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The Preparation and Propertis of Fatty Alcohol esters of Monohalogenbenzoie Acids

by

CELAL TÜZÜN AND REFİK ÖZKAN

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The Preparation and Propertis of Fatty Alcohol esters of Monohalogenbenzoie Acids*

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CELAL TÜZÜN** AND REFİK ÖZKAN***

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ABSTARCT

In this work some esters of o-, m- and p- substituted monohalogenbenzoic acids with fatty alcohols (hexadecanol, oleyl alcohol, octadecanol and eicosanol) have been prepared. Monohalogenbenzoic acids converted to acid chlorides by means of thionyl chloride, then reacted with fatty alcohols. Purification of esters were affected by column chromatograhpy or recrystallization. So far 48 new fatty alcohol esters of monohalogenbenzoic acids were synthesited and melting points, IR and proton NMR spectral data determined.

INTORUCTION

In the literature, some alkyl esters of monohalogenbenzoic acids, inwhich alkyl group having 1–12 carbon atoms have been prepared. Recent work on thes subject has been done by Johsi and Giri[1] who synthesized dodecyl asters of p-fluorobenzoic acid p-fluorobenzoyl chloride and dodecyl alcohol. In this work higher fatty alcohols were chosen. For the preparation of esters, Schotten-Baumann esterification method was used. First, monolalogenbenzoic acids were converted to acid chlorides by means of $SOCl_2$, then acid chlorides were heated with equivalent amount of fatty alcohols in the presence of pyridine:

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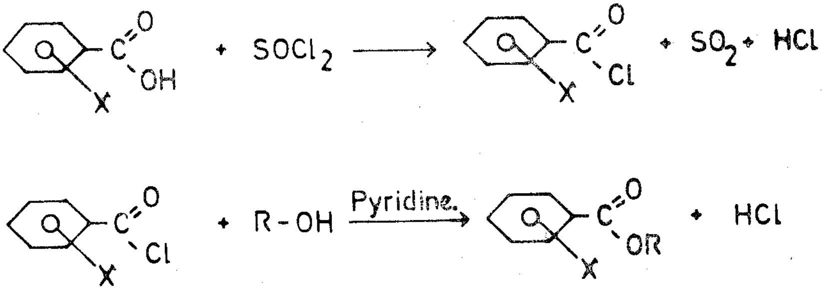
** Department of General Chemistry, Faculty of Science, Ankara University, ANKARA, TURKEY

*** Department of Chemistry, College of Basic Science, Atatürk University, ERZURUM, TURKEY.



X : F, Cl, Br and I

R : $C_{16}H_{31}$–, $C_{18}H_{35}$–, $C_{18}H_{37}$– and $C_{20}H_{41}$–

EXPERIMENTAL

For the synthesis of esters: Fluka (Switzerland) and E. Merk (W. Germany) chemicals and solvents were used. Only p-iodobenzoic acid was prepared from p-aminobenzoic acid by diazotization.

The common applied method for the synthesis of the esters:

Into 250 ml round bottom, two neck flask, 0.05 moles of monohalogenbenzoic acid was put and equipped with a reflux condenser, and mechanical stirrer.

The apparatus was set on a water bath and two drops of pyridine and 12 ml of thionyl chloride were added into the flask. The mixture was refluexd for 20 minutes. Excess of thionyl chloride was removed under diminished pressure and acid chloride left as an oil. 0.05 moles of fatty alcohol was introduced into the flask, and mixture was stirred for 10 minutes. Then 8 ml of pyridine was added into the flask and heated on the water bath while stirring for 30 minutes. Afterwards the flask was cooled down in the ice bath an 10 ml of HCl (1:2 diluted) was added slowly. Yielded ester was extracted by means of dietthy ether, and ether evaporated and the crude ester left in flask.

The crude ester of haxadecyl, actadecyl and eicosyl alcohols were purified by recystallization from the mixture of aceton: methy alcohol (20: 80). The crude esters of oleyl alcohol were purified by column chromatography, adsorbent was silicagel and eluent carbontetrachloride. Pure esters of hexadecyl, octadeyl and eicosyl alcohols are white crystalline substances, while oleyl esters are colourless liquids. Owerall yields of the esters were around 70 percent.

