Synthesis and Characterization of Some Xanthene Fluorophors - Markers for Petroleum Products

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The article presents experimental data regarding synthesis and characterization of some xanthene derivatives. Reaction products were purified and characterized by means of elemental analysis, UV-Vis absorption, fluorescence emission, IR absorption, ^{1}H-NMR and ^{13}C-NMR spectroscopy. There were obtained compounds with hydrophobic properties especially for their usage as markers for petroleum products.

Keywords : marker, xanthene dyes, petroleum products

It is known that in the marking domain of petroleum products there are used specific markers either on the initiative of governments to verify payment of afferent excises for the type of product sold, or on the initiative of producing companies for marking their products quality and prevent the marketing of products mixtures of different quality at higher prices [1,2].

Some products commonly used for marking in this area, present a number of disadvantages related to current loss of the color properties in time, difficult detection of marking product after prolonged storage of petroleum products, difficult handling of developing products, relatively high toxicity of used products, environmental issues related to the destruction of submitted samples under examination, or passage of marking agents in the presented aqueous phase in most cases in tanks of petroleum products where thei are stored [3-6].

Along the time there were made a series of researches on marking product of combustibles and derived fuels from oil manufacture especially by big producing companies and therefore the big majority of obtained results being particularly the subject of patents. Structurally, for marking petroleum products have been proposed various carbonyl compounds [7-9], azo dyes [10-17], antraquinone dyes [18,19], fluorescent coumarin derivatives [20-22].

The present paper illustrates the experimental data regarding nine new organic compounds with xanthene structure synthesized by acylation reaction of hydroyl groups with acetic anhydride, benzoyl xhloride and lauroyl chloride, respectively.

Experimental part

Method for obtaining 3',6'-diacetyloxyspiro[2-benzofuran-3,9'-xanthene]-1-one derivatives

It is dissolved at 20-25^0 C under stirring in 600 mL water containing 16 g sodium hydroxide solution 50% (0.2 moles), 0.1 moles xanthene derivative (33.2g fluorescein, 64.8g eosin, 83.6g erythrosine). Over the solution thus formed is added during 15 min under stirring 12 g of anhydrous sodium carbonate (0.113 moles) and then 160÷264÷325 mL xylene (mixed isomers) (related to xanthene derivative: fluorescein, eosin, erythrosine) and stirred for homogenizing at 20-25^{0}C for one hour. Then, over the reaction mass are added for one hour, 25g acetic anhydride (0.245 moles), then heated to reflux temperature where they are maintained 3 h for reaction concluding. In proportion as the reaction progress intense color and fluorescence of the aqueous phase diminished and the product passes into xylene phase to form a weak colored solution (reddish yellow depending on started fluorophore). After the reaction, allow to cool the reaction mass at 20^{0}C, then allow to rest 30 min when were separated two phases. Further it was separated xylene phase containing the reaction product of aqueous phase. Over xylene phase is added under stirring 50 mL N-methylpyrrolidone, after which the reaction mass is subjected to disstillation under vacuum (400 mmHg) for the residual water elimination and mixture and a mixture of xylene and N-methylpyrrolidone distillation until to a concentration of about 24% of diacetyl product in xylene concentrate. Obtained: 160 g xylene solution containing 38.27 g diacetyl fluorescein (global yield 92%), 277 g of xylene solution containing 66.61 g diacetyl eosin (global yield 91%),345 g of xylene solution containing 82.8 g diacetyl erythrosine (global yield 90%).

Method for obtaining 3',6'-dibenzoyloxyspiro[2-benzofuran-3,9'-xanthene]-1-one derivatives

