portions. The mixture was stirred for 1 h at rt, cooled to 0°C and 3.3 ml (23.5 mmol) of heptene-1 added. A solution of triethylamine (1.8 ml) in dimethylformamide (35 ml) was added dropwise and the resulting mixture stirred for 12 h at rt. Chloroform (50 ml) and diluted hydrochloric acid (1/5) was added. The organic layer was separated and the aqueous layer extracted twice with chloroform. The combined organic extracts were washed twice with brine and dried over sodium sulphate. Solvent was removed *in vacuo* and the residue diluted with water; the solid was filtered off and washed with water. Crystallization from toluene/ethyl acetate afforded 1.9 g of compound **3**. Yield 70%, m.p. 109.5–111°C. IR, cm^{-1}: 3595, 3530–3080 (O–H), 3010 (C–$H_{arom.}$), 2955, 2930, 2860 (C–$H_{alkyl.}$), 1605, 1515 (C=$C_{arom.}$), 1270 (C–O). ^{1}H NMR (δ, ppm): 0.84 (3H, t, J=6.5 Hz, CH_3), 1.14–1.82 (8H, m, CH_2-alkyl.), 2.90 (1H, dd, J_1=8.2 Hz, J_2=16.5 Hz), 3.32 (1H, dd, J_1=10.2 Hz, J_2=16.5 Hz) {4-CH_2}, 4.54–4.74 (1H, m, 5-CH), 6.92 (2H, d, J=8.5 Hz), 7.47 (2H, d, J=8.5 Hz) {arom. protons}.

Table 3. Transition temperatures (°C) of 2-isoxazolines **11c** and **11g** [3].



Compound	*R*	Cr	*SmC*	*SmA*	*N*	I
11c	C_5H_{11}	• 137.5	— —	•	146.5 •	160 •
11g	C_9H_{19}	• 118.4	• 154	•	— —	162.5 •

3.2. *1-(4-Hydroxyphenyl)-3-hydroxyoctan-1-one (**4**)*

A solution of 3.17 g (13.6 mmol) of a 2-isoxazoline **3** and 8.4 g (135.5 mmol) of boric acid in a methanol water mixture (5/1, 72 ml) was hydrogenated over Ni-Ra catalyst (2 g). After the reaction was completed the catalyst was filtered off and washed with chloroform (100 ml). Water (200 ml) was added to filtrate and the organic layer was separated. The aqueous layer was extracted with chloroform (2 × 50 ml); the combined organic extracts were washed with brine (100 ml) and water (50 ml) and dried over sodium sulphate. Solvent was removed *in vacuo* and the residue was recrystalized from toluene/petroleum ether, affording 2.44 g of β-hydroxyketone **4**. Yield 76%, m. p. 76.5–77.5°C. IR, cm^{-1}: 3575, 3460–3100 (O–H), 3010 (C–$H_{arom.}$), 2950, 2925, 2850 (C–$H_{alkyl.}$), 1664 (C=O), 1600, 1590, 1505 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.88 (3H, t, J=7 Hz, 8-CH_3), 1.16–1.66 (8H, m, CH_2-alkyl.), 2.95 (1H, dd, J_1=9 Hz, J_2=18 Hz), 3.11 (1H, dd, J_1=2.4 Hz, J_2=18 Hz) {2-CH_2}, 3.65 (1H, br. s, 3-OH), 4.16–4.25 (1H, m, 3-CH), 6.80–6.98 (1H, m, 4′-OH), 6.85 (2H, d, J=9 Hz), 7.85 (2H, d, J=9 Hz) {arom. protons}.

