Rapid and Simple Method for the Simultaneous Determination of Glycidol and 3-MCPD Fatty Acid Ester in Edible Oils by LC/MS-MS

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Introduction

3-Monochloro-1,2-propanediol (3-MCPD), a known food processing contaminant, is detected in various types of food, such as acid-hydrolyzed vegetable proteins, soy sources, crackers, meat products. Recently, it has been reported that some edible oils contain relatively high levels of 3-MCPD and/or 3-MCPD fatty acid esters(3-MCPDEs). Furthermore, the Chemical and Veterinary Test Agency (CVUA) Stuttgart detected glycidol fatty acid esters (GEs) in refined vegetable oils, which seems to be one reason why high levels of 3-MCPD and/or 3-MCPDEs occur in the oils. However, there is no analytical method simultaneous determination of GEs and 3-MCPDs for reliable risk assessment. This work describes a novel analytical method for the simultaneous determination of GEs and 3-MCPDEs by LC/MS-MS and LC/TOFMS.

Experimental

Instruments

Table.1 LC/MSMS condition for GEs and 3-MCPDEs

HPLC	: Agilent 1290
Column	: ZORBAX Eclipse plus C8 (100mm,2.1mm,1.8μm)
Mobile phase	: A:0.1%HCOOH+10mMHCOONH$_4$ B:IPA
	60%B----(10min)----100%B
Column temp	: 40°C
Sample volume	: 3ul
Flow rate	: 0.25ml/min
MS	: Agilent 6460 triple quadrupole LC/MS
Ionization	: AJS (Positive)
Nebulizer gas	: 345kPa
Vcap	: 4000V
Fragmentor	: 100V(GEs), 169V(3-MCPDEs)

Name	Precursor	Product	CE
Glycidyl linoleate	354.3	337.3	5
Glycidyl palmitate	330.3	313.3	5
Glycidyl oleate	356.3	339.3	5
3-MCPD dipalmitate	604.6	331.3	15
3-MCPD dioleate	656.6	357.3	15

Table.2 LC/TOFMS condition for GEs and 3-MCPDEs

HPLC	:Agilent 1290
Column	: ZORBAX Eclipse plus C8 (100mm,2.1mm,1.8μm)
Mobile phase	: A:0.1%HCOOH+10mMHCOONH$_4$ B:IPA
	60%B----(10min)----100%B
Column temp	: 40°C
Sample volume	: 5ul
Flow rate	: 0.25ml/min
MS	: Agilent 6230 time-of-flight LC/MS
Ionization	: Dual-ESI (Positive)
Mass range	: m/z 100-1000
EIC ion and mass range	: Base peak ion and 0.01 Da
Drying gas	: 10 L/min at 300°C
Nebulizer gas	: 345kPa
Vcap	: 4000V
Fragmentor : 120V	
Resolution	: >8000 at m/z=322.0481
Reference mass	: m/z=121.050873,922.009798

Experimental

Sample Preparation

Glycidyl palmitate (C16:0-GE), glycidyl oleate (C18:1-GE), glycidyl linoleate (C18:2-GE), 3-MCPD dipalmitate (C16:0-3-MCPDDE) and 3-MCPD dioleate (C18:1-3-MCPDDE) were used for this study. Eight commercial edible oils (Table. 3) were purchased from Japanese markets. 0.1g of each oil was weighed into a glass vial and dissolved in 100 mL hexane. These hexane solutions were directly analyzed by LC/MSMS and LC/TOFMS.

Table.3 Commercial edible oil

A	Roasted sesame oil	E	Palm oil
B	Cold pressed sesame oil	F	Rapeseed oil
C	Pomace olive oil	G	Argan oil
D	Extra virgin olive oil		

Fig.1 Commercial edible oil

Results and Discussion

Mass Spectra of GEs and 3-MCPDEs

GEs and 3-MCPDEs were analyzed by LC/MSMS and LC/TOFMS. Mass spectra of all esters showed prominent ions of ammonium adduct ion and these ions were selected as the precursor ions in product ion scan mode by LC/MSMS. These spectra were shown in Fig.2 and 3.

