The role of volatile sulfur compounds in the flavor profiles of rapeseed oil and application in variety selecting and processing

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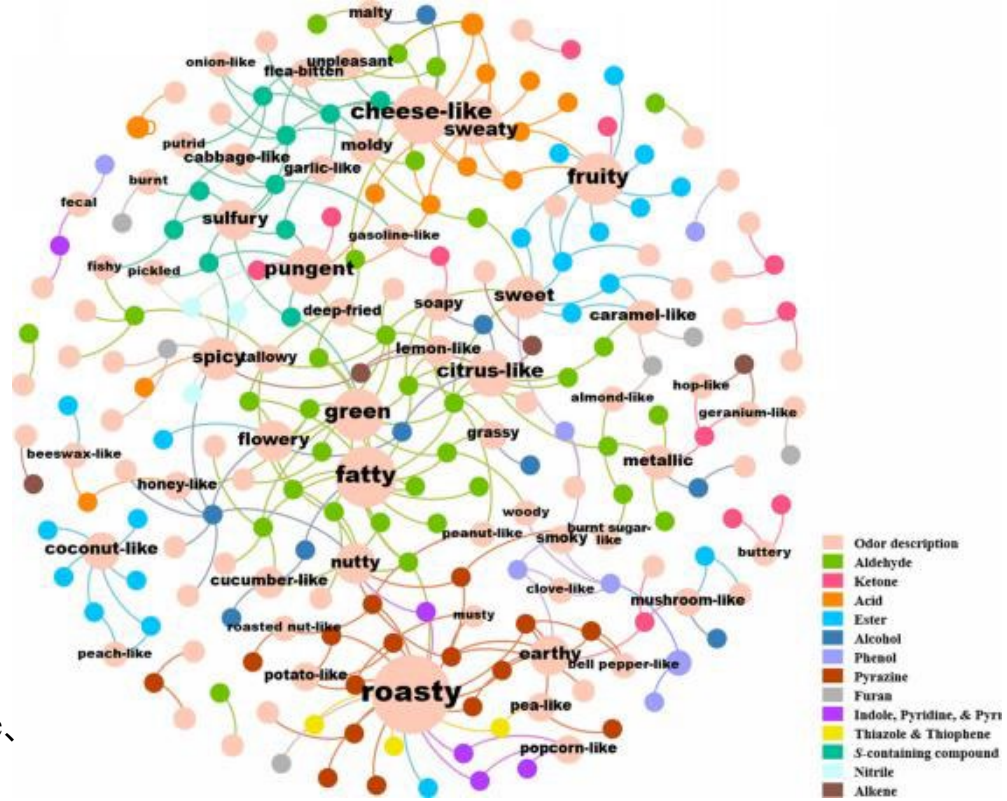
Sydney 2023.9.26

CONTENTS

1.1 Unique aroma in rapeseed oil

Rapeseed is put into a kettle, slowly fried over a gentle fire, permeated with aroma, and then crushed and subjected to steam.
--Tian Gong Kai Wu, Song Dynasty.

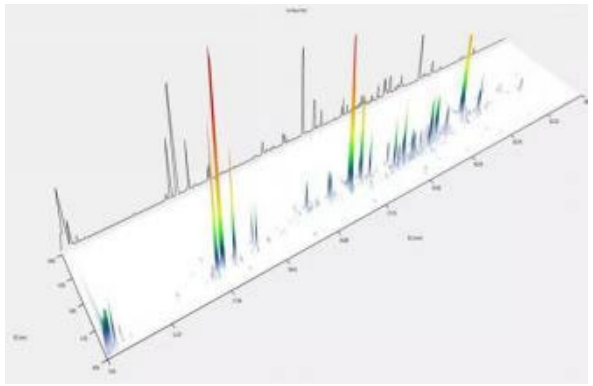
rapeseed oil	2-Butenenitrile、Acetaldehyde、2,5-Dimethyl pyrazine、4-Isothiocyanatobut-1-ene, etc.
peanut oil	Pentanal、2-Pentylfuran、isoamyl alcohol、2,5-Dimethyl pyrazine、2,3,5-Trimethylpyrazine
sesame oil	Thiophene、Hexanal、2,5-Dimethyl pyrazine、2-Ethyl-5-methylpyrazine、Octanoic acid、Nonanoic acid, etc.
sunflower oil	Pinene、Heptaldehyde、Octanal、Nononal、2-Undecenal、Octanoic acid、Nonanoic acid, Hexanoic acid, etc.
soybean oil	Hexanal, 2-Heptanone, 2-Octanone, Heptanoic acid, Octanoic acid, 2-Undecenal, Hexanoic acid, etc.



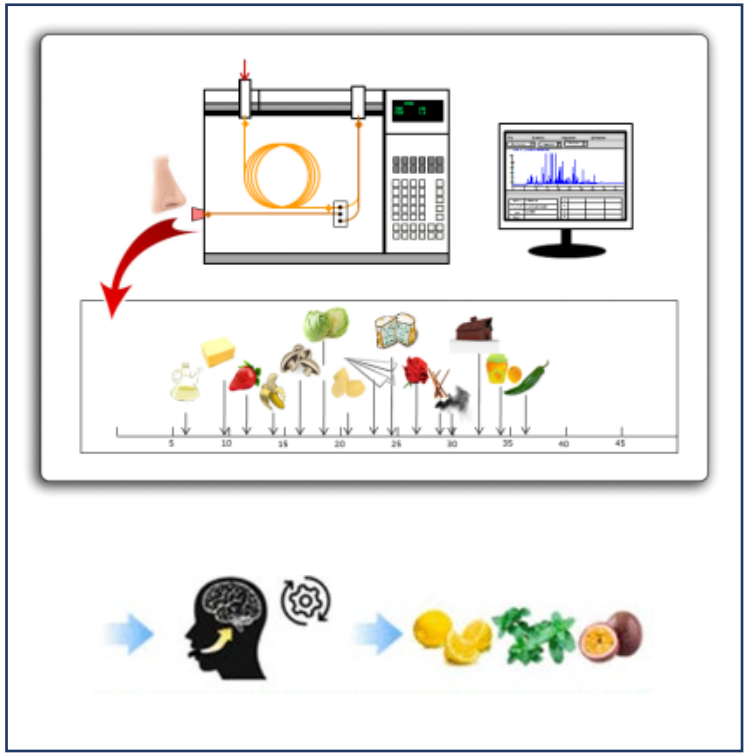
Correlation between aroma properties and aroma substances in rapeseed oils

A complex flavour composition with aroma attributes：nutty, pungent, burnt, pickle, grassy, fishy, fatty