Molecular weight of these esters were determined by the Rast method[2]. For these, camphor was used as solvent. Carbon, hydrogen and oxygen analysis of the esters have been done with Perkin-Elmer Model 240 Elemental Analyzer. Halogen of the esters were determined by the peroxide fusion method[3,4,5].

IR Spectra of the esters were recorded on Perkin-Elmer Model 337 Grating Infrared Spectrohptometer. The sample of oleyl esters for IR spectra were prepared as meat liquid films in KBr pellets. The samples of hexadecyl, octadecyl and eicosyl esters were prepared in CCl_4 and were used with CCl_4 referance sample.

NMR spectra of the esters were recorded on Varian Anaspect EM-360 Spectrometer in CCl_4.

RESULTS AND DISCUSSION

Elemental analysis, molecular weight determinations and spectral data showed that molecular structure of the 48 fatty alcohol esters are consistent with the predicted structure.

IR spectra of the esters show C–H and C = 0 stretching bands at 2940 cm^{-1} and 1740 cm^{-1} respectively, (Fig. 1–4). Splitting of the C–H stretching band is due to symmetric and antisymmetric vibrations[6].

NMR spectra of oleyl esters have five absorption bands, but hexadecyl, octadecyl and eicosyl esters have four (Fig. 5–8). Methyl protons of the esters give deformed triplets at 0,85 ppm. Closely spaced multiplets of methylene protons are seen as a singlet at 1,25 ppm. Protons of the metylene group which is nearest to ester

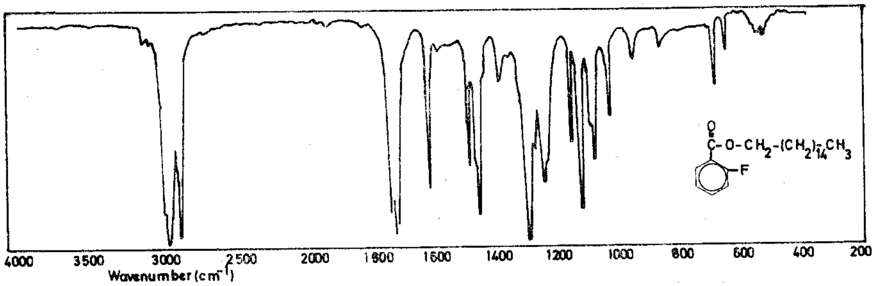


Fig. 1. The IR spectrum of hexadecyl-o-fluorobenzoate (in CCl_4)

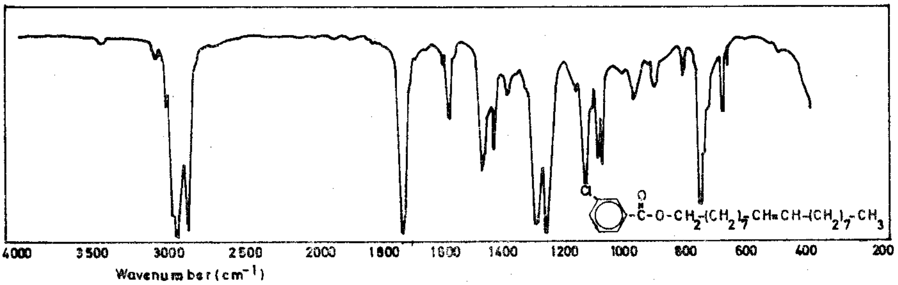


Fig. 2. The IR spectrum of oleyl-m-chlorobenzoate (neat liquid film)

oxygen (–0–CH_2–) correspond to triplet peak art 4.40 ppm. Vinyl protons of oleyl esters are chemically equivalent, therefore they give same spaced triplets at 5,45 ppm, (Fig. 6) Aromatic protons are less shielded than the other protons and they correspond to multiplets at around 8,00 ppm, but multiplets of the aromatic protons of p-chloro and p-bromobenzoates are seen as quartets, (Fig. 7). Aromatic protons of p-iodobenzates give only one singlet peak, (Fig. 8). This is attributed to chemically equivalence of four aromatic protons of p-iodobenzoates.

