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Synthesis of New Liquid Crystalline Compounds Containing a β-Hydroxyketone Fragment in the Side Chain

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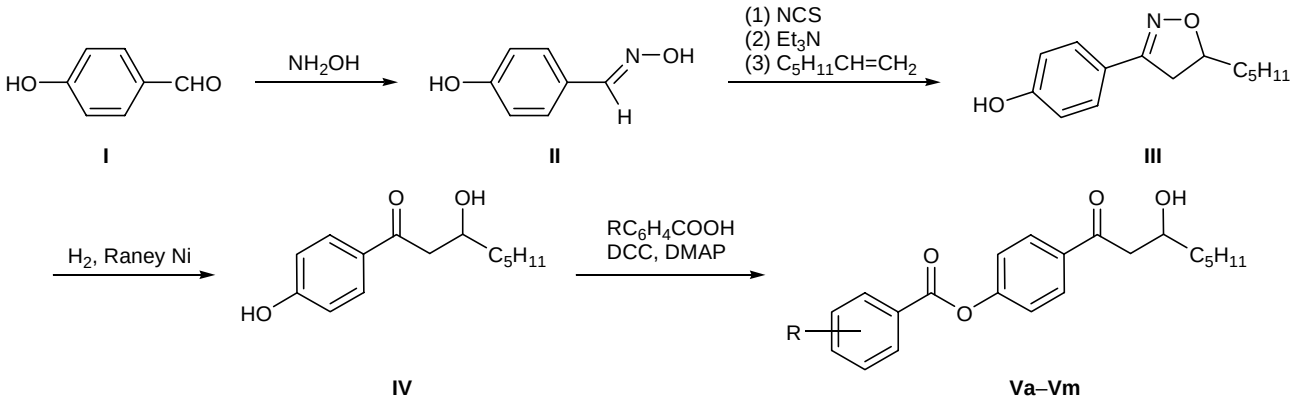
Abstract—Liquid crystalline benzoates with a smectic meso phase were synthesized on the basis of 3-hydroxy-1-(4-hydroxyphenyl)-1-octanone by esterification of 4-alkoxybenzoic acids.

We previously reported on the synthesis of liquid crystals on the basis of 4,5-dihydroisoxazoles [1–4]. Opening of the heteroring in substituted 4,5-dihydroisoxazoles could lead to various difunctional compounds [5, 6]. For example, β-hydroxy ketones, α,β-unsaturated ketones, and amino alcohols can be obtained in this way [5, 6]. We presumed that such transformations of appropriate 4,5-dihydroisoxazoles may be used to prepare new liquid crystalline compounds having a functionalized side chain. As first subjects for study we selected liquid crystalline compounds containing a β-hydroxyketone fragment in the side chain.

The scheme proposed previously [1] for the synthesis of liquid crystalline compounds on the basis of 4,5-dihydroisoxazoles includes transformation of initial *p*-hydroxybenzaldehyde (**I**) into oxime **II** which is then converted into the corresponding nitrile oxide via successive treatment with *N*-chlorosuccinimide and triethylamine. 1,3-Dipolar cycloaddition of the nitrile oxide to 1-heptene gives substituted 4,5-dihydroisoxazole **III**. We believed that opening of the heteroring in **III** could give rise to liquid crystalline compounds having a β-hydroxyketone fragment in the side chain. Most frequently, substituted 4,5-dihydroisoxazoles are subjected to ring opening by catalytic hydrogenation over Raney nickel in the presence of boric or acetic acid [7, 8]. The primary reduction products are the corresponding β-hydroxy imines, and their acid hydrolysis leads to substituted β-hydroxy ketones [5–7]. By hydrogenation of dihydroisoxazole **III** over Raney nickel in the presence of boric acid we obtained 3-hydroxy-1-(4-hydroxyphenyl)-1-octanone (**IV**) in 76% yield (Scheme 1).

The structure of product **IV** was proved by IR and ^{1}H NMR spectroscopy. The IR spectrum of compound

Scheme 1.



