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The Component Acids of Icelandic Herring Oil

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Abstract: A sample of Icelandic herring oil has been analysed for component acids with the following results (wt. %): Saturated acids: Myristic 6.6, palmitic 12.3, stearic 1.3 and arachidic 0.3. Unsaturated acids: C_{14} (2.0 H) 1.6, C_{16} (2.6 H) 11.3, C_{18} (4.0 H) 20.9, C_{20} (4.7 H) 26.4, C_{22} (4.1 H) 19.3.

The component acids of herring oil have been determined previously by Lovern (1) and by Ó. B. Bjarnason and M. L. Meara (2) in their work on the component glyserides of herring oil. The main constituents of the oil are C_{16}, C_{18}, C_{20} and C_{22} — unsaturated acids — and saturated C_{14} and C_{16}.

The sample analysed by the author was kindly provided by the firm Alliance h.f. The analytical characteristics of the sample were as follows: Saponification equivalent 301.4, iodine value (Wijs) 140.0, unsaponifiable matter 1.2% (by weight), free fatty acid 2.9% (as oleic).

The determination of the component fatty acids was carried out as follows: 400 g of the oil were saponified by refluxing with alcoholic potassium hydroxide for ca. 1 hour, the alcohol distilled off and, after dilution with distilled water, most of the unsaponifiable matter extracted with ether. The acids (375.3 g) were then dissolved in acetone (4 ml pr. g of acids) and the hot solution titrated with a 4 N solution of lithium hydroxide until just alkaline to phenolphthalein. The lithium soaps were converted into acids and esterified, whereupon the esters were fractionally distilled through an EHP-column described by Longenecker (3). The acids from the insolube lithium-salts were then submitted to a lead-salt-alcohol-separation. Each of the acid groups was then esterfied and fractionated by distillation in vacuo. The exact procedure is described by Hilditch (4) and Hilditch and Maddison (5).

The results of the lithium- and lead-salt-separation are given in Table I.

Table I

Li-salt-acetone- and Pb-salt-alcohol-separation

			Corresponding esters	
	g	%	S. E.	I.V.
Acids from insoluble lead salts	97.6	25.8	286.8	36.5
— — soluble lead salts	186.4	49.2	297.7	96.1
— — soluble lithium salts	91.2	24.1	309.0	306.1
Unsaponifiable matter extracted ..	3.6	0.9		(116.8)

The distillation of each methyl ester group together with the calculated composition of each fraction is given in Table II A—C.

The deduced iodine values and saponification equivalents in each group of unsaturated esters were the following:

	Group A Esters from insol. Pb-salts			Group B Esters from sol. Pb-salts			Group C Esters from sol. Li-salts	
	S.E.	I.V.		S.E.	I.V.		S.E.	I.V.
C_{14}	240.0	105.8	C_{14}	240.0	105.8	C_{14}	240.0	105.8
C_{16}	268.0	94.8	C_{16}	268.0	94.8	C_{16}	266.6	162.0
C_{18}	296.0	85.8	C_{18}	295.1	124.8	C_{18}	291.5	283.2
C_{20}	324.0	78.4	C_{20}	323.2	110.0	C_{20}	316.8	368.6
C_{22}	351.8	79.5	C_{22}	351.5	90.3	C_{22}	343.3	395.8

The composition of the individual ester fractions were calculated from their iodine values and saponification equivalents, it being assumed following Hilditch and Maddison (5), that fractions with comparatively low iodine values are mixtures of 2 saturated and 2 unsaturated esters, where S.E. of saturated esters = S.E. of unsaturated esters = S.E. of fraction.

The final results of the calculation of the component acids in each group together with the component acids of the whole fat are shown in Table III.

Table II. A.