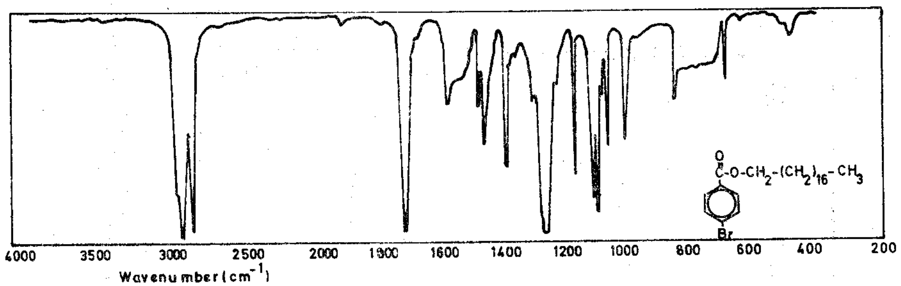


Fig. 3. The IR spectrum of octadecyl-p-bromobenzoate (in CCl_4)

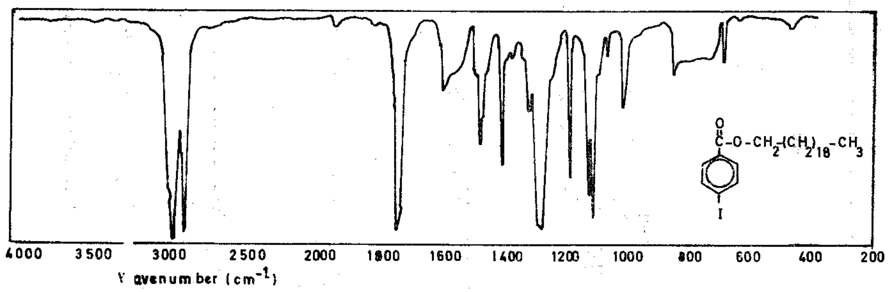


Fig. 4. The IR spectrum of eicosyl-p-iodobenzoate (in CCl_4)

IR absorbtion band frequencies, NMR chemical shift values and melting points of the esters can be seen at the Table 1 and 2.

The results of IR and NMR spectra are consistent with the reference values[7].

