Ultrasonics Sonochemistry 19 (2012) 387–389

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Short Communication

Ultrasound-assisted synthesis of aliphatic acid esters at room temperature

Cristiane B. Hobuss [a], Dalila Venzke [a], Bruna S. Pacheco [a], Alexander O. Souza [a], Marco A.Z. Santos [a], Sidnei Moura [b], Frank H. Quina [c], Karina G. Fiametti [d], J. Vladimir Oliveira [d], Claudio M.P. Pereira [a,*]

[a] Laboratório de Heterociclos Bioativos e Bioprospecção (LAHBBio), Universidade Federal de Pelotas, Centro de Ciências Químicas, Farmacêuticas e de Alimentos, 96010-900 Pelotas, RS, Brazil
[b] Universidade de Caxias do Sul, Instituto de Química, 96070-560 Caxias do Sul, RS, Brazil
[c] Universidade de São Paulo, Instituto de Química, 05513-970 São Paulo, SP, Brazil
[d] Universidade Regional Integrada URI, RS, Brazil

ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form 25 April 2011
Accepted 29 June 2011
Available online 13 July 2011

Keywords:
Ultrasound irradiation
Aliphatic esters
Sonochemistry

ABSTRACT

This work describes the ultrasound-assisted synthesis of saturated aliphatic esters from synthetic aliphatic acids and either methanol or ethanol. The products were isolated in good yields after short reaction times under mild conditions.

1. Introduction

Fatty acid esters and derivatives find widespread applications in the food, cosmetics and pharmaceutical industries owing to their biodegradability and low toxicity [1–3]. Esters of short chain fatty acids are important flavor and aroma compounds and esters of long chain fatty acids are being explored for their use as biodiesel and as waxes in the oleo-chemical industries [3,4]. In general, their preparation by purely chemical means requires vigorous conditions, acid catalysis, and high temperatures with incomplete conversions [5,6]. Free fatty acids are typically esterified by refluxing in methanol with 10% sulfuric acid [7]. Very long reflux times (up to 6 h), high sulfuric acid concentrations (20%) [8] or high temperatures (170 °C) [9,10] can lead to the formation of colored by-products and to the destruction of polyenoic fatty acids.

The favorable effects of ultrasonic irradiation are playing an increasing role in chemical processes, especially in cases where classical methods require onerous conditions or prolonged reaction times [11]. As part of our continuing work on the use of ultrasound irradiation to improve organic reactions [12–18], we report here a rapid and facile procedure for the synthesis of saturated aliphatic acid esters by the ultrasound irradiation induced reaction of aliphatic acids with methanol or ethanol in acidic media at room temperature [11].

2. Method

2.1. Apparatus and analysis

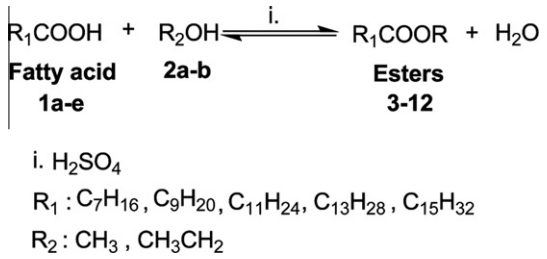
All solvents and chemicals were of research grade and were used as received from Aldrich. The reactions were carried out with a microtip probe connected to a 500W Sonics Vibracell ultrasonic processor operating at 20 kHz at 25% of the maximum power output. The progress of the reactions was monitored on a Shimadzu 2010 Gas Chromatograph equipped with a Rtx-Wax polyethylene glycol capillary column (0.32 mm × 30 m). The mass spectra were obtained on a Hewlett Packard 6890/MSD5973 GC–MS with a split–splitless injector and equipped with a HP-Innowax capillary column (30 m × 250 μm); helium was used as the carrier gas (56 Kpa). The IR spectra were taken on a Shimadzu IR Prestige-21 spectrometer in KBr pellets.

2.2. Synthesis of esters by ultrasound irradiation

In a 25 ml beaker, the fatty acid (4.0 mmol) and sulfuric acid (2.0 mmol) were mixed with ethanol (27.6 ml) or methanol (16.8 ml) and sonicated for 15–30 min at room temperature (25 °C) (Scheme 1). After the time indicated (Table 1), the alcohol was evaporated under reduced pressure. The solid residue was dissolved in water (35 ml), the product was extracted into ethyl ether (3 × 20 ml) and the combined organic fractions were dried ($MgSO_4$). The solvent was evaporated under vacuum to give the pure esters.

