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Synthesis of Banana-Like 1,3-Dihydroxybenzene and 2,7-Dihydroxynaphthalene Esters and Luminescence of Their Terbium(III) Complexes

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Abstract—New esters of 1,3-dihydroxybenzene and 2,7-dihydroxynaphthalene with 4-(4-alkoxybenzoyloxy)-2-(or 3-)methoxybenzoic acids were synthesized. The correlation between their structure and liquid crystal properties was examined, and the luminescence characteristics of terbium(III) complexes with these esters were studied.

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The advantages of liquid crystal displays (LCDs), which are widely used today, are low power consumption and flat screens. However, they also have certain drawbacks such as limited angle of vision and low brightness. Luminescent LCDs, which are emitting displays and contain luminescent lanthanide complexes, are more promising. Therefore, synthesis of luminescent lanthanide complexes and elucidation of the influence exerted by the ligand structure on the luminescence intensity are very topical for the development of such displays [1].

Liquid crystal lanthanide complexes containing as ligands Schiff bases, β-enamino ketonates, β-diketonates, and cholesterol esters with benzo crown ether fragment are known [1]. The luminescence properties of mesomorphic lanthanide complexes were examined in a number of studies [2–4].

Previously [5] we demonstrated for the first time the possibility of using liquid crystal banana-like compounds, 4-methoxy-1,3-benzenedicarboxylic acid esters, as ligands for the formation of complexes with Tb(III) ion.

This paper deals with the synthesis of banana-like compounds containing a methoxy group in lateral fragments of the molecules, study of their mesomorphism, and examination of the possibility of the formation of luminescent Tb(III) complexes with these compounds.

