Characterization of the Aroma Properties in Fragrant Rapeseed Oil and Aroma Variation during Critical Roasting Phase

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Symbols and Abbreviations

1D GC	one-dimensional gas chromatography
AEDA	aroma extract dilution analysis
AF	acidic fraction
CORR	correlation analysis
CPO	cold-pressed oil
CPOP	cold-pressed oil from peeled seeds
DHS	dynamic headspace
DTD	direct thermal desorption
DVB/CAR/PDMS	divinylbenzene/carboxen/polydimethylsiloxane
FD	flavor dilution
FID	flame ionization detector
FPD	flame photometric detector
FRO	fragrant rapeseed oil
FT-IR	Fourier transform-infrared
GC×GC	comprehensive two-dimensional gas chromatography
GC×GC-TOF-MS	two-dimensional gas chromatography-time-of-flight mass spectrometry
GLS	glucosinolate
GPC	gel permeation chromatography
HCA	hierarchical cluster analysis
HPLC	high-performance liquid chromatography
HPO	hot-pressed oil
HRGC-MS	high resolution gas chromatography-mass spectrometry
HS	headspace

HSSE	headspace stir bar sorptive extraction
HS-SPME-GC-MS	headspace-solid phase microextraction-gas chromatography-mass spectrometry
HS-SPME-GC-O-MS	headspace-solid phase microextraction-gas chromatography-olfactometry-mass spectrometry
HS-SPME-GC-TOF-MS	headspace-solid phase microextraction-gas chromatography-time of flight-mass spectrometry
HS-trap	headspace-trap
HVT	high vacuum transfer
IMS-MS	ion-mobility spectrometry-mass spectrometry
IR	infrared spectroscopy
LDA	linear discriminant analysis
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantification
MDGC	multi-dimensional gas chromatography
MMSE	monolithic material sorptive extraction
MOS	metal-oxide-semiconductor
MS/MS	tandem mass spectrometry
MS	mass spectrometry
NBF	neutral/basic fraction
NMR	nuclear magnetic resonance spectroscopy
O	olfactory
OAV	odor activity value
ODP	olfactometry detection port
PCA	principal component analysis

PCR	principal component regression
PLSR	partial least squares analysis
QDA	quantitative descriptive analysis
RawS	raw rapeseed
RF	random forest
RoaS	roasted rapeseed
RSD	relative standard deviation
SAFE	solvent-assisted flavor evaporation
SBSE	stir-bar sorptive extraction
SDE	simultaneous distillation extraction
SFE	supercritical fluid extraction
SHS	static headspace
SIDAs	stable isotope dilution assays
SPE	solid phase extraction
SPME	solid-phase microextraction
STO	steam-treated oil
STOF	steam-treated oil with fishy off-flavor
SVM	support vector machine
TDU	thermal desorption unit
TOF-MS	time-of-flight-mass spectrometry

Summary

Rapeseed oil is one of the third most-produced vegetable oil in the world, which is appreciated for its characteristic flavor and high nutritional value. Fragrant rapeseed oil (FRO) produced by a typical roasting process is popular for its characteristic aroma, which has an annual consumption exceeding 1.5 million tons. However, the changes in aroma blueprint of FRO during the typical roasting processing are still unclear, which challenges rapeseed oil quality and consumer acceptance. Accordingly, the aim of this work was to investigate the aroma characteristics and their precursor's pyrolysis behavior of FRO to provide a basis and guidance for the control of FRO aroma quality during production processing.

First, a systematic review on summarizing, comparing, and critiquing the literature regarding the flavor of rapeseed oil, especially about employed analysis techniques (i.e., extraction, qualitative, quantitative, sensorial, and chemometric methods), identified representative/off-flavor compounds, and effects of different treatments during the processes (dehulling, roasting, microwave, flavoring with herbs, refining, oil heating, and storage) was performed. One hundred and thirty-seven odorants found in rapeseed oil from literature are listed, including aldehydes, ketones, acids, esters, alcohols, phenols, pyrazines, furans, pyrrolines, indoles, pyridines, thiazoles, thiophenes, further *S*-containing compounds, nitriles, and alkenes, and possible formation pathways of some key aroma-active compounds are also proposed. Nevertheless, some of these compounds require further validation (e.g., nitriles) due to lack of recombination experiments in the previous work. To wrap up, advanced flavor analysis techniques should be evolved toward time-saving, portability, real-time monitoring, and visualization, which aims to obtain a “complete” flavor profile of rapeseed oil. Aparting from that, studies to elucidate the influence of key roasting processing on the formation of aroma-active compounds are needed to deepen understanding of factors resulting in flavor variations of rapeseed oil.

Following, a systematic comparison among five flavor trapping techniques including solid-phase microextraction (SPME), SPME-Arrow, headspace stir bar sorptive extraction (HSSE), direct thermal desorption (DTD), and solvent-assisted flavor evaporation (SAFE) for hot-pressed rapeseed oil was conducted. Besides, methodological validation of these five approaches for 31 aroma standards found in rapeseed oil was conducted to compare their stability, reliability, and robustness. For the qualification of the odorants in hot-pressed rapeseed oil, SAFE gave the best performance, mainly due to the high sample volumes, but it

performed worse than other methods regarding linearity, recovery, and repeatability. SPME-Arrow gave good performances in not only odorant extraction but also quantification, which is considered most suitable for quantifying odorants in hot-pressed rapeseed oil. Taking cost/performance ratio into account, SPME is still an efficient flavor extraction method. Multi-method combination of flavor capturing techniques might also be an option of aroma analysis for oil matrix.

Afterwards, by application of the Sensomics approach the key odorants in representative commercial FRO samples were decoded. On the basis of the aroma blueprint, changes of overall aroma profiles of oils and their key odorants were studied and compared in different roasting conditions. To better simulate industrial conditions, high temperatures (150-200 ºC) were used in our roasting study, which was rarely studied before. Identification and quantitation of the key odorants in FRO were well performed by means of the Sensomics concept. Glucosinolate degradation products were a special kind of key odorants existing in rapeseed oil. Most of the odorants showed first rising and then decline trends as the roasting process progressed. Aroma profile results showed that high-temperature-short time and low-temperature-long time conditions could have similar effects on the aroma profiles of roasted rapeseed oils, which could provide a reference for the time cost savings in industrial production.

To gain the fundamental knowledge of the aroma formation in FRO, the thermal degradation behavior of progoitrin (the main glucosinolate of rapeseed) and the corresponding generated volatile products were investigated in liquid (phosphate buffer at a pH value of 5.0, 7.0, or 9.0) and solid phase systems (sea sand and rapeseed powder). The highest thermal degradation rate of progoitrin at high temperatures (150-200 ºC) was observed at a pH value of 9.0, followed by sea sand and then rapeseed powder. It could be inferred that bimolecular nucleophilic substitution reaction (S_N2) was mainly taken place under basic conditions. The highest degradation rate under basic conditions might result from the high nucleophilicity of present hydroxide ions. Under the applied conditions in this study, 2,4-pentadienenitrile was the major nitrile formed from progoitrin during thermal degradation at high temperature compared to l-cyano-2-hydroxy-3-butene, which might be less stable. The possible formation pathways of major *S*-containing (thiophenes) and *N*-containing (nitriles) volatile (flavor) compounds were proposed. Hydrogen sulfide, as a degradation product of glucosinolates, could act as a sulfur source to react further with glucose to generate thiophenes.

Overall, the present work comprehensively documented the effects of thermal conditions and matrices on the aroma characteristics, aroma profiles, and key odorants of hot-pressed rapeseed

oil, which could provide data and theoretical basis for the flavor control of FRO under thermal treatment at actual production temperatures (150-200 °C).

Zusammenfassung

Rapsöl ist eines der am dritthäufigsten produzierten Pflanzenöle der Welt, welches für seinen charakteristischen Geschmack und hohen Nährwert geschätzt wird. Geröstetes Rapsöl (fragrant rapeseed oil, FRO), das durch ein typisches Röstverfahren hergestellt wird, ist wegen seines charakteristischen Aromas beliebt und jährlich werden mehr als 1,5 Millionen Tonnen produziert. Allerdings sind die Veränderungen im Aromaprofil von FRO während der typischen Röstverarbeitung noch unklar, was die Rapsölqualität und die Verbraucherakzeptanz herausfordert. Dementsprechend war das Ziel dieser Arbeit, die Aromaeigenschaften und das Pyrolyseverhalten der Vorläuferverbindungen von FRO zu untersuchen, um eine Grundlage und Anleitung für die Kontrolle der FRO-Aromaqualität während des Herstellungsprozesses zu liefern.

Zuerst wurde eine systematische Übersicht aus der Literatur über die Zusammenfassung, den Vergleich und die Kritik zum Aroma von Rapsöl, insbesondere zu den verwendeten Analysetechniken (d. h. Extraktion, qualitative, quantitative, sensorische und chemometrische Methoden), identifizierte repräsentative Verbindungen und Fehlaromen, und Auswirkungen verschiedener Prozesse während der Herstellung (Schälen, Rösten, Mikrowellenbehandlung, Aromatisierung mit Kräutern, Raffination, Ölerhitzung und Lagerung) durchgeführt. Einhundertsiebenunddreißig in Rapsöl beschriebene Aromastoffe sind aufgelistet, darunter Aldehyde, Ketone, Säuren, Ester, Alkohole, Phenole, Pyrazine, Furane, Pyrroline, Indole, Pyridine, Thiazole, Thiophene, weitere S-haltige Verbindungen, Nitrile und Alkene. Die mögliche Bildungswege einiger wichtiger aromaaktiver Verbindungen werden ebenfalls vorgeschlagen. Dennoch erfordern einige dieser Verbindungen eine weitere Validierung (z. B. Nitrile) aufgrund fehlender Rekombinationsexperimente in den vorherigen Arbeiten. Abschließend sollten fortschrittliche Aromaanalysetechniken in Richtung Zeitersparnis, Übertragung, Echtzeitüberwachung und Visualisierung weiterentwickelt werden, um ein „vollständiges“ Aromaprofil von Rapsöl zu erhalten. Abgesehen davon sind Studien zur Aufklärung des Einflusses wichtiger Röstverfahren auf die Bildung aromaaktiver Verbindungen erforderlich, um das Verständnis der Faktoren zu vertiefen, die zu Aromavariationen von Rapsöl führen.

Im nächsten Schritt wurde in systematischer Vergleich zwischen fünf Techniken zur Extraktion von Aromastoffen, darunter Festphasen-Mikroextraktion (solidphase microextraction, SPME),

SPME-Arrow, headspace sorptive extraction (HSSE), direkte thermische Desorption (DTD) und lösungsmittelunterstützte Aromaverdampfung (solvent assisted flavor evaporation, SAFE) für heißgepresstes Rapsöl durchgeführt. Außerdem wurde eine methodische Validierung dieser fünf Ansätze für einunddreißig in Rapsöl gefundene Aromastoffe durchgeführt, um ihre Stabilität, Zuverlässigkeit und Robustheit zu vergleichen. Bei der Qualifizierung der Aromasstoffe in heißgepresstem Rapsöl erzielte die SAFE, vor allem aufgrund der hohen Probenvolumina, die beste Performance, schnitt aber hinsichtlich Linearität, Wiederfindung und Reproduzierbarkeit schlechter ab als andere Methoden. SPME-Arrow zeigte gute Leistungen nicht nur bei der Extraktion von Aromastoffen, sondern auch bei der Quantifizierung. Sie wurde daher als am besten geeignet für die Quantifizierung von Aromastoffen in heißgepresstem Rapsöl angesehen. Unter Berücksichtigung des Preis-Leistungs-Verhältnisses ist die klassiche SPME aber immer noch eine effiziente Aromaextraktionsmethode. Eine Kombination aus mehreren Methoden zur Erfassung von Aromen könnte auch eine Option der Aromaanalyse für die Ölmatrix sein.