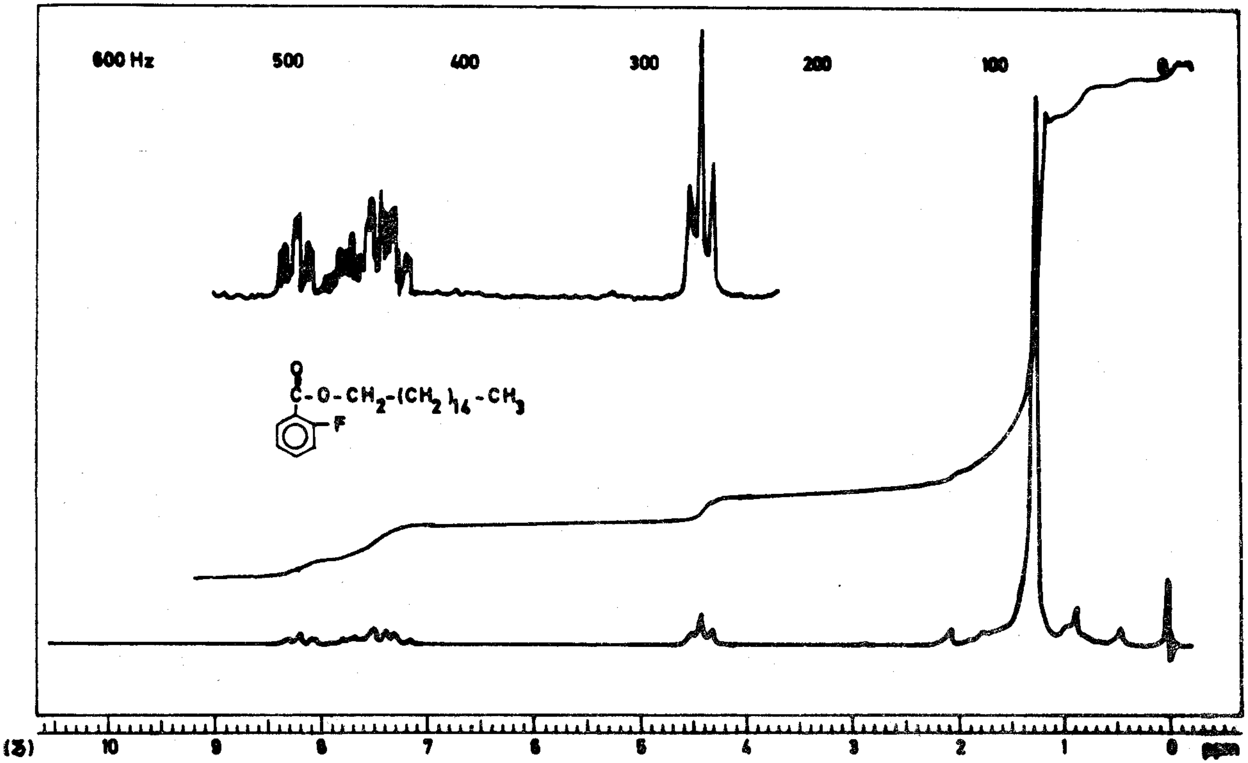


Fig. 5. The NMR spectrum of hexadecyl-o-fluorobenzoate (in CCl_4)

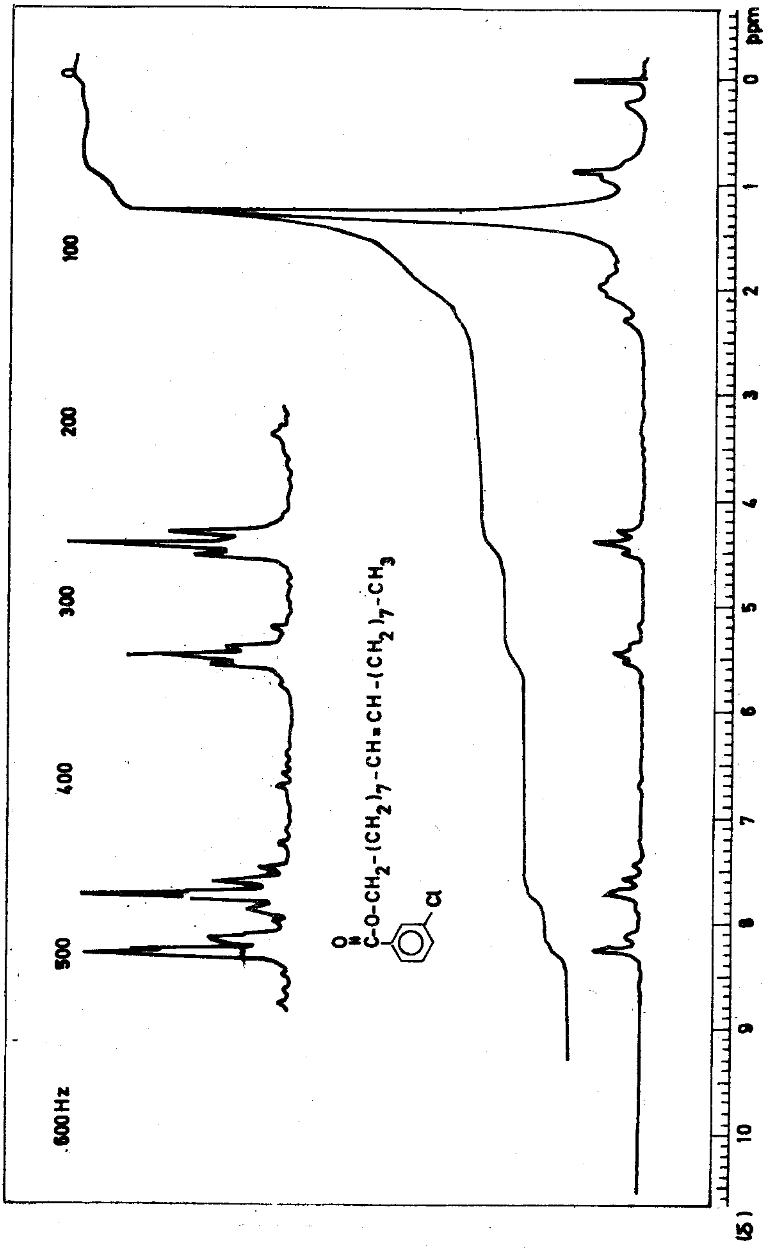


Fig. 6. The NMR spectrum of oleyl-m-chlorobenzoate (in CCl_4)