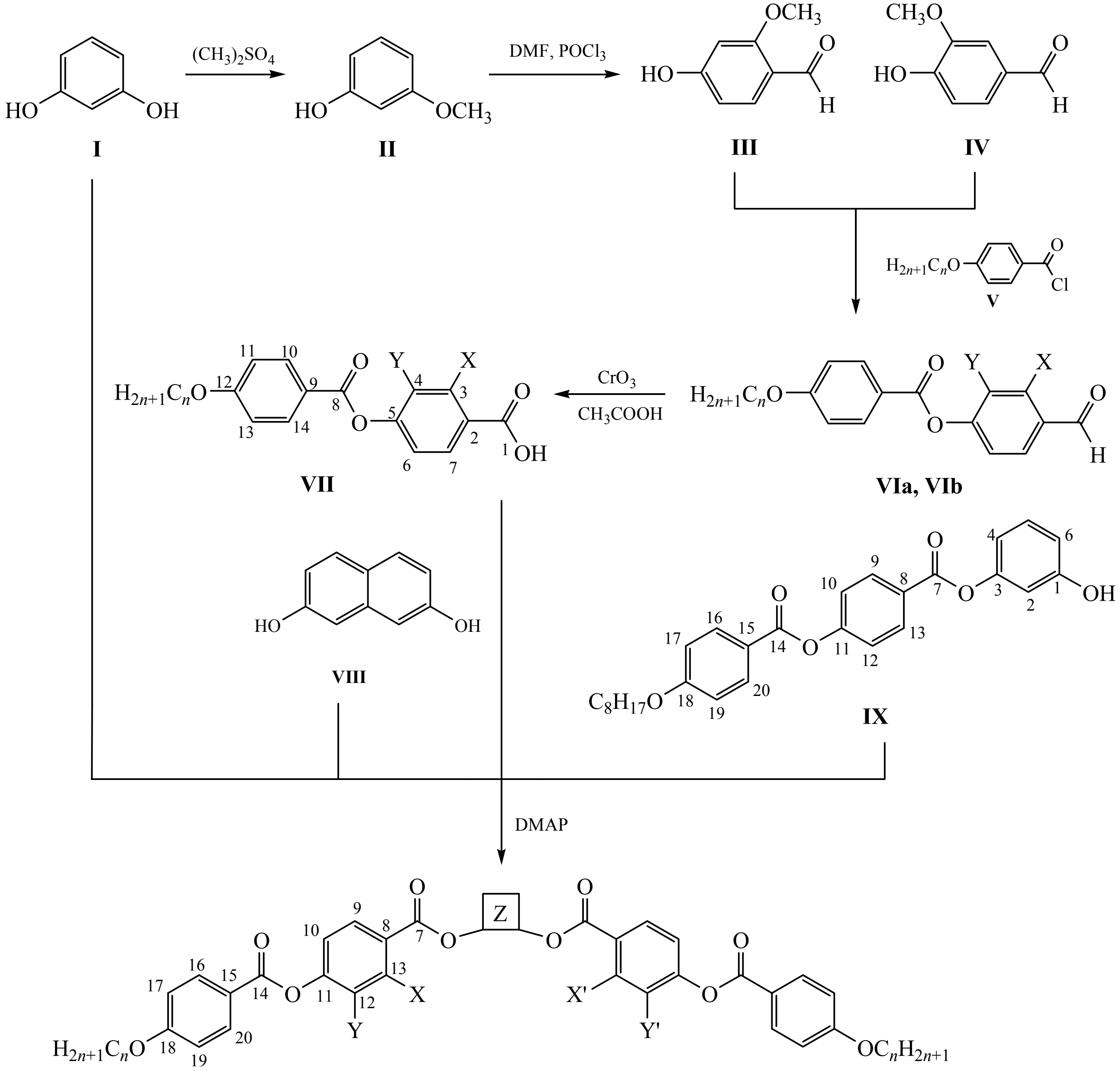
EXPERIMENTAL

1,3-Dihydroxybenzene esters **X–XIII** were prepared following Scheme 1. The first step was the synthesis of 1,3-dihydroxybenzene monomethyl ether **II** using dimethyl sulfate as alkylating agent. Then the aldehyde group was introduced by Vilsmeier formylation with dimethylformamide and phosphorus oxychloride, performed on cooling.

Because the reaction yielded two products, 4-hydroxy-2-methoxybenzaldehyde **III** and its isomer, 2-hydroxy-4-methoxybenzaldehyde, the procedure was modified to ensure their separation. Nevertheless, the yield of **III** did not exceed 20%. The subsequent acylation of 4-hydroxy-2-methoxybenzaldehyde **III** and 4-hydroxy-3-methoxybenzaldehyde **IV** was performed with the corresponding 4-alkoxybenzoyl chlorides **V** in anhydrous pyridine.

The structures of **VIa** and **VIb** were confirmed by IR spectroscopy. Along with the band at ~1680 cm^{-1}, assigned to stretching vibrations of the aldehyde carbonyl group, a band of stretching vibrations of the ester carbonyl group appears at ~1720 cm^{-1}. The band characteristic of stretching vibrations of the ether bond C–O–C appears at ~1240 cm^{-1}. The aldehydes prepared, **VIa** and **VIb**, do not exhibit mesomorphic properties, which is caused by distortion of the

Scheme 1.



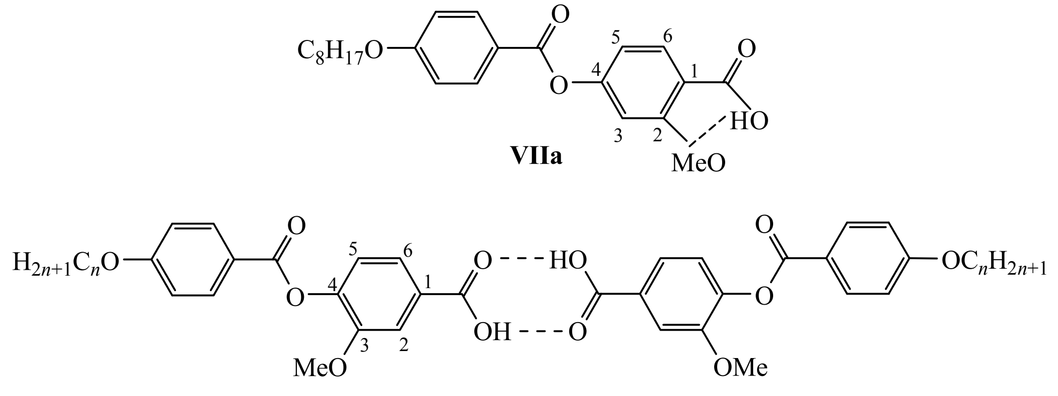
$X = X' = OCH_3$, $Y = Y' = H$, $Z = C_6H_4$, $n = 8$ (**X**); $X = X' = H$, $Y = Y' = OCH_3$, $Z = C_6H_4$, $n = 10$ (**XI**); $X = X' = H$, $Y = Y' = OCH_3$, $Z = C_{10}H_6$, $n = 12$ (**XII**); $X = Y = H$, $X' = OCH_3$, $Y' = H$, $Z = C_6H_4$, $n = 8$ (**XIII**).

geometric anisotropy of the molecule on introduction of a bulky lateral substituent, methoxy group.

