Natural Fish Oil from Fishery Biowaste via a Circular Economy Process

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Outlook of the presentation

- ✓ The problem with today's omega-3 dietary supplements
- ✓ New circular approach to fish oil production
- ✓ The future: whole fish oil from fishery biowaste

Omega-3 dietary supplements: a twofold problem

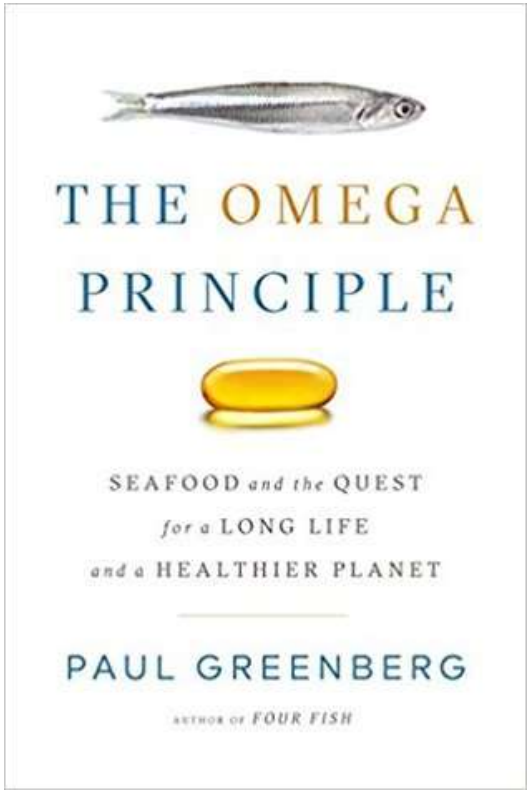
- ✓ Chemically refined fish oil is in ethyl ester form, releasing toxic ethanol in the liver, and devoid of natural antioxidants with many oils found highly oxidised (rancidity)

- ✓ Chiefly derived from anchovy and sardine stocks (and also from krill), the large and increasing demand of fish oil for omega-3 dietary supplements significantly worsens overfishing

Marine omega-3 poor sustainability

- ✓ Fish oil is amid the most popular dietary supplement both in Europe (taken by approximately 20% of adults) and in the USA growing at an annual rate of >10%, the $2.6 billion EPA/DHA ingredient global market in 2018 is estimated to almost triple by 2026

- ✓ "The miracle pill is only the latest product of the reduction industry, a vast, global endeavor that over the last century has boiled down trillions of pounds of marine life into animal feed, fertilizer, margarine, and dietary supplements. The creatures that are the victims of that industry seem insignificant to the untrained eye, but turn out to be essential to the survival of whales, penguins, and fish of all kinds, including many that we love to eat".



What happens if mankind follows recommended daily intake?

- ✓ In brief, 6.5 out of 7 billion people comprising the current world's population do not get sufficient intake of EPA and DHA. Considering a daily dosage of 250 mg, a daily production of 1,625 t of EPA and DHA would be needed (>593,000 t/a), not including the demand of fatty acids by hatcheries.

- ✓ Current yearly production of EPA and DHA enriched oils does not exceed 85,000 t which renders the scope of the effort needed to meet tomorrow's demand.

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Enhancing and improving the extraction of omega-3 from fish oil

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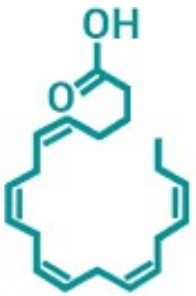
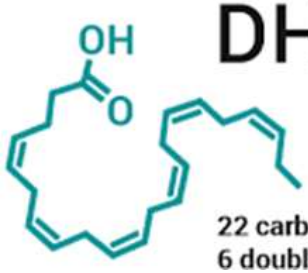
ABSTRACT

Omega-3 fatty acids DHA and EPA derived from fish oil are widely marketed across the world as valued dietary supplements offering numerous health benefits to children and adults alike. Traditional extraction processes are energy intensive and use organic solvents. Green and sustainable alternatives are needed with the aim to significantly expand and improve the production of omega-3 extracts, especially with the aim to obtain these essential polyunsaturated fatty acids from fish processing waste available in > 20 million tonnes/year amount.



EPA

20 carbon
5 double bonds



DHA

22 carbon
6 double bonds

Phlorotannins are removed upon refinement of fish oil

- ✓ The conventional industrial processes used to extract and purify fish oil remove the lipophilic polyphenols naturally present in the fish fat, including the powerful antioxidant and anti-inflammatory phlorotannins obtained by fish eating brown algae.