3.3. *1-(4-Hydroxyphenyl)oct-2-en-1-one (**5**)*

A solution of β-hydroxyketone (0.44 g) **4** and perchloric acid (0.3 ml, 70% solution in water) in

dioxane (15 ml) was stirred for 18 h at 15–17°C. Ethyl acetate (40 ml) and brine (40 ml) were then added. The aqueous layer was extracted with ethyl acetate (2 × 15 ml). The combined organic extracts were washed with a saturated solution of sodium bicarbonate (20 ml) and brine (20 ml) and then dried over sodium sulphate. Solvent was removed *in vacuo* and the residue was recrystalized from toluene/petroleum ether affording 0.27 g of α,β-unsaturated ketone **5**. Yield 65%, m. p. 67–68°C. IR, cm^{-1}: 3590, 3500–3100 (O–H), 3035, 3015 (C–$H_{arom.}$), 2965, 2935, 2875, 2865 (C–$H_{alkyl.}$), 1662 (C=O), 1618 (C=C), 1605, 1585, 1513 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.88 (3H, t, J=7.2 Hz, 8-CH_3), 1.20–1.40 (4H, m, 6-CH_2, 7-CH_2), 1.50 (2H, quintet, J=7 Hz, 5-CH_2), 2.28 (2H, distorted q, J=7 Hz, 4-CH_2), 6.82–6.98 (2H, m, 2-CH and 4′-OH), 7.05 (1H, td, J_1=7 Hz, J_2=15 Hz, 3-CH), 6.90 (2H, d, J=8.5 Hz), 7.89 (2H, d, J=8.5 Hz) {arom. protons}.

3.4. *1-(4-Hydroxyphenyl)-3-chlorooctan-1-one (**6**)*

A solution of β-hydroxyketone **4** (0.766 g) and concentrated hydrochloric acid (1.5 ml) in dioxane (20 ml) was stirred for 22.5 h at 20°C. Toluene (40 ml) and brine (50 ml) were then added. The aqueous layer was extracted with toluene (2 × 20 ml). Combined organic extracts were washed with a saturated solution of sodium bicarbonate (30 ml) and brine (30 ml) and then dried over sodium sulphate. Solvent was removed *in vacuo* and the residue recrystalized from toluene/petroleum ether, affording 0.577 g of β-choroketone **6**. Yield 70%. m. p. 56–57°C (decomp.). UV (λ_{max}, nm): 221.1, 279.8. IR, cm^{-1}: 3585, 3500–3100 (O–H), 3025, 3010 (C–$H_{arom.}$), 2960, 2930, 2875, 2865 (C–$H_{alkyl.}$), 1675 (C=O), 1605, 1585, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.88 (3H, t, J=6.8 Hz, 8-CH_3), 1.20–1.38 (4H, m, 6-CH_2, 7-CH_2), 1.40–1.62 (2H, m, 5-CH_2), 1.69–1.89 (2H, m, 4-CH_2), 3.18 (1H, dd, J_1=5.6 Hz, J_2=16.4 Hz), 3.50 (1H, dd, J_1=8 Hz, J_2=16.4 Hz) {2-CH_2}, 4.48–4.57 (1H, m, 3-CH–Cl), 5.74 (1H, br. s, 4′-OH), 6.88 (2H, d, J=8.8 Hz), 7.89 (2H, d, J=8.8 Hz) {arom. protons}.