4-(4-Alkoxybenzoyloxy)-2(3)methoxybenzaldehydes **VIa** and **VIb** were oxidized to the corresponding acids **VIIa** and **VIIb** with the Jones reagent in acetone [6]. It should be noted that the oxidation of 4-(4-*n*-octyloxybenzoyloxy)-2-methoxybenzaldehyde **VIa** requires elevated temperature and takes longer time. The structures of 4-(4-octyloxy-benzoyloxy)-2-methoxybenzoic acid **VIIa** and 4-(4-alkoxybenzoyloxy)-3-methoxy-benzoic acids **VIIb** and **VIIc** were determined from the ^{1}H NMR spectra.

4-(4-Octyloxybenzoyloxy)-2-methoxybenzoic acid **VIIa** showed no mesomorphic properties, whereas

Scheme 2.



VIIa

VIIb

acids **VIIb** and **VIIc** containing the methoxy group in the 3-position formed a nematic mesophase at lower temperatures than did their unsubstituted analogs [7].

The phase transition temperatures for 4-(4-decyloxybenzoyloxy)-3-methoxybenzoic acid **VIIb** are as follows (°C): crystal (Cr) → isotropic liquid (**I**) 141.1, **I** → nematic mesophase (N) 136.6, N → Cr 117.8. The nematic phase is formed on cooling from the isotropic liquid, i.e., it is monotropic. With the extension of the terminal alkoxy group to 12 C atoms (compound **VIIc**), the mesophase becomes enantiotropic, i.e., it is detected in the course of both heating and cooling. The phase transition temperatures for **VIIc** are as follows (°C): Cr → N 120, N → I 137.8, I → N 137.2, N → Cr 98.

The lack of mesomorphism of **VIIa** can be attributed to the formation of an intramolecular hydrogen bond between the carboxyl proton and oxygen atom of the methoxy group, which prevents formation of dimers and restoration of the geometric anisotropy of the molecule. The presence of an intramolecular hydrogen bond is confirmed by the IR data (ν_{OH} = 3500 cm^{-1}). When the methoxy group is in the *m*-position relative to the carboxy group (acid **VIIb**), the intramolecular hydrogen bonding is impossible, and dimers are formed via intermolecular hydrogen bonding (ν_{OH} = 3050 cm^{-1}), as shown in Scheme 2.

The final banana-like esters of the synthesized acids and 1,3-dihydroxybenzene (**X**, **XI**, **XIII**) and 2,7-dihydroxynaphthalene (**XII**) were prepared by the carbodiimide procedure in anhydrous methylene chloride. Their structure was proved by ^1H NMR spectroscopy. The results of examining compounds **X**–**XII** by polarization microscopy show that they exhibit no mesomorphism. The spectral characteristics, yields, and melting points of the final diesters are given in the table.

Mixing a methanol solution of terbium trichloride [Tb(III) concentration 1×10^{-5} M] and a benzene solution of ligands **X–XIII** (ligand concentration 1×10^{-4} M) led to the formation of luminescent complexes (see figure).

The lowest luminescence intensity was observed with the diester of 1,3-dihydroxybenzene and 4-(4-octyloxybenzoyloxy)-2-methoxybenzoic acid **X**. The shift of the methoxy group to the 3-position of the aromatic ring of the intermediate acid (compound **XI**) led to an increase in the luminescence intensity by a factor of 3. Replacement of the central benzene ring by the naphthalene ring did not affect noticeably the luminescence intensity (compound **XII**). The complexation with ligand **X** could be prevented by a steric factor (close arrangement of two bulky substituents). To check this assumption, we synthesized unsymmetrical banana-like resorcinol ester **XIII** containing a methoxy group only in one lateral fragment (Scheme 1). 3-[4-(4-Octyloxybenzoyloxy)benzoyloxy]-1-hydroxybenzene **IX** was synthesized by the reaction of chloride **V** with a fourfold excess of resorcinol in dry benzene and absolute pyridine as an agent for binding HCl, following the procedure described in [8]. The final 3-[4-(4-octyloxybenzoyloxy)benzoyloxy]-1-[4-(4-octyloxybenzoyloxy)-2-methoxybenzoyloxy]benzene **XIII** was synthesized by the carbodiimide method. The structure of **XIII** was determined from the ^1H NMR data. Examination by