- ✓ Thanks to the pioneering studies of Østerud and co-workers, it is now increasingly understood that natural polyphenols present in marine oils (phlorotannins) play an essential role in protecting omega-3 lipids from oxidation and autoxidation, ensuring that no proinflammatory products are formed after intake as often happens with assumption of refined omega-3 concentrates.

ACS FOOD SCIENCE & TECHNOLOGY
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Review

Sustainably Sourced Olive Polyphenols and Omega-3 Marine Lipids: A Synergy Fostering Public Health

Mario Pagliaro, Daniela M. Pizzone, Antonino Scurria, Claudia Lino, Emilia Paone, Francesco Mauriello,* and Rosaria Ciriminna*

Cite This: *ACS Food Sci. Technol.* 2021, 1, 139–145

ABSTRACT: Thanks to the pioneering studies of Østerud and co-workers, it is now increasingly understood that natural polyphenols present in marine oils play an essential role in protecting omega-3 lipids from oxidation and autoxidation, ensuring that no proinflammatory products are formed after intake as often happens with assumption of refined omega-3 concentrates. Strong antioxidants exerting multiple biological functions, olive biophenols are ideally suited to functionalize marine oils, creating a synergy that has the potential to improve public health across the world. This study identifies suitable avenues for advancing the sustainable production of health-beneficial formulations based on newly obtained natural marine oils and olive phenolic extracts. Important educational outcomes conclude the study.

KEYWORDS: *omega-3, olive, polyphenols, hydroxytyrosol, limonene, circular economy*

Marine oils in natural form are better!

- ✓ In 1986, studying the effect of 8 weeks of daily intake of omega-3 lipids in the form of fish oil or omega-3 capsules, Østerud found modest benefits in the activity of blood cells, suggesting that concentrated omega-3 lipids did not have the same health effects as marine oils in natural form

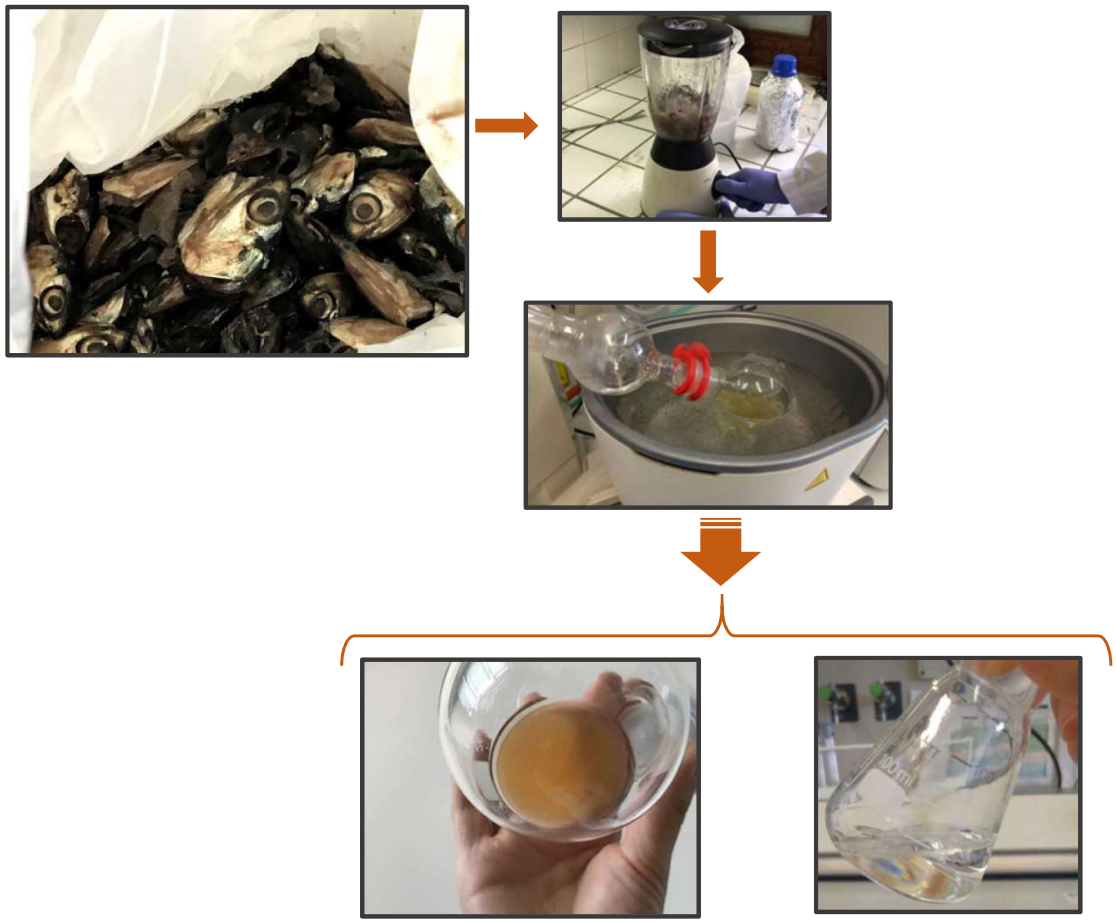
- ✓ In 2001, Østerud and Elvevoll reported the results of administering cold-pressed versus refined marine oils to healthy volunteers. Better results, seen as a consistent improvement in parameters related to the development of cardiovascular disease, were noted by supplementation with cold-pressed seal oil, despite a lower content of n-3 fatty acids in the unrefined oil