* Corresponding author. Tel.: +55 13 33629367; fax: +55 13 33629363.
E-mail address: claudio.martin@pq.cnpq.br (C.M.P. Pereira).

1350-4177/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2011.06.020



Scheme 1. Synthesis of aliphatic acid esters.

2.3. Spectral data of products 3–12

Methyl octanoate: $C_9H_{18}O_2$, MW: 158.24. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 158 (M^+1, 2), 127 (19), 115 (11), 101(10), 87(48), 74(100), 55(27), 43(38).

Methyl decanoate: $C_{11}H_{22}O_2$, MW: 186.29. IR: ν (cm^{-1}) 1720–1760, 1120–1200, 2800–2960; *m/z* (%) 186(M^+1, 3), 155 (12), 143 (26), 101 (9), 87 (55), 74 (100), 55 (26), 43 (34).

Methyl dodecanoate: $C_{13}H_{26}O_2$, MW: 214.34. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 214 (M^+1, 3), 183 (8), 171(12), 143(17), 87(67), 74(100), 55(28), 43(33).

Methyl tetradecanoate: $C_{15}H_{30}O_2$, MW: 242.40. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 242(M^+1, 9), 211(9), 199(17), 143(26), 87(70), 74(100), 55(30), 43(35).

Methyl palmitate: $C_{17}H_{34}O_2$, MW: 270.45. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 270(M^+1, 10), 239(7), 143(33), 87(74), 74(100), 55(35), 43(43).

Ethyl octanoate: $C_{10}H_{20}O_2$, MW: 172.26. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 172(M^+1, 2), 127 (36), 115 (11), 101 (40), 88 (100), 73 (20), 57 (40), 41 (31).

Ethyl decanoate: $C_{12}H_{24}O_2$, MW: 200.32. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 200(M^+1,3), 155(21), 143(5), 88(100), 73(19), 55(26), 43(30).

Ethyl dodecanoate: $C_{14}H_{28}O_2$, MW: 228.37. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 228(M^+1, 7), 183(15), 157(17), 143(8), 129(8), 115(8), 101(54), 88(100), 73(18), 55(27), 43(33).

Ethyl tetradecanoate: $C_{16}H_{32}O_2$, MW: 256.42. IR: ν (cm^{-1}) 1720–1760, 1120–1200, 2800–2960; *m/z* (%) 256 (M^+1, 7), 211(9), 157(17), 101(60), 88(100), 73(17), 55(26), 43(35).

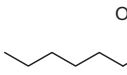
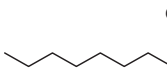
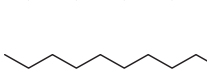
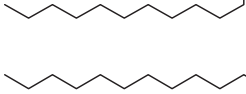
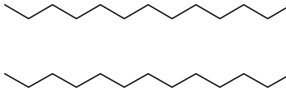
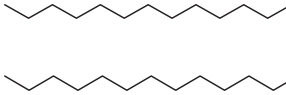
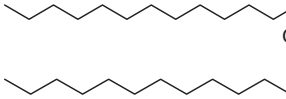
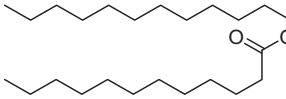
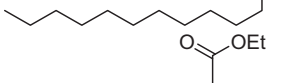
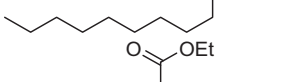
Ethyl palmitate: $C_{18}H_{36}O_2$, MW: 284.48. IR: ν (cm^{-1}) 1720–1760, 1160–1200, 2800–2960; *m/z* (%) 284(M^+1, 9), 241(9), 157(17), 143(9), 101(61), 88(100), 70(17), 55(26), 43(35).

3. Results and discussion

The direct synthesis of esters from fatty acids and alcohols by an enzymatic process has been studied [19]. Ionic liquids are also an attractive alternative, although they have the disadvantage of high cost [20]. Recently, esterification has been investigated with a variety of catalysts, but all require very long reaction times [21–27].

In particular, the ultrasound has been employed to improve the transesterification reaction in two ways: (a) a reduction of reaction time and (b) an increase in the biodiesel yield. The origin of the enhancement of transesterification reactions by ultrasound was studied by Kalva and co-authors and the effect found to be due to a physical rather than a chemical mechanism [28]. However, the reaction times required to prepare biodiesel by using ultrasound are often similar to those of traditional routes, with little or no advantages. For instance, the synthesis of isopropyl esters from palm fatty acids and isopropyl alcohol via sonochemistry reported Deshmane and co-authors [29] required long reaction time

Table 1
Ultrasound-assisted ester synthesis.