Properties of 1,3-dihydroxybenzene and 2,7-dihydroxynaphthalene esters **X–XIII**

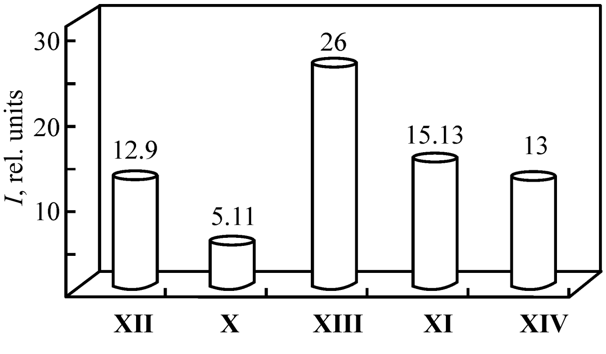
Comp. no.	Yield, %	*T*, °C	Found, % Calculated, %		Formula	^{1}H NMR spectrum, δ, ppm ($CDCl_3$; 300 MHz)
			C	H		
X	67.8	106.0	71.27 71.39	6.80 6.64	$C_{52}H_{58}O_{12}$	0.90 t (6H, CH_3), 1.22–1.55 m (20H, CH_2), 1.77–1.89 m (4H, $C\mathit{H}_2CH_2O$), 3.95 s (6H, OCH_3), 4.09 t (4H, OCH_2), 6.90–7.06 m (8H, H^{10,12,17,19}), 7.13–7.21 m (3H, H^{2,4,6}), 7.48 t (1H, H^5), 8.09–8.20 m (6H, H^{9,16,20})
XI	70.0	99.5 glass	73.17 73.02	7.34 7.50	$C_{60}H_{74}O_{12}$	0.92 t (6H, CH_3), 1.25–1.45 m (24H, CH_2), 1.47–1.56 m (4H, $C\mathit{H}_2CH_2CH_2O$), 1.81–1.90 m (4H, $C\mathit{H}_2CH_2O$), 3.94 br.s (6H, OCH_3), 4.08 t (4H, CH_2O), 7.01 d (4H, H^{17,19}), 7.19–7.25 m (3H, resorcinol H – 2,4,6,), 7.32 d (2H, H^{12}), 7.53 t (1H, resorcinol H^5), 7.85 d (2H, H^9), 7.91, 7.93 d.d (2H, H^{13}), 8.19 d (4H, H^{16,20})
XII	28.0	71.0	74.31 74.13	7.20 7.33	$C_{64}H_{76}O_{12}$	0.89 t (3H, CH_3), 1.55–1.20 m (36H, CH_2), 1.89–1.77 m (4H, $C\mathit{H}_2CH_2O$), 3.95 br.s (6H, OCH_3), 4.05 t (4H, CH_2O), 6.99 d (4H, H^{19,21}), 7.32 d (2H, H^{14}), 7.39, 7.36 d.d (2H, H^{3,6}), 7.70 d (2H, H^{1,8}), 8.00–7.85 m (6H, 2H^{4,5}, 4H^{11,15}), 8.17 d (4H, H^{18,22})
XIII	50.0	135.6	72.32 72.51	6. 80 6.63	$C_{51}H_{56}O_{11}$	0.90 t (6H, CH_3), 1.23–1.55 m (20H, CH_2), 1.77–1.88 m (4H, $C\mathit{H}_2CH_2O$), 3.95 s (3H, OCH_3), 4.05 t (4H, OCH_2), 6.9–7.02 m (6H, H$^{10,12,17,19,17',19'}$), 7.13–7.22 m (3H, H^{2,4,6}), 7.37 d (2H, H$^{10',12'}$), 7.48 t (1H, H^5), 8.09–8.20 m (5H, H$^{9,16,16',20,20'}$), 8.28 d (2H, H$^{9',13'}$)

polarization microscopy showed that the compound had no mesomorphic properties. The intensity of the luminescence of the complex of unsymmetrical banana-like compound **XIII** with terbium(III) chloride was 26 rel. units. For comparison, we show in the figure the luminescence intensity for the previously prepared [5] 4-methoxy-1,3-bis[4-(4-decyloxyphenoxycarbonyl)phenoxycarbonyl]benzene **XIV** containing the methoxy group in the 4-position of the central aromatic ring.