Professors Østerud and Elvevoll, University of Tromsø, Norway, image retrieved from: https://www.aftenposten.no/norge/i/wOwa5/foedselshjelper-for-forskere

New circular route to fish oil invented in Italy

- ✓ Fish oil rich is extracted in high yield from anchovy filleting waste using limonene, a green biosolvent renewably derived from the orange peel, in a simple solid-liquid extraction performed by maceration under stirring followed by limonene removal and recovery via evaporation under reduced pressure.

- ✓ The method closes the materials cycle and establishes a circular economy process to obtain high quality fish oil from biowaste available worldwide in >20 million t/year amount.



R. Ciriminna, A. Scurria, G. Avellone, M. Pagliaro, A Circular Economy Approach to Fish Oil Extraction, *ChemistrySelect* 4 (2019) 5106-5109.

The process enables the marine bioeconomy

- ✓ Because it is completely general, applicable to any fishery biowaste
- ✓ For example, along with Prof. F. Chemat we applied it successfully to shrimp biowaste obtaining a valued marine oil rich in omega-3 lipids and astaxanthin

ACS OMEGA

http://pubs.acs.org/journal/acsodf Article

High Yields of Shrimp Oil Rich in Omega-3 and Natural Astaxanthin from Shrimp Waste

Antonino Scurria, Anne-Sylvie Fabiano Tixier, Claudia Lino, Mario Pagliaro, Fabio D'Agostino, Giuseppe Avellone,* Farid Chemat,* and Rosaria Ciriminna*

Cite This: *ACS Omega* 2020, 5, 17500−17505 Read Online

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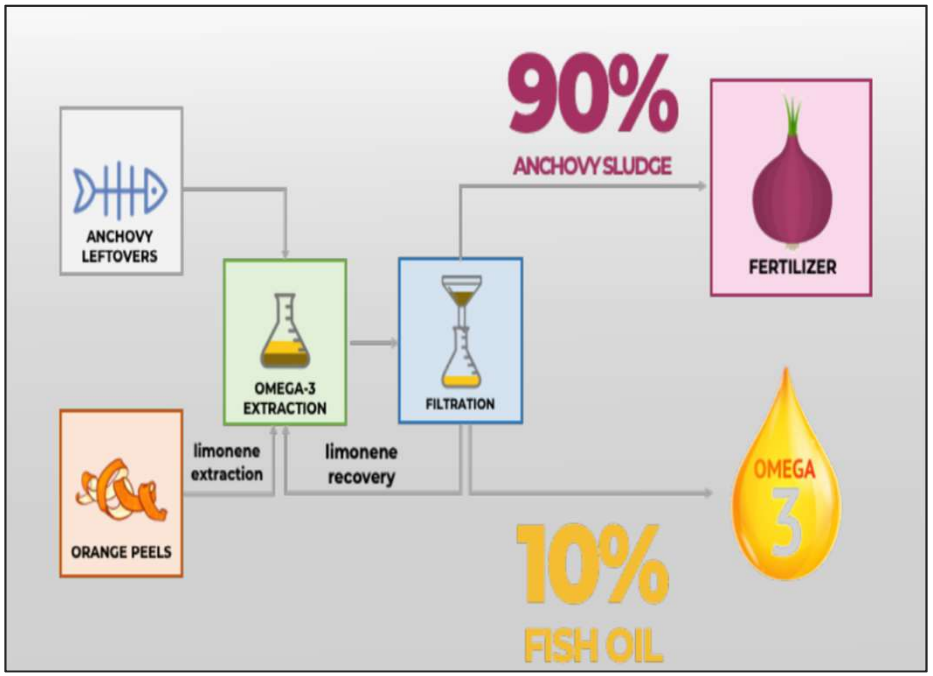
ABSTRACT: A valued marine oil rich in omega-3 lipids and natural astaxanthin is obtained with remarkably high yield (up to 5 wt %) extending to pink shrimp waste (head and carapace) using the approach to extract fish oil from fish processing byproducts using D-limonene. Biobased limonene is an excellent solvent for both unsaturated lipids and astaxanthin-based carotenoids preventing oxidative degradation during the extraction cycle including solvent separation at 85 °C. Explaining the deep red color of the shrimp oil obtained, computational simulation suggests that D-limonene is also a good solvent for natural astaxanthin abundant in shrimp.