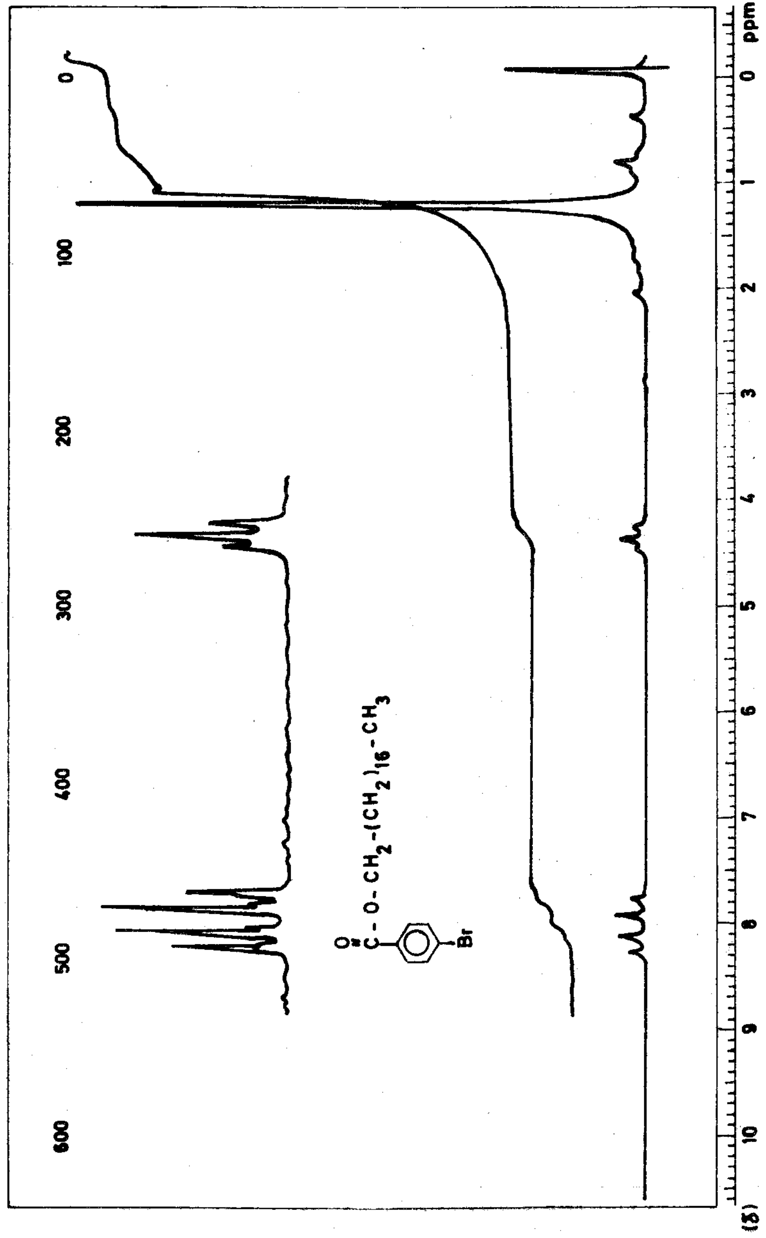


Fig. 7. The NMR spectrum of octadecyl-p-bromobenzoate (in CCl$_4$)