In 150 ÷ 292 ÷ 378 mL pyridine (xanthene derivative related to: fluorescein, eosin, erythrosine) is added at 20-25^{0}C under stirring 0.1 moles xanthene derivative (33.2g fluorescein, 64.8g eosin, 83.6g erythrosine) and maintainig at this temperature for one hour to complete dissolution. Further over the reaction mass is added by dripping during 1 hour 31 g benzoyl chloride (0.22 moles), then heated to reflux temperature (125^{0}C) which is maintained 24 h for conluding of the esterification reaction. After esterification, the reaction mass is cooled at 20^{0}C and poured in thin thread over 1000 mL water and *p*H value is adjusted from 12 to 3 by addition of 10% hydrochloric acid solution when the product precipitated abundant when the stirring is stopped to avoid its transformation into a fine suspension. Dibenzoyl fluorophore is extracted from reaction mass by adding: 160 ÷ 250 ÷ 300 mL toluene (in correlation with xanthene derivative: fluorescein, eosin, erythrosine). It was separated the toluene phase containing the reaction product of pyridine aqueous phase. Toluene solution is subjected to disstillation under vacuum (400 mmHg) for the residual water elimination until to a concentration of about 27% of dibenzoyl product in toluene concentrate. There were obtained: 85 g toluene solution containing 49.86g dibenzoyl fluorescein (global yield 92%), 289 g of toluene solution containing 78g dibenzoyl eosin (global yield 91%), 349g of toluene solution containing 94.14 g dibenzoyl erythrosine (global yield 90%).

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Method for obtaining 3',6'-didodecanoyloxyspiro[2-benzofuran-3,9'-xanthene]-1-one derivatives

In 75 ÷ 196 ÷ 189 mL pyridine (related to xanthene derivative: fluorescein, eosin, erythrosine) is added at 20-25°C under stirring 0.05 moles xanthene derivative (16.6g fluorescein, 32.4g eosin, 41.8g erythrosine) and maintained at this temperature for one hour to complete dissolution. Further over the reaction mass is added by dripping during 1 hour 24.06 g lauroyl chloride (0.11 moles), then heated to reflux temperature (115-125°C) maintained 24 hours for concluding the esterification reaction. After esterification oily reaction mass is cooled at 20°C and poured in thin line over 500 mL water, then *p*H value is adjusted from 12 to 3 by adding 10% hydrochloric acid solution (about 280 mL). It is obtained a glue paste which is washed with water until the disappearance of pyridine odor. For purification glue paste is dissolved in 25 mL ethyl acetate and solution is poured over 25 mL petroleum ether, was allowed to cool 12 h, then was filtered. The filtrate is evaporated, then the residue is dissolved in toluene upto a concentration of about 25% of dilauroyl product. There were obtained: 111 g toluene solution containing 27.85 g dilauroyl fluorescein (global yield 80%), 164 g of toluene solution containing 41 g dilauroyl eosin (global yield 81%), 192 g of toluene solution containing 48 g dilauroyl erythrosine (global yield 80%).

The purification of obtained compounds was accomplished by recrystallization from absolute alcohol. Purified substances were subjected to elemental analysis. Measurements were made with a Carlo-Erba analyzer M 1106. The results are presented in table 3 and are in good accordance with those calculated theoretically. Absorption spectra in the UV-Vis and fluorescence emisson spectra were performed on ethanol solutions at concentrations of 10^{-5} ÷ 10^{-4} molar, at 25 ± 0,5°C in rectangular quartz cuvettes with a thickness of 1 cm, on a UV-Vis-NIR spectrometer JASCO V 570, respectively on a JASCO Spectrofluorimeter FP 6500 (results and working conditions are presented in tables 3 and 4) and infrared spectra were recorded on Specac Golden Gate ATR device attached to a JASCO spectrometer FT-IR 6300 (results and working conditions are presented in table 5). ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at a temperature of 25°C (results and working conditions are presented in table 6).

Results and discussion

The studied organic compounds were obtained by condensation of xanthene derivatives (fluorescein and their halogenated derivatives), with an acylation agent (acetic anhydride, benzoyl chloride, lauroyl chloride) in an organic solvent, followed by isolation of compounds by an appropriate process of used solvent type (by dilution and / or extraction), completed through the water traces elimination by vacuum distillation and the marker obtaining as a solution in an aromatic hydrocarbon.