A circular economy, closed process

- ✓ The process is circular and closed because both bioproducts, fish oil and the solid fish sludge, are highly valued functional products
- ✓ The process contributes to valorize waste from citrus industry through the use of Limonene as biosolvent: a versatile chemical of bioeconomy



R. Ciriminna et al., *Chem. Commun.* **2014**, 50, 15288
R. Ciriminna et al., *ACS Sustainable Chem. Eng.* **2016**, 4, 2243

The process is technically and economically viable

- ✓ The capital investment in the low-energy extraction setup, including the bio-based solvent and the solar air dryer, is relatively modest, and the operational costs are mostly due to labor and electricity to separate the oil from the agro solvent

ACS OMEGA

Article

Cite This: ACS Omega 2019, 4, 15359−15363

http://pubs.acs.org/journal/acsodf

Omega-3 Extraction from Anchovy Fillet Leftovers with Limonene: Chemical, Economic, and Technical Aspects

Rosaria Ciriminna,[†] Antonino Scurria,[†] Anne-Sylvie Fabiano-Tixier,[‡] Claudia Lino,[†] Giuseppe Avellone,[§] Farid Chemat,[*,‡] and Mario Pagliaro[*,†]

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ABSTRACT: We investigate selected chemical, technical, and economic aspects of the production of fish oil rich in polyunsaturated omega-3 fatty acids from anchovy filleting leftovers using *d*-limonene as the extraction solvent at ambient temperature and pressure. Entirely derived from the orange peel prior to orange squeezing for juice production, the bio-based solvent is easily recovered, affording a circular economy process with significant potential for practical applications.

AnchoisOil: rich in omega-3 lipids and oleic acid

- ✓ We called the new oil "AnchoisOil": the new marine oil rich in polyunsaturated fatty acid "omega-3" lipids, particularly in DHA (12.4%) followed by EPA (5.4%)
- ✓ Oleic acid (24%) is the main fatty acid present in the oil. It is an highly beneficial, monounsaturated fatty acid with modulatory effects on inflammatory diseases and health, studied for the development of novel therapeutic approaches for infections, inflammatory, immune, and cardiovascular diseases

Fatty acid		weight%	
Myristic acid (14:0)		9,95	SFA
Pentadecanoic (15:0)		10,38	
Palmitic (16:0)		10,61	
Margaric (17:0)		11,1	
Stearic (18:0)		11,34	
(6,Z)-7 methyl-6-Hexadecenoic (16:1, n-10)		11,04	MUFA
Oleic (18:1, n-9)		11,39	
Gadoleic (20:1, n-11)		12,18	
11-Docosenoic (22:1, n-11)		13,02	
Linoleic (18:2, n-6)		11,6	Omega-6
alpha-Linolenic (18:3, n-3)		11,78	Omega-3
Stearidonic (18:4, n-3)		11,86	
Eicosapentenoic (20:5, n-3)	**EPA**	12,07	
Docosahexaenoic (22:6, n-3)	**DHA**	13,90	

n-3/n-6 > 10

R. Ciriminna et al., *Preprints* **2019**, 2019020023

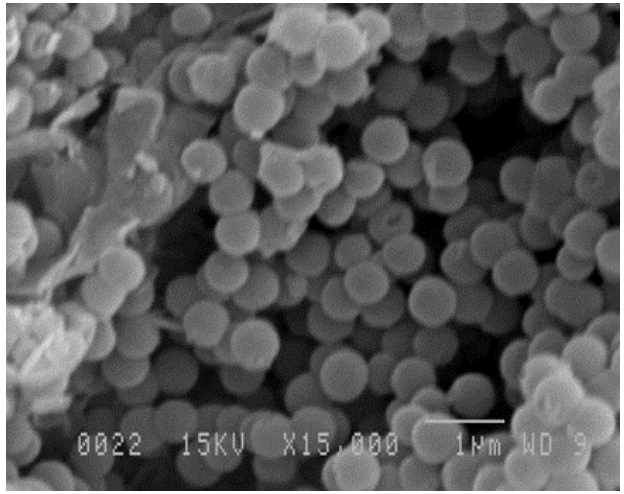
AnchoisOil: rich in vitamin D3

- ✓ The oil is rich in vitamin D3, the physiologically active form of vitamin D
- ✓ The sum of the quantities of the three isomers of vitamin D3 amounts to 0.082 µg vitamin D3 per g oil, namely a 82 µg/kg content, in good agreement with the typical amounts of vitamin D3 in fish oils (ranging from 18 to 350 µg/kg).