3.5. *4-Propyloxybenzoic acid 4-(3-hydroxyoctanoyl)phenyl ester (**7a**)*

To a solution of 0.1 g (0.42 mol) of β-hydroxyketone **4**, 0.084 g (0.47 mmol) of 4-propyloxybenzoic acid and 0.17 g (0.83 mmol) of *N,N′*-dicyclohexylcarbodiimide in dichloromethane (15 ml), was added a catalytic amount of 4-*N,N*-dimethylaminopyridine. The reaction mixture was stirred for 20.5 h and than filtered through aluminium oxide. The sorbent was washed with dichloromethane (40 ml); then the dichloromethane solution was washed with a saturated solution of sodium bicarbonate (30 ml) and water (30 ml). After the drying over sodium sulphate the solvent was removed and crude product crystallized from 2-propanol. Yield 0.147 g of ester **7a** (87%). IR, cm^{-1}: 3650–3250 (O–H), 3035, 3015 (C–$H_{arom.}$), 2965, 2935, 2875, 2860 (C–$H_{alkyl.}$), 1740 (C=O ester), 1680 (C=O), 1605, 1580, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.89 (3H, t, J=7 Hz), 1.05 (3H, t, J=7 Hz) {3′-CH_3 and 8″-CH_3}, 1.22–1.55 (6H, m, 5″-CH_2, 6″-CH_2, 7″-CH_2), 1.56–1.66 (2H, m, 4″-CH_2), 1.84 (2H, sextet, J=7 Hz, 2′-CH_2), 3.03 (1H, dd, J_1=9 Hz, J_2=17.6 Hz), 3.16 (1H, dd, J_1=2.4 Hz, J_2=17.6 Hz) {2″-CH_2}, 3.23 (1H, d, J=3.2 Hz, OH), 4.00 (2H, t, J=7 Hz, 1′-O–CH_2), 4.17–4.26 (1H, m, 3″-CH), 6.96 (2H, d, J=9 Hz), 7.31 (2H, d, J=9 Hz), 8.02 (2H, d, J=9 Hz), 8.12 (2H, d, J=9 Hz) {arom. protons}.

Compounds **7b**–**k**, **8c**,**m**,**n**, **9a**,**d**,**k**,**l**,**n** were prepared from phenols **4**, **5** and **6**, respectively, by the same procedure.

3.6. *4-Hexylbenzoic acid 4-(3-hydroxyoctanoyl)phenyl ester (**7j**)*

Yield 67%. IR, cm^{-1}: 3630–3200 (O–H), 3010 (C–$H_{arom.}$), 2955, 2930, 2855 (C–$H_{alkyl.}$), 1735 (C=O ester), 1670 (C=O), 1600, 1500 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.88 (3H, t, J=6.8 Hz), 0.89 (3H, t, J=6.8 Hz) {6′-CH_3 and 8″-CH_3}, 1.22–1.69 (16H, m, CH_2-alkyl.), 2.69 (2H, t, J=8 Hz, 1′-CH_2), 3.04 (1H, dd, J_1=9 Hz, J_2=17.6 Hz), 3.17 (1H, dd, J_1=2.4 Hz, J_2=17.6 Hz) {2″-CH_2}, 3.22 (1H, d, J=3.2 Hz, OH), 4.17–4.26 (1H, m, 3″-CH), 7.31 (2H, d, J=8.8 Hz), 7.32 (2H, d, J=8.4 Hz), 8.03 (2H, d, J=8.8 Hz), 8.09 (2H, d, J=8.4 Hz) {arom. protons}.

3.7. *4-Fluorobenzoic acid 4-(3-hydroxyoctanoyl)phenyl ester (**7k**)*

Yield 86%. IR, cm^{-1}: 3030, 3015 (C–$H_{arom.}$), 2965, 2935, 2865 (C–$H_{alkyl.}$), 1745 (C=O ester), 1680 (C=O), 1605, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.89 (3H, t, J=6.8 Hz, 8′-CH_3), 1.22–1.67 (8H, m, CH_2-alkyl.), 3.04 (1H, dd, J_1=9.2 Hz, J_2=17.6 Hz), 3.16 (1H, dd, J_1=2.4 Hz, J_2=17.6 Hz) {2′-CH_2}, 3.19 (1H, d, J=3.2 Hz, OH), 4.17–4.27 (1H, m, 3′-CH), 7.19 (2H, t, J=8.8 Hz), 7.32 (2H, d, J=8.8 Hz), 8.04 (2H, d, J=8.8 Hz), 8.21 (2H, dd, J_1=5.6 Hz, J_2=8.8 Hz) {arom. protons}.

