1-O-alkyl-2-(omega-oxo)acyl-sn-glycerols from shark oil and human milk fat are potential precursors of PAF mimics and GHR

This study examines the feasibility that peroxidation and lipolysis of 1-O-alkyl-2,3-diacyl-sn-glycerols (DAGE) found in shark liver oil and human milk fat constitutes a potential source of dietary precursors of platelet activating factor (PAF) mimics and of gamma-hydroxybutyrate (GHB). Purified DAGE were converted into 1-O-alkyl-2-acyl-sn-glycerols by pancreatic lipase, without isomerization, and transformed into 1-O-alkyl-2-oxoacyl-sn-glycerols by mild autooxidation. The various core aldehydes without derivatization, as well as the corresponding dinitrophenylhydrazones, were characterized by chromatographic retention time and diagnostic ions by online electrospray mass spectrometry. Core aldehydes of oxidized shark liver oil yielded 23 molecular species of 1-O-alkyl-sn-glycerols with short-chain sn-2 oxoacyl groups, ranging from 4 to 13 carbons, some unsaturated. Autooxidation of human milk fat yielded 1-O-octadecyl-2-(9-oxo)nonanoyl-sn-glycerol, as the major core aldehyde. Because diradylglycerols with short fatty chains are absorbed in the intestine and react with cytidine diphosphate-choline in the enterocytes, it is concluded that formation of such PAF mimics as 1-O-alkyl-2-(omega-oxo)acyl-sn-glycerophosphocholine from unsaturated dietary DAGE is a realistic possibility. Likewise, a C-4 core alcohol produced by aldol-keto reduction of a C-4 core aldehyde constitutes a dietary precursor of the neuromodulator and recreational drug GHB, which has not been previously pointed out.
Lipid oxidation in fish oil enriched mayonnaise: Calcium disodium ethylenediaminetetraacetate, but not gallic acid, strongly inhibited oxidative deterioration

The antioxidative effects of gallic acid, EDTA, and extra emulsifier Panodan DATEM TR in mayonnaise enriched with 16% fish oil were investigated. EDTA reduced the formation of free radicals, lipid hydroperoxides, volatiles, and fishy and rancid off-flavors. The antioxidative effect of EDTA was attributed to its ability to chelate free metal ions and iron from egg yolk located at the oil-water interface. Gallic acid reduced the levels of both free radicals and lipid hydroperoxides but promoted slightly the oxidative flavor deterioration in mayonnaise and influenced the profile of volatiles. Gallic acid may therefore promote the decomposition of lipid hydroperoxides to volatile oxidation products. Addition of extra emulsifier reduced the lipid hydroperoxide levels but did not influence the level of free radicals or the oxidative flavor deterioration in mayonnaise; however, it appeared to alter the profile of volatiles. The effect of the emulsifier on the physical structure and rheological properties depended on the presence of antioxidants.

General information

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Organisations: Section for Aquatic Lipids and Oxidation, National Institute of Aquatic Resources, Department of Biotechnology, Department of Systems Biology, Department of Biochemistry and Nutrition
Authors: Jacobsen, C. (Intern), Hartvigsen, K. (Intern), Thomsen, M. H. (Ekstern), Hansen, L. (Ekstern), Lund, P. (Intern), Skibsted, L. (Ekstern), Helmer, G. K. (Intern), Adler-Nissen, J. (Intern), Meyer, A. S. (Intern)
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Oxidation in fish oil-enriched mayonnaise 4: Effect of tocopherol concentration on oxidative deterioration

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Organisations: Section for Aquatic Lipids and Oxidation, National Institute of Aquatic Resources, Department of Biotechnology, Department of Systems Biology, Department of Biochemistry and Nutrition
Authors: Jacobsen, C. (Intern), Hartvigsen, K. (Intern), Lund, P. (Intern), Thomsen, M. (Ekstern), Skibsted, L. (Ekstern), Hølmer, G. K. (Intern), Adler-Nissen, J. (Intern), Meyer, A. S. (Intern)
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ISI indexed (2012): ISI indexed yes
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Scopus rating (2011): SJR 1.009 SNIP 1.097 CiteScore 1.87
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Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.931 SNIP 0.901
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.917 SNIP 0.845
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Rancidity in fish oil enriched foods

General information
State: Published
Organisations: Food Biotechnology and Engineering Group, Department of Systems Biology
Authors: Jacobsen, C. (Ekstern), Hartvigsen, K. (Intern), Meyer, A. B. S. (Intern)
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Regiospecific analysis of neutral ether lipids by liquid chromatography/electrospray ionization/single quadrupole mass spectrometry: validation with synthetic compounds