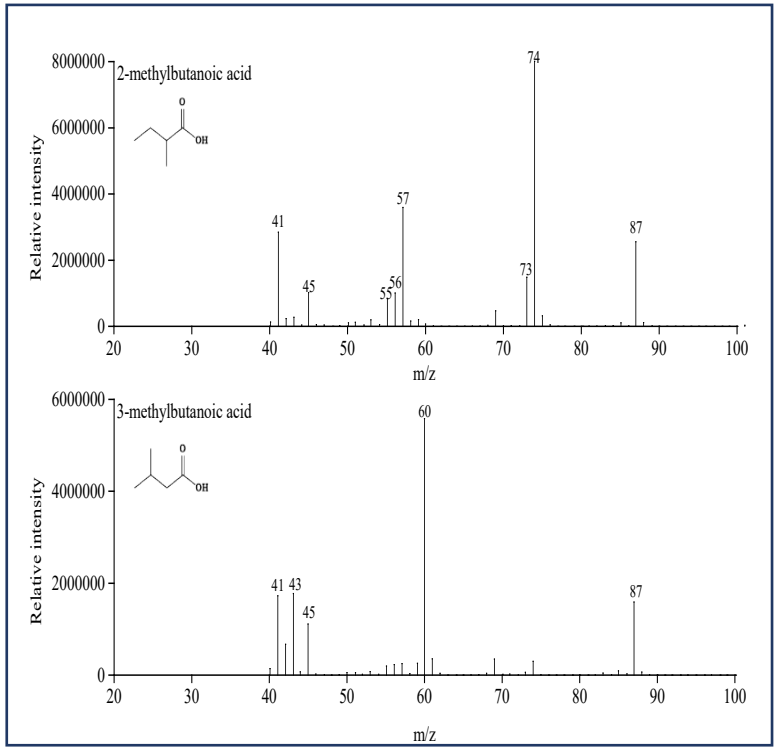
1.2 Aroma Identification of rapeseed oil



Analysis of full two-dimensional time-of-flight mass spectrometry couplings



GC-O Olfactory Characterisation



Isomerism resolution (different aroma characteristics)

- ✓ **A total of 478 volatile components were identified in more than 100 rapeseed oils by full two-dimensional time-of-flight mass spectrometry separation of co-effluents**
- ✓ **A total of 113 aroma components were identified by GC-O analysis, standards and retention time indices**
- ✓ **37 aroma substances in cold-pressed rapeseed oil (predominantly grassy notes) and 97 aroma substances in fragrant rapeseed oil (roasted, pungent)**

Chinese Journal of Oilseed Crops, 2018

1.3 Characteristics and classification of volatile sulfur compounds

sulfur compound

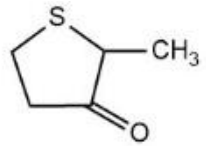
VSCs

- ✓ thiol
- ✓ sulfide
- ✓ Thiolate
- ✓ thiazole

- ✓ Highly volatility
- ✓ low threshold
- ✓ Strong flavour intensity
- ✓ Variety of odours

Dihydro-2-methyl-3(2H)-thiophenone

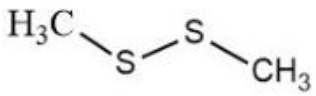
oniony



Dihydro-2-methyl-3(2H)-thiophenone

*** Dimethyl disulphide**

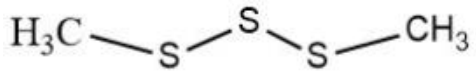
oniony



dimethyl disulfide

*** Dimethyl trisulphide**

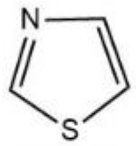
garlic-spicy



Dimethyl trisulfide

*** thiazole**

roasted flavour



thiazole

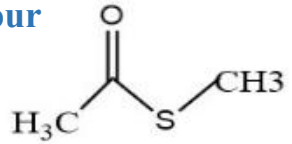
*** methanethiol**

rotten egg odour

methanethiol

Methylthioacetate

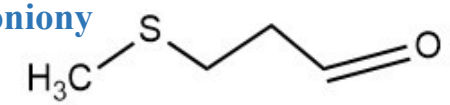
garlic odour



S-methyl thioacetate

3-Methylthiopropanal

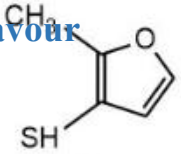
oniony



3-methylthiopropanal

*** 2-Methyl-3-furanethiol**

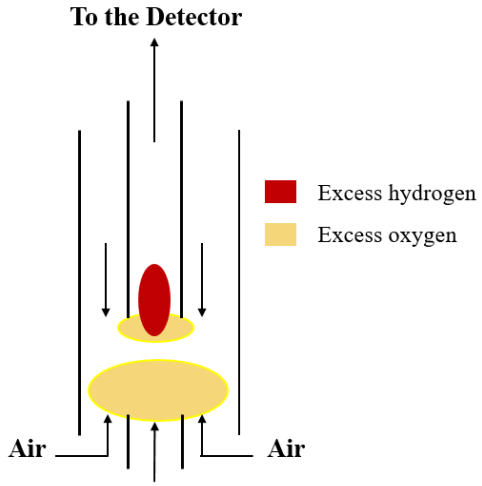
Popcorn flavour



2-methylfuran-3-thiol

Song X , Food Chemistry, 2019, 297:34286.

2.1 A VSCs database based on SCD (Sulfur Chemiluminescence Detector)

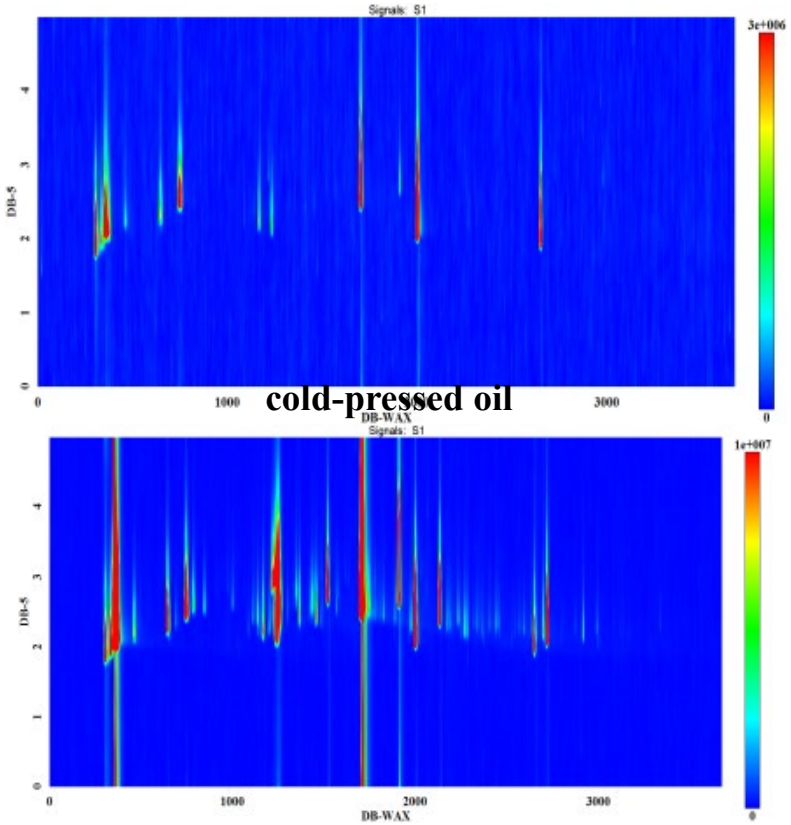


$$SO + O_3 \longrightarrow SO_2^* + O_2$$

$$SO_2^* \longrightarrow SO_2 + h\nu$$

GC-SCD Principle

Full two-dimensional coupled with SCD



The response of GC-SCD to elemental sulfur is isomolar and linearly distributed, with little interference from hydrocarbon compounds.