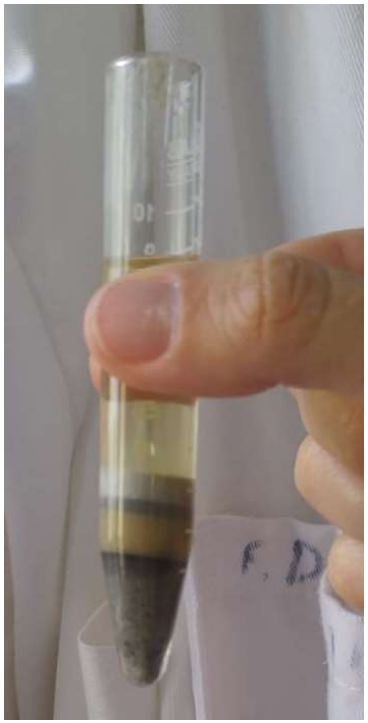
A. Scurria, C. Lino, R. Pitonzo, M. Pagliaro, G. Avellone, R. Ciriminna, Vitamin D3 in Fish Oil Extracted with Limonene from Anchovy Leftovers, *Chemical Data Collections* 25 (2020) 100311.

R&D opportunities

- Extraction efficiency/selectivity
- Quality assessment
- Stability studies
- New formulations
- Biomedical investigations
- Residue characterization



R.Ciriminna et al., *Chem. Soc. Rev.* **2013**, 42, 9243



blog.marketresearch.com
nutraingredients-asia.com

The solid residue of the extraction is an exceptional fertilizer

- ✓ Results to be reported soon in the scientific literature along with the teams of Professors. F. Mauriello and A. Muscolo, Università Mediterranea di Reggio Calabria

Omeg@Silica: AnchoisOiladsorbed on silica

- ✓ AnchoisOil is conveniently loaded on periodic mesoporous silicas affording Omeg@Silica microparticles with 50 wt % fish oil load
- ✓ "The simplicity of the process, the high load of fish oil, and the biocompatible nature of silica support numerous forthcoming applications of this new class of 'Omeg@Silica' materials"

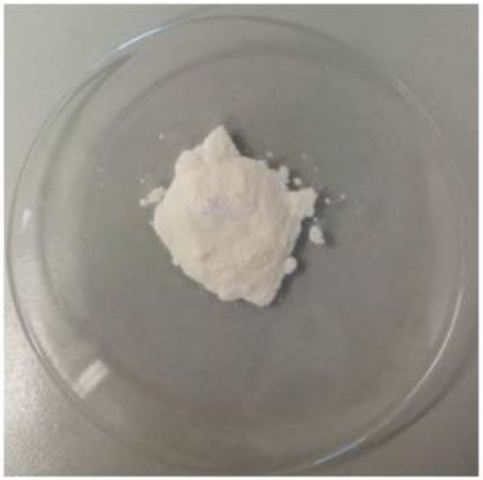
ChemistryOpen | Full Papers | doi.org/10.1002/open.202100038 | Chemistry Europe

Special Collection

Omeg@Silica: Entrapment and Stabilization of Sustainably Sourced Fish Oil

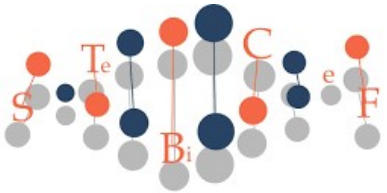
Rosaria Ciriminna, Claudia Lino, and Mario Pagliaro*[a]

Fish oil rich in long-chain polyunsaturated fatty acids, vitamin D_3 and carotenoid pigments have been sustainably extracted from anchovy fillet leftovers using biobased limonene. The oil is conveniently stabilized by adsorption on periodic mesoporous silicas. The simplicity of the process, the high load of fish oil, and the biocompatible nature of mesoporous silica support numerous forthcoming applications of this new class of "Omeg@Silica" materials.



Bioeconomy @ISMN-CNR Palermo

- Bioproduct extraction from *citrus* and *opuntia ficus indica* peel waste
- Green chemical conversion of bioproducts into valued chemicals
- Microencapsulation of bioactive molecules



DIPARTIMENTO DI SCIENZE E TECNOLOGIE
BIOLOGICHE CHIMICHE E FARMACEUTICHE (STEBICEF)

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