3.8. *4-Cyanobenzoic acid 4-(3-hydroxyoctanoyl)phenyl ester (**7l**)*

Yield 80%. IR, cm^{-1}: 3650–3230 (O–H), 3030, 3020 (C–$H_{arom.}$), 2965, 2935, 2865 (C–$H_{alkyl.}$), 2240 (C≡N),

1750 (C=O ester), 1680 (C=O), 1605, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.89 (3H, t, J=6.6 Hz, 8′-CH_3), 1.20–1.64 (8H, m, CH_2-alkyl.), 3.05 (1H, dd, J_1=8.8 Hz, J_2=17.6 Hz), 3.16 (1H, dd, J_1=2.7 Hz, J_2=17.6 Hz) {2′-CH_2}, 3.16 (1H, d, J=3.2 Hz, OH), 4.17–4.27 (1H, m, 3′-CH), 7.33 (2H, d, J=9 Hz), 7.82 (2H, d, J=9 Hz), 8.06 (2H, d, J=9 Hz), 8.30 (2H, d, J=9 Hz) {arom. protons}.

3.9. *4-Pentyloxybenzoic acid 4-(oct-2-enoyl)phenyl ester (**8c**)*

Yield 61%. IR, cm^{-1}: 3010 (C–$H_{arom.}$), 2965, 2925, 2870, 2855 (C–$H_{alkyl.}$), 1732 (C=O ester), 1668 (C=O, *s-cis*), 1648 (C=O, *s-trans*), 1599, 1580, 1511, 1506 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.90 (3H, t, J=6.8 Hz), 0.93 (3H, t, J=7.2 Hz) {5′-CH_3 and 8″-CH_3}, 1.26–1.58 (10H, m, CH_2-alkyl.), 1.82 (2H, quintet, J=7 Hz, 2′-CH_2), 2.31 (2H, dq, J_1=1.2 Hz, J_2=7.2 Hz, 4″-CH_2), 4.04 (2H, t, J=7 Hz, 1′-O–CH_2), 6.87 (1H, distorted d, J=15.2 Hz, 2″-CH), 7.08 (1H, td, J_1=7.2 Hz, J_2=15.2 Hz, 3″-CH), 6.96 (2H, d, J=8.8 Hz), 7.30 (2H, d, J=8.8 Hz), 8.00 (2H, d, J=8.8 Hz), 8.13 (2H, d, J=8.8 Hz) {arom. protons}.

3.10. *4′-Pentylbicyclohexyl-4-carboxylic acid 4-(oct-2-enoyl)phenyl ester (**8n**)*

Yield 91%. IR, cm^{-1}: 3025, 3015 (C–$H_{arom.}$), 2930, 2860 (C–$H_{alkyl.}$), 1750 (C=O ester), 1668 (C=O, *s-cis*), 1648 (C=O, *s-trans*), 1618 (C=C), 1600, 1505 (C=$C_{apoм}$). ^{1}H NMR (δ, ppm): 0.87 (3H, t, J=7 Hz), 0.90 (3H, t, J=7 Hz) {5″-CH_3 and 8‴-CH_3}, 0.80–1.38 (22H, m), 1.45–1.59 (3H, m), 1.66–1.79 (4H, m), 1.80–1.88 (2H, m), 2.10–2.22 (2H, m) {CH_2-alkyl. and protons of cyclohex. rings}, 2.29 (2H, dq, J_1=1.2 Hz, J_2=6.8 Hz, 4‴-CH_2), 2.46 (1H, tt, J_1=3.6 Hz, J_2=12.4 Hz, 4-CH–COOR), 6.83 (1H, distorted d, J=15.6 Hz, 2‴-CH), 7.05 (1H, td, J_1=6.8 Hz, J_2=15.6 Hz, 3‴-CH), 7.15 (2H, d, J=8.8 Hz), 7.94 (2H, d, J=8.8 Hz) {arom. protons}.