Methyl esters of acids from alcohol-insoluble lead salts

Fraction No.	Wt. g	Boiling points °C	S. E.	I. V.	Calculated composition of ester-fractions: Saturated C_{14}	Saturated C_{16}	Saturated C_{18}	Saturated C_{20}	Unsaturated C_{14} (-2.0H)	Unsaturated C_{16} (-2.0H)	Unsaturated C_{18} (-2.0H)	Unsaturated C_{20} (-2.0H)	Unsaturated C_{22} (-2.2H)	N-S
1	3.49	102—108	242.5	1.7	3.36	0.07	—	—	0.05	0.01	—	—	—	—
2	3.25	108—109	245.7	2.1	2.72	0.46	—	—	0.05	0.02	—	—	—	—
3	4.41	109—115	251.7	3.8	2.67	1.58	—	—	0.09	0.07	—	—	—	—
4	4.76	115—117	255.6	4.2	2.22	2.34	—	—	0.08	0.12	—	—	—	—
5	6.36	117—121	263.0	6.0	1.39	4.61	—	—	0.06	0.30	—	—	—	—
6	8.12	121	264.0	7.1	1.48	6.04	—	—	0.08	0.52	—	—	—	—
7	5.72	121—125	265.6	7.2	0.76	4.53	—	—	0.03	0.40	—	—	—	—
8	7.91	126—130	271.3	13.4	—	6.43	0.35	—	—	0.99	0.14	—	—	—
9	8.78	130—133	275.9	21.4	—	5.21	1.53	—	—	1.43	0.61	—	—	—
10	5.53	133—141	283.2	37.1	—	1.63	1.61	—	—	0.99	1.30	—	—	—
11	3.54	141—150	295.5	57.4	—	0.10	1.07	—	—	0.05	2.32	—	—	—
12	6.48	155—162	321.0	72.3	—	—	0.09	0.47	—	—	0.59	5.33	—	—
13	8.00	162—170	336.5	74.8	—	—	—	0.37	—	—	—	3.91	3.72	—
14	13.43	170—176	350.8	78.0	—	—	—	0.06	—	—	—	0.40	12.97	—
15	4.61	Residue	352.8	82.2	—	—	—	—	—	—	—	0.12	4.47	0.02
	94.39				Weights 14.60	33.08	4.65	0.90	0.44	4.90	4.96	9.76	21.16	0.02
No. 15. Esters freed from unsaponifiable matter, S. E. 351.0.					% Esters. 15.5	35.0	4.9	0.9	0.5	5.2	5.3	10.3	22.4	Trace
					% Acids. 15.3	34.9	4.9	0.9	0.5	5.2	5.3	10.4	22.6	Trace

Table II B

Methyl esters of acids from alcohol-soluble lead salts

Fraction No.	Wt. g	Boiling points °C	S. E.	I. V.	Calculated composition of ester-fractions: Saturated C_{14}	Saturated C_{16}	Unsaturated C_{14} (-2.0H)	Unsaturated C_{16} (-2.0H)	Unsaturated C_{18} (-2.9H)	Unsaturated C_{20} (-2.8H)	Unsaturated C_{22} (-2.5H)	N-S
1	4.98	106—110	247.4	18.9	3.36	0.89	0.52	0.21	—	—	—	—
2	6.86	110—113	251.3	39.3	2.69	1.50	1.52	1.15	—	—	—	—
3	5.45	113—115	258.0	51.9	1.03	1.54	0.96	1.92	—	—	—	—
4	3.50	115—120	260.4	60.0	0.43	0.92	0.54	1.61	—	—	—	—
5	5.04	120—122	263.2	68.8	0.32	1.12	0.53	3.07	—	—	—	—
6	7.93	122—131	269.1	76.6	0.05	1.84	—	4.85	1.19	—	—	—
7	8.47	131—140	282.3	97.8	—	1.21	—	2.69	4.57	—	—	—
8	10.36	140—143	289.2	113.1	—	0.60	—	1.57	8.19	—	—	—
9	10.16	143—145	293.4	115.0	—	—	—	0.57	9.59	—	—	—
10	10.99	145—152	300.9	120.0	—	—	—	—	8.55	2.44	—	—
11	11.00	152—161	312.7	116.0	—	—	—	—	3.88	7.12	—	—
12	14.29	161—167	321.7	112.2	—	—	—	—	0.70	13.59	—	—
13	9.30	167—170	326.0	107.1	—	—	—	—	—	8.31	0.99	—
14	12.31	170—175	335.6	96.1	—	—	—	—	—	6.66	5.65	—
15	11.51	175	338.7	95.1	—	—	—	—	—	4.97	6.54	—
16	9.53	175—182	345.6	92.5	—	—	—	—	—	1.89	7.64	—
17	7.72	Residue	352.6	127.8	—	—	—	—	—	0.68	6.96	0.08
	149.40				Weights	7.88	9.62	4.07	17.64	36.67	45.66	27.78	0.08
No. 17. Esters freed from unsaponifiable matter, S.E. 348.8					% Esters	5.3	6.4	2.7	11.8	24.5	30.6	18.6	0.1
					% Acids	5.2	6.4	2.7	11.7	24.5	30.7	18.7	0.1