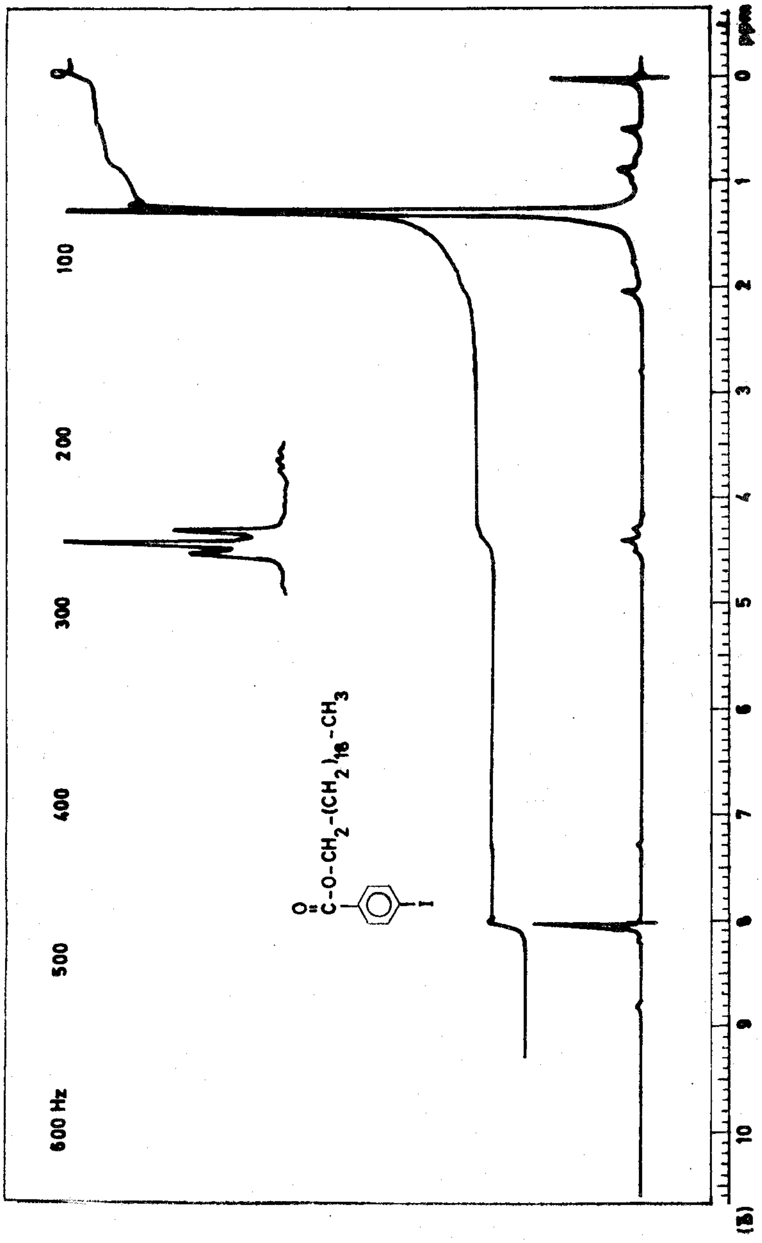


Fig. 8. The NMR spectrum of eicosyl-p-iodobenzoate (in CCl_4)

