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Identification of fatty acids in edible wild plants by gas chromatography

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Abstract

The total lipidic content and the distribution of fatty acids in twenty edible wild plants in S.E. Spain was determined by GC. The lipidic content was higher than usual in the common vegetables. The high ratio of the $\omega 3$ series of unsaturated fatty acids relative to the $\omega 6$ series demonstrates the good nutritional qualities of these plants.

1. Introduction

The $\omega 3$ series of unsaturated fatty acids are present mainly in fish oils (cod, salmon, sardine, sole, etc.), whereas the $\omega 6$ series are more common in vegetable oils (seeds of grape, corn, sunflower, etc.). C₂₀ and C₂₂ fatty acids may reach ca. 30% of the total amount of triglycerides present in fish oils, but in vegetable oils the concentration of these fatty acids is usually lower than 1%. Higher homologues in the $\omega 6$ series are biogenetic precursors of some physiologically important thromboxanes, leukotrienes and prostaglandins, hormones which are related to the inflammatory response. Moreover, the nutritional value of these $\omega 3$ and $\omega 6$ acids is widely known for its beneficial effects in the prevention of several cardiovascular diseases [1].

The role of each of these acids in the mentioned activities is a matter of controversy. Linoleic acid (C18:2 ω 6) can be transformed in animal tissues into arachidonic acid (C20:4 ω 6),

ω6

ω3

 CH_3 - $(CH_2)_4$ -CH=CH- CH_2 -CH=CH- $(CH_2)_7$ -COOHLinoleic acid (C18:2 ω 6)

 $\label{eq:ch3} \text{CH}_3\text{-}\left(\text{CH}_2\right)_4\text{-}\left(\text{CH=CH-CH}_2\right)_3\text{-}\text{CH=CH-}\left(\text{CH}_2\right)_3\text{-}\text{COOH}$ Arachidonic acid (C20:4 ω 6)

 CH_3 - CH_2 - $(CH=CH-CH_2)_2$ -CH=CH- $(CH_2)_7$ -COOHLinolenic acid $(C18:3\omega3)$

CH₃-CH₂-(CH=CH-CH₂)₄-CH=CH-(CH₂)₃-COOH Eicosapentaenoic acid (C20:5ω3)

Fig. 1. Structures of $\omega 3$ and $\omega 6$ acids.

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but linolenic acid (C18:3 ω 3) cannot be transformed into eicosapentaenoic acid (C20:5 ω 3) (Fig. 1). On the other hand, the ω 3 fatty acids series is believed to have beneficial effects in the prevention of thrombosis and arterioscelerosis, mainly the eicosapentaenoic acid. This opens up the discussion on the essentiality of linolenic acid [2].

Of the above-mentioned acids, eicosapentaenoic acid has preventive and therapeutic effects in cardiovascular disease. Therefore, it would be healthy to enrich the daily diet in microalgae, which are rich in this compound. Among others, several attempts have been made with the alga *Nannochloropsis* [3].

The ratio (saturated fatty acids)/(ω 3 fatty acids), which should be low for "good quality",

and the ratio (ω 3 fatty acids)/(ω 6 fatty acids), which should be high, have been proposed as a means of measuring the quality of the fatty acids present in food [4,5].

The amount of lipids present in the most common vegetables is low, and the fatty acids of these lipids are mainly $\omega 3$ and $\omega 6$ with 16 and 18 carbons. On the other hand, the content in fatty acids present in edible wild plants has hardly been studied. A total of twenty wild vegetables have been reported to be used for human consumption in the area of this study (S.E. Spain) [6-9]. The seed is the most studied organ of these wild vegetables, such as goosefoot (Chenopodium album L.), plantain (Plantago major L.) and some species of amaranth (Amarantus sp.) [10-12], showing a content of

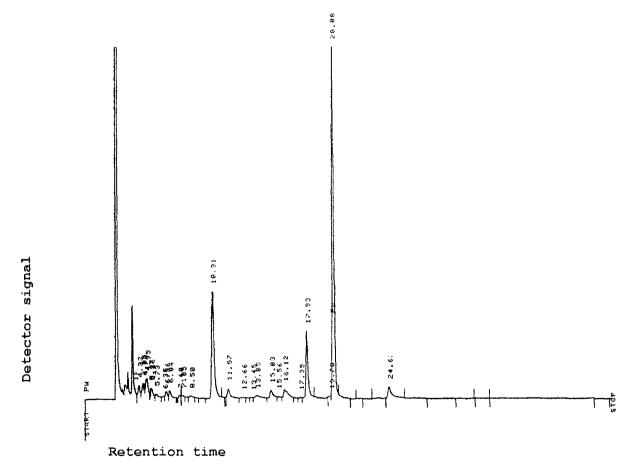


Fig. 2. Gas chromatogram of common mallow (Malva sylvestris L.) fatty acids.