V, R = 4-C_3H_7O (**a**), 4-C_4H_9O (**b**), 4-$C_5H_{11}O$ (**c**), 4-$C_6H_{13}O$ (**d**), 4-$C_7H_{15}O$ (**e**), 4-$C_8H_{17}O$ (**f**), 4-$C_9H_{19}O$ (**g**), 4-$C_{12}H_{25}O$ (**h**), 4-$C_{16}H_{33}O$ (**i**), 4-C_6H_{13} (**j**), 3-F (**k**), 4-F (**l**), 4-CN (**m**).

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Phase transition temperatures of compounds **Vb**–**Vi**

Comp. no.	mp, °C	Smectic phase (C)	T_{tr},[a] °C	Smectic phase (A)	T_{cl},[b] °C
Vb	118.5	–	(112)	●	–
Vc	108	●	118.5	●	119.5
Vd	106	●	122.5	●	124.5
Ve	103	●	124	●	126
Vf	98	●	128.5	●	130
Vg	107	●	126.5	●	127.5
Vh	108	●	124	●	129.5
Vi	104	–	–	●	124

[a] Transition temperature.
[b] Clarification temperature.

IV contained a strong band at 1664 cm^{-1}, which is typical of stretching vibrations of a carbonyl group. In the ^1H NMR spectrum of **IV**, protons of the methylene group in the β-hydroxyketone fragment appear as two doublets of doublets at δ 2.95 and 3.11 ppm with a geminal coupling constant ^2J of 18 Hz. Vicinal couplings of these protons with the CH proton are characterized by ^3J constants of 9 and 2.4, respectively. The CH proton gives rise to a downfield multiplet at δ 4.16–4.25 ppm. The broadened singlet at δ 3.65 ppm belongs to the alcoholic hydroxy group in **IV**; no such signal is present in the spectrum of initial dihydroisoxazole **III**, while the phenolic hydroxy proton gives a multiplet at δ 6.80–6.98 ppm.

Further design of liquid crystalline compounds on the basis of phenol **IV** requires a rigid polycyclic central fragment to be created in the target molecule. This may be achieved, e.g., by esterification of substituted benzoic acids with phenol **IV** to obtain bicyclic compounds like **V** having a bridging ester moiety. We have found that benzoates **Va**–**Vm** are formed with high regioselectivity by reaction of compound **IV** with a small excess of the corresponding benzoic acid in the presence of a twofold amount of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-dimethylaminopyridine (DMAP). Following this procedure, esters **Va**–**Vm** were synthesized in 65–93% yield.

The structure of compounds **Va**–**Vm** was confirmed by the data of IR and ^1H NMR spectroscopy. In the IR spectra of **Va**–**Vm** we observed absorption bands belonging to stretching vibrations of the ester and ketone carbonyl groups at 1730–1750 and 1670–1680 cm^{-1}, respectively. The aromatic region of the ^1H NMR spectra of esters **Va**–**Vm** contained two doublets from protons of the phenol ring and multiplets from the substituted benzoic acid fragment. The intensity ratio of these signals indicates that only one benzoic acid residue is involved in the esterification. The signals from the β-hydroxyketone moiety almost did not change their positions. Broadened signals from the alcoholic hydroxy group were present in the spectra, while multiplets from the phenolic OH proton were absent. These data confirm chemoselective formation of substituted aryl benzoates rather than isomeric alkyl benzoates. We believe that the observed selectivity originates from the reduced nucleophilicity of the alcoholic hydroxy group as compared to phenolic due to steric hindrances (secondary OH group) and participation of the hydroxy group in intramolecular hydrogen bonding with the ketone carbonyl group.