There were used two solvents: xylene (mixed isomers) and pyridine. If it was used xylene as solvent it was necessary preconditioning xanthene derivative (fluorescein, tetrabromo and tetraiodoflurescein) as disodium salt solution (concentration 5.53 - 10.8 - 13.93 % of xanthene derivative) in water with adding of sodium hydroxide solution 50% (molar ratio 1:2) and adjustment of *p*H value with sodium carbonate at 8.5-9. The variant was used for acylation with acetic anhydride. In the case of pyridine usage as solvent it was necessary preconditioning xanthene derivative, because of its solubility in reaction medium at a convenient concentration of about 23%, the variant being used for acylation with lauroyl chloride and benzoyl chloride, pyridine playing in this case the role of proton acceptor, too.

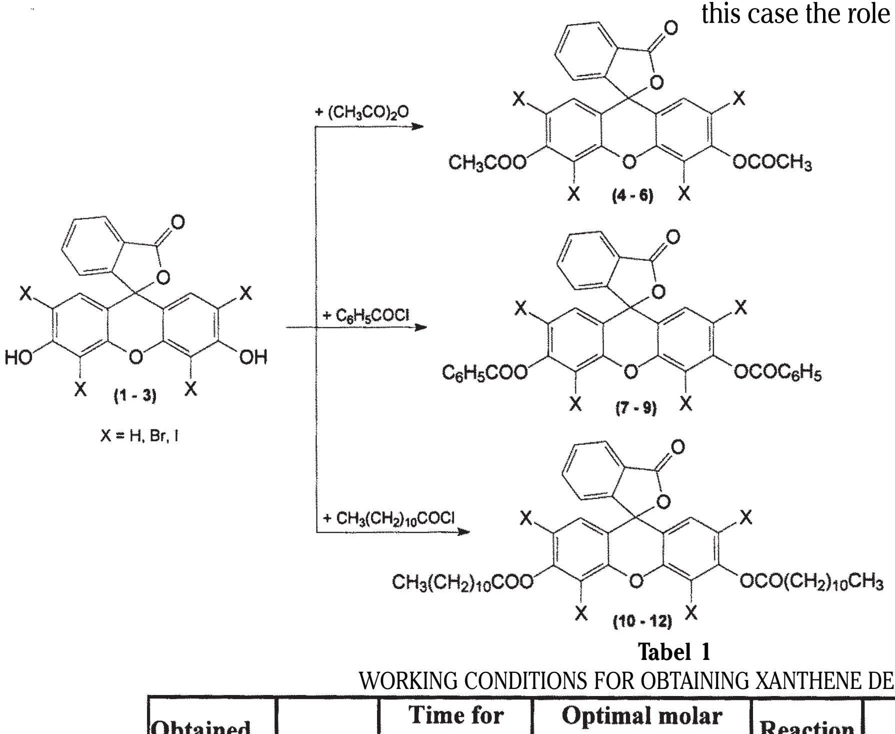

Fig. 1. Reactions for obtaining xanthene fluorophores

Tabel 1

WORKING CONDITIONS FOR OBTAINING XANTHENE DERIVATIVES

Obtained compounds	Reaction medium	Time for reactants introducing [h]	Optimal molar ratio xantene derivative : acylation agent	Reaction temp. [^{0} C]	Isolation products medium	Yield %
4-6	Xylene	1	1 : 2	130	Xylene – N-methylpyrrolidone	90 - 92
7-9	Pyridines	1	1 : 2.3	115	Toluene	90 - 92
10-12	Pyridines	0.5	1 : 2.2	115	Toluene	80 - 81

Table 2
WORKING CONDITIONS AND THE Rf VALUES OF XANTHENE DERIVATIVES

Sationary phase	Mobile phase	Separated compounds	Fluorescence	Rf value
Silicagel Merck 60 F254	n-propanol : n-butanol : ethyl acetate 2 : 4 : 1	4	Green - yellow	0.97
		1	Yellow-orange	0.92
		5	Blue	0.97
		6	Blue	0.94
		7	Green - yellow	0.93
		8	Orange	0.92
		2	Yellow	0.85
		9	Orange	0.93
		3	Orange - ginger	0.86
	pyridine: ammonia: n-amyl alcohol 1.1 : 1 : 1	10	Green - yellow	0.95
		1	Yellow	0.85
		11	Orange	0.92
		12	Yellow	0.82