Table A VSCs database based on SCD

Methanethiol	74-93-1
carbon disulfide	75-15-0
Ethanethiol	1975/8/1
Dimethyl sulfide	75-18-3
propane-1-thiol	107-03-9
Allyl methyl sulfide	10152-76-8
Thiophene	110-02-1
1-Pentanethiol	110-66-7
Methyl thiolacetate	1534-08-3
Dimethyl disulfide	624-92-0
Ethanethioic acid S-ethyl ester	625-60-5
Diallyl sulfide	592-88-1
S-propyl ethanethioate	2307-10-0
2-Methylthiazole	3581-87-1
thiazole	288-47-1
allyl methyl disulfide	2179-58-0
Bis(methylthio)methane	1618-26-4
2-methylfuran-3-thiol	28588-74-1
1-methylsulfanylbutan-2-one	13678-58-5
2-Methoxythiazole	14542-13-3
Dimethyl trisulfide	3658-80-8
Furfuryl Mercaptan	1998/2/2
3-(Methylthio)butanal	16630-52-7
3-methylthiopropanal	3268-49-3
Furfuryl methyl sulfide	1438-91-1
Dihydro-2-methyl-3(2H)-thiophenone	13679-85-1
Tetrahydrothiophen-3-one	1003-04-9
Dimethyl sulfoxide	67-68-5
Benzyl mercaptan	100-53-8
1-(1,3-thiazol-2-yl)ethanone	24295-03-2
ethyl methanesulfonate	62-50-0
formylthiophene	1998/3/3
5-Methylthiophene-2-carboxaldehyde	13679-70-4
Furfuryl thioacetate	13678-68-7
3-Acetylthiophene	1468-83-3
Diallyl trisulfide	2050-87-5
1-benzothiophene	95-15-8
Methyl 2-thiofuroate	13679-61-3
3-mercaptohexanol	51755-83-0
sulfonyldimethane	67-71-0
2-Thiophenemethanol	636-72-6
3-Thiophenemethanol	71637-34-8

42 VSCs standards were identified and more than 20 new compounds were found.

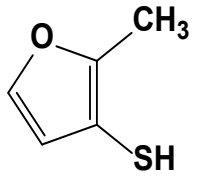
Yu et al□ Food Chemistry 367 (2022) 130741

2.2 Identification of markers of "sulfur notes" in cold-pressed rapeseed oils

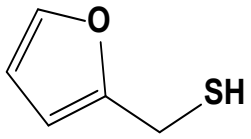
NO	Compound identified	Odor notes	Odor threshold (μg/kg)	OAV range	Number of samples with OAV >1
1	dimethyl sulfide	cabbage, sulfur, gasoline	2.6	7-14574	21
2	Allyl methyl sulphide	garlic,onion	0.017	102-508	13
3	Dimethyl disulphide	onion, cabbage, putrid	0.74	2-678	15
4	Allyl methyl disulfide	green ,onion	18.00	4-4	1
5	Dimethyl trisulphide	sulfur, fish, cabbage	0.03	4-683	11
6	Diallyl disulfide	garlic	5.645	1-57	7
7	Furfuryl methyl sulphide	garlic, vegetable	0.294	12-2195	4
8	Diallyl trisulfide	garlic, green	0.758	4-135	15
9	Methyl thioacetate	cheesy, garlic	1.38	1-78	6
10	Ethyl thioacetate	onion, garlic	0.038	12-726	7
11	Propyl thioacetate	green, onion, garlic	15.225	3-57	11
12	2-Methylthiazole	green,vegetable	3.077	1-7	2
13	Thiazole	nut, sulfur	13.44	1-125	5
14	3-Acetylthiophene	sulfur	6.458	1-70	3
15	Methanethiol	sulfur, gasoline, garlic	0.36	2-138	16
16	Dimethylthiomethane	garlic, sulfur	3.2	1-6	8
17	3-Methylthiobutyraldehyde	vegetable, tomato, fish	0.680	3-2330	13
18	5-Methyl-2-thiophenecarboxaldehyde	cherry, sweet	0.031	204-3165	13
19	Dimethyl sulfoxide	garlic	100	2-6	6

Twelve sulfur compounds were detected for the first time in cold-pressed rapeseed oil,
By OAV, dimethyl sulfide occupies the most important position

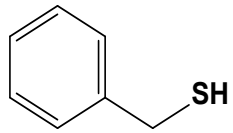
2.3 Thiols as a source of "sesame notes" in fragrant rapeseed oils