Table II C

Methyl esters of acids from acetone-soluble lithium salts

Fraction No.	Wt. g	Boiling points °C	S. E.	I. V.	Calculated composition of ester-fractions: Unsaturated C_{14} (−2,0H)	C_{16} (−3,4H)	C_{18} (−6,5H)	C_{20} (−9,2H)	C_{22} (−10,7H)	N-S
1	2.80	112—123	261.3	124.2	0.51	2.29	—	—	—	—
2	6.24	125—130	269.6	163.6	—	5.40	0.84	—	—	—
3	5.58	130—138	274.7	200.0	—	3.65	1.93	—	—	—
4	8.74	138—140	283.8	240.8	—	2.54	6.20	—	—	—
5	8.60	140—145	292.6	285.6	—	—	8.20	0.40	—	—
6	11.08	145—148	304.4	346.7	—	—	5.19	5.89	—	—
7	10.04	148—158	311.3	366.2	—	—	2.04	8.00	—	—
8	8.20	158—162	322.1	376.3	—	—	—	6.45	1.75	—
9	7.94	162—170	329.5	386.0	—	—	—	3.97	3.97	—
10	6.64	170	342.2	358.1	—	—	—	2.78	3.65	0.21
11	5.46	Residue	402.5	198.5	—	—	—	0.51	4.10	0.85
	81.32				Weights	0.51	13.88	24.40	28.00	13.47	1.06
No. 10. Esters freed from unsaponifiable matter, S.E. 331.3					% Esters.	0.6	17.1	30.0	34.4	16.6	1.3
No. 11. Esters freed from unsaponifiable matter, S.E. 339.9					% Acids.	0.6	16.9	29.9	34.5	16.7	1.4

Table III

The component acids of herring oil

Acids	From Insol.Pb-salts (Group A) (25.8%)	From Sol.Pb-salts (Group B) (49.2%)	From Sol.Li-salts (Group C) (24.1%)	N-S (0.9%)	Total	Component acids wt.%	Component acids mol.%	Component acids Mean unsaturation
Myristic	3.95	2.57	—	—	6.52	6.6	8.2	—
Palmitic	8.99	3.15	—	—	12.14	12.3	13.6	—
Stearic	1.27	—	—	—	1,27	1.3	1.3	—
Arachidic	0.25	—	—	—	0.25	0.3	0.2	—
Unsaturated C_{14}	0.12(—2.0 H)	1.32(—2.0 H)	0.15(—2.0 H)	—	1.59	1.6	2.0	— 2.0 H
— C_{16}	1.33(—2.0 H)	5.78(—2.0 H)	4.08(—3.4 H)	—	11.19	11.3	12.7	— 2.6 H
— C_{18}	1.36(—2.0 H)	12.06(—2.9 H)	7.21(—6.5 H)	—	20.63	20.9	21.2	— 4.0 H
— C_{20}	2.68(—2.0 H)	15.08(—2.8 H)	8.31(—9.2 H)	—	26.07	26.4	24.4	— 4.7 H
— C_{22}	5.84(—2.2 H)	9.21(—2.5 H)	4.02(–10.7 H)	—	19.07	19.3	16.4	— 4.1 H
Unsaponifiable	0.01	0.03	0.33	0.90	1.27			

Analytical characteristics of oil.

	Calculated from data in Table III	Determined on original oil
S.E.	300.2	301.4
I.V.	129.8	140.0

The results resemble fairly closely the following results found by Ó. B. Bjarnason and M. L. Meara (2): Saturated C_{12} 0.1, C_{14} 7.0. C_{16} 11.7, C_{18} 0.8, C_{20} 0.1 wt.%. Unsaturated C_{14} 1.2(—2.0), C_{16} 11.8(—2.4), C_{18} 19.6(—3.5), C_{20} 25.9(—5.2), C_{22} 21.6(—4.3), C_{24} 0.1(—3.8) wt.%.

In the present sample however none of the C_{12} or C_{24} — acids have been found.

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