Table 3
RESULTS OF ELEMENTAL ANALYSIS AND UV-Vis ABSORPTION SPECTRA

Comp. Nr.	Molecular mass	Elemental analysis (%)						Absorption spectra (Ethanol)			
		C		H		Halogen		C x 10^5 (mol/l)	λ (nm)	ε	lgε
		Calc.	found	Calc.	found	Calc.	found				
4	416.14	69.21	69.33	3.87	3.78	---	---	1.35	226	43915	4.643
5	731.75	39.36	39.43	1.65	1.53	43.68	43.75	1.36	234.5	20576	4.313
6	919.71	31.31	31.42	1.31	1.22	55.19	55.24	0.63	246	19329	4.286
7	540.18	75.53	75.65	3.73	3.67	---	---	1.33	232	49546	4.695
8	855.8	47.68	47.72	1.88	1.71	37.34	37.48	0.63	236.5	65456	4.816
9	1043.75	39.09	39.11	1.54	1.51	48.63	48.78	0.67	247	38990	4.591
10	696.92	75.76	75.83	8.03	7.98	---	---	8.29	229	21243	4.327
11	1012.51	52.15	52.24	5.14	5.02	31.60	31.75	5.86	232	24467	4.389
12	1200.51	43.98	43.99	4.33	4.26	42.31	42.44	4.87	225	12755	4.106

Table 4
MAXIMUM FLUORESCENCE EMISSION (λ_{em}) AND RELATIVE FLUORESCENCE INTENSITIES (I_f)

Compound Number	λ_{ex} (nm)	λ_{em} (nm)	I_f, a.u.	Sensitivity	Conc.x10^4 M (ethanol)	Shift Stokes (nm)
4	365	528	5379	12x1/10	3.84	172
5		548	57		4	314
6		542	31		1.74	296
7		430	890		2.96	198
		509	941			276
8		562	3236		2.53	326
9		566	323		0.64	319
10		442	84		20.7	213
		521	403			292
11		443	46		14.6	211
		561	372			329
12		536	3		12.2	311

Reaction conditions for obtaining xanthene O-acyl derivatives are presented in table 1, together with conditions of isolation of markers for petroleum products as solutions in organic solvents.

Purity of synthesized compounds and control during the synthesis was performed by thin layer chromatography, working conditions being presented in table 2. Solubility of samples was done in ethyl alcohol at a concentration of 0.2% and the identification of individual spots was made after exposure to ultraviolet light (365 nm) and by direct visualization of colored spots.

Analyzing the ultraviolet absorption spectra it was remarked for all synthesized compounds that acylation determined effects disturbance of auxochrome conjugation (hydroxyl) – xanthene chromogene (existing in the starting compounds) with conjugation effect hindrance, which lead to the disappearance of absoption bands in the visible and increasing of ultraviolet absorption bands. They are located in 226 to 246 nm domain and have the corresponding intensities of some overlapping n-π* with π-π*electronic transitions. This properties are used for marking petroleum products with compounds which do not absorb in the