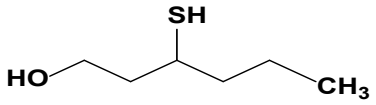
2-Methyl-3-furanthiol



2-Furylmethanthiol

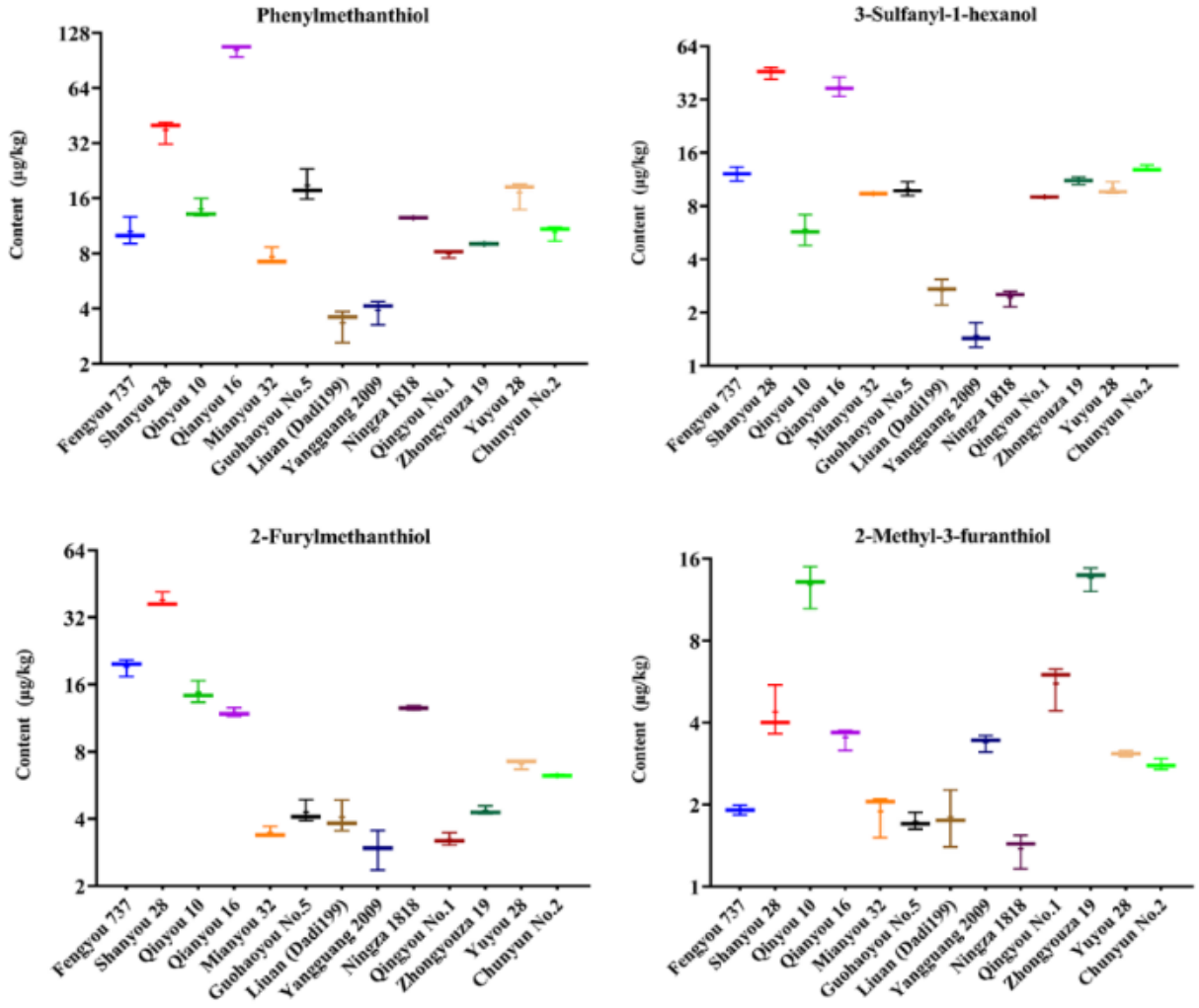


Phenylmethanethiol



3-Sulfanyl-1-hexanol

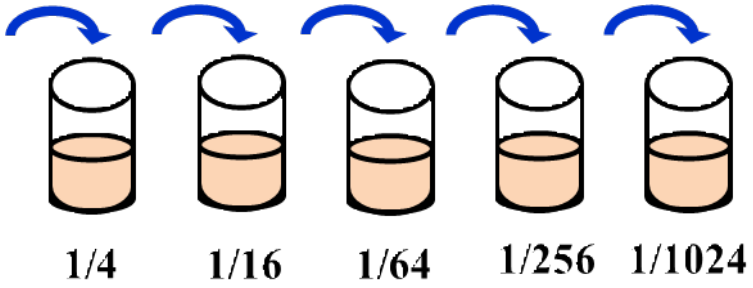
No	RT(min)	Name	Odor	Thresholds(μg/L)	Range of OAV
1	9.938	2-Methyl-3-furanthiol	meaty	0.481	1-21
2	13.758	2-Furylmethanthiol	roasted sesame	0.061	51-357
3	19.933	Phenylmethanthiol	sesame	0.029	39-16445
4	26.994	3-Sulfanyl-1-hexanol	sulfur	0.006	33-7104



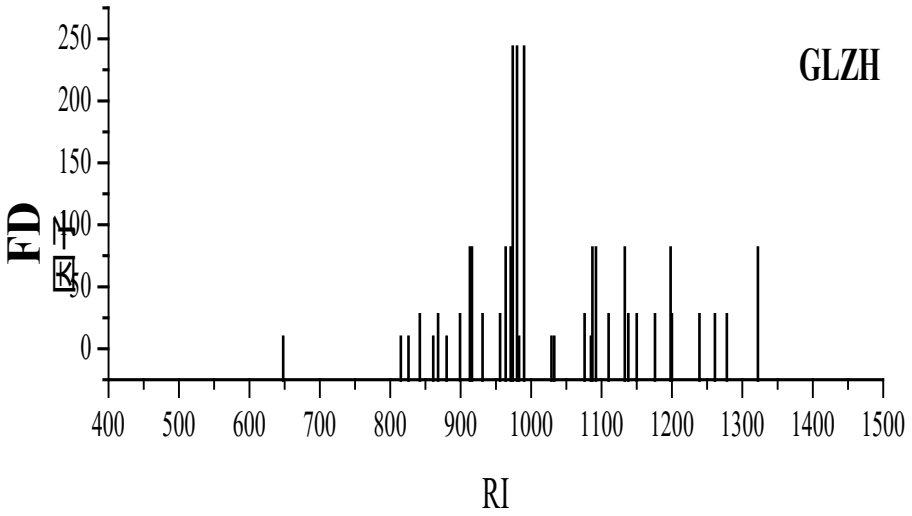
Distribution of 2-methyl-3-furanothiols, 2-Furylmethanthiol, phenylmethanthiol, and 3-Sulfanyl-1-hexanol in 13 different varieties of rapeseed oil was investigated

Yang et al□ Food Chemistry□ 2021

3.1 Molecular sensory science -AEDA and OAV calculations



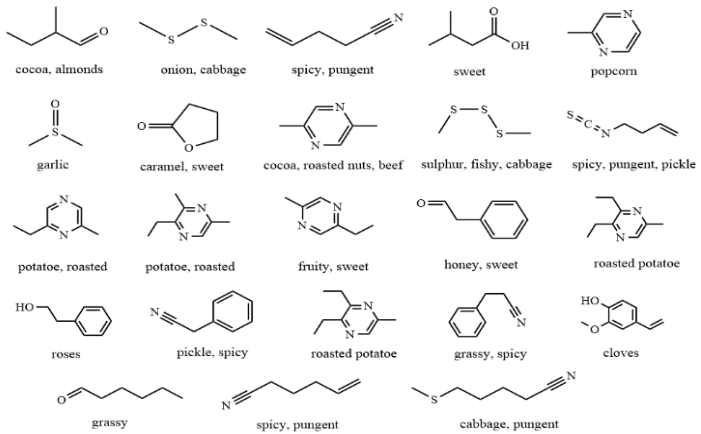
Determination of background system threshold in rapeseed oil Combined with OAV calculation



AEDA

Aroma FD Value Comparison Chart

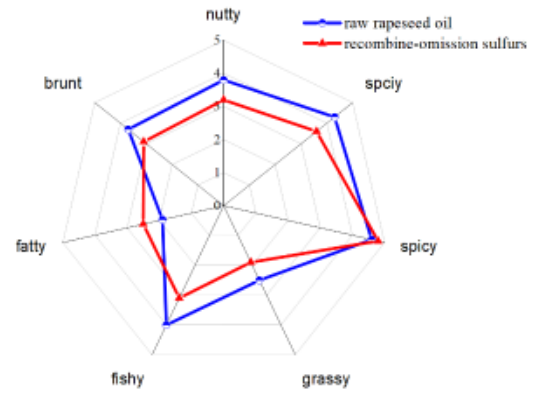
Odor compounds	OT (mg/kg)	Odor compounds	OT (mg/kg)
5-Methylthiazole	0.002	3-Methylthiopropyl isothiocyanate	0.1
2-Methyl-3,5-diethylpyrazine	0.014	6-Methylthiohexonitrile	0.15
1-methyl-1H-pyrrole-2-formaldehyde	0.02	Cyclopentyl isothiocyanate	0.15
6-Methyl-2-Vinylpyrazine	0.026	2-Butenenitrile	0.5
5-hydroxymethylfurfural	0.05	Methylthioacetonitrile	0.5
Butyl isothiocyanate	0.05	3-Butenenitrile	0.7
5-Ethylthiazole	0.05	phenylacetaldehyde	0.8