We examined phase transitions of compounds **Va**–**Vm** and found that eight of these, namely 4-alkoxybenzoates **Vb**–**Vi**, possess mesomorphic properties (see table). Compounds **Vb**–**Vi** give rise to a smectic liquid crystalline phase. Molecules **Va**–**Vm** differ by substituents in positions *3* and *4* of the benzoic acid residue. In this connection, it was important to elucidate the role of the substituent in the presence or absence of liquid crystalline properties of the compounds under study. For example, ester **Va** having a 4-propoxybenzoate moiety does not form liquid crystalline phase, while butyl benzoate **Vb** gives rise to only monotropic smectic phase A in the temperature range 6.5°C. This means that the length of the alkoxy group in esters **Va** and **Vb** is insufficient for formation and stabilization of thermotropic liquid crystalline state. Homologous compounds **Vc**–**Vh** give rise to thermotropic smectic phase C which is converted into smectic phase A on further heating. Extension of the alkoxy substituent in going from ester **Vc** to ester **Vf** enhances intermolecular interaction between the alkyl groups and hence stabilizes more ordered phase C. This is the reason why the temperature range for smectic phase of esters **Vc**–**Vf** increases from 10.5 (**Vc**) to 30.5°C (**Vf**). The temperature range for smectic phase A of compounds **Vc**–**Vg** is 1–2.5°C. Further extension of the alkoxy radical increases its mobility thus reducing thermal stability of smectic phase C of benzoates **Vg** and **Vh** to 19.5 and 16°C, respectively, and increasing the temperature range of less ordered smectic phase A for compound **Vh** to 5.5°C. Benzoate **Vi** in which the alkoxy radical consists of 16 carbon atoms produces only thermotropic smectic phase A in the temperature range 20°C. It is known that stabilization of smectic mesophases is strongly affected by lateral interaction between polar

groups of the molecules. In the case of esters **Vb**–**Vi**, the interaction involving the β-hydroxyketone fragment is also important. As a result, the temperature range of thermotropic smectic phase of esters **Va**–**Vf** and **Vh** increases relative to the corresponding parameter of esters derived from 1-(4-hydroxyphenyl)-1-octanone and 4-alkoxybenzoic acids [9], which differ from compounds **V** by the absence of hydroxy group in the alkyl chain. Moreover, the esters described in [9] give rise to only less ordered smectic phase A [9].

The absence of oxygen atom in the side chain is responsible for weakening of intermolecular interaction [10]. Presumably, this is the reason why ester **Vj** does not produce mesophase. It should be noted that introduction of polar groups into the terminal part of the molecule (esters **Vk**–**Vm**) also leads to loss of liquid crystalline properties.

EXPERIMENTAL

The IR spectra were recorded from solutions in chloroform using a Specord 75-IR spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker Avance-400 spectrometer (400 MHz) from solutions in chloroform-*d*; HMDS was used as internal reference. The phase transition temperatures were determined on a heating device coupled with a polarizing microscope.

