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Composition Characterization of Fatty Acid Zinc Salts by Chromatographic and NMR Spectroscopic Analyses on their Fatty Acid Methyl Esters

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Supplementary Materials

The supplementary data consist of the following Tables S1-S3 and Picture S1 :

Table S1. Retention times and concentrations of 37 FAMEs in the standard solution.
Table S2. Calculation of total fatty acids from GC-MS analysis on FAMEs using an internal standard method (an example with FAMEs from industrial chemical B)
Table S3. ^{1}H NMR data of (a) the hydrolysed products and (b) the methyl esterified products from fatty acid zinc salts.

Picture S1: Pictures of white precipitation formed in a clear aqueous solution of aqueous work-up solution in 2.3.3.1 upon increase of alkalinity suggesting the formation of $Zn(OH)_2$. The same phenomenon was observed in the aqueous work-up solution in 2.3.1.

Table S1: Retention times and concentrations of 37 FAMEs in the standard solution.

Peak No.	RT (min)	Substance Name	Carbon : Double Bond	CAS No.	Certified Conc. (%)	U_{CRM} (%)
1	12.21	Methyl butyrate	C4:0	623-42-7	4.00	± 0.021
2	14.30	Methyl hexanoate	C6:0	106-70-7	4.00	± 0.021
3	17.91	Methyl octadecanoate	C8:0	111-11-5	4.00	± 0.021
4	22.84	Methyl decanoate	C10:0	110-42-9	4.00	± 0.021
5	25.51	Methyl undecanoate	C11:0	1731-86-8	2.00	± 0.011
6	28.20	Methyl laurate	C12:0	111-82-0	4.00	± 0.021
7	30.82	Methyl tridecanoate	C13:0	1731-88-0	2.00	± 0.011
8	33.36	Methyl myristate	C14:0	124-10-7	4.00	± 0.021
9	35.39	Methyl myristoleate	C14:1	56219-06-8	2.00	± 0.011
10	35.78	Methyl pentadecanoate	C15:0	7132-64-1	2.00	± 0.011
11	37.76	Methyl *cis*-10-pentadecenoate	C15:1	90176-52-6	2.00	± 0.011
12	38.13	Methyl palmitate	C16:0	112-39-0	6.00	± 0.032
13	39.72	Methyl *cis*-9-hexadecenoate	C16:1	1120-25-8	2.00	± 0.011
14	40.31	Methyl heptadecanoate	C17:0	1731-92-6	2.00	± 0.011
15	41.89	Methyl *cis*-10-heptadecenoate	C17:1	75190-82-8	2.00	± 0.011
16	42.46	Methyl stearate	C18:0	112-61-8	4.00	± 0.021
17	43.39	Methyl *trans*-9-eladate	C18:1n9t	1937-62-8	2.00	± 0.011
18	43.80	Methyl *cis*-9-oleate	C18:1n9c	112-62-9	4.00	± 0.021
19	44.87	Methyl linolelaidate	C18:2n6t	2566-97-4	2.00	± 0.011
20	45.75	Methyl linoleate	C18:2n6c*	112-63-0	2.00	± 0.011
21	46.44	Methyl arachidate	C20:0	1120-28-1	4.00	± 0.021
22	47.20	Methyl γ-linolenate	C18:3n6	16326-32-2	2.00	± 0.011
23	47.66	Methyl *cis*-11-eicosenoate	C20:1n9	2390-09-02	2.00	± 0.011
24	47.97	Methyl linolenate	C18:3n3	301-00-8	2.00	± 0.011
25	48.28	Methyl heneicosanoate	C21:0	6064-90-0	2.00	± 0.011
26	49.52	Methyl *cis*-11,14-eicosadienoate	C20:2	2463-02-07	2.00	± 0.011
27	50.11	Methyl behenate	C22:0	929-77-1	4.00	± 0.021
28	50.87	Methyl *cis*-8,11,14-eicosatrienoate	C20:3n6	21061-10-9	2.00	± 0.011
29	51.27	Methyl *cis*-13-docosenoate	C22:1n9	1120-34-9	2.00	± 0.011
30	51.60	Methyl *cis*-11,14,17-eicosatrienoate	C20:3n3	55682-88-7	2.00	± 0.011
31	51.83	Methyl tricosanate	C23:0	2433-97-8	2.00	± 0.011
32	51.92	Methyl *cis*-5,8,11,14-eicosatetraenoate	C20:4n6	2566-89-4	2.00	± 0.011
33	53.09	Methyl *cis*-13,16-docosadienoate	C22:2	61012-47-3	2.00	± 0.011
34	53.64	Methyl tetracosanoate	C24:0	2442-49-1	4.00	± 0.021
35	54.20	Methyl *cis*-5,8,11,14,17-eicosapentaenoate	C20:5n3	2734-47-6	2.00	± 0.011
36	54.87	Methyl *cis*-15-tetracosenoate	C24:1n9	2733-88-2	2.00	± 0.011
37	59.66	Methyl *cis*-4,7,10,13,16,19-docosahexaenoate	C22:6n3	2566-90-7	2.00	± 0.011