EXPERIMENTAL

The ^{1}H NMR spectra of 5–10% solutions of the compounds were recorded with a Varian VXR-300 spectrometer operating at 300 MHz, and the IR spectra, with a Specord IR-75 spectrophotometer ($CHCl_3$ solutions). The luminescence spectra were recorded with an SDL-1 spectrometer. The luminescence was excited with the light of a DRSh-250 mercury quartz lamp. Radiation with wavelengths of 313 and 365 nm was cut out using light filters. The purity of the compounds prepared was evaluated by TLC on Silufol UV-254 plates in the system chloroform : acetone = 5 : 2. The phase transition temperatures of the synthesized compounds were determined by polarization microscopy with a POLAM R-312 microscope.

4-Alkoxybenzoyl chlorides **V** were synthesized by the standard procedure [9]. 3-[4-(4-Octyloxybenzoyloxy)benzoyloxy]-1-hydroxybenzene **IX** was synthesized by the procedure described in [8].



Intensity *I* of the luminescence of lanthanide complexes in relation to the ligand structure. **X–XIII**: methoxy group in lateral fragments of the molecule; **XIV**: methoxy group in the central aromatic ring.

3-Methoxyphenol II. To 18.1 g (0.164 mol) of recrystallized 1,3-dihydroxybenzene **I**, we added with vigorous stirring 130 ml of a 10% KOH solution. Then we slowly added dropwise 15.5 ml (0.164 mol) of dimethyl sulfate, avoiding warm-up of the mixture above 40°C. After that, the mixture was stirred for 2 h at room temperature. To bring the reaction to completion and decompose unchanged dimethyl sulfate, the mixture was heated on a boiling water bath for 0.5 h. After cooling, the mixture was acidified with dilute HCl to pH 6 and extracted with benzene (3 × 100 ml), and the benzene extract was washed with a 10% NaOH solution (3 × 200 ml) and with water to pH 7 and was dried over $MgSO_4$. After removing the solvent, the residue was transferred into a distillation flask and subjected to vacuum fractionation, with collection of the fraction boiling at 82–86°C/3 mm Hg. Yield 48.3%, n_D^{20} 1.5520 (published data [10]: n_D^{20} 1.5520).

4-Hydroxy-2-methoxybenzaldehyde III. A four-necked flask was charged with 7.7 ml (0.1 mol) of anhydrous dimethylformamide. The flask was cooled with an ice–salt mixture to –12°C, after which 15.3 g (0.1 mol) of phosphorus oxychloride was added dropwise with stirring. Then 12.2 g (0.1 mol) of 3-methoxyphenol **II** was slowly added dropwise, with the cooling continued, so as to keep the temperature no higher than –5°C. After 2.5 h, the mixture was allowed to warm up to 15°C. A sample was taken, hydrolyzed with a sodium hydrocarbonate solution, and subjected to TLC analysis (chloroform : methanol = 5 : 1), visualization by UV irradiation. Two spots were observed, suggesting formation of the desired 4-hydroxy-2-methoxybenzaldehyde **III** and its isomer, 2-hydroxy-4-methoxybenzaldehyde. The flask was again cooled in an ice bath, and finely crushed ice (100 g) was added with stirring. After the reaction mixture dissolved, a 5 N NaOH solution was added until the solution became alkaline. In the process, brown oil separated out. The alkaline solution was carefully decanted into a beaker, and within 15 min a white flaky precipitated formed throughout the solution volume. The precipitate was filtered off, dried, and suspended in a 1 : 1 mixture of benzene and hexane. The mixture was heated to reflux. The precipitate was filtered off and dried. A white powder was obtained, yield 17.8%, mp 163°C (published data [11]: mp 154–156°C).