Table 5
RESULTS OF IR ABSORPTION SPECTROMETRY

Compound Number	**Characteristic frequencies (cm $^{-1)}$ and intensities** (**vi** - very intense, **i** - intense, **m** - medium, **w** – weak, **vw** - very weak,**sh** - shoulder)
4	3854w, 3735w, 3420m, 2360vi, 2342i, 1766vi, 1612vi, 1496m, 1370i, 1287m, 1208vi, 1156i, 1111i, 1104m, 995m, 892m, 852s, 761i, 668i, 587w,419w
5	3511w, 3027sh, 2360m, 2342w, 1779vi, 1600m, 1551m, 1442i, 1412vi, 1369i, 1287m, 1251i, 1180vi, 1105m, 1067i, 1030m, 1011m, 933i, 880i, 823m, 792m, 701i, 650w, 618w, 596w, 489w
6	3903w, 3854w, 3712m, 2996sh, 2868m, 2360i, 2342m, 1774vi, 1699m,1684m, 1653m, 1508m, 1474m, 1457m, 1396vi, 1369m, 1287m, 1248m, 1182vi, 1802m, 1053m, 881m, 735w, 669w, 419sh
7	3774w, 3727w, 3405w,3076w, 2880m, 2360vi, 2342i, 1765vi, 1745vi,, 1610vi, 1583w, 1551m, 1451i, 1424vi, 1242vi, 1161vi, 1110vi, 1078i, 1024i, 992i, 880w, 795m, 763i, 706vi, 695m, 669m, 580w
8	3421sh, 3066w, 2360i, 2342i, 1756vi, 1601m, 1466m, 1440m, 1411vi, 1243vi, 1214vi, 1076i, 1020i, 874m, 750m, 750m, 704vi, 669m, 574w
9	3903w, 3726w, 3421m, 3063sh, 2869m, 2360vi, 2343i, 1751i, 1702m, 1559i, 1508m, 1488m, 1419w, 1314m, 1250w, 1216w, 1054w, 951w, 872w, 761m, 680m, 669m, 650i, 605m, 569w, 420w
10	3332sh, 2919vi, 2850i, 1765vi, 1702w, 1611i, 1495s, 1464m, 1424i, 1284s, 1244m, 1219m, 1154vi, 1109vi, 995m, 965w, 892m, 828w, 793w, 760m, 720m, 692m, 632vi, 601m, 533vi, 468m, 418w
11	2918vi, 2849i, 1774vi, 1700i, 1600w, 1553vw, 1466m, 1442m, 1409vi, 1375w, 1328w, 1302m, 1289m, 1249i, 1201vi, 1132m, 1078vi, 1013w, 913m, 877m, 749w, 720m, 696i, 635m, 539i, 496i, 465m, 416i
12	3053sh, 2918vi, 2849i, 1700i, 1589i, 1462vi, 1385m, 1302w, 1245w, 1208s, 1168w, 1108m, 1083w, 1033vw, 992vw, 938s, 864s, 846m, 753w, 721w, 684w, 641w, 600w, 532w, 495m, 457m, 417w.

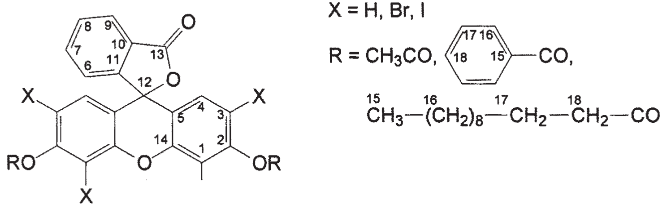

Fig. 2. Atoms localization for ^{1}H and ^{13}C-NMR spectra

visible domain. The marked products with colorless esters are subjected of development by alcaline hydrolysis of esters with regeneration of chromogene system which presented intense absoption in the visible domain.

Fluorescence is mainly due to the appearance of polar mezomer structures in interaction with bright radiation. The existance of a single emission maximum indicates a high purity of color which gives the opportunity of using such compounds in unconventional fields also. The studied florophores are characterized by the presence in the molecule of some condensed heterocyclic with flat structure and appearance by exciting of some charge transfer complex lead to increasing of flurescence.

With regard to the basic terms of the series it was found that by acetylation, respectively benzoylation it was occurred disappearance of the visible absorption maxima, emission maxima being shifted to 530 to 550 nm for diacetyl compounds and over 550 nm for dibenzoyl compounds, respectively. The fact is expained through appearance in excited state of some new structures with charge transfer in which the rigid aromatic rings influence leads to increasing of fluorescence intensity nearby bathochromically shift of emission maximum.

Very large Stokes shifts of about 300 nm show a minimum coverage between absoption and emission spectra, and the obtained values indicate that through excitement the resulted species are more polar than molecules in ground state.

Concerning the absoption spectra in the infrared domain the compounds 4 to 12 have characteristic vibration $n_{C=O}$ ester linkages located at 1751 to 1779 cm^{-1}, respectively ν_{CO} displaced to 1242 to 1250 cm^{-1} for benzoic acid esters derivatives and to 1248- 1251 cm^{-1} for acetates.