Anschließend wurden durch Anwendung des Sensomics-Ansatzes die wichtigsten Aromastoffe in repräsentativen kommerziellen FRO-Proben entschlüsselt. Auf der Grundlage des Aroma-Blueprints wurden Änderungen im Gesamtaromaprofil der Öle und ihrer Schlüsselaromastoffe unter verschiedenen Röstbedingungen untersucht und verglichen. Um industrielle Bedingungen besser zu simulieren, wurden in unserer Röststudie hohe Temperaturen (150-200 ºC) verwendet, die zuvor selten untersucht wurden. Die Identifizierung und Quantifizierung der wichtigsten Aromastoffe in FRO wurde mithilfe des Sensomics-Konzepts gut durchgeführt. Glucosinolat-Abbauprodukte waren eine besondere Art von Hauptaromastoffen, die in Rapsöl vorhanden sind. Die meisten Aromastoffe zeigten mit fortschreitendem Röstvorgang zunächst steigende und dann fallende Tendenzen. Die Ergebnisse der Aromaprofile zeigten, dass Hochtemperatur-Kurzzeit- und Niedrigtemperatur-Langzeit-Bedingungen ähnliche Auswirkungen auf die Aromaprofile von gerösteten Rapsölen haben könnten, was eine Referenz für die Zeitkosteneinsparungen in der industriellen Produktion liefern könnte.

Um grundlegende Erkenntnisse über die Aromabildung bei FRO zu gewinnen, wurde das thermische Abbauverhalten von Progoitrin (dem Hauptglucosinolat in Rapssamen) und den entsprechend entstehenden flüchtigen Produkten in Flüssigkeits- (Phosphatpuffer bei einem pH-Wert von 5,0, 7,0 oder 9,0) und Festphasensystemen (Seesand und Rapspulver) untersucht. Die höchste thermische Abbaurate von Progoitrin bei hohen Temperaturen (150-200 ºC) wurde bei einem pH-Wert von 9,0 beobachtet, gefolgt von Seesand und Rapspulver. Es konnte

gefolgert werden, dass die bimolekulare nukleophile Substitutionsreaktion (S_N2) hauptsächlich unter basischen Bedingungen stattfand. Die höchste Abbaurate unter basischen Bedingungen könnte aus der hohen Nukleophilie der vorhandenen Hydroxidionen resultieren. Unter den angewandten Bedingungen in dieser Studie war 2,4-Pentadiennitril das Hauptnitril, das während des thermischen Abbaus bei hoher Temperatur aus Progoitrin gebildet wurde, verglichen mit l-Cyano-2-hydroxy-3-buten, das weniger stabil sein könnte. Die möglichen Bildungswege der wichtigsten S-haltigen (Thiophene) und N-haltigen (Nitrile) flüchtigen (Aroma-)Verbindungen wurden vorgeschlagen. Schwefelwasserstoff als Abbauprodukt von Glucosinolaten könnte als Schwefelquelle dienen, die dann weiter mit Glucose zu reagieren, um Thiophene zu erzeugen.

Insgesamt dokumentiert die vorliegende Arbeit umfassend die Auswirkungen thermischer Bedingungen und Matrizes auf die Aromaeigenschaften, Aromaprofile und Hauptaromastoffe von heißgepresstem Rapsöl, die Daten und theoretische Grundlagen für die Aromakontrolle von FRO unter thermischer Behandlung bei den in der Produktion tatsächlichen verwendeten Temperaturen (150-200 °C).

摘要

菜籽油是世界三大植物油之一，因其特征的风味和较高的营养价值而受到人们的喜爱。采用典型焙炒工艺生产的浓香菜籽油（FRO）以其特有的香气而广受欢迎，FRO 年消费量已超过 150 万吨。然而，FRO 在焙炒过程中香气物质的变化规律尚不明晰，这对菜籽油的质量和消费者的接受度提出了挑战。 据此，本工作旨在研究 FRO 的香气特征及其香气物质前体的热解行为，为 FRO 生产过程中香气品质的控制提供依据和指导。

首先，对菜籽油风味的文献进行了系统综述，综述主要包含菜籽油风味的分析技术（即提取技术、定性分析、定量分析、感官分析和化学计量学方法），菜籽油代表性香气物质和异味化合物， 以及菜籽油加工过程中不同处理方式（脱皮、焙炒、微波、风味萃取、精炼、油加热和储存）对风味的影响。共有 137 种香气物质在菜籽油中被报道，包括醛类、酮类、酸类、酯类、醇类、酚类、吡嗪类、呋喃类、吡咯啉类、吲哚类、吡啶类、噻唑类、噻吩类、其他含硫化合物、腈类 和烯烃。本章还综述了一些关键香气活性物质的可能形成途径。 由于前人研究中缺乏重组实验，菜籽油中的一些香气物质需要进一步验证（例如腈类）。未来的风味分析技术应该向省时、便携、实时监控和可视化的方向发展，以期获得菜籽油的“完整”风味特征。此外，关键焙炒工艺对香气物质形成的影响有待进一步研究阐明，以探明影响菜籽油风味变化的因素。

其次，系统比较了固相微萃取（SPME）、SPME-Arrow、顶空搅拌棒吸附萃取（HSSE)）、直接热解吸（DTD）和溶剂辅助蒸馏萃取（SAFE）等五种风味萃取技术提取热榨菜籽油风味物质。同时，对菜籽油中 31 种香气成分进行了方法学验证，比较了五种方法的可靠性和稳健性。结果显示，对于热榨菜籽油中香气物质的定性，SAFE 呈现最优的效果，分析主要原因为提取样品量最大，但它在线性、回收率和重复性方面的表现不如其他四种方法。SPME-Arrow 风味提取效果好，数据显示其对于热榨菜籽油中香气成分的定量效果最好。考虑到性价比，SPME 仍然是一种高效的风味提取方法。风味提取技术的多方法联用也是以油为基质的香气分析的一种潜在策略。

再次，基于分子感官科学理论，分析了代表性 FRO 产品中的关键香气物质，并比较了不同焙炒条件下的菜籽油的香气轮廓及香气物质的变化。为了更好地模拟工业条件，采用了高温炒籽条件（150-200 ℃），相关的研究较少。采用分子感官科学方法对 FRO 中关键香气物质进行了有效的定性和定量。硫代葡萄糖苷降解产物是菜籽油中存在的

一类主要的特征风味物质。随着焙炒过程的进行，大多数香气物质呈现先增后减的趋势。香气轮廓分析结果表明，在特定高温短时和低温长时焙炒条件下的热榨菜籽油会有相似的香气轮廓，结果可为实际生产提供参考。

最后，为了进一步了解 FRO 中香气的形成，研究了 2-羟基-3-丁烯基硫代葡萄糖苷（油菜籽的主要硫代葡萄糖苷）在液相体系（pH 为 5.0、7.0 或 9.0 的磷酸盐缓冲液）和固相体系（海沙和菜籽粉）中的热解行为及其挥发性产物。在高温条件（150-200 ºC）下，pH 为 9.0 的液态体系中硫代葡萄糖苷的降解率最高，其次是海沙，再是菜籽粉。推断双分子亲核取代反应（S_N2）主要在碱性条件下发生。碱性条件下的降解率最高可能是存在的大量氢氧根离子具有高亲核性。基于本研究所应用的条件，相比于较不稳定的l-氰基-2-羟基-3-丁烯，2,4-戊二烯腈是主要的腈类挥发性产物。提出了主要含硫（噻吩）和含氮（腈）挥发性物质的可能形成途径。硫化氢作为硫代葡萄糖苷的降解产物，可以作为硫的来源与葡萄糖进一步反应生成噻吩。

综上，本文全面研究了加热条件和基质对热榨菜籽油的香气特征、香气轮廓和关键香气物质的影响，可为实际生产条件下（150-200 °C）FRO 的风味控制提供数据和理论依据。

I. CHAPTER General Introduction and Outline

Flavor of Rapeseed Oil: An Overview of Odorants, Analytical Techniques, and Impact of Treatment

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COMPREHENSIVE REVIEWS IN FOOD SCIENCE AND FOOD SAFETY

Flavor of rapeseed oil: An overview of odorants, analytical techniques, and impact of treatment

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Abstract

As one of the three major vegetable oils in the world, rapeseed oil is appreciated for its high nutritional value and characteristic flavor. Flavor is an essential attribute, determining rapeseed oil quality and consumer acceptance. The present manuscript provides a systematic literature review of recent advances and knowledge on the flavor of rapeseed oil, which focuses on aroma-active as well as off-flavor compounds, flavor analysis techniques (i.e., extraction, qualitative, quantitative, sensory, and chemometric methods), and effects of treatments (storage, dehulling, roasting, microwave, flavoring with herbs, refining, and oil heating) on flavor from sensory and molecular perspectives. One hundred thirty-seven odorants found in rapeseed oil from literature are listed and possible formation pathways of some key aroma-active compounds are also proposed. Future flavor analysis techniques will evolve toward time-saving, portability, real-time monitoring, and visualization, which aims to obtain a "complete" flavor profile of rapeseed oil. The changes of volatile compounds in rapeseed oil under different treatments are summarized in this view. Studies to elucidate the influence of different treatments on the formation of aroma-active compounds are needed to get a deeper understanding of factors leading to the variations of rapeseed oil flavor.

KEYWORDS
analytical techniques, aroma, flavor, rapeseed oil, treatment

1 | INTRODUCTION

Rapeseed oil, one of the most consumed vegetable oils globally, is the third most-produced vegetable oil in the world with an annual production (2019–2020) of 27.98 million metric tons, after palm oil and soybean oil (73.18 and 57.92 million metric tons, respectively) (United States Department of Agriculture, 2020). The world's major producers of rapeseed oil are the European Union, China, Canada, and India, with 9.66, 6.04, 4.43, and 2.66 million metric tons of rapeseed oil in 2019–2020, respectively (United States Department of Agriculture, 2020). In North America, Europe, Australia, and Japan, significant amounts of rapeseed oil with low erucic acid content are used as cooking oil. In North America and Australia, the rapeseed (*Brassica napus* and *Brassica rapa*) with low amounts of glucosinolates and erucic acid is known as "canola." However, rapeseed oil with a high amount of erucic acid still predominates in some rapeseed producing areas such as China and India that did not take part in the development and conversion to canola-type rapeseed (Przybylski et al., 2005; Zhang, Wu, et al., 2020). Widespread attention has also been paid to a type of high-oleic rapeseed oil that contains a higher percentage of oleic acid and shows therefore more oxidative stability. Thus, high-oleic rapeseed oil is confirmed to be suitable for cooking processes at elevated temperatures, including frying (Matthäus et al., 2009; Rękas et al., 2015). However, besides significant contents of unsaturated fatty acids, rapeseed oil also contains tocopherols, sterols, and polyphenols, which help to improve the nutritional value and oxidative stability (Tynek et al., 2012; Wei et al., 2012).

The main methods used for the extraction of rapeseed oil include cold pressing, hot pressing, and solvent extraction. Cold pressing is an oil extraction method without chemical or thermal treatments (Kiralan & Ramadan, 2016), leading to oils with an astringent, slightly nutty, and seed-like flavor. The low temperature used during cold pressing contributes to the retention of bioactive compounds (Gracka et al., 2016; Matthäus & Brühl, 2004). Virgin rapeseed oil is a kind of cold-pressed rapeseed oil that suffers no additional treatment except for sedimentation or filtration, which is popular in Europe (e.g., Germany, Switzerland, Austria, and Denmark) because of its mild and fresh taste and cabbage-like flavor (Brühl & Matthäus, 2008; Matheis & Granvogl, 2016a; Matthäus & Brühl, 2003). In China, virgin rapeseed oil produced by hot pressing also gains massive popularity among consumers due to its intensive color, smooth taste, and characteristic flavor (roasted, caramel, and pungent flavor). A moderate roasting of the seeds helps to improve the yield of oil and oxidative stability by increasing the content of tocopherols in the oil on the one side, and also causes the generation of the characteristic oil aroma on the other side. Thereby, seed roasting leads to the formation of volatiles from the Maillard reaction, mostly heterocyclic compounds including pyrazines, contributing to the pleasant roasted flavor. Currently, the consumption of virgin hot-pressed rapeseed oil has accounted for almost 30% of the rapeseed oil market in China with around 1.5 million tons per year, which is expected to grow by approximately 10% per year (Kraljić et al., 2018; Zhang, Zhu, et al., 2020; Zhou et al., 2019). Solvent-extracted canola oils usually undergo several chemical refining steps to become oil products with a light flavor and color, mainly used as cooking oil and salad oil. Flavor is one of the most critical criteria for customers to choose edible oils. At the same time, improper storage and processing of seeds and oils can lead to off-flavors in rapeseed oil (fusty, musty, and rancid) (Bonte et al., 2017; Matheis & Granvogl, 2016b, 2019a, 2019b). During the past decade, more and more attention has been paid to the flavor of rapeseed oil, odorants in particular. As far as we know, there is no systematic review on summarizing, comparing, and critiquing the literature regarding the flavor of rapeseed oil, especially about analysis techniques, aroma-active compounds, and effects of different treatments during the production processes.

