Conditions-related Analysis of Trimethylolpropane Esterification and Transesterification with Oil Components for Lipase-catalyzed Synthesis of Biolubricants

Surinenaite B[1], Dienys G[1], Bendikiene V[2], Asadauskas S[3], Grigiskis S[4]

[1]Institute of Biotechnology, Vilnius, Lithuania
Contacting E-mail: birute@ibt.lt

BACKGROUND

Lipase-catalyzed synthesis of trimethylolpropane (TMP) esters converting oil components is of great interest to provide biodegradable, low toxic and environment-friendly biolubricants. Screening of lipases can determine effective process, desirable content and high yield of final products. ***Subject:*** Commercial lipases Resinase HT (RHT, *Novozymes*), Lipozyme RM IM (LRM IM, *Novozymes*) and lipase produced by *Enterobacter aerogenes* (E13, *JSC Biocentras*) were tested for transesterification of TMP with pure or emulsified rapeseed, linseed and camelina oils, with trioleate, methyl-, ethyl- and butyl-oleates and for esterification with capric, myristic and oleic acids at 60°C up to 96 hours with or without vacuum control. Titrimetric, TLC and GC methods were used for product analysis.

RESULTS

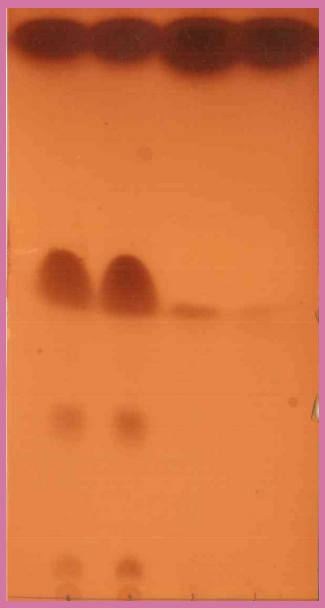
➢ Highest yield of fatty acid TMP esters was **84%** for E13 lipase-catalyzed transesterification of methyl oleate while RHT-catalyzed conversion of the ester was only **21%** (Figure). Other oleates were transesterified by both enzymes up to **66%** product yield without vacuum control. TMP esterification with fatty acids was less effective (10-60%). LRM IM catalysis provided **80%** of TMP triesters converting rapeseed oil methyl esters and **70%** of products in esterification with oleic acid at 20 mbar control.

Table. RHT-catalyzed transesterification of oils with TMP.

Emulsifiers / Oils	Camelina	Linseed	Rapeseed
	Fatty acid TMP esters, % (after 96 h at 60°C without vacuum)		
Pure oil	25	19	31
AWE 400 (logP 0.750)	49	33	55
ENE 6P9 (logP 0.739)	23	20	28
ENE CO5 (logP 1.719)	30	24	39
FAS FX1 (logP 2.616)	16	17	19
GLY SMO (logP -0.386)	35	30	41

➢ Efficiency of TMP transesterification with oils catalyzed by RHT lipase was determined by the source. Commercial emulsifiers (derivatives of acids AWE 400 and FAS FX1, alcohols ENE 6P9, glycerol ENE CO5 and sorbitan GLY SMO) activated or depressed the enzyme (Table). Two TMP esters (preferably mono- and di-) were synthesized after 72 h conversion of rapeseed oil emulsified with AWE 400 and GLY SMO and of linseed oil emulsified with AWE 400 and ENE CO5.

Figure. Transesterification of methyl oleate with TMP catalyzed by RHT (1-2 panels, 72 h and 96 h) and by E13 (3-4 panels, 72 h and 96 h).



CONCLUSIONS

1. **Transesterification** of TMP with oleates was **more effective than esterification** with fatty acids in catalysis of three lipases tested.
2. **Emulsifiers depressed or activated** RHT lipase comparing to transesterification of pure oils. The effect was suggested to be determined by properties of emulsifying agents including logP.
3. **Hydrolysis** step was **not crucial** for the yield of TMP esters in conversion of oils. TMP **mono- and di- esters** were **predominant** rather due to **RHT specificity** as triester **hydrolysis** was very **weak**.

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[1]Institute of Biotechnology: www.ibt.lt
[2]Vilnius University: www.gf.vu.lt
[3]Institute of Chemistry: www.chi.lt
[4]JCS Biocentras: www.biocentras.lt