3-Hydroxy-1-(4-hydroxyphenyl)-1-octanone (IV). A suspension of 2 g of Raney nickel in 60 ml of methanol and 12 ml of water was saturated with hydrogen over a period of 1 h while stirring. Dihydroisoxazole **III** [1], 3.17 g (13.6 mmol), and boric acid, 8.4 g (135.5 mmol), were added, and the mixture was stirred under hydrogen until it no longer absorbed. The catalyst was filtered off and washed with 100 ml of chloroform on a filter, 200 ml of water was added to the filtrate, and the organic phase was separated. The aqueous phase was treated with chloroform (2×50 ml), and the chloroform extracts were combined, washed with 100 ml of a saturated solution of sodium chloride and 50 of water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was recrystallized from a toluene–petroleum ether mixture. Yield of hydroxy ketone **IV** 2.44 g (76%), mp 76.5–77.5°C (from toluene–petroleum ether). IR spectrum, ν, cm^{-1}: 3575, 3460–3100 (OH); 3010 (C–H$_{arom}$); 2950, 2925, 2850 (C–H$_{aliph}$); 1664 (C=O); 1600, 1590, 1505 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, C^{8}H$_3$, *J* = 7 Hz), 1.16–1.66 m (8H, CH$_2$, alkyl), 2.95 d.d (1H, J_1 = 9, J_2 = 18 Hz), 3.11 d.d (1H, C^{2}H$_2$, J_1 = 2.4, J_2 = 18 Hz), 3.65 br.s (1H, 3-OH), 4.16–4.25 m (1H, 3-H), 6.80–6.98 m (1H, 4'-OH), 6.85 d (2H, *J* = 9 Hz), 7.85 d (2H, H$_{arom}$, *J* = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-propoxybenzoate (Va). A catalytic amount of 4-(dimethylamino)-pyridine was added to a solution of 0.1 g (0.42 mmol) of hydroxy ketone **IV**, 0.084 g (0.47 mmol) of 4-propoxybenzoic acid, and 0.17 g (0.83 mmol) of *N*,*N'*-dicyclohexylcarbodiimide in 15 ml of methylene chloride. The mixture was stirred for 23 h at 20°C, and the precipitate was separated by filtering through a layer of aluminum oxide and washed with 40 ml of methylene chloride. The filtrate was washed with 30 ml of a saturated solution of sodium hydrogen carbonate and 30 ml of water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was recrystallized from 2-propanol. Yield 0.147 g (87%), mp 126–126.5°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 3250–3650 (OH); 3035, 3015 (C–H$_{arom}$); 2965, 2935, 2875, 2860 (C–H$_{aliph}$); 1740 (C=O, ester); 1680 (C=O, ketone); 1605, 1580, 1510 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, C$^{3'}$H$_3$, C$^{8''}$H$_3$, *J* = 7 Hz); 1.05 t (3H, C$^{3'}$H$_3$, C$^{8''}$H$_3$, *J* = 7 Hz); 1.22–1.55 m (6H, C$^{5''}$H$_2$, C$^{6''}$H$_2$, C$^{7''}$H$_2$); 1.56–1.66 m (2H, C$^{4''}$H$_2$); 1.84 sext (2H, C$^{2'}$H$_2$, *J* = 7 Hz); 3.03 d.d (1H, C$^{2''}$H$_2$, J_1 = 9, J_2 = 17.6 Hz); 3.16 d.d (1H, C$^{2''}$H$_2$, J_1 = 2.4, J_2 = 17.6 Hz); 3.23 d (1H, OH, *J* = 3.2 Hz); 4.00 t (2H, C$^{1'}$CH$_2$, *J* = 7 Hz); 4.17–4.26 m (1H, 3''-H); 6.96 d (2H, *J* = 9 Hz), 7.31 d (2H, *J* = 9 Hz), 8.02 d (2H, *J* = 9 Hz), 8.12 d (2H, *J* = 9 Hz) (H$_{arom}$).

Compounds **Vb**–**Vm** were synthesized following a similar procedure.

4-(3-Hydroxyoctanoyl)phenyl 4-butoxybenzoate (Vb). Yield 78%. IR spectrum, ν, cm^{-1}: 3230–3640 (OH); 3030, 3015 (C–H$_{arom}$); 2960, 2935, 2875 (C–H$_{alkyl}$); 1735 (C=O, ester); 1680 (C=O, ketone); 1600, 1585, 1510 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, C$^{4'}$H$_3$, C$^{8''}$H$_3$, *J* = 6.4 Hz), 0.98 t (3H, C$^{4'}$H$_3$, C$^{8''}$H$_3$, *J* = 7 Hz), 1.18–1.56 m (8H, CH$_2$, alkyl), 1.56–1.67 m (2H, C$^{4''}$H$_2$), 1.80 quint (2H, C$^{2'}$H$_2$, *J* = 7 Hz), 3.03 d.d (1H, C$^{2''}$H$_2$, J_1 = 9, J_2 = 17.6 Hz), 3.16 d.d (1H, C$^{2''}$H$_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.23 d (1H, OH, *J* = 3 Hz), 4.04 t (2H, C$^{1'}$H$_2$, *J* = 7 Hz), 4.16–4.26 m (1H, 3''-H), 6.96 d (2H, H$_{arom}$, *J* = 9 Hz), 7.31 d (2H, H$_{arom}$, *J* = 9 Hz), 8.02 d (2H, H$_{arom}$, *J* = 9 Hz), 8.12 d (2H, H$_{arom}$, *J* = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-pentyloxybenzoate (Vc). Yield 93%. IR spectrum, ν, cm^{-1}: 3035, 3020 (C–H$_{arom}$); 2965, 2940, 2875 (C–H$_{aliph}$); 1740 (C=O, ester); 1685 (C=O); 1610, 1520 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, C$^{5'}$H$_3$, C$^{8''}$H$_3$,