Thus, this review systematically evaluates and discusses current knowledge on the flavor compounds in rapeseed oil, focusing on the roles of the key aroma compounds, off-flavor development, and flavor analytical techniques (including extraction, qualitative, quantitative, sensory, and chemometric methods). In addition, the effects of different treatments on the flavor of rapeseed oil are summarized. This article aims at a better understanding of rapeseed oil flavor and providing promising and insightful information to obtain rapeseed oil products with the desired quality, especially with regard to flavor.

2 | FLAVOR COMPOUNDS IN RAPESEED OIL

More than 300 volatile compounds in rapeseed oil have been reported so far. However, only a part of these compounds is aroma-active and can contribute to the overall aroma of rapeseed oil. In this review, 137 aroma-active compounds found in rapeseed oil in previous studies were collected and collated in Table 1 including aldehydes, ketones, acids, esters, alcohols, phenols, pyrazines, pyrrolines, indoles, pyridines, thiazoles, thiophenes, furans, sulfur (*S*)-containing compounds, nitriles, and alkenes. The selection criteria of aroma-active compounds in this table are as follows: compounds were judged to be aroma-active based on their gas chromatography–olfactometry/mass spectrometry (GC–O/MS) results. In addition, a network map based on the relation between these 137 odorants and

TABLE 1 Aroma-active compounds found in rapeseed and rapeseed oils

Name	Odor description (as mentioned in the reference)	Sources and FD factors (if mentioned in the reference)	References
Aldehydes			
Benzaldehyde	Almond-like, burnt sugar-like	HPO	j
Butanal	Cheese-like, unpleasant	CPO	f
(*E*,*E*)-2,4-Decadienal	Deep-fried, fatty, flowery	RoaS^{4}, CPO$^{8, 64}$, CPOP^{8}, HPO, STO^{256}, STOF^{512}	b, c, d, e, h, j
(*E*,*Z*)-2,4-Decadienal	Cheese-like, deep-fried	CPO^{64}, STO^{64}, STOF^{16}	d, e, h
(*E*)-2-Decenal	Fatty, nutty, tallowy	RawS^{16}, RoaS^{8}, CPO^{32}, CPOP^{32}, STO^{16}, STOF^{128}	b, c, d, e, h
(*Z*)-2-Decenal	Fatty	STO^{16}, STOF^{128}	h
trans-4,5-Epoxy-(*E*)-2-decenal	Metallic	RawS^{32}, RoaS^{32}, CPO$^{16, 512}$, CPOP^{32}, STO^{2048}, STOF^{2048}	b, c, d, e, h
trans-2,3-Epoxyundecanal	Citrus-like, metallic	CPO^{64}, STO^{16}, STOF^{8}	d, e, h
Geranial	Citrus-like	CPO^{64}	d, e
(*E*,*E*)-2,4-Heptadienal	Fatty, flowery, lard-like, nutty	CPO^{8}, HPO, STO^{8}, STOF^{4}	b, h, j
Heptanal	Flowery, green, lemon-like, pungent, rancid, sweet, tallowy	HPO	f, i, j
(*Z*)-4-Heptenal	Biscuit-like, creamy, fishy, tallowy	CPO^{8}, CPOP^{4}, HPO, STO^{4}, STOF^{32}	a, b, h
Hexanal	Fatty, grassy, green, woody	RawS^{64}, RoaS^{32}, CPO$^{32, 1024}$, CPOP^{512}, HPO, STO^{32}, STOF^{32}	a, b, c, d, f, h, i, j
(*E*)-2-Hexenal	Apple-like, green	HPO	j
4-Hydroxy-3-methoxybenzaldehyde	Vanilla-like	RawS^{8}, RoaS^{4}, CPO$^{16, 32}$, CPOP^{8}, STO^{128}, STOF^{128}	b, c, d, e, h
2-Methylbutanal	Malty	RoaS^{1}, CPO^{32}, CPOP^{16}	b, c, d, e
3-Methylbutanal	Butanoic acid, cheese-like, flea-bitten, malty	RoaS^{2}, CPO^{32}, CPOP^{16}	b, c, d, e, f
2-Methylpropanal	Moldy, sweet	CPO	f
3-(Methylthio)propanal	Cooked potato-like	RawS^{32}, RoaS^{128}	c
(*E*,*E*)-2,4-Nonadienal	Deep-fried, fatty, green	CPO$^{64, 128}$, CPOP^{64}, STO^{64}, STOF^{64}	b, d, e, h
(*E*,*Z*)-2,6-Nonadienal	Cucumber-like, fatty	CPO$^{32, 2048}$, CPOP^{64}, STO^{64}, STOF^{32}	b, e, h
(*Z*,*Z*)-3,6-Nonadienal	Fatty, green	STO^{32}, STOF^{16}	h
Nonanal	Citrus-like, detergent-like, fatty, green, lemon-like, peanut-like, soapy, sweet	CPO^{16}, CPOP^{64}, HPO	a, b, i, f
(*E*,*E*,*Z*)-2,4,6-Nonatrienal	Oat flakes-like	CPO^{16}, CPOP^{16}	b
(*E*)-2-Nonenal	Cardboard-like, cucumber-like, fatty, green, orris-like	RawS^{32}, RoaS^{16}, CPO$^{32, 16}$, CPOP^{128}, HPO, STO^{256}, STOF^{256}	a, b, c, d, e, h
(*Z*)-2-Nonenal	Fatty	CPOP^{16}	b
(*Z*)-6-Nonenal	Caramel-like, citrus-like	CPO^{32}	d, e
Octanal	Citrus-like, fatty, grassy, green, lemon-like, soapy	RawS^{32}, RoaS^{4}, CPO$^{512, 1024}$, CPOP^{128}, HPO, STO^{16}, STOF^{8}	a, b, c, d, e, f, h
(*E*)-2-Octenal	Fatty, green, nutty, roasty	CPO$^{2, 8}$, CPOP^{4}, HPO	b, d, e, f, i
Pentanal	Cheese-like, moldy	CPO	f
Phenylacetaldehyde	Flowery, green, honey-like	RoaS^{4}, HPO	a, c
(*E*)-2-Tridecenal	Metallic	STO^{16}, STOF^{16}	h

(Continues)

TABLE 1 (Continued)

Name	Odor description (as mentioned in the reference)	Sources and FD factors (if mentioned in the reference)	References
Ketones			
2-Aminoacetophenone	Foxy	RawS^{256}, RoaS^{512}, CPO^{2048}, STO^{32}, STOF^{8}	c, d, e, h
2,3-Butanedione	Buttery	RawS^{8}, RoaS^{64}, CPO^{8}, CPOP^{8}, HPO	a, b, c
(*E*)-*β*-Damascenone	Fruity	CPO^{8}	d, e
1-Hexen-3-one	Pungent	STO^{32}, STOF^{4}	h
4-Mercapto-4-methylpentan-2-one	Black currant-like, catty	RawS^{32}, RoaS^{64}	c
3-Methylnonane-2,4-dione	Corn-like, straw-like	CPO^{8}, CPOP^{8}	b
(*Z*)-1,5-Octadien-3-one	Geranium-like, hop-like, metallic	CPO^{32}, STO^{16}, STOF^{64}	d, e, h
2-Octanone	Gasoline-like, soapy	HPO	j
1-Octen-3-one	Earthy, herbal, mushroom-like	RawS^{16}, RoaS^{32}, CPO^{128}, CPOP$^{512, 4096}$, HPO, STO^{256}, STOF^{64}	a, b, c, d, e, h
2,3-Pentanedione	Buttery	RawS^{4}, RoaS^{8}	c
1-Penten-3-one	Pungent	STOF^{8}	h
Acids			
Acetic acid	Vinegar-like, acetic acid	RawS^{32}, RoaS^{8}, CPO^{8}, CPOP^{32}, STO^{8}, STOF^{128}	b, c, h, f
Butanoic acid	Cheese-like, sweaty	RawS^{64}, RoaS^{32}, CPO^{32}, CPOP^{64}, STO^{64}, STOF^{1024}	b, c, d, e, h
Heptanoic acid	Sweaty	CPO^{16}, STO^{32}, STOF^{16}	e, h
Hexanoic acid	Pungent, sweaty	RawS^{8}, CPO^{4}, CPOP^{4}	b, c
2-Methylbutanoic acid	Cheese-like, sweaty, fruity	RawS^{64}, RoaS^{128}, CPO$^{32, 256}$, CPOP^{256}, STO^{128}, STOF^{256}	b, c, d, e, h
3-Methylbutanoic acid	Cheese-like, sweaty, fruity	RawS^{64}, RoaS^{128}, CPO$^{32, 256}$, CPOP^{256}, STO^{128}, STOF^{256}	b, c, d, e, h
3-Methylpentanoic acid	Cheese-like, sweaty	CPOP^{4}	b
2-Methylpropanoic acid	Cheese-like, sweaty	RawS^{8}, RoaS^{4}, CPO^{8}, CPOP^{8}	b, c
Octanoic acid	Spicy	HPO	i
Pentanoic acid	Cheese-like, pungent, sweaty	RawS^{32}, RoaS^{4}, CPO$^{8, 16}$, CPOP^{32}	b, c, d, e
Phenylacetic acid	Beeswax-like, honey-like	RawS^{32}, RoaS^{128}, CPO$^{16, 32}$, CPOP^{32}, STO^{512}, STOF^{128}	b, c, d, e, h
Propanoic acid	Sweaty	CPO^{8}	b
Esters			
Butyrolactone	Caramel-like, sweet	HPO	j
γ-Decalactone	Coconut-like, peach-like	CPO^{128}, STO^{256}, STOF^{64}	d, e, h
Ethyl acetate	Caramel-like, sweet, sugar-like	CPO	f
Ethyl butanoate	Ananas-like, gummi bear-like, fruity, sweet	CPO^{4}, CPOP^{2}	b, f
Ethyl 2-methylbutanoate	Fruity	CPO^{16}, CPOP^{8}	b
Ethyl 3-methylbutanoate	Fruity	CPOP^{4}	b
Ethyl 3-methylpentanoate	Fruity	STO^{8}	h
Ethyl 2-methylpropanoate	Fruity	CPO, CPOP^{2}	b, f
Ethyl 4-pentenoate	Fruity, sweet	CPO	f
Ethyl phenylacetate	Beeswax-like	RoaS^{4}	c

(Continues)

TABLE 1 (Continued)