lipids of ca. 10% and a distribution of fatty acids where those with 18 carbons of the $\omega 3$ and $\omega 6$ series prevail. Leaves have been studied in chickweed (*Stellaria media* Villars) [13], where α -linolenic acid was the major component at more than 50% of the total content of fatty acids.

One of these plants, purslane (Portulaca

oleracea L.), has been proposed as an alternative to fish oils owing to its richness in $\omega 3$ fatty acids [14,15]. In this plant a high percentage of fatty acids with 20 and 22 carbons was reported [14], but it was refuted later [17-20].

Our target was to determine the distribution of the fatty acids and the total content in lipids of

Table 1 Lipidic and C_{14} – C_{16} fatty acid percentage contents in edible wild plants

Species	Lipids (%) ^a	14:0	16:0	$16:3\omega 3$	$16:2\omega 6$	16:1ω7	16:1ω9
Amaranthus viridis L.	0.29 (85.93)	0.78	21.08	0.40	0.35	1.59	0.00
(amaranth)							
Beta maritima L.	0.22 (92.34)	0.81	22.56	0.45	0.42	3.87	0.52
(wild beet)							
Cakile maritima Scopoli	0.29 (72.67)	0.84	11.77	0.46	0.26	1.39	0.89
(sea rocket)							
Cardaria draba L.	0.31 (82.34)	1.97	19.18	0.72	7.82	1.94	0.00
(hoary cress)							
Chenopodium album L.	0.59 (87.55)	0.66	15.68	0.31	0.31	0.00	0.00
(goosefoot)							
Ch. murale L.	0.43 (88.13)	0.48	16.82	0.00	0.43	1.46	0.00
(goosefoot)							
Ch. opulifolium Schrader	0.40 (82.04)	0.95	15.10	0.62	1.47	0.00	2.84
(goosefoot)							
Crithmum maritimum L.	0.42 (89.79)	1.75	9.41	0.16	0.22	0.62	0.00
(rock samphire)							
Malva sylvestris L.	0.47 (83.72)	0.77	15.60	0.81	0.27	1.99	0.00
(common mallow)							
Parietaria diffusa Mert.	0.59 (83.43)	0.74	20.39	0.47	0.54	1.99	0.00
(pelitory-of-the-wall)							
Pichris echioides L.	0.16 (83.81)	0.67	17.60	0.62	0.17	1.75	0.00
(ox-tongue)							
Plantago major L.	0.18 (82.44)	1.79	15.90	1.00	0.43	1.47	0.12
(plantain)							
Portulaca oleracea L.	0.39 (89.04)	0.71	17.40	0.38	0.86	20.96	0.00
(purslane)							
Rumex crispus L.	0.24 (75.36)	0.48	12.32	0.87	0.24	0.00	1.93
(curly dock)							
Salicornia europaea L.	0.34 (94.11)	1.33	21.57	0.76	0.64	1.40	0.00
(glasswort)	, ,						
Sisymbrium irio L.	0.31 (71.03)	0.86	13.91	0.28	0.40	1.57	0.00
(hedge mustard)	, ,						
Sonchus oleraceus L.	0.75 (86.50)	1.77	19.07	0.56	0.13	0.00	0.00
(sow-thistle)	(,			0.00	0.10	0.00	0.00
Sonchus tenerrimus L.	0.52 (83.19)	9.54	16.14	0.55	3.60	1.53	4.08
(sow-thistle-of-the-wall)	· · · · · · · · · · · · · · · · · · ·		• • • •		2.00		
Stellaria media Villars	0.14 (84.75)	1.22	19.54	1.70	0.00	1.58	0.00
(chickweed)				1.70	0.00	1.50	0.00
Verbena officinalis L.	0.51 (92.75)	1.28	11.61	0.40	0.00	1.80	0.00
(vervain)	(> 2)	1.20		0.10	0.00	1.00	0.00

^a Identified percentage of fatty acids in parentheses.

these species, in order to establish the possible beneficial effects of consumption.