J = 7 Hz), 0.93 t (3H, $C^{5'}H_3$, $C^{8''}H_3$, J = 7 Hz), 1.30–1.68 m (12H, CH_2, alkyl), 1.82 quint (2H, $C^{2'}H_2$, J = 7 Hz), 3.04 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 18 Hz), 3.16 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 18 Hz), 3.23 d (1H, 3-OH, J = 3 Hz), 4.04 t (2H, $C^{1'}H_2$, J = 7 Hz), 4.16–4.26 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 9 Hz), 7.31 d (2H, H_{arom}, J = 9 Hz), 8.02 d (2H, H_{arom}, J = 9 Hz), 8.12 d (2H, H_{arom}, J = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-hexyloxybenzoate (Vd). Yield 84%. IR spectrum, ν, cm^{-1}: 3200–3650 (OH); 3035, 3015 (C–H_{arom}); 2960, 2935, 2875, 2860 (C–H_{alkyl}); 1735 (C=O, ester); 1680 (C=O, ketone); 1605, 1585, 1515 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.85–0.94 m (6H, $C^{6'}H_3$, $C^{8''}H_3$), 1.20–1.67 m (14H, CH_2, alkyl), 1.81 quintet (2H, $C^{2'}H_2$, J = 7 Hz), 3.03 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 18 Hz), 3.16 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 18 Hz), 3.24 d (1H, OH, J = 3.2 Hz), 4.03 t (2H, $C^{1'}H_2$, J = 7 Hz), 4.17–4.26 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 9 Hz), 7.31 d (2H, H_{arom}, J = 9 Hz), 8.02 d (2H, H_{arom}, J = 9 Hz), 8.12 d (2H, H_{arom}, J = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-heptyloxybenzoate (Ve). Yield 65%. IR spectrum, ν, cm^{-1}: 3250–3630 (OH); 3030, 3010 (C–H_{arom}); 2955, 2930, 2870, 2855 (C–H_{aliph}); 1735 (C=O, ester); 1675 (C=O, ketone); 1600, 1580, 1505 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.84–0.95 m (6H, $C^{7'}H_3$, $C^{8''}H_3$), 1.20–1.67 m (16H, CH_2, alkyl), 1.81 quint (2H, $C^{2'}H_2$, J = 7 Hz), 3.03 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 17.6 Hz), 3.16 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.22 d (1H, OH, J = 3.2 Hz), 4.03 t (2H, $C^{1'}H_2$, J = 7 Hz), 4.17–4.26 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 9 Hz), 7.31 d (2H, H_{arom}, J = 9 Hz), 8.02 d (2H, H_{arom}, J = 9 Hz), 8.12 d (2H, H_{arom}, J = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-octyloxybenzoate (Vf). Yield 86%. IR spectrum, ν, cm^{-1}: 3260–3650 (OH); 3035, 3015 (C–H_{arom}); 2960, 2935, 2870, 2860 (C–H_{aliph}); 1735 (C=O, ester); 1680 (C=O, ketone); 1605, 1580, 1515 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.85–0.95 m (6H, $C^{8'}H_3$, $C^{8''}H_3$), 1.20–1.68 m (18H, CH_2, alkyl), 1.81 quint (2H, $C^{2'}H_2$, J = 7 Hz), 3.03 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 17.6 Hz), 3.16 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.23 d (1H, OH, J = 3.2 Hz), 4.03 t (2H, $C^{1'}H_2$, J = 7 Hz), 4.16–4.26 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 9 Hz), 7.31 d (2H, H_{arom}, J = 9 Hz), 8.02 d (2H, H_{arom}, J = 9 Hz), 8.12 d (2H, H_{arom}, J = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-nonyloxybenzoate (Vg). Yield 70.4%. IR spectrum, ν, cm^{-1}: 3035, 3015 (C–H_{arom}); 2960, 2940, 2865 (C–H_{alkyl}); 1735 (C=O, ester); 1680 (C=O, ketone); 