



Original research article

Furan fatty acid content and homologue patterns of fresh green matrices

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ABSTRACT

Furan fatty acids (furan-FAs) are valuable antioxidants which are supposed to play an important role in the protection of polyunsaturated fatty acids from getting oxidised. Scattered literature reports indicated that these fatty acids are widely present at low concentrations in various biological and food samples. Here, we determined the furan-FA composition in 35 samples including seven fresh herb matrices, as well as in spinach and grass. Samples were transesterified and furan-FAs were enriched from the fatty acid methyl ester fraction by means of silver ion chromatography followed by analysis with gas chromatography with mass spectrometry operated in selected ion monitoring mode (GC/MS-SIM). The samples featured between one (rosemary) and eight different furan-FAs (curly-leaf parsley). Six saturated and four unsaturated furan-FAs were identified with clear dominance of β,β' -dimethyl-substituted representatives. The total amount of furan-FAs ranged from 15 to 2650 $\mu\text{g}/100\text{ g}$ fresh weight with dill, grass and curly-leaf parsley being the richest sources among the sample matrices. The rarely described unsaturated furan-FAs were detected in eight of the nine matrices and were predominant in flat-leaf parsley. Curly-leaf and flat-leaf parsley as well as fresh and deep-frozen spinach samples showed remarkable differences in the furan-FA pattern.

1. Introduction

Furan fatty acids (furan-FAs) are a class of heterocyclic fatty acids bearing a furan moiety in the central part of the fatty acid chain. A carboxyalkyl chain (typically consisting of 7, 9, 11 or 13 carbon atoms) is attached to the α -position of the furan moiety, whereas the α' -position carries a short alkyl chain (typically consisting of 3 or 5 carbon atoms). Most commonly, the β -position is substituted with a methyl group and the β' -position with either hydrogen (monomethyl-substituted furan-FAs) or with another methyl group (dimethyl-substituted furan-FAs). The main furan-FAs in marine animals, oils and plants were found to be 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid (11D5), 12,15-epoxy-13,14-dimethyloctadeca-12,14-dienoic acid (11D3), 10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoic acid (9D5), 12,15-epoxy-13-methyleicosa-12,14-dienoic acid (11M5), and 10,13-epoxy-11-methyloctadeca-10,12-dienoic acid (9M5) (Balzano et al., 2017; Boselli et al., 2000; Chvalová and Špička, 2016; Glass et al., 1974; Gunstone et al., 1978; Guth and Grosch, 1991; Hannemann et al., 1989; Masanetz et al., 1998; Masanetz and Grosch, 1998; Mawlong et al., 2016; Pacetti et al., 2013, 2010; Sigrist et al., 2001; Vetter et al., 2016; Wahl et al., 1994b, 1994a; Wendlinger and Vetter, 2014). Occasionally, unsaturated furan-FAs bearing a double bond in either the carboxyalkyl or the alkyl side chain have also been described (Boselli et al., 2000; Ishii et al., 1988; Pacetti et al., 2010; Wendlinger et al.,

2016). In addition, furan-FAs without methyl substituents in β - and β' -positions (“non-methylated” furan-FAs) were recently detected in fish (Vetter et al., 2016).

Despite being minor constituents, the presence of furan-FAs has been documented in a wide range of matrices like fish (Chvalová and Špička, 2016; Glass et al., 1977; Gunstone et al., 1978; Pacetti et al., 2010; Wahl et al., 1994b; Vetter et al., 2016), fats and oils (Boselli et al., 2000; Guth and Grosch, 1992, 1991; Wahl et al., 1994a; Wendlinger and Vetter, 2014) and plants (Hannemann et al., 1989; Masanetz et al., 1998; Masanetz and Grosch, 1998; Sigrist et al., 2001). The most abundant dietary source of furan-FAs is fish, followed by milk fat and (refined) soybean oil (Wendlinger and Vetter, 2014). Furan-FAs originate from algae, marine bacteria or plants, while their presence in animals arises from nutritional intake (Batna et al., 1993; Shirasaka et al., 1997; Spiteller, 2005). Antioxidative properties of these valuable, bioactive fatty acids (Spiteller, 2005; Vetter and Wendlinger, 2013) have been described in several studies (Lemke et al., 2014; Okada et al., 1996, 1990; Teixeira et al., 2013; Wakimoto et al., 2011). In plants, where furan-FAs are mainly bound to phospholipids, they can protect polyunsaturated fatty acids (PUFAs) from lipid peroxidation and thus, they may play an important role in the protection mechanism against oxidative stress (Mawlong et al., 2016; Spiteller, 2005).