Name	Odor description (as mentioned in the reference)	Sources and FD factors (if mentioned in the reference)	References
Ethyl 3-phenylpropanoate	Flowery	STO[8]	h
γ-Hexalactone	Coconut-like	RawS[32], RoaS[4]	c
δ-Hexalactone	Roasty	HPO	i
Methyl 2-methylbutanoate	Fruity	CPO[8]	d, e
Methyl 2-methylpropanoate	Fruity	CPOP[4]	b
γ-Nonalactone	Coconut-like, peach-like	RawS[16], RoaS[4], CPO[8, 64], STO[256], STOF[128]	b, c, d, e, g
δ-Nonalactone	Coconut-like	CPO[64], STO[16], STOF[32]	d, e, h
γ-Octalactone	Coconut-like	CPO[32, 64], CPOP[16], STO[16], STOF[32]	b, d, e, h
δ-Octalactone	Coconut-like	CPO[8]	d
γ-Valerolactone	Mushroom-like, earth-moist	CPO	f
Alcohols			
2,3-Butanediol	Solvent-like, metallic	CPO	f
1-Hexanol	Grassy	CPO[2], CPOP[8]	b
(*Z*)-3-Hexen-1-ol	Cucumber-like, fatty	CPO[16], STO[32], STOF[64]	d, e, h
Linalool	Citrus-like, flowery	CPO[4, 32], CPOP[32]	b, d, e
3-Methyl-1-butanol	Cheese-like, malty	CPO[4]	b, f
(*E*,*Z*)-2,6-Nonadien-1-ol	Cucumber-like	CPO[16], CPOP[32]	b
1-Octanol	Citrus-like, soapy	CPO[32], CPOP[4], STO[16], STOF[64]	b, e, h
1-Octen-3-ol	Mushroom-like	CPO[32]	d, e
2-Phenylethanol	Flowery, honey-like, rose-like, spicy, gum-like, nutty, rye-like	RoaS[32], CPO[32, 64], CPOP[128], STO[256], STOF[256], HPO	a, b, c, d, e, h, j
Phenols			
4-Allyl-2-methoxyphenol	Clove-like, smoky	STO[4], STOF[8]	h
2-Methoxyphenol	Gammon-like, smoky, sweet	CPO[32]	d, e
2-Methoxy-4-vinylphenol	Clove-like, phenolic, smoky, woody	RawS[1024], RoaS[1024], CPO[32], HPO	c, d, e, j
4-Methylphenol	Fecal	CPO[32], STO[256], STOF[256]	d, e, h
3-Propylphenol	Leather-like	STO[8], STOF[32]	h
4-Vinylphenol	Phenolic	CPO[8]	d, e
Pyrazines			
Acetylpyrazine	Roasty	RoaS[64]	c
2-*sec*-Butyl-3-methoxypyrazine	Bell pepper-like, earthy, pea-like, roasty	CPO[16, 32], CPOP[128], STO[32], STOF[64]	b, d, e, h
2,3-Diethyl-5-methylpyrazine	Earthy, musty, toasted, nutty	RawS[32], RoaS[2048], HPO	a, c
2,3-Dimethylpyrazine	Roasty, roast meat-like	HPO	i
2,5-Dimethylpyrazine	Peanut-like, roasted nut-like, roasty	HPO	i, j
2,6-Dimethylpyrazine	Cocoa-like, roast beef-like	HPO	j
2-Ethyl-3,5-dimethylpyrazine	Earthy, roasty	RoaS[4], CPO[32]	c, e
2-Ethyl-3,6-dimethylpyrazine	Earthy, roasty	RoaS[256], CPO[32]	c, e

(Continues)

TABLE 1 (Continued)

Name	Odor description (as mentioned in the reference)	Sources and FD factors (if mentioned in the reference)	References
3-Ethyl-2,5-dimethylpyrazine	Nutty, burnt sugar-like, roasty	HPO	i, j
2-Ethyl-5-methylpyrazine	Potato-like, roasty	RoaS^{4}, HPO	c, j
2-Ethyl-6-methylpyrazine	Potato-like, roasty	RoaS^{4}, HPO	c, i, j
Ethylpyrazine	Roasted nut-like	RoaS^{4}, HPO	c, i
2-Isobutyl-3-methoxypyrazine	Bell pepper-like, earthy	RawS^{256}, RoaS^{8}, CPO$^{256, 2048}$, CPOP^{8192}, STO^{32}, STOF^{32}	b, c, e, h
2-Isopropyl-3-methoxypyrazine	Earthy, pea-like	RawS^{256}, RoaS^{1024}, CPO$^{2048, 8192}$, CPOP^{8192}, HPO, STO^{256}, STOF^{1024}	a, b, c, d, e, h
Methylpyrazine	Roasty	HPO	j
Trimethylpyrazine	Potato-like, musty, roasty	HPO	j
Furans			
2-Furanmethanethiol	Coffee-like	RoaS^{128}	c
2-Furanmethanol	Burnt	HPO	j
2(5*H*)-Furanone	Roasty	HPO	j
3-Hydroxy-4,5-dimethylfuran-2(5*H*)-one	Lovage-like, spicy, seasoning-like	CPO$^{8, 64}$, CPOP^{16}, STO^{512}, STOF^{512}	b, d, e, h
4-Hydroxy-2,5-dimethylfuran-3(2*H*)-one	Caramel-like	RoaS^{2048}, CPO^{64}	c, d, e
5-Methyl-2-furancarboxaldehyde	Almond-like, caramel-like	HPO	j
Indole, pyridines, and pyrrolines			
2-Acetylpyridine	Nutty, roasty	CPO^{32}	d, e
2-Acetyl-1-pyrroline	Popcorn-like	RoaS^{256}	c
2-Acetyl-3,4,5,6-tetrahydropyridine	Popcorn-like, roasty	RoaS^{4}	c
Indole	Fecal, mothball-like	RawS^{8}	c
2-Propionyl-1-pyrroline	Popcorn-like, roasty	RoaS^{128}	c
Thiazoles and thiophene			
2,4-Dimethylthiazole	Roasty	HPO	j
2-Formylthiophene	Roasty	RoaS^{4}	c
2-Propionylthiazole	Pea-like, roasty	CPO^{512}, STO^{64}, STOF^{32}	d, e, h
***S*-containing compounds**			
Allyl isothiocyanate	Green, sulfury, pungent	CPO$^{2, 16, 128}$, HPO$^{2, 16}$	g, j
Dimethyl disulfide	Moldy, onion-like, putrid, unpleasant, cabbage-like	RoaS^{4}, CPO^{2}, HPO$^{4, 8}$	c, g
Dimethyl sulfide	Asparagus-like, cheese-like, flea-bitten, moldy, onion-like, sulfury, cabbage-like	RawS^{32}, RoaS^{32}, CPO$^{2, 8}$, CPOP^{128}, HPO$^{4, 32}$	a, b, c, f, g
Dimethyl sulfone	Burnt, sulfury	CPO^{2}, HPO$^{2, 4}$	g, j
Dimethyl sulfoxide	Cheese-like, compost-like, flea-bitten, garlic-like	CPO$^{2, 8}$, HPO$^{4, 8, 64}$	f, g, j
Dimethyl trisulfide	Cabbage-like, fishy, sulfury	RoaS^{1024}, CPO$^{2, 4, 32, 128}$, CPOP^{16}, HPO$^{32, 128}$, STO^{64}, STOF^{128}	a, b, c, d, e, g, h, j

(Continues)

TABLE 1 (Continued)

Name	Odor description (as mentioned in the reference)	Sources and FD factors (if mentioned in the reference)	References
2,4-Dithiapentane	Moldy, unpleasant	CPO	j
1-Isothiocyanatobutane	Garlic-like, pungent, sulfury	CPO[4, 16], HPO[2]	g
4-Isothiocyanato-1-butene	Pickled, pungent, spicy, sulfury	CPO[16, 32, 256], HPO[2, 32]	g, i, j
Methanethiol	Cabbage-like, garlic-like, gasoline-like, putrid, sulfury	RawS[1], RoaS[5], CPO[2], HPO[4, 8]	c, g
Nitriles			
Benzyl nitrile	Pickled, pungent, spicy	HPO	i, j
5-Cyano-1-pentene	Spicy	HPO	i
Heptanenitrile	Pungent, spicy	HPO	i
Alkenes			
D-Limonene	Citrus-like, mint-like	HPO	j
Limonene (dipentene)	Citrus-like, spicy, lemon-like	CPO[2], CPOP[16], HPO	b, f, i
Myrcene	Geranium-like, hop-like	CPO[64]	d, e
α-Pinene	Resinous	CPO[8], CPOP[16]	b

Abbreviations: CPO, cold-pressed oil; CPOP, cold-pressed oil from peeled seeds; HPO, hot-pressed oil; RawS, raw rapeseed; RoaS, roasted rapeseed; STO, steam-treated oil; STOF, steam-treated oil with fishy off-flavor.
References (time order): a, Gracka et al. (2016); b, Pollner and Schieberle (2016); c, Ortner et al. (2016); d, Matheis and Granvogl (2016a); e, Matheis and Granvogl (2016b); f, Bonte et al. (2017); g, Zhou et al. (2018); h, Matheis and Granvogl (2019a); i, Su et al. (2019); j, Zhou et al. (2019).

odor descriptions was made using *Gephi* 0.9.2 software (https://gephi.org/) (Figure 1). In Figure 1, the light pink (first color in the legend) nodes represent different odor descriptions and other nodes with different colors represent different kinds of aroma-active compounds. The size of the light pink nodes (odor description) represents the number of connected nodes (corresponding odorants). The larger the size of the light pink nodes, the more the number of corresponding odorants. These aroma-active compounds elicit mainly roasty, fatty, cheese-like, green, fruity, pungent, citrus-like, sweaty, sweet, spicy, flowery, nutty, earthy, sulfury, and coconut-like aroma notes, contributing to the overall flavor of rapeseed oil. Figure 1 nicely illustrates that heterocyclic compounds including pyrazines, pyrrolines, pyridines, thiazoles, and thiophene are responsible for the roasty flavor, aldehydes mainly contribute to the fatty and green flavor, acids impart cheese-like and sweaty flavor to the oil, esters contribute to the fruity and coconut-like smell of rapeseed oil, and *S*-containing compounds are responsible for the sulfury odor note in rapeseed oil. Beside key aroma compounds, this section also describes other volatiles that have been found in rapeseed oil but have not been proven as key odorants in these oils as well as their formation pathways.

2.1 | Aldehydes

Aldehydes are common volatiles in vegetable oils formed by the oxidation of fatty acids, which make up the largest proportion of total volatiles in most cold-pressed or non-roasted rapeseed oils (Gracka et al., 2016; Ivanova-Petropulos et al., 2015; Mao et al., 2019). Thirty-two aldehydes were reported to be aroma-active compounds in rapeseed and rapeseed oil, which have the highest proportion of odorants in Table 1. Most of the reported aldehydes in rapeseed oil are related to the fatty flavor of the oil, but some are responsible for green, nutty, and even rancid odor (Kraljić et al., 2018; Matheis & Granvogl, 2016b, 2019a, 2019b). Raghavan et al. (1994) verified that the predominant volatile compounds from fresh and aged canola oils were (*E*,*Z*)-2,4-heptadienal and (*E*,*E*)-2,4-heptadienal, which are generated from the degradation of linolenic acid and are responsible for the fatty and nutty aroma. In both high-oleic rapeseed oil and conventional rapeseed oil, (*E*,*E*)-2,4-heptadienal, (*E*,*Z*)-2,4-decadienal, and propanal were found to be the major volatile compounds (Petersen et al., 2012). Pollner and Schieberle (2016) reported that (*E*,*Z*)-2,6-nonadienal (fatty and cucumber-like) and (*E*,*E*)-2,4-nonadienal (fatty, deep-fried, and green) had the