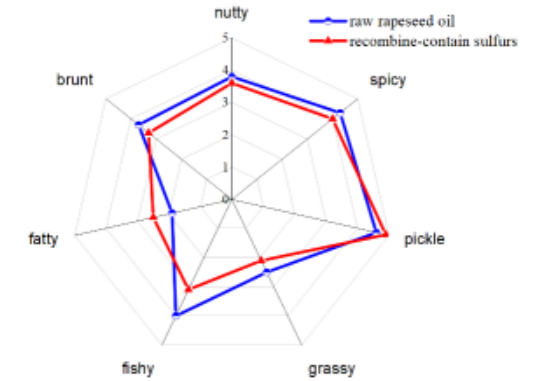


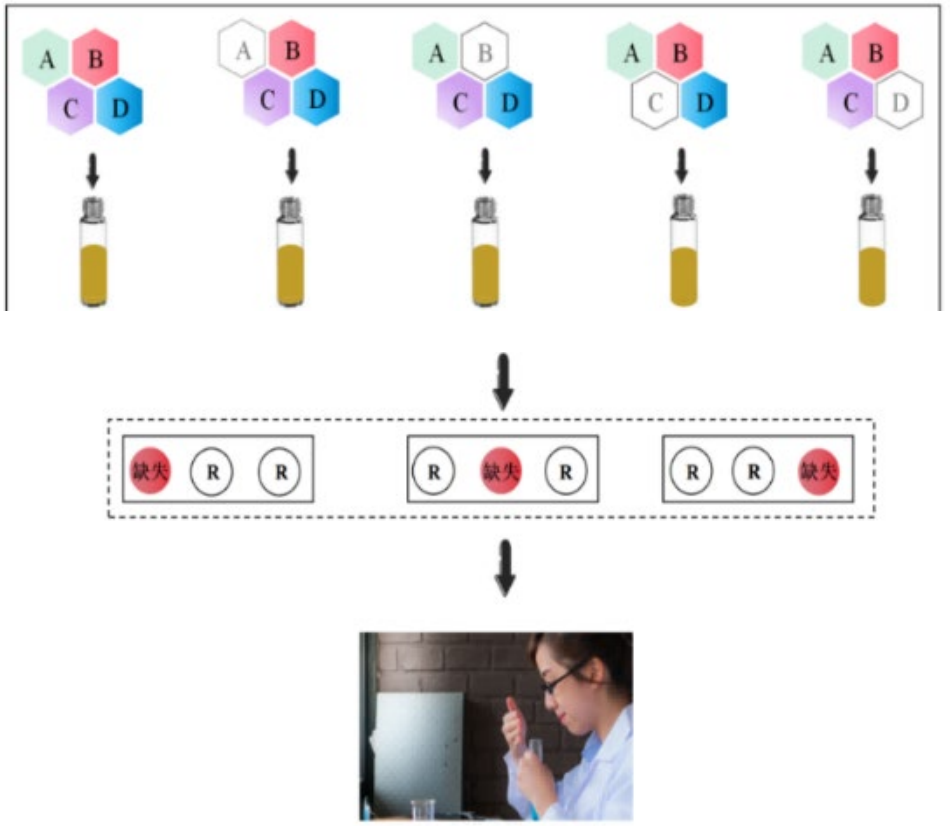
Screening of characteristic flavour substances

3.2 Aroma recombination and omission of fragrant rapeseed oils

Aroma recombination







omission experiment

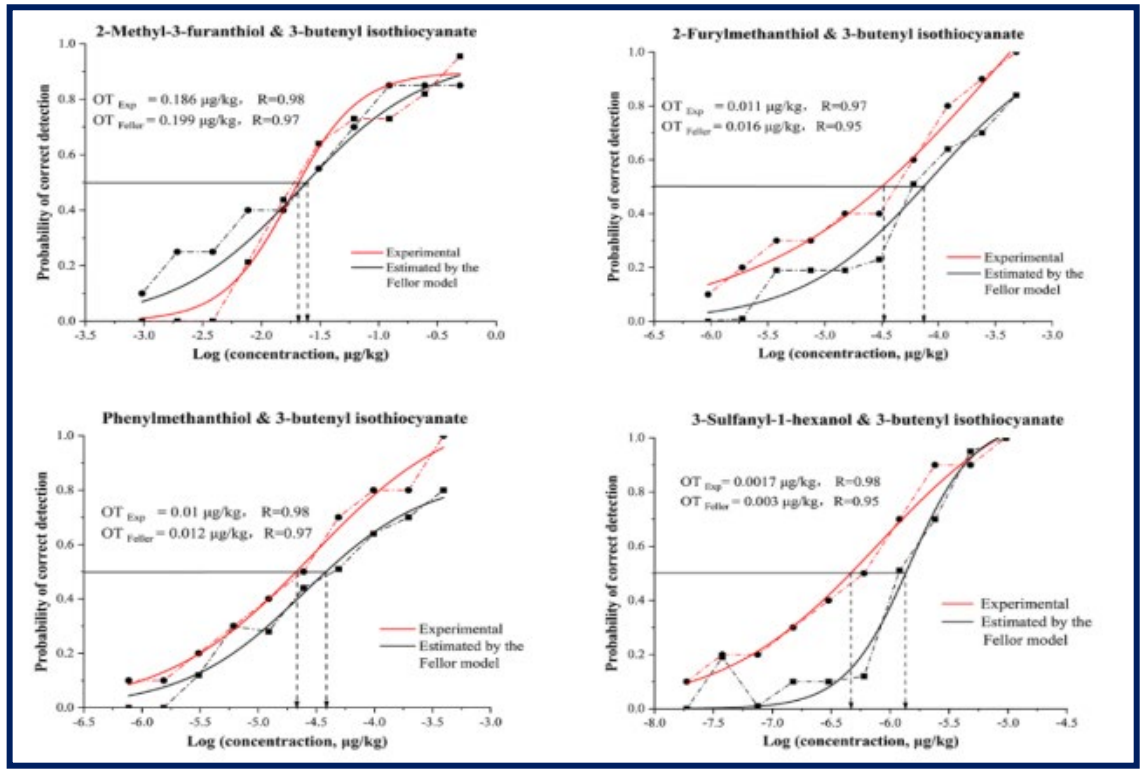
compounds	sinigifcant
isothiocyanate	***
nitrile	*
alcohol	**
aldehyde	*
acid	-
ketone	-
lactone	-
furan	***
Sulfur compounds	***

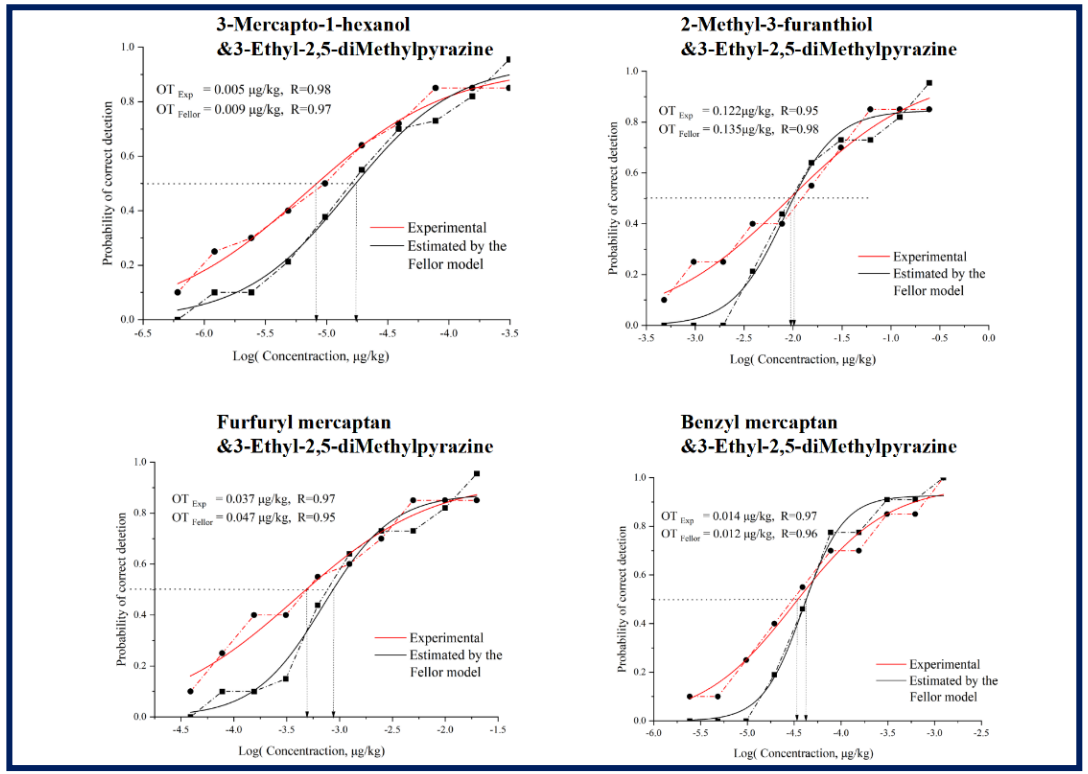
The key aroma recombination of rapeseed oil was achieved; Sulfur-containing compounds such as FFT are indispensable components, and the recombination similarity has increased from 82% to 93%.