4-(4-Alkoxybenzoyloxy)-2-(and 3-)methoxybenzaldehydes VIa–VIc. Aldehyde **III** or **IV** (17.8 mmol) was dissolved in 15 ml of anhydrous pyridine, after which 16.8 mmol of appropriate 4-alkoxybenzoyl chloride **V** was added with stirring over a period of 10 min. After adding the whole amount of **V**, a dense white precipitate formed throughout the solution volume. Then 30 ml of alcohol was added, and the precipitate was filtered off, washed with alcohol (3 × 25 ml), and dried in air.

4-(4-*n*-Octyloxybenzoyloxy)-2-methoxybenzaldehyde VIa. Yield 55.8%, mp 107°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 2925, 2840 (CH_2, CH_3); 1720 (C=O ester); 1680 (C=O aldehyde); 1600, 1460 ($C–C_{arom}$); 1240 (C–O–C).

4-(4-*n*-Decyloxybenzoyloxy)-3-methoxybenzaldehyde VIb. Yield 86%, mp 68.2°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 2930, 2840 (CH_2, CH_3); 1720 (C=O ester); 1680 (C=O aldehyde); 1595, 1465 ($C–C_{arom}$); 1240 (C–O–C).

4-(4-*n*-Dodecyloxybenzoyloxy)-3-methoxybenzaldehyde VIc. Yield 73%, mp 127.2°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 2930, 2835 (CH_2, CH_3); 1720 (C=O ester); 1680 (C=O aldehyde); 1595, 1470 ($C–C_{arom}$); 1240 (C–O–C).

4-(4-Octyloxybenzoyloxy)-2-methoxybenzoic acid VIIa. To a suspension of 3.5 g (0.009 mol) of acylated aldehyde **VIa** in 50 ml of anhydrous acetone, we added with stirring a solution of 2.32 g of chromic anhydride in 2.4 ml of concentrated H_2SO_4 and 7.2 ml of water. The mixture was stirred for 1.5 h at room temperature and then for 2 h at 40°C and left overnight. After that, 300 g of crushed ice was added, the mixture was stirred for 0.5 h, and, after thawing, the fine colorless precipitate was filtered off. The precipitate was washed with water on the filter (3 × 50 ml) and dried. Yield 61%, mp 128°C. ^1H NMR spectrum, δ, ppm ($CDCl_3$, 300 MHz): 0.87 t (3H, CH_3), 1.20–1.50 m (10H, CH_2), 1.67–1.82 m (2H, $\underline{CH_2}CH_2O$), 3.82 s (3H, OCH_3), 4.09 t (2H, OCH_2), 6.91 d (1H, 6-H), 7.07 m (3H, 4,11,13-H), 7.75 d (1H, 3-H), 8.07 d (2H, 10,14-H).

4-(4-Decyloxybenzoyloxy)-3-methoxybenzoic acid VIIb was prepared similarly, crystallized from alcohol, and dried. Yield 57.4%. ^1H NMR spectrum, δ, ppm (DMSO, 500 MHz): 0.88 t (3H, CH_3), 1.21–1.38 m (12H, CH_2), 1.39–1.48 m (2H, $\underline{CH_2}CH_2CH_2O$), 1.71–1.80 m (2H, $\underline{CH_2}CH_2O$), 3.84 s (3H, OCH_3), 4.10 t (2H, OCH_2), 7.12 d (1H, 11,13-H), 7.36 d (1H, 6-H), 7.61–7.69 m (2H, 3,7-H), 8.07 d (2H, 10,14-H).

4-(4-Dodecyloxybenzoyloxy)-3-methoxybenzoic acid VIIc was prepared similarly, recrystallized from alcohol, and purified by column chromatography (aluminum oxide L 40/250, eluent methylene chloride :

methanol = 10 : 1). The solvent was distilled off at reduced pressure, and the residue was washed with dry hexane. Yield 30%, M^+ 456. ^{1}H NMR spectrum, δ, ppm (DMSO, 300 MHz): 0.85 t (3H, CH_3), 1.1–1.5 m (18H, CH_2), 1.67–1.83 m (2H, $\underline{CH_2}CH_2O$), 3.82 s (3H, OCH_3), 4.08 t (2H, OCH_2), 7.12 d (1H, 11,13-H), 7.34 d (1H, 6-H), 7.62–7.68 m (2H, 3,7-H), 8.05 d (2H, 10,14-H).