1600, 1580, 1510 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, $C^{9'}H_3$, $C^{8''}H_3$, J = 7 Hz), 0.89 t (3H, $C^{9'}H_3$, $C^{8''}H_3$, J = 7 Hz), 1.16–1.69 m (20H, CH_2, alkyl), 1.81 quintet (2H, $C^{2'}H_2$, J = 7 Hz), 3.03 d.d (1H, $C^{2''}$H2, J_1 = 9, J_2 = 18 Hz), 3.17 d.d (1H, $C^{2''}H_2$, J_1 = 2.5, J_2 = 18 Hz), 3.25 br.s (1H, OH), 4.03 t (2H, $C^{1'}H_2$, J = 7 Hz), 4.18–4.26 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 9 Hz), 7.31 d (2H, H_{arom}, J = 9 Hz), 8.02 d (2H, H_{arom}, J = 9 Hz), 8.12 d (2H, H_{arom}, J = 9 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-dodecyloxybenzoate (Vh). Yield 72%. IR spectrum, ν, cm^{-1}: 3240–3630 (OH); 3015 (C–H_{arom}); 2955, 2930, 2855 (C–H_{aliph}); 1735 (C=O, ester); 1675 (C=O, ketone); 1600, 1580, 1505 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, $C^{12'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 0.91 t (3H, $C^{12'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 1.18–1.68 m (26H, CH_2, alkyl), 1.82 quintet (2H, $C^{2'}H_2$, J = 6.8 Hz), 3.04 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 17.6 Hz), 3.18 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.23 d (1H, OH, J = 2.9 Hz), 4.06 t (2H, $C^{1'}H_2$, J = 6.8 Hz), 4.17–4.27 m (1H, 3''-H), 6.98 d (2H, H_{arom}, J = 8.8 Hz), 7.32 d (2H, H_{arom}, J = 8.8 Hz), 8.04 d (2H, H_{arom}, J = 8.8 Hz), 8.13 d (2H, H_{arom}, J = 8.8 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-hexadecyloxybenzoate (Vi). Yield 92%. IR spectrum, ν, cm^{-1}: 3200–3630 (OH); 3025 (C–H_{arom}); 2925, 2850 (C–H_{aliph}); 1730 (C=O, ester); 1675 (C=O, ketone); 1600, 1580, 1505 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.86 t (3H, $C^{16'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 0.89 t (3H, $C^{16'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 1.17–1.67 m (34H, CH_2, alkyl), 1.81 quintet (2H, $C^{2'}H_2$, J = 6.8 Hz), 3.03 d.d (1H, $C^{2''}H_2$, J_1 = 8.8, J_2 = 18 Hz), 3.17 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 18 Hz), 3.22 d (1H, OH, J = 2.4 Hz), 4.03 t (2H, $C^{1'}H_2$, J = 6.8 Hz), 4.17–4.27 m (1H, 3''-H), 6.96 d (2H, H_{arom}, J = 8.8 Hz), 7.31 d (2H, H_{arom}, J = 8.8 Hz), 8.02 d (2H, H_{arom}, J = 8.8 Hz), 8.12 d (2H, H_{arom}, J = 8.8 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-hexylbenzoate (Vj). Yield 67.4%, mp 104–104.5°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 3200–3630 (OH); 3010 (C–H_{arom}); 2955, 2930, 2855 (C–H_{aliph}); 1735 (C=O, ester); 1670 (C=O, ketone); 1600, 1500 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, $C^{6'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 0.89 t (3H, $C^{6'}H_3$, $C^{8''}H_3$, J = 6.8 Hz), 1.22–1.69 m (16H, CH_2 alkyl), 2.69 t (2H, $C^{1'}H_2$, J = 8 Hz), 3.04 d.d (1H, $C^{2''}H_2$, J_1 = 9, J_2 = 17.6 Hz), 3.17 d.d (1H, $C^{2''}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.22 d (1H, OH, J = 3.2 Hz), 4.17–4.26 m (1H, 3''-H), 7.31 d (2H, H_{arom}, J = 8.8 Hz), 7.32 d (2H, H_{arom}, J = 8.4 Hz),

