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Novel non-methylated furan fatty acids in fish from a zero discharge aquaculture system

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ABSTRACT

Background: Furan fatty acids (F-acids) are valuable minor fatty acids which are appraised for their protective role against lipid oxidation of polyunsaturated fatty acids (PUFAs). The most relevant dietary source for F-acids is fish with the predominant occurrence of up to five dimethyl- or monomethyl-substituted homologues. During the screening of fish from a zero discharge aquaculture (ZDA) system we noted the potential presence of unusual F-acids.
Methods: We developed a method by gas chromatography with mass spectrometry operated in the selected ion monitoring mode for elucidation of the structures of the uncommon F-acids.
Results: Carp from the ZDA system contained seven non-methylated F-acids with dominance of 8-(5-hexylfuran-2-yl)-octanoic acid (8F6). Non-methylated F-acids have never been detected before in fish. Subsequent analysis of other fish species and a batch of the fish feed confirmed the presence of non-methylated F-acids.
Conclusions: F-acids in fish are derived from the feed. Our investigation indicates that more emphasis should be put on the F-acid concentrations in fish from aquaculture, which appears to depend on the quality of the fish feed.

1. Introduction

Furan fatty acids (F-acids) are a group of heterocyclic fatty acids which have been found to be valuable radical scavengers (antioxidants) in food [1,2]. The richest food sources for F-acids are fish, milk fat, soy beans, and different green plants [1–7]. Broadly speaking, F-acids are found virtually in all samples where polyunsaturated fatty acids (PUFAs) are present, although the concentrations of F-acids are usually low. In Germany, fish is the major food source for the average intake of F-acids [4]. Due to the notably low average daily intake of fish and seafood in Germany (~14.4 kg/year fish and seafood in 2013) [8], fish is most likely also the prevalent dietary source of F-acids in many other countries with similar or higher fish intake. The presence of F-acids in fish may protect against mortality from heart disease [1]. Recently, up to 22 different F-acid structures have been identified in fish liver by means of a thorough GC/MS-SIM method [9]. These 22 F-acids originated from two classic families, i.e. methyl- and dimethyl-substituted F-acids (Fig. 1). Typically, five classic F-acids (9M5, 9D5, 11M5, 11D5, 11D3) are representing the majority of F-acids in fish [3,9].

Fish populations are systematically declining worldwide due to excessive fishing, pollution and destruction of spawning grounds and natural habitats [10]. Higher demand for seafood in a world of substantial depletion of fish in natural aquatic bodies has led to the rapid development of aquaculture, i.e. the managed production of aquatic animals under controlled conditions [10]. Negative impact of conventional aquaculture systems on the environment (e.g. due to chemical treatments, antibiotics, transfer of diseases to wild fish, interbreeding of escaped cultured fish with wild fish, destruction of benthic ecosystems and eutrophication) [11] has prompted the development of recirculating aquaculture systems to overcome some of the problems encountered in conventional aquaculture systems [12,13]. In these land-based systems, fish are grown at high densities and water is purified to such an extent that water replacement is limited to a daily water exchange of 10–20% of the total water volume. Further developments in this field have led to the development of zero discharge aquaculture (ZDA) systems where water is not exchanged throughout the raising of the fish. By means of aerobic and anaerobic biological treatment loops most carbon and nitrogen are released as CO_2 and N_2 in these latter systems whereby water use is restricted to compensation for evaporation losses only [14]. In an ongoing experiment we wish to explore whether fish from ZDA systems are containing F-acids and at what levels. During the initial screening of the samples for the five classic F-acids in carp and other fish we noted peaks in the GC/MS ion chromatograms which indicated the presence of several uncommon F-acids previously unknown to us.

The goal of the present study was to develop a methodology for the verification of the presence and structures of unusual F-acids in fish (especially: carp) from the ZDA system. Different GC/MS screening

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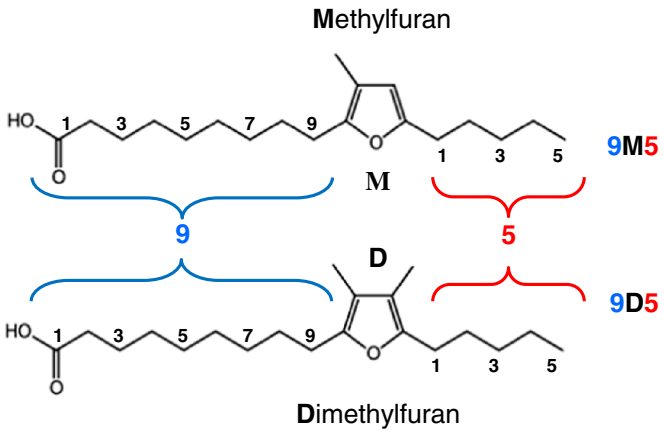

Fig. 1. Structure of top: 9-(3-methyl-5-pentylfuran-2-yl)-nonanoic acid (9M5) and bottom: 9-(3,4-dimethyl-5-pentylfuran-2-yl)-nonanoic acid along with the description of the short terms according to Vetter et al. [16].

methods were used for studying the F-acids in fillet, liver and spleen of a carp sample. Last but not least, we aimed to investigate the potential source for the unusual F-acids in the fish.