Bis-1,3-[4-(4-octyloxybenzoyloxy)-2-methoxybenzoyloxy]benzene X. A mixture of 1.075 g (2.7 mmol) of acid **VIIa**, 0.18 g (1.63 mmol) of 1,3-dihydroxybenzene **I**, and 36 mg (0.3 mmol) of dimethylaminopyridine (DMAP) in 25 ml of anhydrous methylene chloride was stirred for 10 min, after which 0.62 g (3 mmol) of dicyclohexylcarbodiimide (DCC) was added, and the mixture was stirred for 7 h and left overnight. The solvent was removed at reduced pressure, and alcohol was added to the residue to induce crystallization. The precipitate was filtered off, washed with alcohol (3 × 30 ml), and dried.

Bis-1,3-[4-(4-decyloxybenzoyloxy)-3-methoxybenzoyloxy]benzene XI was prepared similarly.

Bis-2,7-[4-(4-*n*-dodecyloxybenzoyloxy)-3-methoxybenzoyloxy]naphthalene XII was prepared similarly.

3-[4-(4-Octyloxybenzoyloxy)benzoyloxy]-1-[4-(4-octyloxybenzoyloxy)-2-methoxybenzoyloxy]benzene XIII was prepared similarly from 0.475 g (1.19 mmol) of 4-(4-octyloxybenzoyloxy)-3-methoxybenzoic acid **VIIa**, 0.548 g (1.19 mmol) of monoacylated phenol **IX**, 0.268 g (1.3 mmol) of DCC, and 0.03 g (0.13 mmol) of DMAP. The product was crystallized from the alcohol : benzene = 3 : 1 mixture.

CONCLUSIONS

(1) Previously unknown esters of 1,3-dihydroxybenzene and 2,7-dihydroxynaphthalene with 4-(4-alkoxybenzoyloxy)-2(3)-methoxybenzoic acids were synthesized, and their capability to form liquid crystals was examined. The presence of the bulky methoxy group in lateral fragments of the banana-like molecules leads to the lack of mesomorphism, whereas intermediate 4-(4-alkoxybenzoyloxy)-3-methoxybenzoic acids form a nematic mesophase.

(2) The luminescence of terbium(III) complexes of the 1,3-dihydroxybenzene esters becomes more intense when the methoxy group in the aromatic ring of the lateral fragment is shifted from the 2-position to the 3-position.

(3) The luminescence of the terbium(III) complexes is the strongest when the methoxy group is present only in one of the lateral fragments of the banana-like 1,3-dihydroxybenzene ester, which is apparently due to the absence of steric hindrance to the complexation.

REFERENCES

1. Binnemans, K. and Gorlle-Walrand, Ch., *Chem. Rev.*, 2002, vol. 102, pp. 2303–2345.
2. Suarez, S., Mamula, O., Imbert, D., et al., *Chem. Commun.*, 2003, pp. 1226–1227.
3. Suarez, S., Mamula, O., Scopelliti, R., et al., *New J. Chem.*, 2005, vol. 29, pp. 1323–1334.
4. Gayvoronsky, V., Yakunin, S., Pergamenshchik, V., et al., *Ukr. J. Phys. Opt.*, 2006, vol. 7, no. 3, pp. 116–118.
5. Novikova, N.S., Kilimenchuk, E.D., Yarkova, M.Yu., et al., *Zh. Prikl. Khim.*, 2008, vol. 81, no. 9, pp. 1602–1607.
6. Kelly Stephen, M. and Buchecker, R., *Helv. Chim. Acta*, 1988, vol. 2, pp. 461–466.
7. Maksimenko, S.I. and Novikova, N.S., *Dopov. Nats. Akad. Nauk Ukr.*, 2009, no. 1, pp. 130–136.
8. Achten, R., Cuypers, R., Giesbers, M., et al., *Liq. Cryst.*, 2004, vol. 31, no. 8, pp. 1167–1174.
9. *Weygand–Hilgetag, Organisch-chemische Experimentierkunst*, Leipzig: Johann Ambrosius Barth, 1964, 3rd ed.
10. *Svoistva organicheskikh soedinenii: Spravochnik* (Properties of Organic Compounds: Handbook), Potekhin, A.A., Ed., Leningrad: Khimiya, 1984.
11. US Patent 6512100.