* C18:2n6c : C18 fatty acid with 2 adjacent cis double bonds starting at C6 counting from the methyl group.

Table S2: Calculation of total fatty acids from GC-MS analysis on FAMEs using an internal standard method (an example with FAMEs from industrial chemical B)

Peak No	RT (min)	Carbon : Double Bond	R_{fi} [a]	P_{ti}	W_{FAMEi} [b]	f_{FAi} [c]	FA (%)	Normalized (%)
5	25.5	C11:0	-	8,982,706	-	0.9300	-	Internal Standard
6	28.2	C12:0	1.0821	4,125,829	0.4294	0.9346	2.56	2.62
8	33.4	C14:0	1.1433	374,575	0.0369	0.9421	0.22	0.23
12	38.1	C16:0	1.1524	7,761,990	0.7586	0.9481	4.58	4.69
16	42.5	C18:0	1.1921	4,000,594	0.3780	0.9530	2.29	2.35
17	43.4	C18:1n9t	1.1650	1,260,657	0.1219	0.9527	0.74	0.76
18	43.8	C18:1n9c	1.1982	133,218,285	12.5225	0.9527	75.99	77.84
20	45.8	C18:2n6c	1.1005	18,095,281	1.8519	0.9524	11.23	11.51
			total				97.62	100

[a,b] R_{fi} and W_{FAMEi} were calculated according to the eqn (1) and (2), respectively.
[b] $f_{FA\,i}$: Conversion factor (fatty acid methyl ester to the corresponding fatty acid)

$$W_{FAMEi} = \frac{P_{ti} * W_{tC11:0} \times 1.0067}{P_{tC11:0} \times R_{fi}} \quad \text{……..eqn (S1)}$$

W_{FAMEi} : Content of each fatty acid methyl ester in test solution
P_{ti} : Peak area of each fatty acid methyl ester in test solution
$W_{tC11:0}$: Weight of internal standard (triundecanoin) added to test portion
1.0067 : Conversion of internal standard (triundecanoin) from triglyceride to FAME
$P_{tC11:0}$: Peak area of internal standard (methyl undecanoate) in test solution
R_{fi} : Response factor of each fatty acid methyl ester

$$R_{fi} = \frac{P_{Si} \times W_{C11:0}}{P_{SC11:0} \times W_i} \quad \text{……..eqn (S2)}$$

P_{Si} : Peak area of each fatty acid methyl ester in standard solution
$P_{SC11:0}$: Peak area of internal standard (methyl undecanoate) in standard solution
$W_{C11:0}$: Weight of internal standard (methyl undecanoate) in standard solution (mg)
W_i : Weight of each fatty acid methyl ester in standard solution (mg)