Product	Sonochemistry		Literature	
	Time (min)	Yield (%)[a]	Time (h)[ref.]	Yield (%)[ref.]
	30	93	21[22]	73[22]
	15	80	48[23]	71[23]
	15	63	4,5[24]	94[24]
	15	77	48[23]	79[23]
	15	80	48[23]	64[23]
	15	80	4.5[24]	90[24]
	15	50	30[25]	90[25]
	15	70	6[26]	65[26]
	15	78	8[27]	86[27]
	30	95	3,5[24]	95[22]

[a] Yields of isolated products.

(6 h) in acidic medium. Similar conditions were used by Hanh et al. [30,31] to obtain of esters of oleic acid (FFA) with short-chain alcohols (ethanol, propanol and butanol) under ultrasonic irradiation.

The esterification of oleic acid was investigated over the range of molar ratios of alcohol to oleic acid of 1:1–10:1, with 0.5–10 wt.% of the acid catalyst (wt. of sulfuric acid/wt. of oleic acid) and irradiation times of 10 h. The optimized condition for the esterification process was a molar ratio of alcohol to oleic acid of 3:1 with 5 wt.% of H_2SO_4 at 60 °C and an irradiation time of 2 h [30,31].

Stavarache and co-authors recently reported two important studies of the transesterification of vegetable oils using ultrasound irradiation at low frequency and an ultrasonic reactor for large-scale synthesis [32–34] using base rather than acid as the catalyst. The reaction times using base are normally much less than those for acid catalysis, reflecting the difference in the thermodynamics of the two processes: the base-catalyzed reaction is exothermic while the acid-catalyzed reaction is endothermic. However, the disadvantages of using base catalysis include side-reactions between the triglyceride and the catalyst and the formation of soap, which are directly dependent on the amount of base. These kinds of side-reactions are not observed when acid is used as the catalyst. Santos et al. [35] reported the preparation of methyl esters from *Oreochromis niloticus* (Nile tilapia) oil and methanol. The reaction was completed by applying low-frequency (40 kHz) and high-intensity ultrasound from an ultrasonic cleaner combined with reflux. However, for organic reactions, the results obtained with ultrasonic cleaners are not always reproducible and, in this particular case, higher temperatures were also necessary to produce the product [35].

In contrast, the procedure reported here is quite simple. The esters were prepared by esterification of the fatty acid, **1**, with ethanol or methanol in the presence of sulfuric acid (20%) under ultrasonic irradiation (20 kHz) for 15–30 min at room temperature (Scheme 1). In comparison with conventional methods described in the literature, the principal advantages of our procedure are the significant decrease in the reaction time (just 15–30 min are required) and the temperature (room temperature) with no sacrifice in the product yields.

4. Conclusion

The procedure described here is an economical and efficient method for carrying out esterification reactions of commercial importance. Significant advantages of the method include the fact that: (i) the reaction is simple to execute; (ii) the reaction can be conducted at ambient temperature; (iii) the required reaction times are short (15–30 min); (iv) the workup is very simple; and (v) the products are isolated in good yields (50–95%). This mild, convenient and improved protocol for the ultrasound-promoted preparation of esters can potentially be explored for biodiesel synthesis.

Acknowledgements

The authors are grateful to INCT de Estudos do Meio Ambiente (573.667/2008-0), CEPEMA-USP (Centro de Capacitação e Pesquisa em Meio Ambiente), CNPq (310472/2007-5, 475575/2008-3), FAPERGS and CAPES for financial and fellowship support. FHQ is affiliated with the INCT for Catalysis in Molecular and Nanostructures Systems (INCT-Catalysis).