8.03 d (2H, H_{arom}, J = 8.8 Hz), 8.09 d (2H, H_{arom}, J = 8.4 Hz).

4-(3-Hydroxyoctanoyl)phenyl 3-fluorobenzoate (Vk). Yield 90%, mp 122°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 3020 (C–H_{arom}); 2955, 2930, 2865 (C–H_{aliph}); 1745 (C=O, ester); 1680 (C=O, ketone); 1600 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{8'}H_3$, J = 6.8 Hz), 1.18–1.67 m (8H, CH_2, alkyl), 3.04 d.d (1H, $C^{2'}H_2$, J_1 = 9, J_2 = 17.6 Hz), 3.16 d.d (1H, $C^{2'}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.18 d (1H, OH, J = 2.8 Hz), 4.18–4.24 m (1H, 3'-H), 7.33 d (2H, H_{arom}, J = 8.8 Hz), 8.04 d (2H, H_{arom}, J = 8.8 Hz), 7.30–7.39 m (1H, H_{arom}), 7.50 d.t (1H, H_{arom}, J_1 = 5.6, J_2 = 8 Hz), 7.87 br.d (1H, H_{arom}, J = 9.6 Hz), 7.99 br.d (1H, H_{arom}, J = 7.2 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-fluorobenzoate (Vl). Yield 86%, mp 129–130°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 3030, 3015 (C–H_{arom}); 2965, 2935, 2865 (C–H_{aliph}); 1745 (C=O, ester); 1680 (C=O, ketone); 1605, 1510 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{8'}H_3$, J = 6.8 Hz), 1.22–1.67 m (8H, CH_2, alkyl), 3.04 d.d (1H, $C^{2'}H_2$, J_1 = 9.2, J_2 = 17.6 Hz), 3.16 d.d (1H, $C^{2'}H_2$, J_1 = 2.4, J_2 = 17.6 Hz), 3.19 d (1H, OH, J = 3.2 Hz), 4.17–4.27 m (1H, 3'-H), 7.19 t (2H, H_{arom}, J = 8.8 Hz), 7.32 d (2H, H_{arom}, J = 8.8 Hz), 8.04 d (2H, H_{arom}, J = 8.8 Hz), 8.21 d.d (2H, H_{arom}, J_1 = 5.6, J_2 = 8.8 Hz).

4-(3-Hydroxyoctanoyl)phenyl 4-cyanobenzoate (Vm). Yield 80%, mp 123–124°C. IR spectrum, ν, cm^{-1}: 3230–3650 (OH); 3030, 3020 (C–H_{arom}); 2965, 2935, 2865 (C–H_{aliph}); 2240 (C≡N); 1750 (C=O, ester); 1680 (C=O, ketone); 1605, 1510 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{8'}H_3$, J = 6.6 Hz), 1.20–1.64 m (8H, CH_2, alkyl), 3.05 d.d (1H, $C^{2'}H_2$, J_1 = 8.8, J_2 = 17.6 Hz), 3.16 d.d (1H, $C^{2'}H_2$, J_1 = 2.7, J_2 = 17.6 Hz), 3.16 d (1H, OH, J = 3.2 Hz), 4.17–4.27 m (1H, 3'-H), 7.33 d (2H, H_{arom}, J = 9 Hz), 7.82 d (2H, H_{arom}, J = 9 Hz), 8.06 d (2H, J = 9 Hz), 8.30 d (2H, H_{arom}, J = 9 Hz).

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