3.11. *4-Propyloxybenzoic acid 4-(3-chlorooctanoyl)phenyl ester (**9a**)*

Yield 81%. IR, cm^{-1}: 3030, 3010 (C–$H_{arom.}$), 2960, 2930, 2875, 2860 (C–$H_{alkyl.}$), 1730 (C=O ester), 1690 (C=O), 1600, 1580, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.89 (3H, t, J=7 Hz, 8″-CH_3), 1.06 (3H, t, J=7 Hz, 3′-CH_3), 1.18–1.38 (4H, m, 6″-CH_2, 7″-CH_2), 1.40–1.64 (2H, m, 5″-CH_2), 1.70–1.92 (2H, m, 4″-CH_2), 1.84 (2H, sextet, J=7 Hz, 2′-CH_2), 3.25 (1H, dd, J_1=5.6 Hz, J_2=17 Hz), 3.56 (1H, dd, J_1=7.6 Hz, J_2=17 Hz) {2″-CH_2}, 4.00 (2H, t, J=7 Hz, 1′-O–CH_2), 4.50–4.60 (1H, m, 3″-CH–Cl), 6.97 (2H, d, J=8.8 Hz), 7.32 (2H, d, J=8.8 Hz), 8.03 (2H, d, J=8.8 Hz), 8.12 (2H, d, J=8.8 Hz) {arom. protons}.

3.12. *4-Fluorobenzoic acid 4-(3-chlorooctanoyl)phenyl ester (**9k**)*

Yield 70%. UV (λ_{max}, nm): 250.4. IR, cm^{-1}: 3025, 3020 (C–$H_{arom.}$), 2955, 2925, 2875, 2855 (C–$H_{alkyl.}$), 1740 (C=O ester), 1690 (C=O), 1600, 1510 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.90 (3H, t, J=7 Hz, 8′-CH_3), 1.20–1.40 (4H, m, 6′-CH_2, 7′-CH_2), 1.42–1.64 (2H, m, 5′-CH_2), 1.71–1.91 (2H, m, 4′-CH_2), 3.25 (1H, dd, J_1=5.6 Hz, J_2=17.2 Hz), 3.56 (1H, dd, J_1=7.6 Hz, J_2=17.2 Hz) {2′-CH_2}, 4.50–4.60 (1H, m, 3′-CH–Cl), 7.19 (2H, distorted t, J=8.8 Hz), 7.32 (2H, d, J=8.8 Hz), 8.04 (2H, d, J=8.8 Hz), 8.22 (2H, distorted dd, J_1=5.6 Hz, J_2=8.8 Hz) {arom. protons}.

3.13. *4-Cyanobenzoic acid 4-(3-chlorooctanoyl)phenyl ester (**9 l**)*

Yield 76%. IR, cm^{-1}: 3025 (C–$H_{arom.}$), 2960, 2930, 2860 (C–$H_{alkyl.}$), 2235 (C≡N), 1745 (C=O ester), 1685 (C=O), 1600, 1500 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.90 (3H, t, J=6.8 Hz, 8′-CH_3), 1.18–1.40 (4H, m, 6′-CH_2, 7′-CH_2), 1.42–1.64 (2H, m, 5′-CH_2), 1.71–1.92 (2H, m, 4′-CH_2), 3.24 (1H, dd, J_1=5.2 Hz, J_2=17.2 Hz), 3.57 (1H, dd, J_1=7.6 Hz, J_2=17.2 Hz) {2′-CH_2}, 4.45–4.59 (1H, m, 3′-CH–Cl), 7.34 (2H, d, J=8.4 Hz), 7.83 (2H, d, J=8.4 Hz), 8.06 (2H, d, J=8.4 Hz), 8.30 (2H, d, J=8.4 Hz) {arom. protons}.