2. Experimental

Plant material harvested in different locations and at diverse growing stages were combined prior to analysis. Vegetable samples were washed with water and, after removing the remaining water, were dried, powdered and stored in a desiccator. Harvesting started in May 1990 and ended in June 1992. The total lipidic content was determined after extracting the dried plant in a Soxhlet apparatus with light petroleum.

Methyl esters were prepared by treatment of

Table 2 C_{18} fatty acid percentage contents in edible wild plants

Species	18:0	18:3ω3	18:4ω3	$18:2\omega 6$	18:3ω6	18:1ω7	18:1ω9
Amaranthus viridis L	3.30	24.34	0.00	20.24	0.25	0.33	8.60
(amaranth)							
Beta maritima L.	2.46	29.44	0.50	19.21	0.17	0.38	5.66
(wild beet)							
Cakile maritima Scopoli	2.08	23.84	0.38	9.29	0.00	0.71	1.00
(sea rocket)							
Cardaria draba L.	2.56	30.56	0.62	7.82	0.60	1.94	6.11
(hoary cress)							
Chenopodium album L.	1.69	44.82	0.17	15.86	0.00	0.00	2.90
(goosefoot)							
Ch. murale L.	1.66	36.04	0.14	17.86	0.00	0.55	6.96
(goosefoot)							
Ch. opulifolium Schrader	0.74	33.02	0.00	9.62	0.57	0.00	2.84
(goosefoot)							
Crithmum maritimum L.	1.49	9.98	0.42	12.03	0.25	0.00	16.11
(rock samphire)							
Malva sylvestris L.	2.07	42.22	0.29	10.40	0.50	1.14	1.73
(common mallow)							
Parietaria diffusa Mert.	2.46	21.18	3.64	18.70	1.99	0.00	5.05
(pelitory-of-the-wall)							
Pichris echioides L.	1.27	43.20	0.20	10.86	0.42	0.00	3.61
(ox-tongue)							
Plantago major L.	2.12	33.32	2.02	11.18	0.00	0.00	2.32
(plantain)							
Portulaca oleracea L.	3.46	32.60	0.00	16.82	0.27	0.74	5.89
(purslane)							
Rumex crispus L.	1.10	41.21	1.73	10.35	0.00	0.06	1.08
(curly dock)							2.00
Salicornia europaea L.	2.85	28.03	0.44	23.49	0.55	1.47	4.42
(glasswort)							
Sisymbrium irio L.	1.31	31.04	0.19	8.39	0.00	1.40	1.30
(hedge mustard)							1.00
Sonchus oleraceus L.	1.84	43.58	0.09	8.10	0.34	0.00	2.15
(sow-thistle)						0.00	2.10
Sonchus tenerrimus L.	0.73	30.33	0.11	8.70	0.35	0.00	4.08
(sow-thistle-of-the-wall)				~		5.55	1.00
Stellaria media Villars	2.80	22.75	4.68	1.93	2.40	0.00	5.68
(chickweed)	-	<u>-</u> _		****		0.00	2.00
Verbena officinalis L. (vervain)	2.21	54.99	0.00	5.67	0.25	0.00	6.49

the crude extract with acetyl chloride and methanol (both from Sigma, Madrid, Spain) [21,22]. The resulting mixture was analysed by GC, the methyl esters of the fatty acids being identified by comparison of their retention times with those for standards (Rapeseed oil mix and PUFAS-1 from Sigma), using a Hewlett-Packard HP5890 Series II chromatograph provided with a flame

ionization detector and HP3394 integrator. A Supelco SP2330 capillary column of fused silica of high polarity was used (30 m \times 0.25 mm I.D.; film thickness 0.2 μ m). The flow-rate of the carrier gas (nitrogen) was 0.8 l/min, the splitting ratio in the injector was 100:1, the injector and detector temperatures were 220°C, the oven temperature was initially 150°C, increased at