The esters	IR absb. band frequencies(cm^{-1})	^{1}H NMR Chemical shift values (ppm)	m.p.(^{o}C)
Hexadecyl-o-fluorobenzoate	2940 ; 1730	0,85(t,3);1,26(s,28);4.43(t,2);7,12-8,40(m,4)	36
Hexadecyl-m-fluorobenzoate	2945 ; 1740	0,86(t,3);1,25(s,28);4,41(t,2);7,20-8,24(m,4)	40
Hexadecyl-p-fluorobenzoate	2945 ; 1743	0,85(t,3);1,28(s,28);4,39(t,2);7,10-8,58(m,4)	44
Hexadecyl-o-chlorobenzoate	2943 ; 1754	0,83(t,3);1,25(s,28);4,38(t,2);7,30-8,20(m,4)	31
Hexadecyl-m-chlorobenzoate	2945 ; 1743	0,85(t,3);1,23(s,28);4,38(t,2);7,40-8,38(m,4)	36
Hexadecyl-p-chlorobenzoate	2945 ; 1740	0,84(t,3);1,29(s,28);4,36(t,2);7,93(q,4)	50
Hexadecyl-o-bromobenzoate	2940 ; 1752	0,86(t,3);1,28(s,28);4,39(t,2);7,40-8,15(m,4)	30
Hexadecyl-m-bromobenzoate	2950 ; 1742	0,87(t,3);1,26(s,28);4,40(t,2);7,32-8,53(m,4)	34
Hexadecyl-p-bromobenzoate	2950 ; 1742	0,87(t,3);1,26(s,28);4,38(t,2);7,99(q,4)	51
Hexadecyl-o-iodobenzoate	2952 ; 1750	0,86(t,3);1,25(s,28);4,40(t,2);7,12-8,36(m,4)	30
Hexadecyl-m-iodobenzoate	2955 ; 1740	0,85(t,3);1,24(s,28);4,39(t,2);7,20-8,73(m,4)	46
Hexadecyl-p-iodobenzoate	2947 ; 1740	0,88(t,3);1,27(s,28);4,38(t,2);8,00(s,4)	53
Oleyl-o-fluorobenzoate	2957 ; 1735	0,87(t,3);1,26(s,28);4,39(t,2);5,44(t,2);7,10-8,37(m,4)	
Oleyl-m-fluorobenzoate	2927 ; 1725	0,86(t,3);1,25(s,28);4,38(t,2);5,45(t,2);7,28-8,25(m,4)	
Oleyl-p-fluorobenzoate	2924 ; 1729	0,86(t,3);1,25(s,28);4,36(t,2);5,44(t,2);7,10-8,55(m,4)	
Oleyl-o-chlorobenzoate	2925 ; 1730	0,86(t,3);1,27(s,28);4,36(t,2);5,53(t,2);7,40-8,33(m,4)	
Oleyl-m-chlorobenzoate	2930 ; 1725	0,88(t,3);1,27(s,28);4,40(t,2);5,45(t,2);7,39-8,35(m,4)	
Oleyl-p-chlorobenzoate	2930 ; 1726	0,85(t,3);1,26(s,28);4,39(t,2);5,45(t,2);7,93(q,4)	
Oleyl-o-bromobenzoate	2924 ; 1733	0,86(t,3);1,26(s,28);4,38(t,2);5,45(t,2);7,37-8,20(m,4)	
Oleyl-m-bromobenzoate	2926 ; 1729	0,87(t,3);1,29(s,28);4,40(t,2);5,49(t,2);7,35-8,52(m,4)	
Oleyl-p-bromobenzoate	2945 ; 1742	0,87(t,3);1,28(s,28);4,39(t,2);5,46(t,2);8,00(q,4)	
Oleyl-o-iodobenzoate	2945 ; 1750	0,87(t,3);1,29(s,28);4,40(t,2);5,43(t,2);8,25-8,40(m,4)	
Oleyl-m-iodobenzoate	2929 ; 1724	0,85(t,3);1,25(s,28);4,39(t,2);5,48(t,2);7,22-8,74(m,4)	
Oleyl-p-iodobenzoate	2947 ; 1743	0,88(t,3);1,26(s,28);4,42(t,2);5,45(t,2);8,00(s,4)	

Table 1, IR absorbtion hand frequencies and proton NMR chemical shift values of kexadecyl and oleyl esters of monohalogenbenzoic acids. Melting of hexadecyl esters of monohalogenbenzoic acids·