A reversed-phase high-performance liquid chromatography (HPLC) method with on-line electrospray ionization/collision-induced dissociation/mass spectrometry (ESI/CID/MS) is presented for the regiospecific analysis of synthetic reference compounds of neutral ether lipids. The reference compounds were characterized by chromatographic retention times, full mass spectra, and fragmentation patterns as an aid to clarify the regiospecificity of ether lipids from natural sources. The results clearly show that single quadrupole mass spectroscopic analysis may elucidate the regiospecific structure of neutral ether lipids. Ether lipid reference compounds were characterized by five to six major ions in the positive ion mode. The 1-O-alkyl-sn-glycerols were analyzed as the diacetyl derivative, and showed the \([M - \text{acetoyl}]^+\) ion as an important diagnostic ion. The diagnostic ions of directly analyzed 1-O-alkyl-2-acyl-sn-glycerols and 1-O-alkyl-3-acyl-sn-glycerols
were the \([M - \text{alkyl}](+), [M + H - \text{H}_2\text{O}](+), \) and \([M + H](+)) ions. Regiospecific characterization of the fatty acid position was evident from the relative ion intensities, as the sn-2 species had relatively high \([M + H](+)) ion intensities compared with \([M + H - \text{H}_2\text{O}](+)), whereas the reverse situation characterized the sn-3 species. Furthermore, corresponding sn-2 and sn-3 species were separated by the chromatographic system. However, loss of water was promoted as fatty acid unsaturation was raised, which may complicate interpretation of the mass spectra. The diagnostic ions of directly analyzed 1-O-alkyl-2,3-diacyl-sn-glycerols were the \([M - \text{alkyl}](+), [M - \text{sn-2-acyl}](+), \) and \([M - \text{sn-3-acyl}](+)) ions. Regiospecific characterization of the fatty acid identity and position was evident from the relative ion intensities, as fragmentation of the sn-2 fatty acids was preferred to the sn-3 fatty acids; however, loss of fatty acids was also promoted by higher degrees of unsaturation. Therefore, both structural and positional effects of the fatty acids affect the spectra of the neutral ether lipids. Fragmentation patterns and optimal capillary exit voltages are suggested for each neutral ether lipid class. The present study demonstrates that reversed-phase HPLC and positive ion ESI/CID/MS provide direct and unambiguous information about the configuration and identity of molecular species in neutral 1-O-alkyl-sn-glycerol classes.

General information
State: Published
Organisations: Department of Systems Biology
Authors: Hartvigsen, K. (Intern), Ravandi, A. (Ekstern), Bukhave, K. (Intern), Hølmer, G. K. (Intern), Kuksis, A. (Ekstern)
Pages: 1116-1124
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BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.956 SNIP 0.911 CiteScore 2.46
BFI (2013): BFI-level 1
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ISI indexed (2011): ISI indexed yes
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Scopus rating (2010): SJR 1.366 SNIP 1.051
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Scopus rating (2008): SJR 1.297 SNIP 1.028
Scopus rating (2007): SJR 1.287 SNIP 1.077
Scopus rating (2006): SJR 1.267 SNIP 1.11
Scopus rating (2005): SJR 1.478 SNIP 1.232
Scopus rating (2004): SJR 1.21 SNIP 1.174
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 1.326 SNIP 1.127
Scopus rating (2002): SJR 1.072 SNIP 1.021
Oxidation in fish-oil-enriched mayonnaise 2: Assessment of the efficacy of different tocopherol antioxidant systems by discriminant partial least squares regression analysis

Oxidative protection of mayonnaises with 16% fish oil was studied during cold storage (5 degrees C) after supplementation with different tocopherol systems: the ternary antioxidant system ascorbic acid, lecithin and tocopherol (A/L/T), and two commercial mixtures, an oil-soluble (Toco 70) preparation and a water-soluble (Grindox 1032) preparation. The physical structure of the fish-oil-enriched mayonnaise was manipulated by adding extra emulsifier (Panodan TR) with the purpose of investigating whether or not this affected the antioxidative activity of the tocopherol mixtures. A number of different analytical techniques (HPLC, high-performance liquid chromatography, gas chromatography mass spectrometry (GC-MS), sensory analysis, confocal laser scanning microscopy and rheological measurements) were employed to elucidate the chemical, sensory, structural and rheological aspects of the oxidation process. Discriminant partial least squares regression was used to analyse the data obtained. The three tocopherol preparations not only affected the oxidative stability of the mayonnaises differently they also influenced the rheological and structural properties of the mayonnaises in different ways. The rheological and structural properties of the mayonnaise were also affected by the addition of extra emulsifier, but this did not influence the formation of fishy and rancid off-flavours. Addition of the A system caused the immediate formation of distinct fish; and rancid off-flavours in the fresh mayonnaises. The volatile compounds trans-2-heptenal, 3-octen-3-one, 1-octen-3-ol, trans,cis-2, 4-heptadienal, trans,trans-2,4-heptadienal, trans-2-octenal, nonanal and trans,cis-3,6-nonadienal were thought to contribute to the fishy and rancid flavours. Addition of Toco 70 did not affect the sensory perception of mayonnaise nor the development of volatile flavour compounds as evaluated by GC-MS, but the peroxide values were slightly increased in mayonnaise containing Toco 70 as compared to the other mayonnaises. Mayonnaise with Grinder 1032 seemed to have fewer fishy and rancid off-flavours than mayonnaises without antioxidant. This flavour-protective effect of Grindox 1032 was correlated to an increase in the size of the droplet diameter of mayonnaises supplemented with Grindox 1032