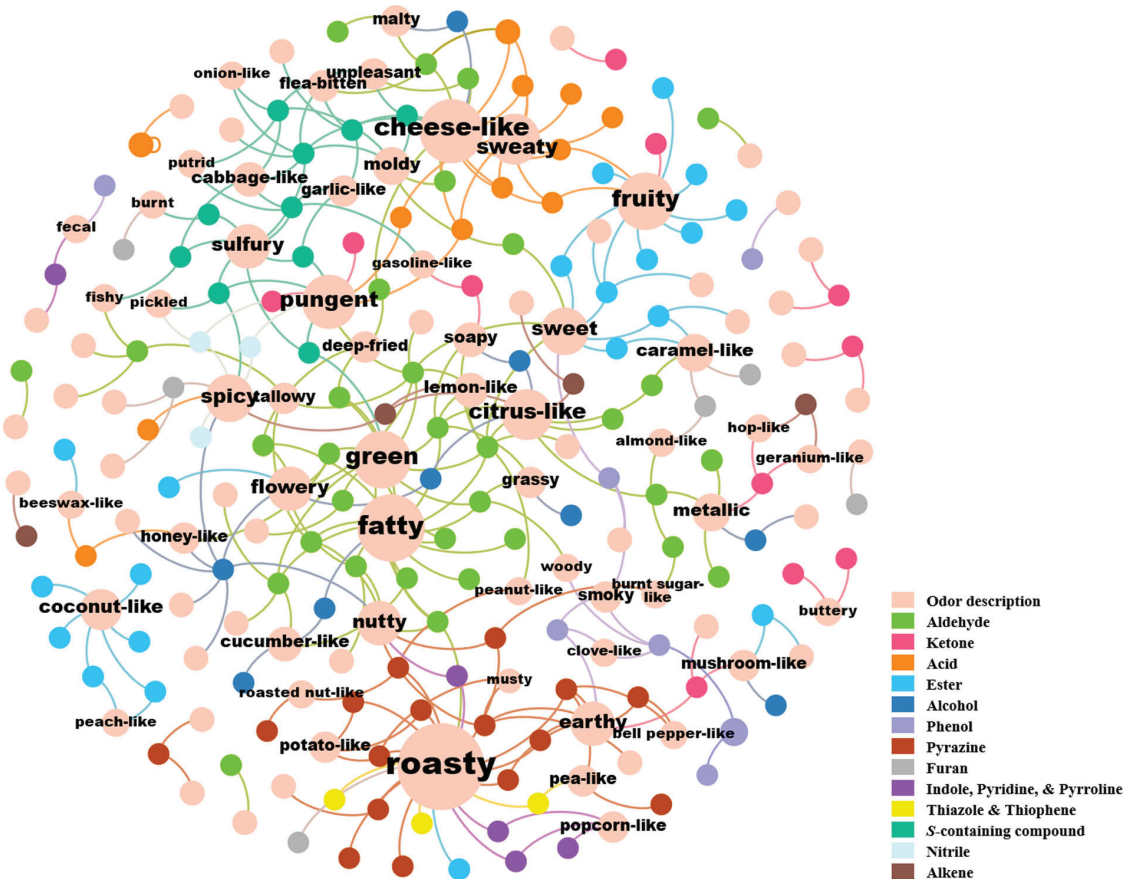

FIGURE 1 Network relation map of odorants and corresponding odor description in rapeseed and rapeseed oils (odor description nodes reported more than once are labeled in the figure)

highest odor activity values (OAVs; ratio of the concentration of an odorant to its corresponding odor threshold) in rapeseed oil. However, these compounds have not been identified in the work of Gracka et al. (2017). In the study of Gracka et al. (2016), the major aldehydes discovered in cold-pressed rapeseed oil were octanal and hexanal, contributing to the grassy aroma notes. They also found high contents of octanal in roasted rapeseed oil. Mao et al. (2019) confirmed that hexanal, nonanal, and octanal were dominant volatiles in non-roasted rapeseed oil, which were related to the grassy and fatty smelling. Hexanal, heptanal, (*E*)-2-hexenal, (*E*,*E*)-2,4-decadienal, and benzaldehyde were reported to be aroma-active compounds in commercial fragrant rapeseed oils (virgin rapeseed oil obtained from roasted seeds) (Zhou et al., 2019). The differences in rapeseed varieties, processing methods, and volatiles extraction methods may lead to the variations seen in the types of aldehydes in these studies.

Aldehydes in rapeseed oil can be formed by two main formation pathways: one is lipid peroxidation and the other is Strecker degradation. Hexanal, (*E*)-2-butenal, (*E*)-2-nonenal, and (*E*,*E*)-2,4-nonadienal are known as compounds originating from the oxidation of linolenic acid, whereas octanal is generated from oleic acid, all of which are major fatty acids in rapeseed oil. (*E*,*Z*)-2,6-Nonadienal is known to be derived from 9-hydroperoxy-(*E*,*Z*,*Z*)-10,12,15-octadecatrienoic acid. 2-Methylbutanal, 3-methylbutanal, and 2-methylpropanal, related to a malty odor in oil, are generated by Strecker degradation of the corresponding amino acids isoleucine, leucine, and valine during roasting of the seeds (Bonte et al., 2017; Gracka et al., 2016; Mao et al., 2019; Matheis & Granvogl, 2016a; Pollner & Schieberle, 2016; Zhou et al., 2019).

2.2 | Ketones

Ketones also impart aroma to rapeseed oils. Guth and Grosch (1990) reported on 23 aroma-active compounds detected via aroma extract dilution analysis (AEDA). 1-Octen-3-one and (*Z*)-1,5-octadien-3-one were found to be aroma-active ketones with the highest flavor dilution (FD) factors for the first time. Eleven aroma-active ketones have been reported in rapeseed oil to date (Table 1).

1-Octen-3-one is a representative ketone of the aroma-active compounds in rapeseed oil, which is the product of the 10-hydroperoxide of linoleic acid through the β-scission route. Its odor has been generally described as herbal mushroom and earthy (Wang et al., 2005). 2-Heptanone and 3-octen-2-one were also reported to contribute to the nutty flavor in rapeseed oil by Kraljić et al. (2018); however, their real impact on the overall aroma remained unclear because no GC–O experiments were performed for these two compounds. High contents of 2,3-pentanedione and 2,3-butanedione (both with buttery odor) were found in roasted rapeseed, whereas the raw seeds showed lower concentrations of the corresponding substances (Ortner et al., 2016). Jing et al. (2020) also found that 2,3-pentanedione, 2,3-butanedione, and 5-hepten-2-one showed high OAVs after thermal treatment of rapeseed. Their contents increased significantly during roasting, and the concentrations of the ketones increased by approximately 13%. However, the concentrations of these volatiles were analyzed with 2-octanol as the internal standard; thus, OAVs calculated in this study are relative values that cannot serve as direct evidence of identifying key aroma compounds. 2,3-Butanedione was not detected in oils from raw or light-roasted seeds in their study, which might be due to differences between rapeseed cultivars. The possible formation pathway of 2,3-pentanedione can be suggested by an aldol reaction from propanal and hydroxyacetaldehyde (glycolaldehyde). The formation of the homologous 2,3-butanedione was postulated by a similar pathway from acetaldehyde and hydroxyacetaldehyde (Ortner et al., 2016). Dicarbonyl compounds are known to be generated during the Maillard reaction, leading to the further formation of heterocyclic compounds (Gracka et al., 2016). Furanones are formed by the degradation of carbohydrates during the thermal processing of foods. 4-Hydroxy-2,5-dimethylfuran-3(2*H*)-one, responsible for a caramel-like aroma, was found in high amounts in roasted rapeseed with a high OAV, whereas it was absent in raw seeds (Ortner et al., 2016). 3-Hydroxy-4,5-dimethylfuran-2(5*H*)-one (sotolone; seasoning-like odor) can originate from threonine that can form 2-ketobutyric acid after enzymatical deamination, which then undergoes an aldol condensation (with acetaldehyde) and a cyclization (Pons et al., 2010). An alternative formation route for sotolone starting with 4-hydroxyisoleucine was also proposed (Blank et al., 1996; Matheis & Granvogl, 2016a).

2.3 | Acids

For acids, butanoic acid, 2- and 3-methylbutanoic acid, phenylacetic acid, pentanoic acid, heptanoic acid, and acetic acid were observed to be typical aroma-active compounds in rapeseed oil based on the molecular sensory science concept (also called the sensomics approach), which contributed sweaty, pungent, and vinegar-like aroma notes (Matheis & Granvogl, 2016a, 2016b, 2019a; Ortner et al., 2016; Pollner & Schieberle, 2016). Interestingly, these acids were found in roasted rapeseed, but they are not currently identified as aroma-active compounds in hot-pressed rapeseed oil. In the study of Ivanova-Petropulos et al. (2015), acetic acid showed the highest relative concentrations in pumpkin seed oil, followed by sesame oil, sunflower oil, and rapeseed oil. 2- and 3-Methylbutanoic acid were found with high FD factors in cold-pressed rapeseed oil, formed from the corresponding amino acids isoleucine and leucine by microorganisms via the so-called Ehrlich pathway during production or storage of rapeseed oil (Matheis & Granvogl, 2016a).

2.4 | Esters

In absolute numbers, esters are the second largest group of odorants that had been reported so far (Table 1). Twenty aroma-active esters were found in rapeseed oils including nine lactones (butyrolactone, γ-decalactone, γ-hexalactone, δ-hexalactone, γ-nonalactone, δ-nonalactone, γ-octalactone, δ-octalactone, and γ-valerolactone). They were related to the fruity and flowery-like odor with relatively low FD factors. Esters accounted for 5%–8% in volatile compounds that were identified in unheated and heated (60°C) refined rapeseed oil (Kasprzak et al., 2020). Six esters were also found among 109 volatiles detected in virgin rapeseed oils (Wang et al., 2020). However, esters account for only a small proportion within the volatiles of rapeseed oil. Moreover, up to now, there are only a few reports on the formation pathways of these compounds in rapeseed oil, which need to be further addressed.

2.5 | Alcohols

As shown in Table 1, nine alcohols with aroma activity were reported in previous studies. Besides aldehydes and ketones, alcohols, including straight-chain and branched alcohols derived from the reduction of Strecker aldehydes, were the third largest group of volatiles observed in rapeseed oils (Gracka et al., 2016).

In cold-pressed rapeseed oil, the major volatile compounds (aldehydes, alcohols, and alkanes) that were found made up 64.4%–82.5% of the total volatiles. 2-Phenylethanol appears most frequently in the group of alcohols (Table 1). Significant contents of 1-hexanol, 3-methyl-1-butanol, and 2-methyl-1-butanol were also

identified in the oil from non-roasted rapeseed (Mao et al., 2019). Flowery and honey-like smelling 2-phenylethanol was found as an important odorant in cold-pressed rapeseed oil, which is also formed via the Ehrlich pathway (Matheis & Granvogl, 2016a). The odor of 1-octen-3-ol has been generally described as mushroom-like (Matheis & Granvogl, 2016a). Kraljić et al. (2018) detected seven alcohols in rapeseed oils. The amounts of alcohols decreased with an increasing roasting temperature, except for 3-hepten-1-ol, which was referred to their volatility at higher temperatures and the generation of the corresponding aldehydes.

2.6 | Phenols

2-Methoxy-4-vinylphenol (also named 4-ethenyl-2-methoxyphenol) is the main aroma-active phenol in rapeseed and rapeseed oil with a clove-like, smoky, and woody flavor (Matheis & Granvogl, 2016a, 2016b; Ortner et al., 2016; Zhou et al., 2019). Kraljić et al. (2018) indicated that 2-methoxy-4-vinylphenol was found only in rapeseed oil preconditioned at 100°C, which was thought to be related to canolol in oil due to its similar molecular structure, and thus, it was inferred that 2-methoxy-4-vinylphenol is generated from canolol.

2.7 | Heterocyclic compounds

Heterocyclic compounds are an essential class of aroma compounds containing pyrazines, pyrroles, pyridines, thiophenes, thiazoles, furans, and so forth that are generated during the Maillard reaction in many heat-processed foods and are often responsible for their roasted aroma. Heterocyclic compounds positively correlate with applied heating temperature and time (Kraljić et al., 2018; Mao et al., 2019; Park et al., 1995).