References

[1] R.P. Yadav, R.K. Saxena, R. Gupta, W.S. Davidson, J. Sci. Ind. Res. 56 (1997) 479.
[2] S. Piccicuto, C. Blecker, J.-C. Brohee, A. Mbampara, G. Lognay, C. Deroanne, M. Paquot, M. Marlier, Biotechnol. Agron. Soc. Environ. 5 (2001) 209.
[3] R.K. Saxena, P.K. Ghosh, R. Gupta, W.S. Daidson, S. Bradoo, R. Gulati, Curr. Sci. 77 (1999) 101.
[4] H.S. Larios, H.S. García, R.M. Oliart, G. Valerio-Alfaro, Appl. Microbiol. Biotechnol. 65 (2004) 373.
[5] R.L. Glass, Lipids 6 (1971) 919.
[6] G. Hubscher, J.N. Hawthorne, P. Kemp, J. Lipid Res. 1 (1960) 433.
[7] M. Rogozinski, J. Gas Chromatogr. 2 (1964) 136.
[8] F.M. Archibald, V.P. Skipski, J. Lipid Res. 7 (1996) 442.
[9] H. Hadorn, K. Zuercher, Mitt. Lebensmittelunters Hyg. 58 (1967) 236.
[10] K.V. Peisker, J. Am. Oil Chem. Soc. 41 (1964) 87.
[11] G. Cravotto, P. Cintas, Chem. Soc. Rev. 35 (2006) 180.
[12] L. Pizzuti, L.A. Piovesan, A.F.C. Flores, F.H. Quina, C.M.P. Pereira, Ultrason. Sonochem. 16 (2009) 728.
[13] F.A.N. Silva, M.P. Galluzzi, L. Pizzuti, V. Gressler, D.P. Rivelli, S.B.M. Barros, C.M.P. Pereira, Lett. Drug Des. Discov. 6 (2009) 323.
[14] L. Pizzuti, P.L.G. Martins, B.A. Ribeiro, F.H. Quina, E. Pinto, A.F.C. Flores, D. Venzke, C.M.P. Pereira, Ultrason. Sonochem. 17 (2010) 34.
[15] A. Duarte, W. Cunico, C.M.P. Pereira, A.F.C. Flores, R.A. Freitag, Ultrason. Sonochem. 17 (2010) 281.
[16] D. Venzke, A.F.C. Flores, F.H. Quina, L. Pizzuti, C.M.P. Pereira, Ultrason. Sonochem. 18 (2011) 370.
[17] P.D. Neuenfeld, A.R. Duval, B.B. Drawanz, P.F. Rosales, C.R.B. Gomes, C.M.P. Pereira, W. Cunico, Ultrason. Sonochem. 18 (2011) 65.
[18] G. Ozyilmaz, E. Gezer, J. Mol. Catal. B: Enzym. 64 (2010) 140.
[19] P. Mahapatra, A. Kumari, V.K. Garlapati, R. Banerjee, A. Nag, J. Mol. Catal. B: Enzym. 60 (2009) 57.
[20] H. Weingärtner, Angew. Chem. Int. Ed. 47 (2008) 654.
[21] A.C. Pinto, L.L.N. Guarieiro, M.J.C. Rezende, N.M. Ribeiro, E.A. Torres, W.A. Lopes, P.A.P. Pereira, J.B. Andrade, J. Braz. Chem. Soc. 16 (2005) 1313.
[22] N. Mori, H. Togo, Tetrahedron 61 (2005) 5915.
[23] R. Gulati, P. Arya, B. Malhotra, A.K. Prasad, R.K. Saxena, J. Kumar, A.C. Watterson, V.S. Parmar, Arkivoc (iii) (2003) 159.
[24] X. Li, W. Eli, J. Mol. Catal. A: Chem. 279 (2008) 159.
[25] S.Y. Sun, Y. Xu, D. Wang, Bioresour. Technol. 100 (2009) 2607.
[26] C. Li, J. Yang, P. Wang, J. Liu, Q. Yang, Microporous Mesoporous Mater. 123 (2009) 228.
[27] K. Qiao, H. Hagiwara, C. Yokoyama, J. Mol. Catal. A: Chem. 246 (2006) 65.
[28] A. Kalva, T. Sivasankar, V.S. Moholkar, Ind. Eng. Chem. Res. 48 (2009) 534.
[29] V.G. Deshmane, P.R. Gogate, A.B. Pandit, Ultrasonics Sonochem. 16 (2009) 345.
[30] H.D. Hanh, N.T. Dong, K. Okitsu, R. Nishimura, Y. Maeda, Renew. Energy 34 (2009) 780.
[31] H.D. Hanh, N.T. Dong, K. Okitsu, R. Nishimura, Y. Maeda, Renew. Energy 34 (2009) 766.
[32] C. Stavarache, M. Vinatoru, Y. Maeda, Ultrasonics Sonochem 13 (2006) 401.
[33] C. Stavarache, M. Vinatoru, Y. Maeda, H. Bandow, Ultrasonics Sonochem. 14 (2007) 413.
[34] C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, Ultrasonics Sonochem. 12 (2005) 367.
[35] F.F.P. Santos, J.Q. Malveira, M.G.A. Cruz, F.A.N. Fernandes, Fuel. 89 (2010) 275.