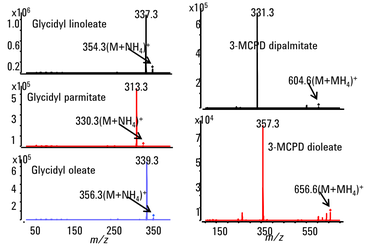

Fig.2 Mass spectra of GEs and 3-MCPDEs by LC/MSMS

Results and Discussion

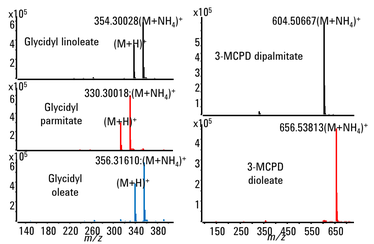

Fig.2 MSMS spectra of GEs and 3-MCPDEs by LC/TOFMS

SRM Chromatograms of GEs and 3-MCPDEs

GEs and 3-MCPDEs were separated using acetonitrile and IPA. The chromatograms were shown in Fig.3. IPA were chosen as the mobile phase because of the intensities of GEs and 3-MCPDEs .

SRM chromatograms of these esters at 0.1 ng/mL were shown in Fig.4. Table.4 showed the detection limits, linearity by LC/MSMS and the relative mass errors by LC/ TOFMS of GEs and 3-MCPDEs .

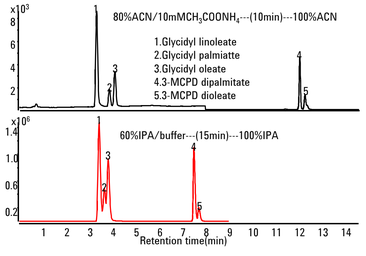

Fig.3 Total ion chromatograms of GEs and 3-MCPDEs by SRM mode with different mobile phase

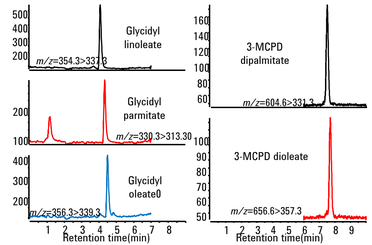

Fig.4 SRM chromatograms of GEs and 3-MCPDEs by LC/MS/MS (concentration: 0.1 ng/mL)

Table.4 Detection limit, linearity and mass error of GEs and 3-MCPDEs

No	Name	S/N 0.1ng/mL	LODs S/N=3	Linearity r2	Mass error ppm
1	Glycidyl linoleate	60	0.005	0.9999	-0.13
2	Glycidyl palmitate	61	0.005	0.9999	0.31
3	Glycidyl oleate	52	0.006	0.9999	-0.52
4	3-MCPD dipalmitate	60	0.005	0.9996	-0.09
5	3-MCPD dioleate	34	0.010	0.9997	-0.37

Ion Suppression by the Matrix in Edible Oil

A 0.1 g of aliquot of the rapeseed oil spiked at 1 μg/g was dissolved in 10, 50 and 100 mL of hexane. These rapeseed oil were analyzed by LC/MSMS and the intensities of all esters were compared with its of standard solution at same concentration. These results were shown in Fig.5. SRM chromatograms of GEs and 3-MCPDEs in the extract of the rapeseed oil spiked at 1ug/g were shown in Fig.6. The detection limits, recovery and RSD were shown in Table.5.