Table 3 C_{20} fatty acid percentage contents in edible wild plants

Species	20:0	20:5ω3	20:3ω6	20:4ω6	20:1ω9
Amaranthus viridis L.	0.57	0.93	0.24	0.00	0.00
(amaranth)					
Beta maritima L.	0.28	0.54	0.22	0.52	0.36
(wild beet)					
Cakile maritima Scopoli	4.30	0.09	0.18	0.00	0.00
(sea rocket)					
Cardaria draba L.	0.96	2.16	0.00	0.56	0.00
(hoary cress)					
Chenopodium album L.	0.23	0.36	0.17	1.30	0.00
(goosefoot)					
Ch. murale L.	0.72	0.41	0.00	1.01	0.00
(goosefoot)					
Ch. opulifolium Schrader	0.00	3.06	0.57	0.00	0.00
(goosefoot)					
Crithmum maritimum L.	1.38	0.76	0.00	0.00	0.54
(rock samphire)					
Malva sylvestris L.	1.04	0.00	1.23	5.30	0.00
(common mallow)					
Parietaria diffusa Mert.	1.17	0.00	1.50	0.00	0.00
(pelitory-of-the-wall)					
Pichris echioides L.	1.04	0.00	0.00	0.00	0.00
(ox-tongue)					
Plantago major L.	1.31	1.27	0.00	1.02	0.00
(plantain)					
Portulaca oleracea L.	0.87	0.00	0.00	0.00	0.00
(purslane)	0.07	0.00	0.00	0.00	3.00
Rumex crispus L.	0.50	0.12	0.00	0.00	1.08
(curly dock)	0.50	0.12	0.00	0.00	1.00
Salicornia europaea L.	2.44	0.39	0.00	0.00	0.00
(glasswort)	2.44	0.57	0.00	0.00	0.00
Sisymbrium irio L.	0.19	0.55	0.00	0.32	0.00
(hedge mustard)	0.19	0.55	0.00	0.32	0.00
Sonchus oleraceus L.	1.48	0.35	0.11	0.00	0.15
(sow-thistle)	1.46	0.55	0.11	0.00	0.15
Sonchus tenerrimus L.	0.65	0.00	0.10	1.83	0.00
(sow-thistle-of-the-wall)	0.05	0.00	0.10	1.65	0.00
Stellaria media Villars	0.00	0.42	0.00	0.41	0.00
	0.00	0.42	0.00	0.41	0.00
(chickweed)	0.45	0.40	0.00	0.62	2.75
Verbena officinalis L.	0.65	0.60	0.00	0.62	2.13
(vervain)					

 3° C/min to 190° C (held for 21 min), the injection volume was 2 μ l, every two analyses a blank was run and the area integration method was used.

Unknown peaks were not considered in further calculations. All the experiments were repeated at least twice and the average values are given here. Fig. 2 shows a typical chromatogram (common mallow).

3. Results and discussion

The total lipidic content, referred to fresh plant weight, is presented in Table 1. The percentages of fatty acids for all the plants studied are given in Tables 1–4. Fig. 3 shows the ratio of the different series of fatty acids.