2.7.1 | Pyrazines

In absolute numbers, pyrazines are the third major group of aroma-active compounds that had been reported up to now (Table 1). They are often present at consistently higher concentrations in oils from roasted rapeseed compared to oils from raw or light-roasted rapeseed, confirming that pyrazines are generated by prolonged thermal treatment. Dicarbonyl compounds generally derive from the degradation of carbohydrates. The reaction of dicarbonyl compounds with free amino acids or polypeptides can form α-amino ketones, and then, generate pyrazines via condensation reaction (Umano et al., 1995). Aldol condensation and subsequent cyclization can also produce pyrazines (Jing et al., 2020; Sacchetti et al., 2016). Eight pyrazines were detected among the flavor compounds of the oil obtained from rapeseed roasted at 100°C, namely, 2-methylpyrazine, 2-ethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-3-methylpyrazine, 2-ethyl-5-methylpyrazine, 2-ethyl-6-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine (Kraljić et al., 2018). 2,5-Dimethylpyrazine and trimethylpyrazine were identified as key odorants in roasted rapeseed oil by GC–O and were associated with a peanut-like and roasty aroma (Gracka et al., 2016). Su et al. (2019) reported on five pyrazines, detected via GC–O, that were responsible for the roasted aroma of rapeseed oils (hot pressing), including ethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine. Similar compounds were also found in commercial fragrant rapeseed oils using monolithic material sorptive extraction (MMSE) and GC–O (Zhou et al., 2019). The possible generation pathways of 2-ethyl-3,6-dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine eliciting an earthy and roasty smell are based on a condensation of two aminoaldehydes, of two aminoketones, or of an aminoaldehyde and an aminoketone; then the addition of the Strecker aldehyde of alanine (acetaldehyde) forms dihydropyrazines, which were suggested as intermediates (Cerny & Grosch, 1994; Ortner et al., 2016). Pollner and Schieberle (2016) detected 2-isopropyl-3-methoxypyrazine (earthy and pea-like odor) with the highest OAV among the volatiles in cold-pressed rapeseed oil despite its extremely low amount. 2-Isopropyl-3-methoxypyrazine might be formed from valine (branched-chain α-amino acid) and glyoxal (α-dicarbonyl compound), as well as 2-isobutyl-3-methoxypyrazine from leucine and 2-*sec*-butyl-3-methoxypyrazine from isoleucine (Matheis & Granvogl, 2016a). It is noteworthy that methoxypyrazines were found as key odorants in rapeseed oils in several studies performed in Germany. Also, Gracka et al. (2016) reported on 2-isopropyl-3-methoxypyrazine in roasted rapeseed oils with OAVs of 3.72 and 3.46. However, there are only a few reports on these compounds in rapeseed oil in other countries. Up to now, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, and 2-*sec*-butyl-3-methoxypyrazine have never been reported in rapeseed oil in China. A possible reason might be the fact that the very low concentrations combined with the very low odor thresholds of these compounds make them difficult to analyze on the one side, but to important odorants on the other side; thus, more attention should be drawn to these compounds in the near future.

2.7.2 | Furans

Furans are a major class of compounds formed by lipid peroxidation, carbohydrate degradation, and Maillard reaction, giving sweet, malty, and caramel-like characteristics to food. As well as pyrazines, furan contents significantly increase with an increase of heating temperature and time in the production of rapeseed oil.

2-Furancarboxaldehyde (furfural) and 5-methyl-2-furancarboxaldehyde (5-methylfurfural) were the major furanoic compounds found in toasted canola oil. Their sensory properties have been described as rotten, sweet, and caramel-like (Park et al., 1995). Furfural was found to be a specific product from thermal reactions, generated, for example, from 1-deoxyosone during the Maillard reaction (Gracka et al., 2016). However, it has not been identified as a key aroma compound in rapeseed or rapeseed oil so far. Kraljić et al. (2018) also detected furfural, 5-methyl-2-furfural, and 2-furanmethanol (furfuryl alcohol) in the oil from rapeseed heated at 100°C. Microwave pretreatment led to the generation of many furans, for example, furfuryl alcohol, dihydro-2(3*H*)-furanone, and 5-butyldihydro-2(3*H*)-furanone, which improved the aroma of rapeseed oil (Ren et al., 2019). Furfuryl alcohol was reported as an odor-active compound (burnt flavor) in fragrant rapeseed oil in a study performed by Zhou et al. (2019). The amount of 2-furanmethanethiol (2-furfurylthiol) with a coffee-like aroma significantly increased during thermal treatment of rapeseed (Ortner et al., 2016). Its generation pathway was studied by model systems by reacting various monosaccharides with glutathione, thiamine, or cysteine as sulfur source, showing that 2-furancarbaldehyde might be the key intermediate (Hofmann & Schieberle, 1995; Wang et al., 2012). 2-Pentylfuran has been determined in many vegetable oils, for example, in olive, linseed, walnut, sunflower, and rapeseed oils (Uriarte et al., 2011). The conjugated diene radical that is involved in its formation pathway derives from the cleavage of the 9-hydroxyradical of linoleic acid that may further react with oxygen to form vinyl hydroperoxide, which then experiences cyclization via the alkoxy radical to end up with 2-pentylfuran (Frankel, 1983). 2-Pentylfuran significantly increased during the roasting process (Zhou et al., 2013). However, no study has shown that 2-pentylfuran is aroma-active in rapeseed oil.

2.7.3 | Indole, pyridines, pyrrolines, thiazoles, and thiophene

According to the study of Kraljić et al. (2018), similar to pyrazines, 1-(1H-pyrrol-2-yl)ethanone (2-acetylpyrrole) was also observed in the oil obtained from rapeseed roasted at 100°C, whereas 4-methyl-2-pyrrolidinone and 2,5-dimethylpyrroline were only determined in the oil extracted from rapeseed heated at temperatures <100°C. Additionally, 2-propionylthiazole and 2-acetylpyridine, both with a roasty aroma note, were found to be present in cold-pressed rapeseed oil, but did finally not contribute to the overall aroma, based on OAV calculation, part of the molecular sensory science concept as state-of-the-art methodology in aroma analysis (Matheis & Granvogl, 2016b). 2-Acetyl-1-pyrroline (popcorn-like smell) and 2-propionyl-1-pyrroline (popcorn-like, roasty) were determined as aroma compounds with high FD factors in roasted rapeseed (Ortner et al., 2016). They are formed by the degradation of proline with reducing carbohydrates, indicating 1-pyrroline as the key intermediate of the thermally induced generation (Hofmann & Schieberle, 1998). There is also a group of heterocyclic sulfur compounds, including thiazoles (2-propionylthiazole and 2,4-dimethylthiazole) and 2-formylthiophene with a roasty flavor (Table 1).

2.8 | *S*-containing volatile compounds

Dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, dimethyl sulfone, dimethyl sulfoxide, allyl isothiocyanate, 4-isothiocyanato-1-butene, and 1-isothiocyanato butane are the main *S*-containing aroma-active compounds in rapeseed oils. They are very crucial and responsible for the characteristic pungent, sulfury, cabbage-like, onion-like, and garlic-like aroma of rapeseed oils (Blažević & Mastelić, 2008).

Based on the molecular sensory science concept, dimethyl trisulfide and dimethyl sulfide were reported by Matheis and Granvogl (2016a) as key odorants with high OAVs in commercially native cold-pressed rapeseed oil. Besides, Gracka et al. (2016) reported that the odor of dimethyl sulfide dominated both the cold-pressed and hot-pressed rapeseed oils with nearly identical OAVs, indicating that a chemical process plays a key role in the formation of dimethyl sulfide compared to an enzymatic process. Dimethyl sulfide and dimethyl disulfide can derive from methionine (Peres et al., 2013). *S*-Methylmethionine was also reported as a precursor of dimethyl sulfide (Scherb et al., 2009). Besides, it was previously reported that isothiocyanates might be hydrolyzed to generate sulfides and disulfides (Pecháček et al., 1997). *S*-Methylcysteine sulfoxide presumably forms dimethyl sulfoxide, which was possibly formed by the involvement of glucosinolate products, nonprotein-bound amino acids, and thiol-methyltransferase (Zhou et al., 2018). High amounts of dimethyl sulfide in rapeseed oil were formed along with a rising temperature up to 80°C. Dimethyl trisulfide, found

with a high OAV in rapeseed oil (Matheis & Granvogl, 2016a), contributed a characteristic flavor note to the overall rapeseed oil aroma, and it was increasingly formed during heating. However, neither dimethyl sulfide nor dimethyl trisulfide was detected in cold-pressed rapeseed oil in a study of Ivanova-Petropulos et al. (2015). It was supposed that headspace (HS) solid phase microextraction (SPME) in combination with GC–MS could not detect further sulfur compounds owing to the limited sensitivity. Roasting temperature and sulfur amino acids determined the content of dimethyl trisulfide that was detected in 13 of 15 commercial fragrant rapeseed oils in a previous study (Zhou et al., 2019). In the study of Zhang, Wu, et al. (2020), dimethyl sulfoxide was detected in 17 out of 33 commercial fragrant rapeseed oil samples, dimethyl trisulfide only in four oils, but neither dimethyl disulfide nor dimethyl sulfide was found in these oils. The distinction might be caused by various genetic types of rapeseed and the treatment conditions. Also, the limits of detection of several applied methods may explain the differing results. Further research should apply more sensitive methods such as GC–O and two-dimensional gas chromatography–time-of-flight-mass spectrometry (GC×GC–TOF-MS) to identify trace odorants.

Allyl isothiocyanate, 4-isothiocyanato-1-butene, and 1-isothiocyanato butane leading to green, sulfury, and pungent aroma impressions in rapeseed oils showed high FD factors. The pungent smell in the oil samples mainly originated from isothiocyanates, formed from glucosinolates. High contents of the pungent-smelling 4-isothiocyanato-1-butene were previously identified in *Brassica campestris* and *B. napus*, whereas allyl isothiocyanate with the same odor impression was identified in *Brassica juncea* (Zhou et al., 2018). Allyl isothiocyanate (sulfury and pungent) has partially existed in commercial fragrant rapeseed oils. Different varieties may cause higher OAVs in certain commercial rapeseed oils. Additionally, 4-isothiocyanato-1-butene was detected in fragrant rapeseed oils, and the highest OAV was 50 (Zhou et al., 2019). 4-Isothiocyanato-1-butene (66.54% in the overall volatile compounds) was reported to be the predominant volatile when no pretreatment was applied to the rapeseed. The proportion of 4-isothiocyanato-1-butene decreased to 1.71% and 4.97% in oil samples after heat processing (110°C) or microwave treatment of the seeds (Wei et al., 2012). Similar trends were also described by Zhou et al. (2013), who compared the concentrations in untreated and microwave-treated rapeseed oils. Thereby, the content of 4-isothiocyanato-1-butene decreased by 97% after microwave treatment, whereas the amounts of 5-cyano-1-pentene and methallyl cyanide increased. Gracka et al. (2016) determined a higher amount of 4-isothiocyanato-1-butene in the oils obtained from roasted (at 140–180°C) rapeseed compared to the oil produced from raw rapeseed. Kraljić et al. (2018) found that 4-isothiocyanato-1-butene, accounting for 56% of overall volatile compounds, was the predominant volatile in cold-pressed rapeseed oils. Its proportion raised and made up >68% after preconditioning the oil at 60°C, caused by long-time contact of glucosinolates and enzymes. However, the higher heating temperatures decreased the proportion of isothiocyanate to the overall volatiles. The optimal temperature to inactivate the myrosinase of rapeseed was suggested to be between 70 and 75°C (Przybylski et al., 2005). Further research might be conducted to investigate the influence of processing on the amounts of odorants formed by glucosinolate degradation in rapeseed oil.

For example, allyl isothiocyanate was reported to derive from hydrolyzed sinigrin via myrosinase (Ren et al., 2019). In canola oil, it might be formed through another pathway due to the absence of sinigrin in rapeseed (Zhou et al., 2018). Further, it was verified that gluconapin can be converted into 4-isothiocyanato-1-butene (Mao et al., 2019). The myrosinase in impaired rapeseed cellula turns sinigrin, hydroxyglucobrassicin, progoitrin, and gluconapin into related volatiles during the hydrolytic process. The corresponding hydrolysates contribute to the pungent odor in rapeseed and its degree is dependent on the proportions of different precursor compounds. Interestingly, these isothiocyanates have not yet been reported as aroma-active volatiles in mustard seeds and rapeseed in Germany, which might be due to differences in genotype. Hanschen et al. (2012) studied the thermal degradation (100 and 130°C) of aliphatic glucosinolates and proposed degradation pathways. They found that the reaction conditions (e.g., water content, matrix, metal ion, vitamin C, pH value, and temperature) impacted the thermal breakdown of glucosinolates and the formation of degradation products. However, a more thorough exploration of the mechanisms of flavor compounds formation from different single glucosinolates via thermally induced degradation with different reaction conditions is still required.

