

Microwave assisted synthesis of tripodal triazines from 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione and fatty acids

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*Abstract: A new fast and direct synthesis for tripodal fatty acid esters of tris-hydroxyethyl isocyanurate **1** under microwave irradiation is developed. The method is valid for saturated and unsaturated acids, but the last produced a mixture of esters cis and trans.*

1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione (**1**), a compound commonly used in the preparation of polymers, presents a C_3 symmetry (Figure 1), which makes it a good template to build fatty acid esters with a tripodal structure (Figure 2).

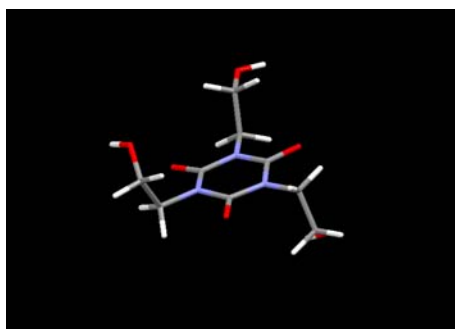


Figure 1. X-ray structure of 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione (**1**)¹

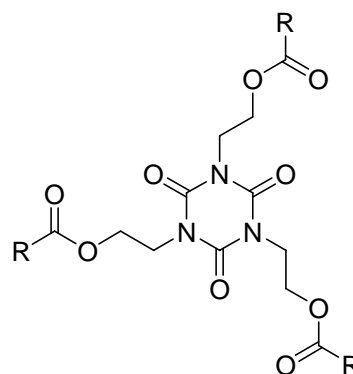
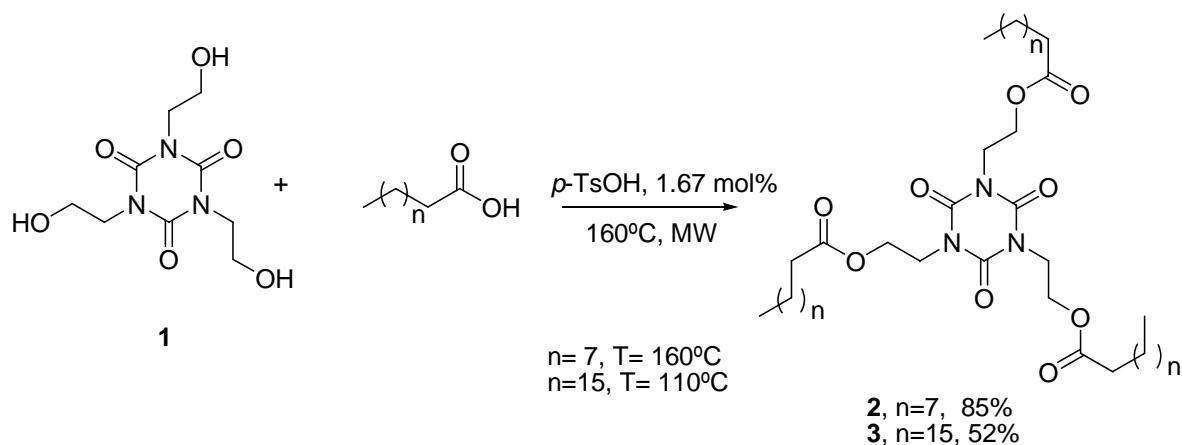


Figure 2

These esters have been reported as fibre treatment agents to improve resistance,² lubricants,³ low viscosity waxes,⁴ melt flow improvers⁵ and heat-resistant finishes for synthetic fibers.⁶ All the previous reports on these compounds used conventional esterification methods, usually with long reaction times.

Microwave assisted organic synthesis (MAOS) seemed to be a good candidate to improve the preparation of these esters. Previous reports have demonstrated the usefulness of this tool in esterification reactions.⁷ Then, we decided to study the esterification of **1** by microwave irradiation, under solvent-free conditions with solid *p*-