Concentrations of furan-FAs in plants are rather low ranging from ~1–800 $\mu\text{g}/\text{g}$ dry matter (Hannemann et al., 1989; Masanetz et al.,

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1998; Masanetz and Grosch, 1998; Sigrist et al., 2001). Hence, they need to be selectively enriched. This can be achieved for example by urea fractionation or silver ion chromatography. Several studies focussing on furan-FAs in plants indicated a fast transformation into volatile secondary products. For instance, exposure of soybean oil to daylight led to a complete degradation of 9D5 and 11D5 (Guth and Grosch, 1997). The resulting (aromatic) photo-oxidation products can significantly contribute to the off-flavour of food (Guth and Grosch, 1991; Masanetz et al., 1998; Masanetz and Grosch, 1998; Sigrist et al., 2001). But despite the fact that processing and drying of food may degrade furan-FAs, information about their distribution in fresh aromatic plants and other (edible) green plants is rather scarce (Boselli et al., 2000; Hannemann et al., 1989).

As most previous studies focused on volatile secondary products of furan-FAs in dried green matrices, the aim of our study was to determine the concentrations and homologue patterns of furan-FAs in several fresh green matrices. Emphasis was also put on the detection of minor furan-FAs including unsaturated ones. Typically, three or four samples per matrix were analysed for this purpose. Furthermore, we were interested to see if noticeable differences occur in relatively similar matrices like fresh and deep-frozen spinach, as well as curly-leaf and flat-leaf parsley. In total, 35 green samples were transesterified and enriched using silver ion chromatography. Furan fatty acid methyl esters (furan-FAME) were then analysed by gas chromatography with mass spectrometry (GC/MS) operated in selected ion monitoring (SIM) mode.

2. Material and methods

2.1. Nomenclature

Furan fatty acids were abbreviated as furan-FAs instead of F-acids in order to exclude false interpretations by non-experts (e.g. fluorinated acids), as recently suggested to Müller et al. (2017) by the handling editor. Individual furan-FAs were abbreviated according to the short term notation by Vetter et al. (2012). Here, 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid is denoted as 11D5 and 12,15-epoxy-13,14-dimethyleicosa-12,14,16-trienoic acid is denoted as 11D5:1 (Fig. 1, Table 1).

2.2. Samples

Thirty-five samples were analysed in total. The set of samples, including 32 samples of sage (*Salvia officinalis*), dill (*Anethum graveolens*), chives (*Allium schoenoprasum*), marjoram (*Origanum majorana*), rosemary (*Rosmarinus officinalis*), curly-leaf parsley (*Petroselinum crispum* var. *crispum*), flat-leaf parsley (*Petroselinum crispum* var. *neapolitanum*), fresh and deep-frozen spinach (*Spinacia oleracea*), was purchased from different supermarkets located in Stuttgart, Germany. All samples originated from Germany, but no further information was given on the label. In addition, three individual grass samples were collected in Stuttgart (near the University of Hohenheim).

2.3. Chemicals and standards

Silica gel 60, AgNO₃ (≥99.5%) and myristic acid (14:0, ≥98%)

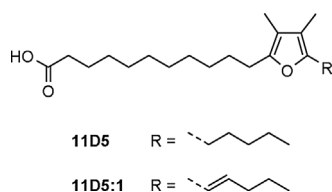


Fig. 1. Chemical structures of 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid (11D5) and 12,15-epoxy-13,14-dimethyleicosa-12,14,16-trienoic acid (11D5:1).

Table 1
Furan-FAs (tentatively) identified in the samples and the GC/MS parameters for their methyl esters.

furan-FA	chemical name	retention time t_R (min)	molecular ion (m/z)	base peak (m/z)	furan moiety fragment ion* (m/z)	identified by
9M5	10,13-epoxy-11-methyloctadeca-10,12-dienoic acid	21.96	322	165	109	reference standard
11M5	12,15-epoxy-13-methyleicosa-12,14-dienoic acid	26.73	350	165	109	reference standard
11D3	12,15-epoxy-13,14-dimethyloctadeca-12,14-dienoic acid	24.49	336	151	123	previous study**
9D5	10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoic acid	23.74	336	179	123	previous study**
11D5	12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid	28.54	364	179	123	reference standard
12D5	13,16-epoxy-14,15-dimethylheneicosa-13,15-dienoic acid	30.93	378	179	123	tentatively
9D5:1	10,13-epoxy-11,12-dimethyloctadeca-10,12,14-trienoic acid	26.46	334	177	135	tentatively
9:1D5	10,13-epoxy-11,12-dimethyloctadeca-8,10,12-trienoic acid	26.98	334	205	135	tentatively
11D5:1	12,15-epoxy-13,14-dimethyleicosa-12,14,16-trienoic acid	31.25	362	177	135	previous study**
11:1D5	12,15-epoxy-13,14-dimethyleicosa-10,12,14-trienoic acid	31.75	362	205	135	previous study**

* McLafferty ion in case of saturated furan-FAs.

** Reference: Wendlinger et al., 2016.

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