3.3 Interactions of thiols with other key aroma

Main aroma: heterocyclic compounds
Special aroma: isothiocyanate, sulfur compounds

Ratio of experimental thresholds to theoretical thresholds





The interaction between the four thiols and the characteristic flavors "roasting" 3-ethyl-2,5-dimethylpyrazine and "pungent" 3-butenyl isothiocyanate was additive/synergistic, promote the relesse characteristic flavor of rapeseed oil

Yang et al□ Food Chemistry□ 2021

4.1 Pathway1-SMM identification-precursor of DMS

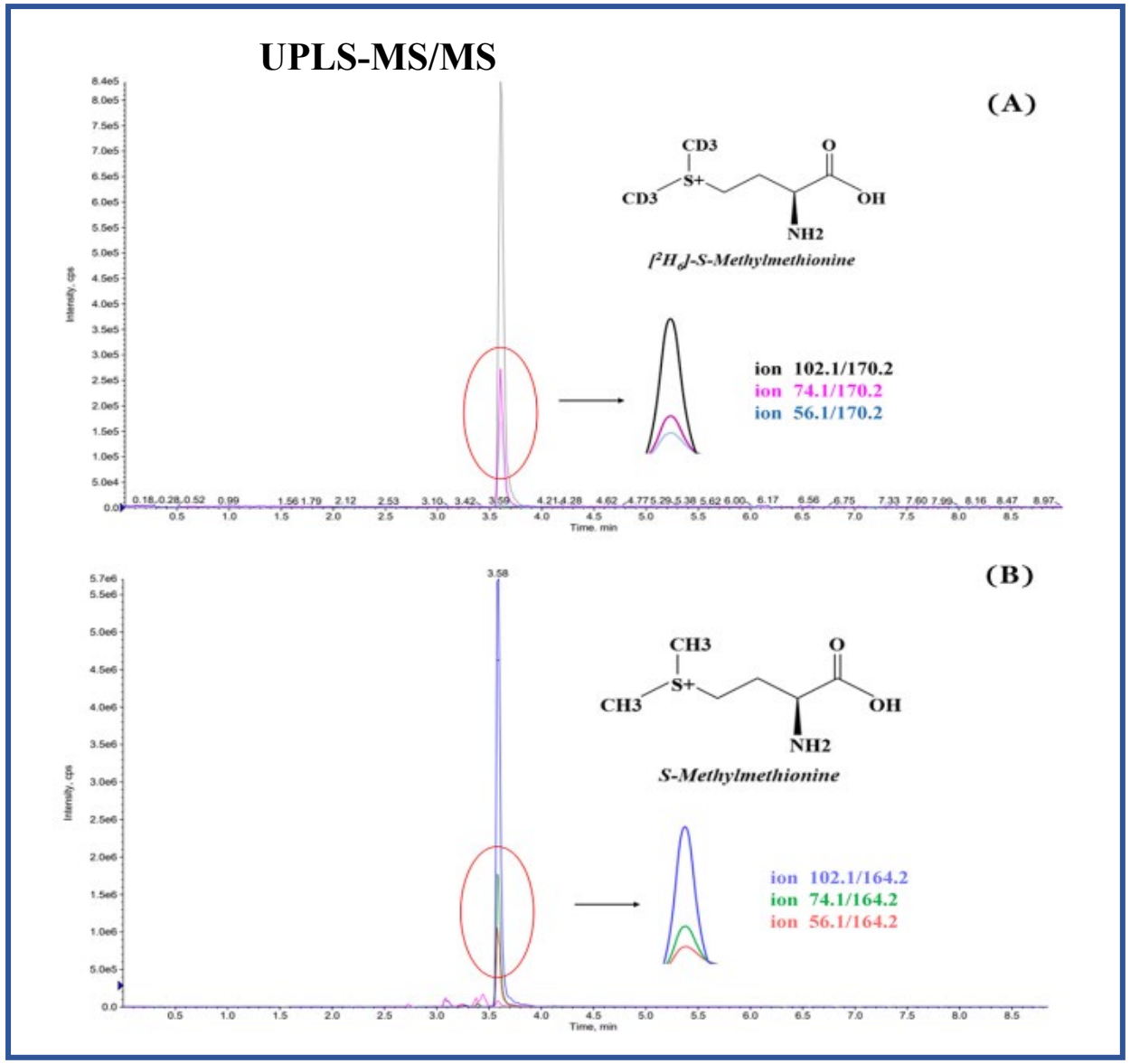


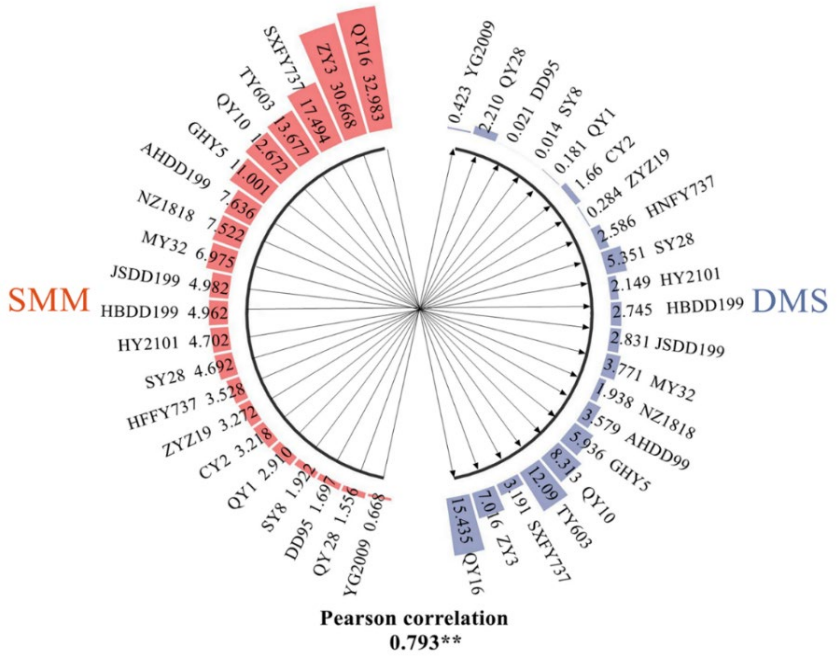
Table Quantitaiton of SMM via Stable isotope

Analyte	Scan mode	Precursor ion (m/z)	Product ion (m/z)	Collisionenergy(V)	Retentiontime(min)
IS-SMM [a]	+	170.2	102.1	13/70	3.6
IS-SMM-1[b]	+	170.2	74.1	23/70	3.6
IS-SMM-2[b]	+	170.2	56.1	28/70	3.6
SMM [a]	+	164.2	102.1	13/70	3.6
SMM-1[b]	+	164.2	74.1	23/70	3.6
SMM-2[b]	+	164.2	56.1	28/70	3.6