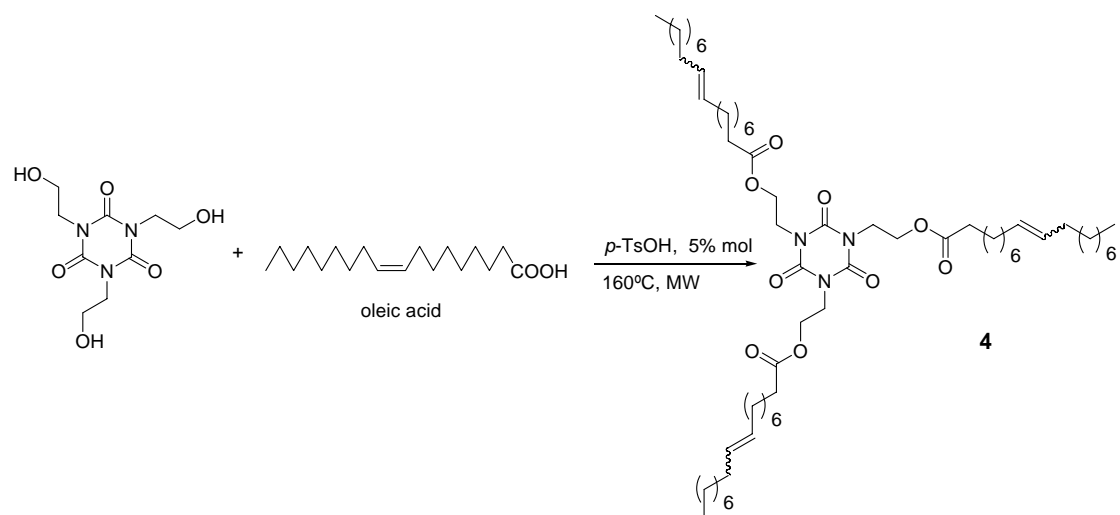
toluenesulfonic acid as catalyst. Thus, a 1:3 mixture of **1** and decanoic acid together with a catalytic amount of TsOH (1.67 mol%) were heated to 160°C for 10 minutes yielding 2,2',2''-(2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl) tris(decanoate) (**2**) in 85%. (Scheme 1).



Scheme 1

Under the same reaction conditions stearic acid suffered pyrolysis. Thus, temperature was decreased in steps of 10 degrees, finding that at 110°C there was no carbonization yielding, after 20 minutes, a 52% of 2,2',2''-(2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl) tristearate (**3**) (Scheme 1).

In order to check the stability of double bonds oleic acid ((9Z)-Octadec-9-enoic acid) was studied. Irradiation for 30 minutes at 160°C yielded 68% of a mixed triester of elaidic (*trans*) and oleic (*cis*) acids as detected by ^1H NMR (Figure 3), in an approximated ratio of 2:1, which could correspond to (9E,9'E)-2,2'-(5-(2-((Z)-nonadec-9-enyloxy)ethyl)-2,4,6-trioxo-1,3,5-triazinane-1,3-diyl)bis(ethane-2,1-diyl) dioctadec-9-enoate where **1** is esterified with two molecules of elaidic acid and one of oleic acid.



Scheme 2

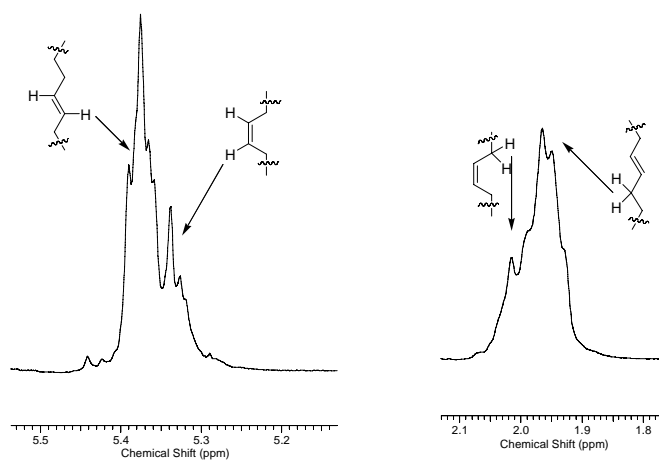


Figure 3

In summary, we developed a new fast and direct synthesis for tripodal fatty acid esters of tris-hydroxyethyl isocyanurate **1**. This allows easy access to this kind of compounds in order to study their properties as lipid analogues (Figure 4).