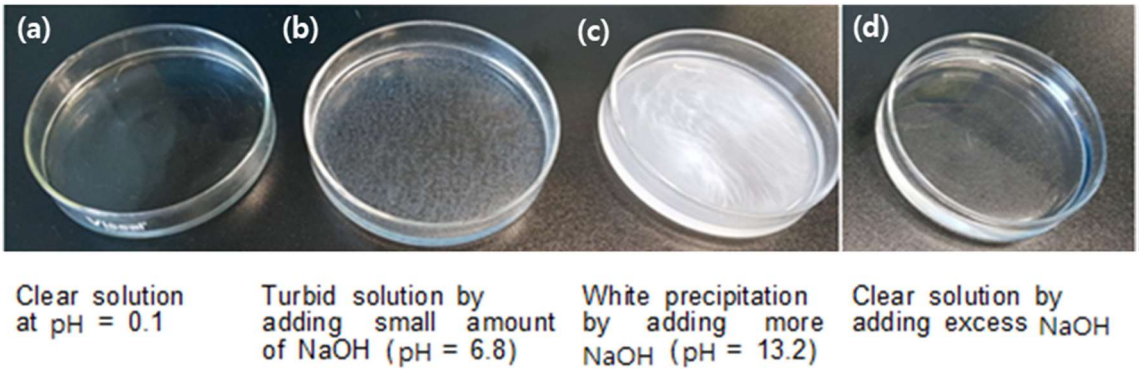
Table S3 : ^{1}H NMR data of (a) the hydrolysed products and (b) the methyl esterified products from fatty acids zinc salts.

(a) Hydrolysed products from fatty acids zinc salts

Peak No.	1.Industrial Chemical A Hydrolyzed (in DMSO-d6)	2.Industrial Chemical B Hydrolysed (in DMSO-d6)	Multiplicity	Assignments
	Chemical shift, ppm (Integration)			
1	0.85 (3.0)	0.85 (3.0)	Triplet (J=8.0Hz)	Protons of terminal methyl
2	1.16-1.36 (22.6)	1.18-1.36 (19.8)	Multiplet	CH_2 of long chain alkyl
3	1.48 (2.0)	1.48 (2.1)	Quintet (J=6.8Hz)	CH_2 of C3
4	1.91-2.04 (2.1)	1.92-2.04 (3.6)	Multiplet	CH_2-Allylic protons
5	2.17 (2.0)	2.17 (2.0)	Triplet (J=7.6Hz)	CH_2 of C2 (α to COOH)
6	2.65-2.76 (0.19)	2.66-2.77 (0.24)	Multiplet	CH_2-bis-allylic protons
7	-	-	-	-
8	5.27-5.38 (1.2)	5.27-5.38 (2.0)	Multiplet	Olefinic protons
9	11.94 (1.0)	11.94 (0.9)	Singlet	Proton of carboxyl acid

(b) Methyl esterified products from fatty acids zinc salts

Peak No.	1.Industrial Chemical A Methyl Esterified (in $CDCl_3$)	2.Industrial Chemical B Methyl Esterified (in DMSO-d6 + $CDCl_3$)	Multiplicity	Assignments
	Chemical shift, ppm (Integration)			
1	0.86 (3.0)	0.85 (3.0)	Triplet (J=8.0Hz)	Protons of terminal methyl
2	1.15-1.36 (22.2)	1.16-1.35 (19.8)	Multiplet	CH_2 of long chain alkyl
3	1.59 (2.0)	1.51 (2.1)	Quintet (J=6.8Hz)	CH_2 of C3
4	1.96-2.05 (2.0)	1.92-2.03 (3.6)	Multiplet	CH_2-Allylic protons
5	2.28 (2.0)	2.26 (2.0)	Triplet (J=7.6Hz)	CH_2 of C2 (α to $COOCH_3$)
6	2.56-2.87 (0.17)	2.66-2.76 (0.23)	Multiplet	CH_2-bis-allylic protons
7	3.64 (2.8)	3.57 (3.0)	Singlet	Methoxy(OCH_3) protons
8	5.27-5.39 (1.1)	5.25-5.36 (2.0)	Multiplet	Olefinic protons
9	-	-	-	-



Picture S1: Pictures of white precipitation formed in a clear aqueous solution of aqueous work-up solution in 2.3.3.1 upon increase of alkalinity suggesting the formation of $Zn(OH)_2$. The same phenomenon was observed in the aqueous work-up solutions in 2.3.1.