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Authors: Jacobsen, C. (Intern), Hartvigsen, K. (Intern), Lund, P. (Intern), Adler-Nissen, J. (Intern), Hølmer, G. K. (Intern), Meyer, A. S. (Intern)
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Scopus rating (2016): SJR 0.742 SNIP 0.882 CiteScore 1.81
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BFI (2015): BFI-level 1
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BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.828 SNIP 0.908 CiteScore 1.71
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.791 SNIP 0.901 CiteScore 1.71
Oxidation in fish oil-enriched mayonnaise 3: Assessment of the influence of the emulsion structure on oxidation by discriminant partial least squares regression analysis

General information
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Organisations: Section for Aquatic Lipids and Oxidation, National Institute of Aquatic Resources, Department of Biotechnology, Department of Systems Biology, Department of Biochemistry and Nutrition, Center for BioProcess Engineering, Department of Chemical and Biochemical Engineering
Authors: Jacobsen, C. (Intern), Hartvigsen, K. (Intern), Lund, P. (Intern), Thomsen, M. (Ekstern), Skibsted, L. (Ekstern), Adler-Nissen, J. (Intern), Hølmer, G. K. (Intern), Meyer, A. S. (Intern)
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Oxidation in fish-oil-enriched mayonnaise 1: Assessment of propyl gallate as an antioxidant by discriminant partial least squares regression analysis

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Authors: Jacobsen, C. (Intern), Hartvigsen, K. (Intern), Lund, P. (Intern), Meyer, A. S. (Intern), Adler-Nissen, J. (Intern), Holstborg, J. (Ekstern), Hølmer, G. K. (Intern)
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BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.791 SNIP 0.901 CiteScore 1.71
ISI indexed (2013): ISI indexed yes
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Scopus rating (2012): SJR 0.872 SNIP 1.038 CiteScore 1.68
ISI indexed (2012): ISI indexed yes
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BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.931 SNIP 0.901
Web of Science (2010): Indexed yes
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Scopus rating (2009): SJR 0.917 SNIP 0.845
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Scopus rating (2008): SJR 0.852 SNIP 0.849
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Scopus rating (2007): SJR 0.707 SNIP 0.842
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 0.749 SNIP 0.824
Web of Science (2006): Indexed yes
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Web of Science (2005): Indexed yes
Absorption and metabolism of the primary oxidation product: hydroperoxy-linoleic acid.

General information
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Organisations: Department of Biochemistry and Nutrition
Authors: Bertelsen, L. S. (Intern), Hartvigsen, K. (Intern), Weber, C. (Intern), Hølmer, G. K. (Intern), Bukhave, K. (Intern)
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Projects:

Oxidationsmekanismer i fiskeolieholdige

Technical University of Denmark
Period: 01/06/1996 → 18/09/2000
Number of participants: 3
Phd Student:
Hartvigsen, Karsten (Intern)
Supervisor:
Bukhave, Klaus (Intern)
Main Supervisor:
Hølmer, Gunhild Kofoed (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Program Stipendium-SU, Eksp
Project: PhD

Oxidation mechanisms in fish oil enriched emulsions
The purpose of the project is to study the oxidation mechanisms in fish oil enriched emulsions in order to develop combined emulsifier and antioxidant systems which are more efficient in protecting fish oil enriched foods against oxidation than existing antioxidant systems. Results obtained in 1999 have shown that the low pH in mayonnaise is a very important factor for the initiation of the oxidation processes in mayonnaise. This is due to the fact that iron ions are released/loosened from the egg yolk components at the oil/water interface when pH is decreased to 4, which is the normal pH in mayonnaise. The released iron promotes decomposition of peroxides to volatiles, which are responsible for the off-
flavour formation in mayonnaise. The metal chelator EDTA was observed to be a very efficient antioxidant in mayonnaise due to its ability to chelate iron. A HPLC method for determination of lipid peroxides has been further optimised and is now fully operational. By the aid of GC-MS a large number of volatiles that correlate to the fishy and rancid off-flavours in oxidised mayonnaise have been identified.

National Institute of Aquatic Resources
Department of Biochemistry and Nutrition
Department of Biotechnology
Danisco Ingredients
Association of Danish Fish Meal and Fish Oil Manufacturers
Royal Veterinary and Agricultural University
Period: 01/05/1996 → 31/12/1999
Number of participants: 11
Project participant:
Vu, Thi Thu Trang (Intern)
Jacobsen, Charlotte (Intern)
Hartvigsen, Karsten (Intern)
Lund, Pia (Intern)
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Green, Else (Intern)
Reitz, Suzie (Intern)
Adler-Nissen, Jens (Intern)
Project Manager, organisational:
Børresen, Torger (Intern)

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