2.9 | Nitriles

Nitriles, as a unique type of volatiles produced in rapeseed oil, are generated during glucosinolate degradation. Hu et al. (2014) reported on 16 volatile compounds in rapeseed oil including benzenepropanenitrile, 5-methyl-hexanenitrile, 3-pentenenitrile, and 5-cyano-1-pentene that distinguish it from soybean, peanut, and sunflower seeds. The volatiles 2,4-pentadienenitrile, 3-butenenitrile, methallyl cyanide, 2-butenenitrile, 5-cyano-1-pentene, 3-pentenenitrile, 5-methylhexanenitrile, benzyl nitrile, 3-phenylpropionitrile, and heptanenitrile were detected in commercial fragrant

rapeseed oil (Zhou et al., 2019). The most abundant nitriles detected in the oil processed from heated rapeseed were methallyl cyanide and 2-methyl-5-hexenenitrile (Gracka et al., 2016). Up to now, a lot of research about nitriles in rapeseed oils has been performed in China due to a high content of glucosinolates. The number of the carbon atoms of the major nitriles was not more than 5, which indicates that nitriles with low molecular weight are derived from glucosinolates during heat treatment (Mao et al., 2019). The contents of nitriles increased remarkably after thermal processing. Results of Kraljić et al. (2018) also showed that the contents of nitriles in rapeseed oil samples increased with ascending heating temperature. Jing et al. (2020) evaluated nitriles in rapeseed oils with different roasting time and reported on significantly increased amounts of nitriles after roasting for 40 min at 150°C. This finding indicated that heating can remarkably facilitate the thermal decomposition of glucosinolates as well as the generation of nitriles. A lowered myrosinase activity, and thus, a reduced decomposition of glucosinolates after heat and microwave processing may also attribute to the increase of nitriles and the formation of distinct odors (Wei et al., 2012).

In contrast to isothiocyanates, nitriles were considered to have no pungent smell (Williams et al., 2009). However, Jing et al. (2020) assumed that the existence of nitriles is largely responsible for the typical spicy attribute in virgin rapeseed oil. They found nitriles as key odorants including 2-butenenitrile (OAV > 2.5), octanenitrile (OAV > 5.8), and 5-(methylthio)-pentanenitrile (OAV > 9.2). As already mentioned above, the OAVs calculated in this study can only be relative values, because only 2-octanol was used as internal standard. Su et al. (2019) applied GC–O and reported on benzyl nitrile that contributed with a pungent-smelling odor note to the overall aroma of rapeseed oil. They also demonstrated that 5-cyano-1-pentene and heptanenitrile were aroma-active volatiles in fragrant rapeseed oils applying odor-specific magnitude estimation. However, an influence of the odor attributes of nitriles on the overall aroma of rapeseed oils has not been confirmed in any other study up to now. Thus, further research about the aroma activity of nitriles in rapeseed oil is needed.

In general, isothiocyanates and nitriles are formed by thermal and/or enzymatic degradation of the corresponding glucosinolates, for example, benzyl nitrile from glucotropaeolin. 5-Cyano-1-pentene might be formed via three possible ways: (i) if glucobrassicanapin eliminates sulfur, glucose, and sulfate; (ii) if gluconapoleiferin eliminates sulfur, sulfate, and glucose, followed by a dehydroxylation; or (iii) if glucoalyssin eliminates a sulfoxide (Mao et al., 2019).

2.10 | Alkanes and alkenes

Alkanes and alkenes are mainly formed during lipid peroxidation via lipid hydroperoxides. Alkanes were found to be the third most abundant volatile compounds in cold-pressed rapeseed oil based on the work of Mao et al. (2019). Generally, hydrocarbons are not regarded as prominent odorants in rapeseed oil. In the case of alkenes, 1-pentene, 2-pentene, 2,3-dimethyl-1-butene, and 4-isothiocyanato-1-butene accounted for 22% of the total volatile compounds in rapeseed oil (Ivanova-Petropulos et al., 2015). In canola oils, terpenes were identified including *p*-cymene, thymoquinone, and limonene (Kiralan & Ramadan, 2016). Ivanova-Petropulos et al. (2015) detected the monoterpenes *β*-pinene (10.5% of the total terpenes) and dl-limonene (18.5% of the total terpenes) at significant relative concentrations in rapeseed oil. Limonene in rapeseed oil increased with the roasting temperature (Kraljić et al., 2018). It was also found in the volatile fraction of refined and cold-pressed rapeseed oil (Kiralan & Ramadan, 2016).

2.11 | Off-flavors of rapeseed oils

The odor attributes nutty and seed-like are the typical descriptors for the sensory evaluation of virgin oil obtained from intact rapeseed. The aroma of refined and deodorized canola oil only presents the characteristics of slightly nutty, buttery, and bland. However, improper storage and processing of seeds and oils can lead to off-flavors in rapeseed oil (fusty, musty, or rancid) (Bonte et al., 2017; Malcolmson et al., 1994). According to the German Society for Fat Science (Deutsche Gesellschaft für Fettwissenschaft [DGF]), the typical sensory attributes of good virgin cold-pressed rapeseed oils from sound seeds include seed-like, nutty, woody, and astringent, whereas rancid, fusty, musty, yeast-like, straw-like, roasty, burnt, and bitter are responsible for off-flavors in rapeseed oil (Matthäus et al., 2008).

Octanal, hexanal, 1-octen-3-one, and (*E*,*Z*)-2,6-nonadienal were reported with higher FD factors in rapeseed (Pollner & Schieberle, 2016), which were considered to impart off-flavors to oil as well (Morales et al., 2005). 1-Octen-3-one, with a mushroom-like smell (off-odor) contribution to canola oil, showed a concentration of 75 ppb (about 750 times above the detection threshold) after the aging process. Due to its low threshold, it influences the aroma characteristic of the oil sample despite its relatively low content (Raghavan et al., 1994). (*E*)-2-Pentenal and 1-penten-3-ol significantly correlated (Pearson correlation coefficients of 0.99 and 0.97 in [$p < 0.01$], respectively) with a rancid off-flavor (evaluated by sensory profile analysis) (Jeleń et al., 2007). Also,

Koprivnjak (2000) showed a correlation between the contents of these two compounds and the intensity of the rancid odor in olives.

Microorganisms were thought to be one reason for the sensory defects of virgin rapeseed oils (Bonte et al., 2017). Volatiles formed from microbial metabolism such as 2- and 3-methylbutanoic acid (via the Ehrlich pathway) and 4-methylphenol were identified as the main differences between sensory good and bad native cold-pressed rapeseed oils, which showed higher contents in off-flavor rapeseed oils. Based on the molecular sensory science concept, these three compounds were deduced to be the indicators for the undesired musty/fusty smell in native cold-pressed rapeseed oil (Matheis & Granvogl, 2016b). Elsden et al. (1976) found that 4-methylphenol emerged from either *p*-hydroxyphenylacetic acid or tyrosine in the presence of *Clostridium scatologenes* and *Clostridium difficile*. As a result, rapeseed with improper storage (high moisture content and/or high temperatures) and low quality leads to an off-flavor in native cold-pressed oils, broadly affecting the final oil quality (Matheis & Granvogl, 2016b).

Moreover, steam treatment may result in a fishy off-flavor in rapeseed oil. It was reported that (*E*,*Z*)-2,6-nonadienal, (*E*,*Z*,*Z*)-2,4,7-decatrienal, (*E*,*Z*)-2,4-heptadienal, (*Z*)-4-heptenal, (*Z*)-1,5-octadien-3-one, 1-penten-3-one, and 1-octen-3-one can contribute to a fishy smell in food (Karahadian & Lindsay, 1989; Venkateshwarlu et al., 2004). Sghaier et al. (2015) identified six volatiles that they related to the fishy odor in rapeseed oil including (*Z*)-4-heptenal, (*E*,*Z*)-2,4-heptadienal, (*E*,*Z*,*Z*)-2,4,7-decatrienal, (*E*,*Z*)-2,6-nonadienal, 1-penten-3-one, and 1-octen-3-one. However, Matheis and Granvogl (2019a) assumed that the previous study did not provide powerful evidence for the fishy odor resulting from these six volatile compounds in rapeseed oil. They found that trimethylamine was the only compound evoking the fishy odor in rapeseed oil via SPME–high-resolution GC (HRGC)–MS technique, calculation of OAVs, and sensory recombination experiments. It was shown that phosphatidylcholine can generate trimethylamine in soybean oil (Jiang et al., 2016). Thus, Matheis and Granvogl (2019a) supposed that trimethylamine was formed during the steaming process from sinapine (bearing a choline ester in the side chain analog to phosphatidylcholine) as a possible precursor. Overall, the fishy smell might be caused by the synergism of several volatile compounds, which needs further research.

When it comes to the pungent flavor in rapeseed oil, 4-isothiocyanato-1-butene (glucosinolate degradation product) was considered as the representative pungent odorant in rapeseed oil, regarded to create an off-flavor (Zhou et al., 2013, 2018). However, fragrant rapeseed oil is widely used in the Sichuan and Hunan cuisine, both of which belong to the Eight Great Cuisines in China, characterized by a pungent and spicy aroma. Fragrant rapeseed oils eliciting an intense roasted and pungent aroma can make these cuisines more characteristic. In a very recent study, Zhang, Wu, et al. (2020) found that glucosinolate degradation products were responsible for the pungent aroma and had a positive correlation with the erucic acid content. This finding might be related to the fact that rapeseed samples with a high erucic acid content (>3.0%) accounted for 92.5% of the whole samples in Sichuan, based on the "2018 National Rapeseed Harvest Quality Survey Report" in China. Thus, the off-flavor of rapeseed oil might be differently recognized according to different dietary habits and preferences in different regions. A large-scale sensory test investigating and comparing the preferences of consumers in different regions regarding the aroma of rapeseed oil has not yet been performed and more research is still needed.

3 | FLAVOR ANALYSIS TECHNIQUES OF RAPESEED OIL

3.1 | Extraction and enrichment techniques

An efficient isolation technique is an essential prerequisite to extract the aroma-active compounds of rapeseed oil for further analysis. Based on separation principles, approaches for the extraction of volatiles in fat/oil can be classified into distillation, HS extraction, solvent extraction, and others (e.g., Tedlar bags) (Buettner, 2017). An overview of extraction and enrichment techniques of aroma compounds from fat/oil is shown in Table 2. Each technique imparts discrimination and incomplete recoveries for flavor compounds in oils. Therefore, there is no perfect technique for the extraction of flavor compounds in a sense.

In the early time, solid phase extraction, which is not suitable for the direct analysis of oil, was employed along with thin-layer chromatography after steam distillation to isolate principal contributors to the aroma of vegetable oils (Shimoda et al., 1996; Vreuls et al., 1999). In addition, the extraction of odorants is mostly accompanied by the extraction of lipids, often limiting the use of simple liquid–liquid extraction (LLE). Hence, flavor compounds in rapeseed oil require preseparation, such as the use of a membrane as a molecular sieve to separate triglycerides from the remaining oil constituents (Chongcharoenyanon et al., 2012). Not any existing solvent-extraction approach provides complete isolation of flavor compounds. For instance, dichloromethane extraction results in better isolation of ketones, esters, and phenols compared to