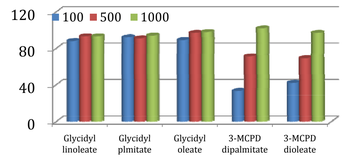

Fig.5 Relative intensity of each ester

Results and Discussion

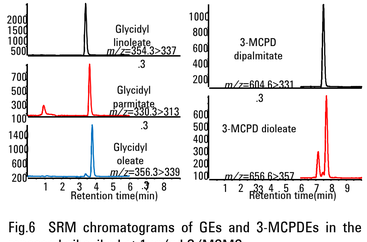

Fig.6 SRM chromatograms of GEs and 3-MCPDEs in the rapeseed oil spiked at 1μg/g LC/MSMS

Table.5 Detection limit, linearity and mass error of GEs and 3-MCPDEs

No	Name	S/N 1 μg/g	LODs μg/g	Recovery 1μg/g	RSD n=5
1	Glycidyl linoleate	458	0.007	93	1.2
2	Glycidyl palmitate	270	0.011	94	2.3
3	Glycidyl oleate	291	0.010	98	1.4
4	3-MCPD dipalmitate	475	0.006	102	1.7
5	3-MCPD dioleate	735	0.004	97	0.9

Analysis of the Edible Oil by LC/MS/MS and LC/TOF/MS

Eight edible oils were analyzed by LC/MSMs and LC/QTOF. SRM chromatograms and extract chromatograms of the rapeseed oil were shown in Fig.7 and 8. The amounts and relative mass errors of them in edible oils were shown in Table.6

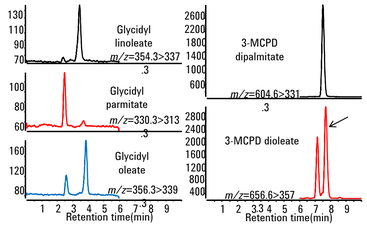

Fig.7 SRM chromatograms of the rapeseed oil by LC/MSMS

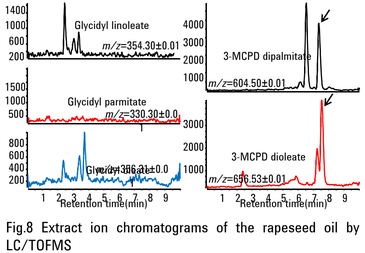

Fig.8 Extract ion chromatograms of the rapeseed oil by LC/TOFMS

Table.6 The concentration by LC/MSMS and the relative mass errors by LC/TOFMS of GEs and 3-MCPDEs in edible oils

No	Name	A	B	C	D 1	D 2	E	F	G
1	Glycidyl linoleate	385	19	18	22	11	ND	51	103
2	Glycidyl palmitate	88	ND	ND	32	ND	ND	ND	89
3	Glycidyl oleate	245	7	92	ND	ND	ND	111	259
4	3-MCPD dipalmitate	2	2	3	3	4	4	2	787
5	3-MCPD dioleate	63	2	91	2	3	105	59	1430

A:Roasted sesame oil D:Extrac virgin olive oil G:Palm oil
B:Cold pressed sesame oil E:Rapeseed oil
C:Pomace olive oil F:Argan oil

No	Name	A	B	C	D 1	D 2	E	F	G
1	Glycidyl linoleate	3.2	ND	ND	ND	ND	ND	ND	ND
2	Glycidyl palmitate	ND	ND	ND	ND	ND	ND	ND	ND
3	Glycidyl oleate	2.3	ND	ND	ND	ND	ND	ND	2.1
4	3-MCPD dipalmitate	ND	ND	ND	ND	ND	ND	ND	0.4
5	3-MCPD dioleate	ND	ND	ND	ND	ND	ND	ND	2.2

A:Roasted sesame oil D:Extrac virgin olive oil G:Palm oil
B:Cold pressed sesame oil E:Rapeseed oil
C:Pomace olive oil F:Argan oil

Conclusions

1. LODs of GEs and 3-MCPDEs standard solution by LC/MS/MS were in the range from 0.05 to 0.01 ng/mL and the r^2 values were over 0.999.
2. Relative mass errors of base peak ion measured by LC/TOF/MS were within 1ppm.
3. Recoveries of GEs and 3-MCPDEs in the rapeseed oil by 1000-times dilution by hexane ranged from 93 to 102 %.
4. LODs of GEs and 3-MCPDEs in the rapeseed oil ranged from 4 to 11 ng/g.
5. The amount of GEs and 3-MCPDEs detected in eight edible oil ranged from 11 to 385 g/g and from 2 to 1430 ng/g