Acylated compounds with lauroyl chloride have characteristic vibrations of methylene group from aliphatic chain ν_{CH2} at 2918 cm^{-1} and 2849 cm^{-1}. Still there are reported for compounds 5, 6, 8, 9, 11, 12 ν_{C-Hal} vibration located at 684 to 706 cm^{-1}.

Atribution of the ^{1}H-NMR signals was done having in mind peaks intensity and multiplicity and shift values verified with selective proton decoupling experiments.

Nuclear magnetic resonance spectrum ^{1}H-NMR shows that the protons of aromatic nuclei from the xanthene rest are found at a shift values situated at δ=6.5-7.3 ppm depending on the presented substituents,while in phtaleine rest the aromatic protons are found more deshilded at a shift values situated at δ =7.6-8.2 ppm. In case of halogenated derivatives it is characteristic the presence of proton H-4 as singlet at the shift values situated at δ=6.9-7.2 ppm.

If for the acetyl compounds the methyl group protons of acetyl rest is situated at δ=2.2-2.4 ppm, for O-benzoyl compounds the aromatic protons may be found in the spectra at the shift values δ=7.3-7.8 ppm. The corresponding protons of aliphatic rest for O-lauroyl compounds are found in spectra at shift values δ=1.1-2.2 ppm depending on the position in the aliphatic chain.

Regarding carbon atoms from the ester group, these are found at a shift values δ=164-176 ppm, depending on the nature of the started acid, while the carbon atom of