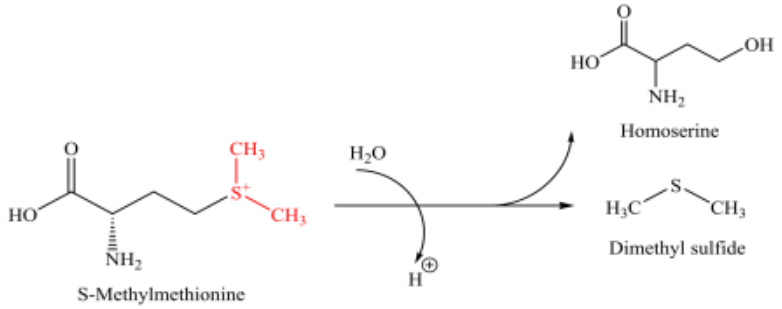
Food Chemistry,2021, 6

4.1 Pathway1-Correlation between SMM and DMS

Samples[a]	Content(mg/kg)	
	SMM [b]	DMS [c]
SXFY737	17.494 ±1.606	3.191 ±0.135
SY28	4.692 ±0.162	5.351 ±0.705
QY10	12.672 ±1.301	8.313 ±0.872
QY16	32.983 ±2.286	15.435 ±0.843
TY603	13.677 ±1.062	12.09 ±0.383
MY32	6.975 ±0.614	3.771 ±0.496
GHY5	11.001 ±0.637	5.936 ±0.007
AHDD199	7.636 ±0.088	3.579 ±0.196
JSDD199	4.982 ±0.509	2.831 ±0.32
SY8	1.922 ±0.023	0.014 ±0.003
NZ1818	7.522 ±0.135	1.938 ±0.131
HBDD199	4.962 ±0.268	2.745 ±0.179
YG2009	0.668 ±0.013	0.423 ±0.077
HY2101	4.702 ±0.241	2.149 ±0.257
QY1	2.91 ±0.201	0.181 ±0.007
ZYZ19	3.272 ±0.147	0.284 ±0.016
QY28	1.556 ±0.031	2.21 ±0.09
ZY3	30.668 ±0.727	7.016 ±0.982
DD95	1.697 ±0.037	0.021 ±0.004
CY2	3.218 ±0.27	1.66 ±0.042
HNFY737	3.528 ±0.172	2.586 ±0.638
Pearson correlation coefficient	0.793**	



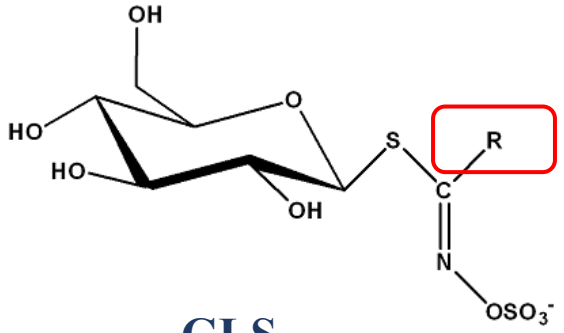
SMM and DMS



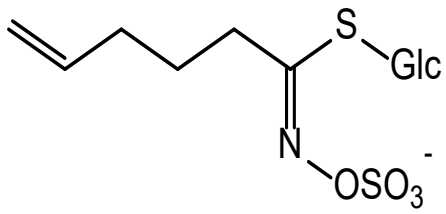
DMS degradation

Flavor of cold-pressed rapeseed oil may be controlled by SMM in rapeseed raw material

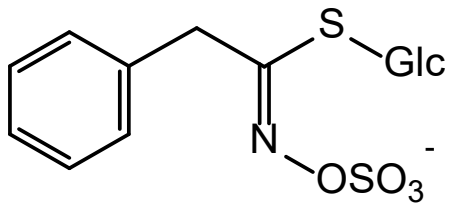
4.2 Pathway 2 - Targeted metabolomics analysis of rapeseed fractions



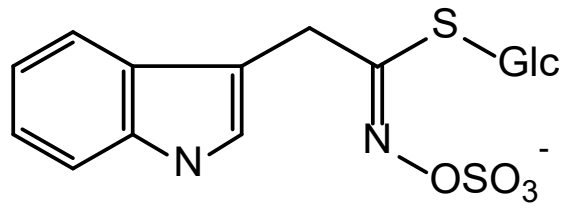
GLS



Aliphatic GLS



Aromatic GLS



Indole GLS

New methods: sample enrichment, high-resolution detection of GLS, standard comparison

	Detection method	debris peak	Sulphur-containing aliphatic structures
1	[M-H]-	406.0322 /259	3-(Methylthio)propyl glucosinolate
2	[M-H]-	406.0322 /259	4-(Methylthio)propyl glucosinolate
3	[M-H]-	420.0443 /195	4-(Methylthio)butyl glucosinolate
4	[M-H]-	434.0597 /259	5-(Methylthio)pentyl glucosinolate
5	[M-H]-	476.0654 /80	7-Methylsulfanyl-3-oxoheptyl glucosinolate

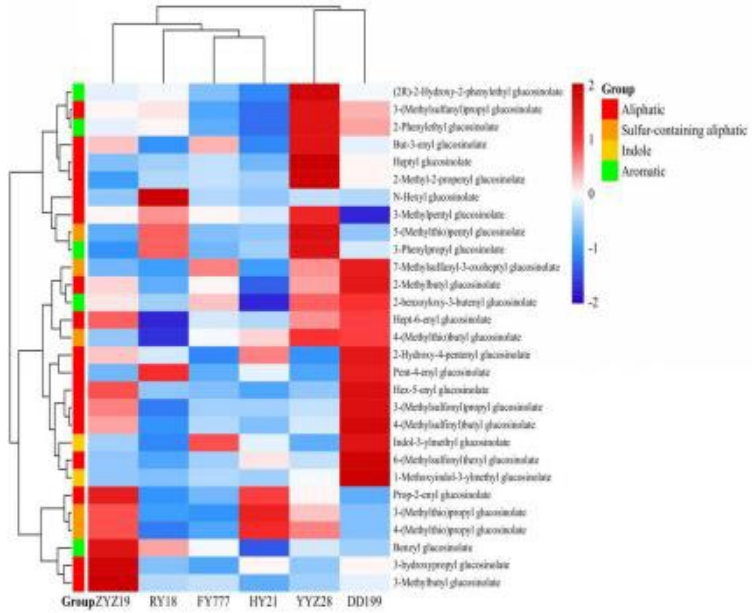
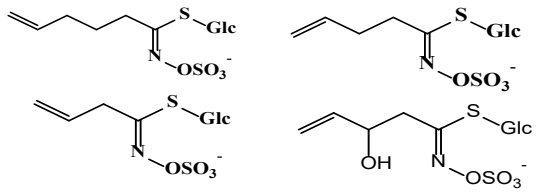


Figure 1. The heatmap of glucosinolate profiles via widely metabolites analysis in different rapeseeds materials

Using targeted metabolomic methods, five new sulfur-containing GLS such as glucoerucin were discovered compared to traditional LC-MS methods

4.3 Degradation of precursors GLSs

A technical roadmap for the construction of degradation models and product identification of 13 major GLS