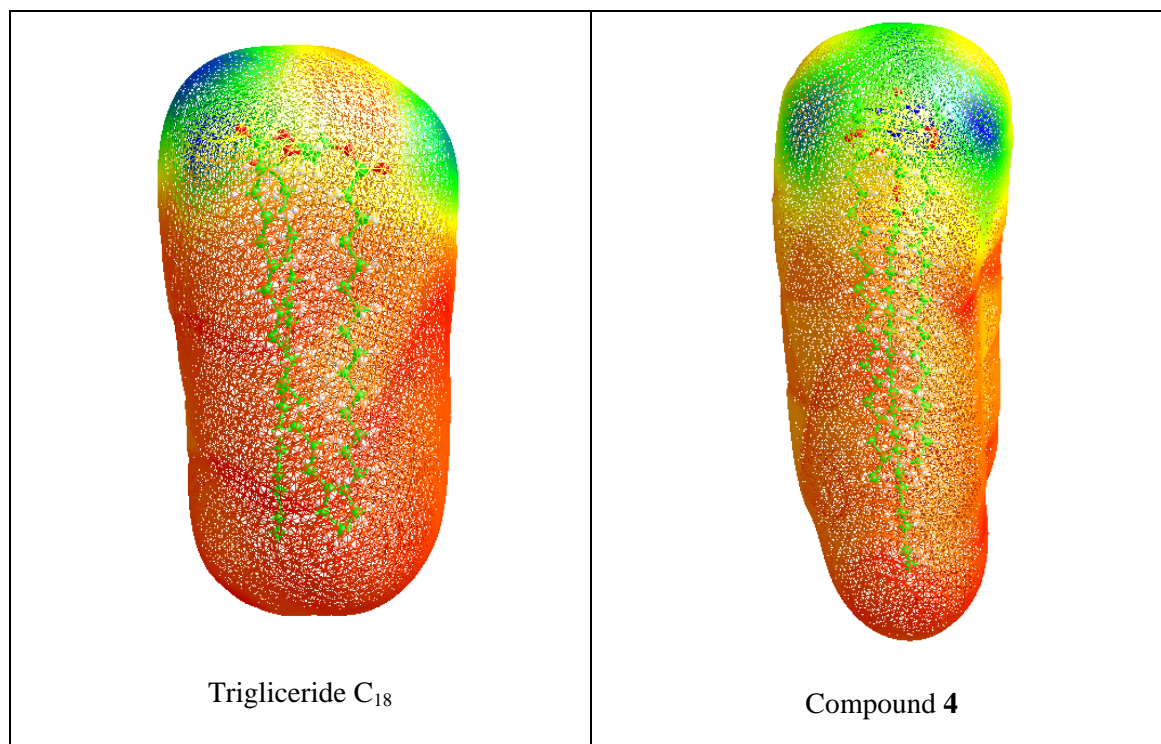


Figure 4. Molecular lipophilic potential⁸

Acknowledgements

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General experimental procedure

Compound **1** (0.199 g, 0.76 mmol) thoroughly mixed with decanoic acid (0.408 g, 2.28 mmol) and *p*-TsOH (7.3 mg), was irradiated in a CEM Discover monomode oven for 10 minutes (200W, 160°C). The crude reaction was dissolved in CH₂Cl₂ and washed with NaOH_{aq} (10%) and water. After evaporation the residue was purified by chromatography on silica column, yielding **2** (0.473 g, 85%) as a thick oil.

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² Yamakita, H.; Ito, Y. *Japan Patent JP2008163489*, **2008**, *Scifinder* CAN 149:202523, **2008**.

³ Gan, X.; Qiu, S.; Lu, X.; Zhang, Z.; Wang, G.; Hu, Z.; Zhang, D.; Xing, Y. *China Patent CN 1583985*, **2005**, *Scifinder* CAN 144:54123, **2005**.

⁴ Kitamura, T.; Doi, K. *Japan Patent 1992 JP 04246589*, *Scifinder* CAN 118:149815 1993

⁵Nakayama, Y. *Japan Patent* JP 04248867 1992, *Scifinder* CAN 118:170302 1993

⁶ Kitamura, K.; Hosomi, H. *Japan Patent* JP 62125079, 1987, *Scifinder* CAN 107:238521, 1987.
Minagawa, M.; Nakahara, Y. *Japan Patent* JP 48071444, 1973, *Scifinder* CAN 80:60580, 1974.

⁷ “*Microwaves in organic synthesis*” 2nd edition, A. Loupy ed. Wiley-VCH, 2006. Sivan Velmathi, Nagahata, R.; Sugiyama, J.; Takeuchi K. *Macromol. Rapid Commun.* **2005**, *26*, 1163–1167.

⁸ Surface calculated with software VEGA ZZ. Pedretti, A.; Villa, L.; Vistoli, G. *J. Comp.-Aid. Mol. Design.*, **2004**, *18*, 167-173. Pedretti, A.; Villa, L.; Vistoli, G. *J. Mol. Graph.*, **2002**, *21*, 47-49. Pedretti, A.; Villa, L.; Vistoli, G. *Chem. Acc.*, **2003**, *109*, 229-32. <http://www.ddl.unimi.it>. The Molecular Lipophilicity Potential (*MLP*) is calculated projecting the Broto-Moreau lipophilicity atomic constants on the molecular surface (Gaillard, P.; Carrupt, P.A.; Testa, B.; Boudon, A. *J. Comp.-Aid. Mol. Design.*, **1994**, *8*, 83).