Table 6
RESULTS FOR NMR SPECTRA

Compound Number	^{1}H-NMR ($(CD_3)_2SO$) – (ppm)	^{13}C-NMR ($(CDCl_3)$) – (ppm)
4	H9 = 8.04(m); H8 = 7.81(m); H7 = 7.76(m); H6 = 7.36(d); H4 = 7.86(d); H1 = 6.61; H3 = 6.55; CH_3 = 2.28	C1 = 109.82; C2 = 159.66; C3 = 110.68; C4 = 113.25; C5 = 124.55; C6 = 126.97; C7 = 130.3; C8 = 125.91; C9 = 130.20; C10 = 130.42; C11 = 137.31; C12 = 81.26; C13 = 168.84; C14 = 152.61; CO =169.12; CH_3 = 20.95
5	H9 =8.07(d); H8 = 7.86(t); H7 = 7.80(t); H6 = 7.58(d); H4 = 7.22(s); CH_3 = 2.44	C1 = 107.69; C2 = 160.32; C3 = 112.31; C4 = 119.62; C5 = 124.52; C6 = 125.84; C7 = 136.49; C8 = 125.44; C9 = 130.32; C10 = 131.37; C11 = 147.62; C12 = 80.35; C13 = 167.72; C14 = 147.97; CO =168.22; CH_3 = 20.35
6	H9 = 8.07(d); H8 = 7.86(t); H7 = 7.80(t); H6 = 7.52(d); H4 = 7.24(s); CH_3 = 2.42	C1 = 84.81; C2 = 153.88; C3 = 86.30; C4 = 119.47; C5 = 124.43; C6 = 125.73; C7 = 137.01; C8 = 125.47; C9 = 131.31; C10 = 136.51; C11 = 150.91; C12 = 79.72; C13 = 167.28; C14 = 151.79; CO =168.08; CH_3 = 21.11
7	H9 = 8.12(d); H8 = 7.94(t); H7 = 7.60(t); H6 = 7.49(d); H4 = 7.11(d); H16 = 7.74(t); H17 = 7.60(d); H18 = 7.39(d)	C1 = 109.83; C2 = 159.71; C3 = 110.86; C4 = 118.87; C5 = 124.33; C6 = 125.93; C7 = 136.87; C8 = 125.29; C9 = 130.55; C10 = 130.82; C11 = 149.47; C12=102.47; C13 = 168.86; C14 = 152.46; CO=164.46; C15 = 134.44; C16 = 129.17; C17=128.75; C18 = 130.00
8	H9 = 8.20(d); H8 = 7.93(t); H7 = 7.85(t); H6 = 7.48(d); H4 = 6.96(s); H16 = 7.81(t);H17 = 7.67(d); H18 = 7.33(d)	C1 = 107.90; C2 = 156.83; C3 = 112.30;C4 = 119.05; C5 = 125.68; C6 = 127.18; C7 = 133.12; C8 = 126.36; C9 = 12941; C10 = 131.28; C11 = 144.22; C12=102.88; C13 = 167.95; C14 = 48.05; CO = 162.63; C15 = 135.32; C16 =129.59; C17 =128.76; C18 = 130.37
9	H9 = 8.15(d); H8 = 7.94(t); H7 = 7.83(t); H6 = 7.50(d); H4 = 6.92(s); H16 = 7.77(t);H17 = 7.67(d); H18 = 7.40(d)	C1 = 85.10; C2 = 154.14; C3 = 89.44; C4 = 121.85; C5 = 127.13; C6 = 128.30; C7 = 133.31; C8 = 125.92; C9 = 130.24; C10 = 130.43; C11 = 145.29; C12=102.93; C13 = 168.14; C14 = 146.51; CO =164.45; C15 = 135.43; C16 = 129.22; C17=128.90; C18 = 130.14
10	H9 = 8.03(d); H8 = 7.83(t); H7 = 7.75(t); H6 = 7.23(d); H3-H4 = 6.58(m); H15 = 0.84(t); H16 = 1.22(q); H17 = 1.48 (q); H18 = 2.19(d)	C1 =110.44; C2 = 160.02; C3 = 113.47; C4 = 124.62; C5 = 125.59; C6 = 126.75; C7 = 131.10; C8 = 130.91; C9 = 129.82; C10 = 152.67; C11 = 136.65; C12 = 103.06; C13 = 170.17; C14 = 152.92; CO =176.37; C15 = 14.66 ; C16 = 22.80-29.62; C17=31.97; C18 = 34.69
11	H9 = 8.15(d); H8 = 7.80(t); H7 = 7.76(t); H6 = 7.37(d); H4 = 6.98(m); H15 = 0.80(t); H16 = 1.18(q); H17 = 1.44(q); H18 = 2.16(d)	C1 =110.38; C2 = 161.12; C3 = 114.74; C4 = 126.26; C5 = 125.76; C6 = 126.43; C7 = 135.21; C8 = 131.14; C9 = 130.08; C10 = 153.04; C11 = 138.97; C12 = 103.53; C13 = 171.25; C14 = 149.43; CO =176.11; C15 = 14.67 ; C16 = 22.81-31.98; C17=32.20; C18 = 34.36
12	H9 = 7.94(d); H8 = 7.74(t); H7 = 7.68(t); H6 = 7.16(d); H4 = 6.50(m); H15 = 0.72(t); H16 = 1.08(q); H17 = 1.38 (q); H18 = 2.12(d)	C1 =110.35; C2 = 159.85; C3 = 113.30; C4 = 124.48; C5 = 125.46; C6 = 126.65; C7 = 130.97; C8 = 129.67; C9 = 128.82; C10 = 152.60; C11 = 136.53; C12 = 103.00; C13 = 170.02; C14 = 152.98; CO =175.88; C15 = 14.22 ; C16 = 22.78-31.37; C17=31.95; C18 = 34.33

carbonyl group from the phtaleine rest is found at shift values δ =168-170 ppm, for all studied compounds.

Conclusions

Nine new fluorescent compounds with xanthene structure have been synthesized, obtained by acylation of fluorescein, eosin and erythrosine, the compounds being characterized by means of elemental analysis, UV-Vis absorption, fluorescence emission, IR absorption, ^{1}H-NMR and ^{13}C-NMR spectroscopy, the results confirming their structures.

The study of structure – fluorescent properties relationship with respect to the nature of the substituents, designates the new synthesized compounds as fluorescent marking agents with applications as markers for petroleum products.

The obtained markers are compounds without absorbtion in visible light domain at the application for petroleum products, having a distinct and intense florescence in both the ultraviolet and in the visible domain after developing with specific agents. Compounds are not affected by any other coloring agents eventualy used and may be applied for marking of petroleum products in very small quantities (ppm).

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