3.14. *4′-Pentylbicyclohexyl-4-carboxylic acid 4-(3-chlorooctanoyl)phenyl ester (**9n**)*

Yield 75%. UV (λ_{max}, nm): 254.2. IR, cm^{-1}: 3030, 3015 (C–$H_{arom.}$), 2930, 2855 (C–$H_{alkyl.}$), 1755 (C=O ester), 1690 (C=O), 1625, 1600, 1505 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm): 0.87 (3H, t, J=7 Hz), 0.89 (3H, t, J=7 Hz) {5″-CH_3 and 8‴-CH_3}, 0.94–1.18 (m), 1.18–1.38 (m), 1.40–1.63 (m), 1.66–1.90 (m) {33 H, CH_2-alkyl. and protons of cyclohex. rings}, 2.11–2.19 (2H, m, equatorial protons of cyclohex. rings 3-CH and 5-CH), 2.46 (1H, tt, J_1=3.6 Hz, J_2=12.4 Hz, 4-CH-COO*R*), 3.22 (1H, dd, J_1=5.6 Hz, J_2=17 Hz), 3.53 (1H, dd, J_1=7.6 Hz, J_2=17 Hz) {2‴-CH_2}, 4.48–4.58 (1H, m, 3‴-CH–Cl), 7.16 (2H, d, J=8.6 Hz), 7.97 (2H, d, J=8.6 Hz) {arom. protons}.

3.15. *4-Dodecyloxybenzoic acid 4-(oct-2-enoyl)phenyl ester (**8h**)*

A stirred solution of compound **7h** (0.056 g, 0.11 mmol) in pyridine (10 ml) was cooled to 0°C and methanesulphonyl chloride (0.03 ml) was added. The mixture was stirred for 30 min at 0°C, the cooling bath

was removed and the mixture stirred for 24 h at 20°C and then for 1 h at 70°C. Ethyl acetate (40 ml) and diluted (1/5) hydrochloric acid (50 ml) were added to the reaction mixture. The organic layer was separated and washed with water (25 ml), a saturated solution of sodium bicarbonate (25 ml) and water (25 ml), then dried over sodium sulphate. Solvent was removed *in vacuo* and the resulting solid recrystallized from 2-propanol to afford 0.032 g (59%) of compound **8h**. UV (λ_{max}, nm): 273.1. IR, cm^{-1}: 3025, 3010 (C–$H_{arom.}$), 2925, 2855 (C–$H_{alkyl.}$), 1732 (C=O ester), 1668 (C=O, *s-cis*), 1648 (C=O, *s-trans*), 1618 (C=C), 1606, 1600, 1581, 1511, 1506 (C=$C_{arom.}$). ^{1}H NMR (δ, ppm.): 0.87 (3H, t, J=7.2 Hz), 0.90 (3H, t, J=7.2 Hz) {12′-CH_3 and 8″-CH_3}, 1.16–1.40 (20H, m), 1.41–1.58 (4H, m) {CH_2-alkyl.}, 1.81 (2H, quintet, J=7 Hz, 2′-CH_2), 2.31 (2H, dq, J_1=1.2 Hz, J_2=6.8 Hz, 4″-CH_2), 4.03 (2H, t, J=7 Hz, 1′-O–CH_2), 6.87 (1H, distorted d, J=15.6 Hz, 2″-CH), 7.08 (1H, td, J_1=6.8 Hz, J_2=15.6 Hz, 3″-CH), 6.96 (2H, d, J=8.8 Hz), 7.30 (2H, d, J=8.4 Hz), 8.00 (2H, d, J=8.4 Hz), 8.13 (2H, d, J=8.8 Hz) {arom. protons}.

4. Conclusion

New liquid crystalline compounds containing β-hydroxy-, β-chloroketone and α,β-unsaturated ketone moieties have been prepared. The key step in the synthesis of these materials is the reductive cleavage of the 2-isoxazoline ring. Further chemical transformations of the resulting β-hydroxyketone moiety, and esterification with corresponding acids, led to liquid crystalline esters with β-chloroketone and α,β-unsaturated ketone moieties. The smectic C phase is dominant in the synthesized compounds containing the β-hydroxyketone moiety. Among compounds with the β-chloroketone moiety, the temperature range of the smectic phase is smaller than for compounds with the β-hydroxyketone group. The α,β-enone moiety leads to mesophase disappearance in the case of two-ring 4-alkoxybenzoates, however three-ring compounds form smectic phase over a wide temperature range.

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