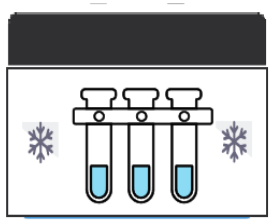
Allylic aliphatic thioglycosides

aromatic thioside

Sulphur-containing aliphatic thiosides

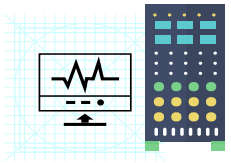
Indole thiosides

Thermal degradation (different systems)



ice bath

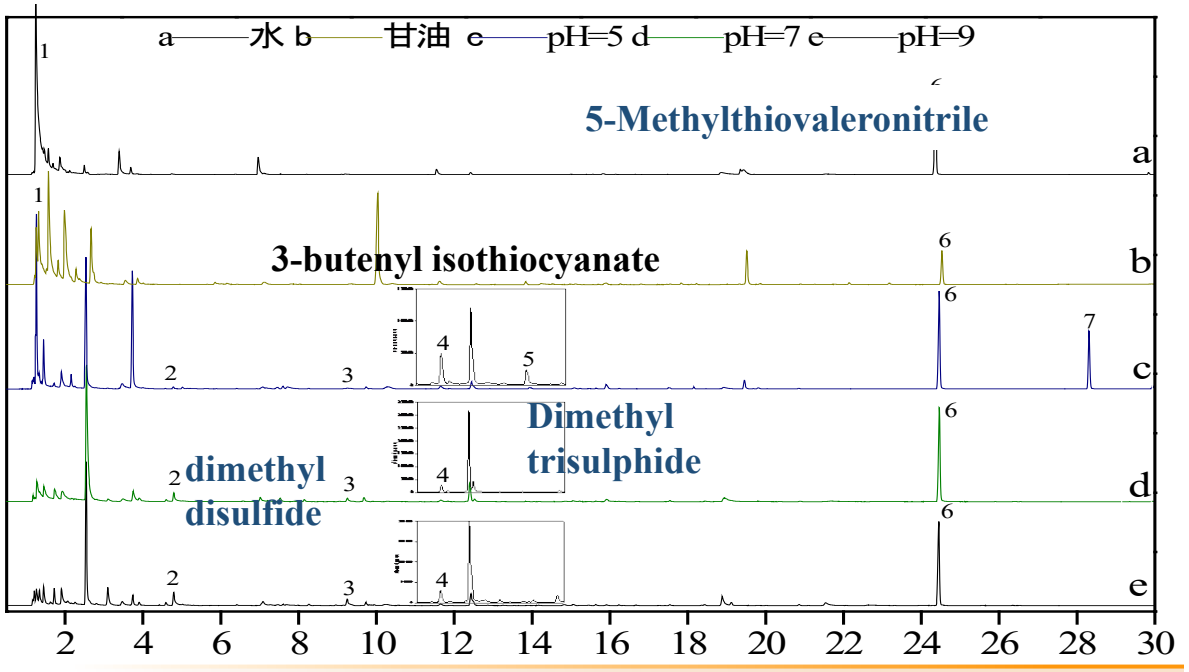
HS-SPME

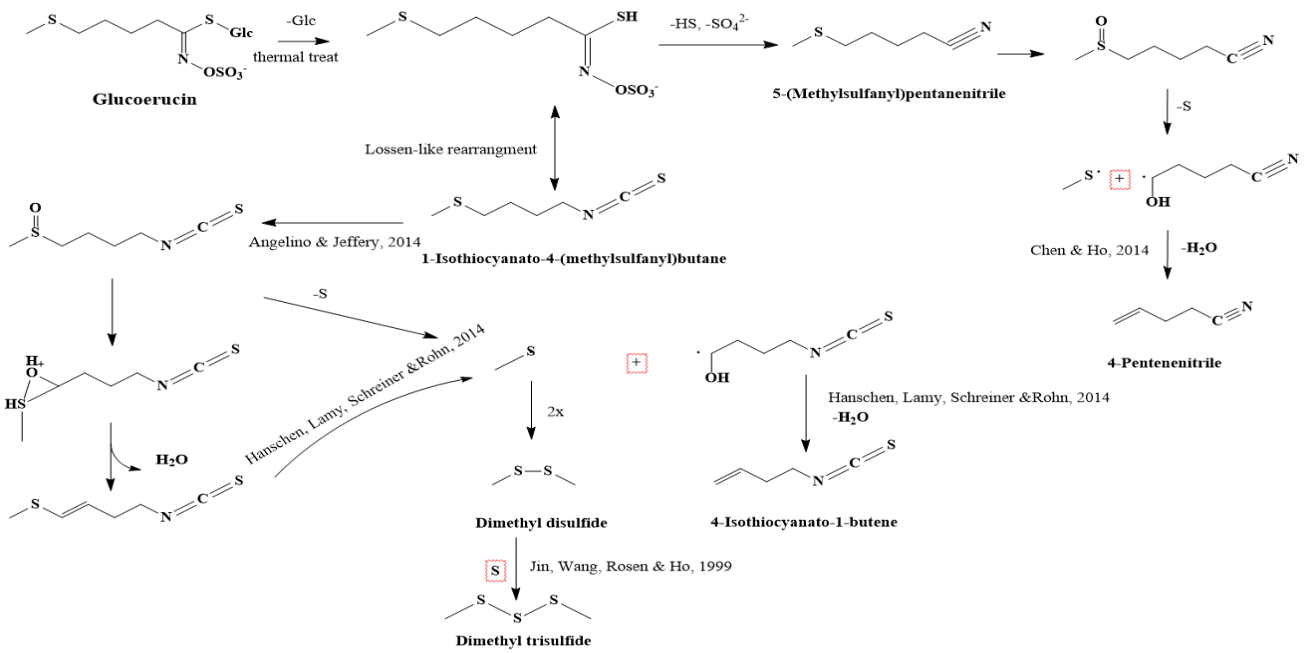


GC-MS

Standard quantitative

GC-O





GER produced dimethyl disulfide (oniony note), Dimethyl Trisulfide (garlic note), and 3-butenyl ISO (pungent note)

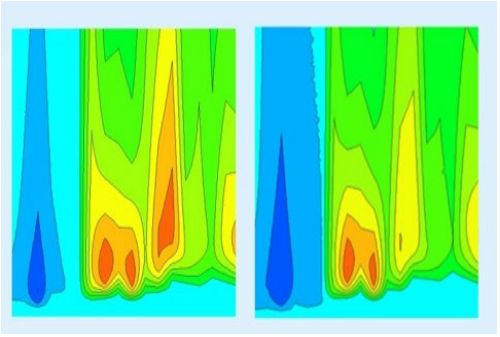
Perspective

selection device

Microwave conditioning device

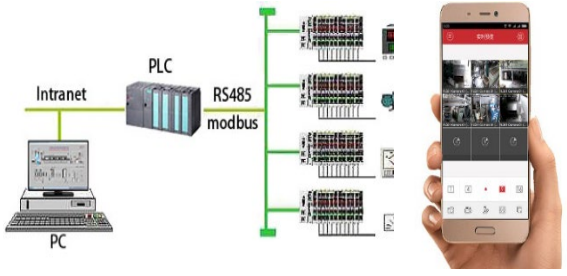
Low-temperature and low-residual oil press

physical refine



Flavor Fingerprint

Full-process control system



intelligent control

Unique microwave low-temperature pressing processing technology provides dual enhancement of flavor and nutrition

Propose new molecular goals through the corresponding logic between key flavor substances and aroma types

Targeted aroma generation technology through research on formation pathways and sensory demand

Key Aroma Retention Techniques for Flavor Release

Warmly welcome you to visit our institute

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