The esters	IR absb.band frequencies(cm^{-1})	^{1}H NMR chemical shift values (ppm)	m.p.(°C)
Octadecyl-o-fluorobenzoate	2957 ; 1738	0,86(t,3);1,26(s,32);4,40(t,2);7,12–8,39(m,4)	43
Octadecyl-m-fluorobenzoate	2952 ; 1748	0,89(t,3);1,26(s,32);4,41(t,2);7,42–8,29(m,4)	48
Octadecyl-p-fluorobenzoate	2960 ; 1743	0,89(t,3);1,28(s,32);4,41(t,2);7,18–8,53(m,4)	53
Octadecyl-o-chlorobenzoate	2958 ; 1750	0,88(t,3);1,27(s,32);4,47(t,2);7,41–8,22(m,4)	41
Octadecyl-m-chlorobenzoate	2947 ; 1743	0,86(t,3);1,24(s,32);4,42(t,2);7,40–8,33(m,4)	40
Octadecyl-p-chlorobenzoate	2959 ; 1745	0,88(t,3);1,25(s,32);4,40(t,2);7,90(q,4)	57
Octadecyl-o-bromobenzoate	2958 ; 1752	0,82(t,3);1,23(s,32);4,39(t,2);7,43–8,20(m,4)	41
Octadecyl-m-bromobenzoate	2962 ; 1741	0,84(t,3);1,22(s,32);4,40(t,2);7,41–8,59(m,4)	44
Octadecyl-p-bromobenzoate	2950 ; 1741	0,86(t,3);1,23(s,32);4,38(t,2);8,01(q,4)	59
Octadecyl-o-iodobenzoate	2957 ; 1751	0,85(t,3);1,27(s,32);4,38(t,2);7,16–8,39(m,4)	41
Octadecyl-m-iodobenzoate	2949 ; 1745	0,84(t,3);1,26(s,32);4,37(t,2);7,20–8,68(m,4)	52
Octadecyl-p-iodobenzoate	2957 ; 1740	0,85(t,3);1,24(s,32);4,40(t,2);8,03(s,4)	61
Eiocosyl- o-fluorobenzoate	2961 ; 1740	0,86(t,3);1,25(s,36);4,40(t,2);7,17–8,48(m,4)	50
Eiocosyl- m-fluorobenzoate	2968 ; 1744	0,87(t,3);1,23(s,36);4,41(t,2);7,39–8,23(m,4)	55
Eiocosyl- p-fluorobenzoate	2970 ; 1742	0,84(t,3);1,22(s,36);4,38(t,2);7,13–8,48(m,4)	61
Eiocosyl- o-chlorobenzoate	2962 ; 1756	0,86(t,3);1,23(s,36);4,40(t,2);7,30–8,27(m,4)	47
Eiocosyl- m-chlorobenzoate	2968 ; 1746	0,87(t,3);1,26(s,36);4,38(t,2);7,37–8,33(m,4)	46
Eiocosyl- p-chlorobenzoate	2949 ; 1743	0,89(t,3);1,28(s,36);4,43(t,2);7,99(q,4)	63
Eiocosyl- o-bromobenzoate	2965 ; 1740	0,89(t,3);1,28(s,36);4,43(t,2);7,42–8,20(m,4)	47
Eiocosyl- m-bromobenzoate	2967 ; 1739	0,88(t,3);1,27(s,36);4,39(t,2);7,40–8,56(m,4)	49
Eiocosyl- p-bromobenzoate	2960 ; 1744	0,83(t,3);1,25(s,36);4,39(t,2);7,99(q,4)	64
Eiocosyl- o-iodobenzoate	2950 ; 1752	0,86(t,3);1,20(s,36);4,39(t,2);7,20–8,37(m,4)	46
Eiocosyl- m-iodobenzoate	2952 ; 1743	0,87(t,3);1,24(s,36);4,38(t,2);7,20–8,69(m,4)	57
Eiocosyl- p-iodobenzoate	2950 ; 1743	0,89(t,3);1,25(s,36);4,40(t,2);8,02(s,4)	66

Table 2. IR absorbtion pand frequencies, protnn NMR chemicol shift values and melting points of octadecyl and eicosyl esters of monohalogenbenzoic acids.

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ÖZET

Bu çalışma o-, m- ve p- halojen (F, C1, Br ve I) benzoik asitlerin bazı yağ alkolleiryle (hekzadekanol, oleil alkol, oktadekanol ve eikosanol) verdikleri esterler sentezlendi.

Elde edilen saf esterlerin erime noktaları ve molekül ağırlıkları tayin edildi; karbon, hidrojen, oksijen ve halojen analizleri yapıldı; IR ve NMR spektrumları alındı. Yapılan tayinler, analizler ve alınan spektrumlar değerlendirilerek, bu çalışmada 48 tane yeni ester elde edildiği sonucuna varıldı.

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