It is remarkable that the total amounts of

Table 4 C_{22} – C_{24} fatty acid percentage contents in edible wild plants

Species	22:0	22:5ω3	22:6ω3	22:4ω6	22:1ω9	22:1ω11	24:0
Amaranthus viridis L.	1.75	0.00	0.00	0.00	0.00	0.00	1.18
(amaranth)					0.00	0.00	0.50
Beta maritima L.	0.92	0.49	0.65	1.34	0.00	0.00	0.59
(wild beet)	2.42	0.00	0.00	0.27	9.53	0.00	2.97
Cakile maritima Scopoli	2.42	0.00	0.00	0.27	9.53	0.00	2.91
(sea rocket) Cardaria draba L.	1.58	0.00	0.00	0.00	1.23	0.00	1.24
(hoary cress)	1.56	0.00	0.00	0.00	1.23	0.00	1.27
Chenopodium album L.	1.00	0.00	0.00	0.00	0.00	0.00	0.61
(goosefoot)	1.00	0.00	0.00	0.00	0.00	0.00	0.0-
Ch. murale L.	1.37	0.00	0.00	0.00	0.00	0.00	2.22
(goosefoot)		0.00					
Ch. opulifolium Schrader	1.52	0.74	2.30	0.00	0.00	1.91	4.84
(goosefoot)							
Crithmum maritimum L.	4.24	0.76	0.00	0.00	0.00	28.03	1.64
(rock samphire)							
Malva sylvestris L.	0.00	0.00	0.00	0.27	0.00	0.44	0.65
(common mallow)							
Parietaria diffusa Mert.	1.39	0.00	0.00	0.00	0.00	0.00	2.22
(pelitory-of-the-wall)							
Pichris echioides L.	1.64	0.15	0.00	0.00	0.00	0.15	0.46
(ox-tongue)							
Plantago major L.	1.31	0.00	1.47	0.00	3.45	0.00	0.98
(plantain)						0.00	0.40
Portulaca oleracea L.	3.33	0.00	0.00	0.00	0.00	0.00	0.49
(purslane)		0.00	0.00	0.00	0.00	0.40	0.24
Rumex crispus L.	0.61	0.00	0.00	0.00	0.00	0.42	0.34
(curly dock)	2.45	0.00	0.00	1 00	0.00	0.00	0.00
Salicornia europaea L.	2.45	0.00	0.00	1.88	0.00	0.00	0.00
(glassswort) Sisymbrium irio L.	0.37	0.21	0.83	0.00	1.69	1.73	4.51
(hedge mustard)	0.57	0.21	0.65	0.00	1.09	1.75	7.51
Sonchus oleraceus L.	3.01	0.25	0.00	0.27	0.00	0.00	1.42
(sow-thistle)	5.01	0.23	0.00	0.27	0.00	0.00	
Sonchus tenerrimus L.	0.75	0.38	0.00	1.83	0.00	0.00	1.99
(sow-thistle-of-the-wall)	V/ / L/	0.50	0.00	1.00	0.00		
Stellaria media Villars	1.34	0.00	0.00	0.00	0.00	0.00	3.30
(chickweed)	***	20 - 20 - 20					
Verbena officinalis L.	1.00	0.00	0.00	0.62	0.00	0.00	1.25
(vervain)							

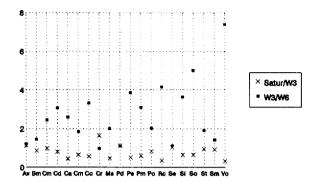


Fig. 3. Ratios between fatty acid series. Av = Amaranthus viridis; Bm = Beta maritima; Cm = Cakile maritima; Cd = Cardaria draba; Ca = Chenopodium album; Cm = Chenopodium murale; Co = Chenopodium opulifolium; Cr = Crithmum maritimum; Ms = Malva sylvestris; Pd = Parietaria diffusa; Pe = Pichris echioides; Pm = Plantago major; Po = Portulaca oleracea; Rc = Rumex crispus; Se = Salicornia europaea; Si = Siymbrium irio; So = Sonchus oleraceus; St = Sonchus tenerrimus; Sm = Stellaria media; Vo = Verbena officinalis.

lipids in the edible wild plants studied are higher than in more common vegetables. Sow-thistle (Sonchus oleraceus L.) has the highest values, with 0.75 g per 100 g of plant. Other plants also with high values were goosefoot (Chenopodium album L.), pellitory-of-the-wall (Parietaria diffusa Mert. & Koch) and sow-thistle-of-the-wall (Sonchus tenerrimus L.). Analyses showed a low content of lipids for chickweed (Stellaria media Villars), ox-tongue (Picris echioides L.) and plantain (Plantago major L.), with values under 0.2 g per 100 g.

The fatty acids of these lipidic fractions are, in general, mainly unsaturated, the highest value being 74.54%. Vervain (*Verbena officinalis* L.) showed the highest ratios of polyenic acids. 63.50%. Glasswort (*Salicornia europaea* L.) and sow-thistle-of-the-wall (*Sonchus tenerrimus* L.) showed ca. 30% of saturated fatty acids.

The highest content of monoenoic acids was found in rock samphire (*Crithmum maritimum* L.), which also had the lowest content of polyenoic acids. The lowest content of these acids was for common mallow (*Malva sylvestris* L.). with 2.31%. In the ω 3 series with 20 and 22 carbons, goosefoot (*Chenopodium opulifolium* Schraeder) had the highest value, 3%. The low

saturated/ ω 3 ratio and the high ω 3/ ω 6 ratio indicate good nutritional qualities with respect to fatty acids in these plants, especially in vervain.

In view of these results, we believe that it would be of interest to grow these species, in order to develop a genetic selection that would increase the ratio of $\omega 3$ and $\omega 6$ fatty acids, and use them for human consumption or as a source of the above-mentioned fatty acids.

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