2. Materials and methods

2.1. Chemicals and standards

2-Propanol (≥99.8%), silica 60, $AgNO_3$ (≥99.5%), myristic acid (14:0) (≥98%), and butylhydroxytoluene (BHT) (≥99%) were from Fluka/Sigma-Aldrich (Steinheim, Germany). Bulk isolute sorbent (isolute HM-N) was from Biotage AB (Uppsala, Schweden). Concentrated sulphuric acid (98%), Diethyl ether (for synthesis, ≥99%), NaCl (≥99.5%) were from Carl Roth (Karlsruhe, Germany). Methanol (HPLC grade, ≥99.85%), and *n*-hexane (HPLC grade, ≥99.5% were from Th. Geyer (Renningen, Germany). The F-acids 11-(3,4-dimethyl-5-pentylfuran-2-yl)-undecanoic acid (11D5) and 11-(3-methyl-5-pentylfuran-2-yl)-undecanoic acid (11M5) were synthesized by Knight and Smith [15], 10-(3-methyl-5-pentylfuran-2-yl)-decanoic

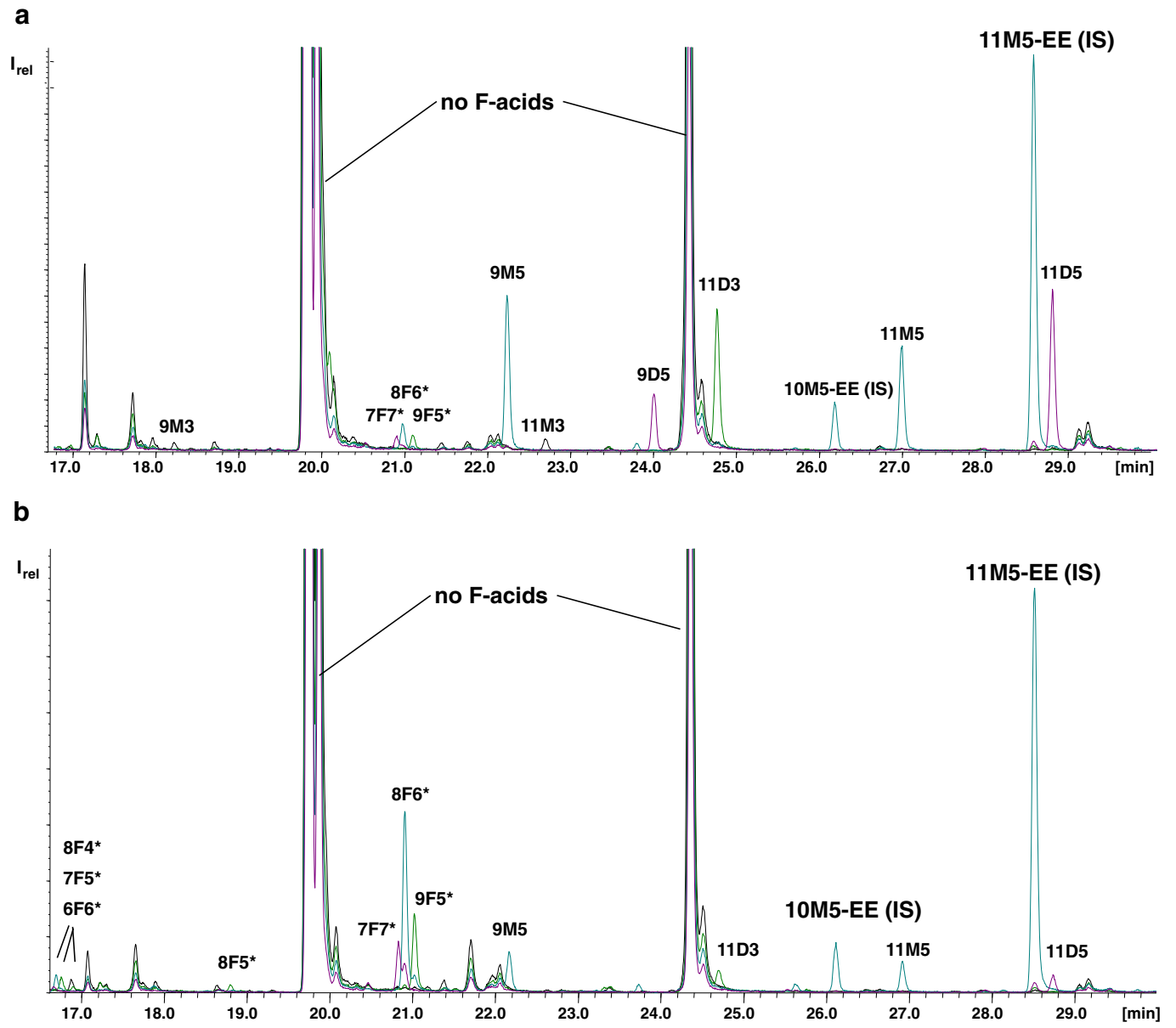

Fig. 2. GC/MS-SIM ion chromatograms (*m/z* 137, *m/z* 151, *m/z* 165, *m/z* 179) of the furan fatty acid methyl ester fraction from (a) muscle and (b) liver of a carp from the zero discharge aquaculture system. Asterisks denote new unusual F-acids described in this article.