TABLE 2 Extraction and enrichment techniques of flavor compounds from fats/oils

Basis	Techniques	Features	Applications
HS	SHS and HS-trap	Trap enrichment device in HS-trap, rapid, easy use, nonselective, HS-trap is more sensitive but also more complex than SHS	1. The characterization of olive oils by the direct coupling of SHS with mass spectrometry (Lorenzo et al., 2002) 2. Characterization of the volatiles responsible for the fishy odor in heated rapeseed oil via HS-trap (Sghaier et al., 2016)
	SPME	Adsorbent (e.g., PDMS/DVB/CAR coated), solvent free, selectivity, 10–50× higher sensitivity than SHS, rapid, automation, liable to low boiling point, more hydrophobic and less volatile compounds are not favorable, limited extraction, suffer from saturation, competition between volatiles (discrimination)	1. Extraction and identification of 32 volatile compounds in refined and cold-pressed rapeseed oils (Jeleń et al., 2000) 2. Determination of the key volatiles of rapeseed oil with and without microwave and thermal pretreatments from different seed varieties (Wei et al., 2012)
	HSSE	HS-trap, PDMS stir bar, a special case of SBSE, high-concentration capacity, accuracy, time-consuming	Analysis of olive oil varieties by comparing HSSE with SPME (Stilo et al., 2019)
	DHS	Cartridges trap, such as Tenax, desorption by SFE, 50–100× higher sensitivity than SPME, selectivity, reproducibility, nondestructive, labor-intensive	1. Investigation on the conditions for SFE desorption of identified seed oil volatiles from sorbents (Chester et al., 1996) 2. Extraction of volatiles for the differentiation of sensory bad (musty/fusty) and good virgin rapeseed oils (Bonte et al., 2017)
	MMSE	Pure silica material (like MonoTrap) with porous monolithic structures combined with octadecyl (ODS) groups that bond to the surface or to activated carbons, large surface area, high adsorption rate, versatility, limited repeatability	Acquirement of aroma-active compounds from rapeseed oil in a more time-effective process (Zhou et al., 2019)
Distillation	SAFE	High vacuum distillation, less heat degradation, reproducibility, accuracy, less analyte losses, no artifact formation, dedicated glassware	Isolation of the volatiles to elucidate thermally induced changes in mustard seeds and rapeseed (Ortner et al., 2016)
	SDE	Simultaneous distillation/extraction by a Likens–Nickerson apparatus, artifact formation, dedicated glassware	Comparison of the extraction efficiency of volatiles by SDE and SPME in olive oil (Buettner, 2017)
	HVT	Evaporation from heated oil (around 50°C), good recovery of semivolatiles, labor-intensive, complexity, solid fat analysis not possible	Extraction of aliphatic alcohols and ketones from butter oil (Forss & Holloway, 1967)
	Short-path distillation	Thin-film distillation based on molecular free paths, continuity, good recovery, high price, solid fat analysis not possible, dedicated glassware	Unraveling of the fishy off-flavor in steam-treated rapeseed oil using the sensomics concept (Matheis & Granvogl, 2019a)
	Steam distillation	Hydro-distillation, low price, artifact formation, poor recovery of polar compounds	The extraction of volatiles by steam distillation of the oil from roasted sesame seeds for flavor identification (Nakamura et al., 1989)
Solvent extraction	SFE (CO_2 mostly)	Variation of the pressure treatment on solutes, evaporation at ambient pressure, green technique, dedicated instrument, expertise required	Recovery of seed oil volatiles to analyze lipid samples that are easily decomposed (Snyder & King, 1994)

(Continues)

TABLE 2 (Continued)

Basis	Techniques	Features	Applications
	LLE with membrane	Low-density polyethylene membrane in the solvent as a molecular sieve, low price, easy use, reproducibility	Recovery of butter oil in a sealed low-density polyethylene membrane pouch in the organic solvent (Chongcharoenyanon et al., 2012)
	LLE	Low price, coupled with other techniques, different distribution coefficients, hard to eliminate triglycerides	Extraction of key volatiles in cold-pressed rapeseed oil (Pollner & Schieberle, 2016)
	SPE	Same lipophilicity sorbent such as C18-bonded silica or polymers, selectivity, easy use, direct analysis of solid fat not possible	Recovery of the flavor compounds in the water phase by the combination with SPE for the analysis of sesame oil flavor (Shimoda et al., 1996)
Others	GPC	Fractionation by gel-selective column, low price, nondestructive	Separation of fat and flavor compounds using a column of Bio-Beads SX-3 with dichloromethane as eluent (Buettner, 2017)
	Tedlar bag	Low price, no concentration or derivatization methods, analysis of trace compounds not possible	Collection of oil fumes to compare emissions of aldehydes during deep-frying with (extra virgin) olive oil and canola oil (Fullana et al., 2004a)

Note: SHS and HS-trap represent static headspace and headspace-trap, respectively; a trap enrichment device in HS-trap is the only difference. Others included gel permeation chromatography (GPC) based on size-exclusion chromatography and Tedlar bag; an enrichment method not an isolation technique in the strict sense.

Abbreviations: DHS, dynamic headspace; HS, headspace; HSSE, headspace sorptive extraction; HVT, high-vacuum transfer; LLE, liquid–liquid extraction; MMSE, monolithic material sorptive extraction; PDMS/DVB/CAR, polydimethylsiloxane/divinylbenzene/carboxen; SAFE, solvent assisted flavor evaporation; SBSE, stir bar sorptive extraction; SDE, simultaneous distillation extraction; SFE, supercritical fluid extraction; SPE, solid phase extraction; SPME, solid phase microextraction.

pentane. Nonetheless, dichloromethane is undesirable for high recovery rates of alkanes and alcohols (Taylor & Linforth, 2010). Thereby, a thorough selection of the proper solvent for the extraction of the volatiles from rapeseed oil is needed. To settle the problem of solvent co-eluting, a specific solvent-based extraction technique, the supercritical fluid extraction (SFE), is used as a green and mild method for recovery of thermosensitive volatiles in oil, usually using CO_2. This technique is prone to extract aryl compounds and esters in plant essential oil; however, SFE has rarely been reported for aroma analysis in edible oils (Pourmortazavi & Hajimirsadeghi, 2007). Snyder and King (1994) compared two different methods (SFE and thermal desorption) to desorb HS volatiles from the trap and concluded that SFE causes less degradation but was not appropriate for the lower boiling volatiles compared to thermal desorption during the analysis of vegetable oil. According to Taylor and Linforth (2010), the simultaneous use of several isolation techniques is crucial to unfold an overall volatile profile.

High-vacuum transfer (HVT), short-path distillation, and steam distillation are classic methods to isolate aroma compounds depending on their volatility. Short-path distillation, commonly practiced for the purification of fatty acids, has much lower recoveries for lactones compared to the solvent assisted flavor evaporation (SAFE) technique (Engel et al., 1999). Early studies reported the isolation of volatiles by steam distillation, for example, from sesame seed oil (Nakamura et al., 1989); however, both steam distillation and simultaneous distillation/extraction (SDE) increase the possibility of artifact formation (Buettner, 2017). By comparing SDE to SPME applied to olive oil, higher percentages of terpenoids and aldehydes, caused by thermal degradation, were detected (Vichi et al., 2007). Taylor and Linforth (2010) reported on HVT linked with molecular distillation as a gentle extraction technique to reduce the degradation of 3-methylnonane-2,4-dione that was formed during the storage of soybean oil. However, this technique has poor reproducibility and underestimates the importance of highly volatile aroma compounds due to losses during isolation and the solvent front during chromatography (Taylor & Linforth, 2010). Engel et al. (1999) verified that the yields of odorants in several foods with low volatility decreased using "normal" HVT compared to the SAFE technique. Otherwise, many of the abovementioned prerequisites for a proper odorant extraction are fulfilled by the SAFE technique, usually used for state-of-the-art aroma analysis within the sensomics approach. SAFE can extract many polar and high-boiling compounds with representative flavor efficiently (Parker, 2015); thus, the overall aroma profile of food can be well presented using this technique. Pollner and Schieberle (2016) used SAFE combined with LLE to iso-

late the acidic (AF) and the neutral/basic (NBF) volatiles to avoid overlap in peaks during GC–O to uncover the aroma differences of cold-pressed rapeseed oils obtained from either unpeeled or peeled rapeseed. Likewise, Matheis and Granvogl (2016b) used the same way to separate NBF and AF, then NBF was further fractionated by polarity using silica gel chromatography with different eluents to characterize the aroma compounds that are crucial for commercially native cold-pressed rapeseed oil. Although SAFE shows excellent extraction purity, complex glassware has to be used. Further, some odorants might also be overlapped by the solvent peak during GC analysis (Parker, 2015). Thus, the HS technique is often applied in parallel to SAFE to identify very volatile aroma-active compounds co-eluting with the solvent peak, for example, dimethyl sulfide and methanethiol (Matheis & Granvogl, 2019a; Ortner et al., 2016). This combination ends up with a suitable analytical approach to detect all aroma-active compounds in food.

Based on the volatility by solvent-free extraction, HS analysis is widely used to yield the natural olfactory image of a sample with little or no pre-preparation. Although a simple and fast technique, static headspace (SHS) is often not suitable for the quantitation of the trace target compounds and has rarely been used for the research of rapeseed oil (Sghaier et al., 2016). Thus, further HS sampling techniques might be used to compensate lower concentrations of HS volatiles by collecting a large volume of the sample, for example, Tenax (or alternative polymer) in dynamic headspace (DHS) to trap the trace compounds, SPME with differently coated fibers (e.g., polydimethylsiloxane/divinylbenzene/carboxen [DVB/CAR/PDMS]) to improve selectivity, or polydimethylsiloxane stir bar sorptive extraction (SBSE) for the enrichment step. A comparison indicated that DHS has a 50- to 100-fold higher sensitivity than SPME, and SPME is 10–50 times more sensitive than SHS (Pfannkoch & Whitecavage, 2000). DHS applied with Tenax is widely used and its characteristic, a high affinity for non-polar compounds, favoring it for the differentiation of volatiles in rapeseed oil. DHS shows higher sensitivity related to SPME despite low adsorption capacity owning to a low superficial area of Tenax. Bonte et al. (2017) found 13 aroma compounds (e.g., 3-methylbutanal and 2-methylpropanal) to evaluate the sensory quality of virgin rapeseed oil using DHS–GC–MS. The exploration of other trapping systems and selective polymers or an extension of the sorptive surface such as MonoTrap in MMSE might make DHS more promising. SPME is selective, sensitive, rapid, and automated. For example, SPME displayed a higher recovery of overlooked trimethylamine (fishy odor) than SAFE during the analysis of steam-treated rapeseed oil (Matheis & Granvogl, 2019a). In recent years, different fiber coatings have been developed to extract various types of volatile analytes. Wei et al. (2012) evaluated five fiber types regarding extraction selectivity and capacity of volatiles in rapeseed oil. Thereby, the DVB/CAR/PDMS fiber achieved the best results, whereas it showed less selectivity for highly volatile compounds compared to CAR/PDMS. SPME technique offers several advantages (low price, less consumption, easy use, etc.) and will have great development potential if researchers focus on improvements for the selectivity and sensitivity. However, the problem of competition among volatiles regarding their adsorption onto the SPME fibers has to be accounted for by using stable isotopically labeled internal standards or standard addition to get reliable quantitative data. A good perspective might be given by the recent establishment of the so-called SPME arrow technique, a technology for microextraction, combining trace-level sensitivity with high mechanical robustness. MMSE was verified to show higher recovery and less time consumption than SPME, which is more liable to absorb compounds with a low boiling point (Buettner, 2017). Zhou et al. (2019) applied MMSE to rapeseed oil for the first time and detected 29 volatiles. Besides, SBSE, which has been used for olive oil, compensates drawbacks of SPME such as limited extraction capability for ultra-trace odorant analysis and HS saturation (Stilo et al., 2019). Thus, SBSE has potential as an extraction technique for flavor analysis in rapeseed oil, although it has scarcely been used up to now. For both SPME and SBSE, also the possibility of artifact formation during thermodesorption of the adsorbed volatiles at elevated temperatures has to be considered (Christlbauer et al., 2004).

In conclusion, further advanced extraction techniques should comply with proper extraction selectivity, reproducibility, and efficiency, particularly focused on ultra-trace volatiles with high contribution to flavor. Mild treatment to avoid any artifact formation and a good combination of several isolation techniques to set up an automated and handy system are needed to meet various objectives, such as (i) monitoring key aroma-active compounds in general, (ii) unraveling the compounds causing distinct off-flavors during processing or storage, and (iii) obtaining a "complete" aroma profile to discriminate various types of foods, for example, vegetable oils with regard to their labeled quality.

3.2 | Qualitative and quantitative techniques

3.2.1 | Detectors and qualitative techniques

Different detectors/sensors and chromatographic systems for flavor analysis in edible oils are shown in Table 3. Multiple chromatographic systems connected to detectors are used to characterize key aroma compounds in food. Flame

TABLE 3 Different detectors/sensors and chromatographic systems for flavor analysis in edible oils

Detectors/sensors	Features	Chromatographic systems	Applications
MS	Sort the ions by mass-to-charge ratio, vacuum, background interference is possible	1D GC	Monitoring of changes of key volatiles in rapeseed oil during ambient storage by HS-SPME-GC–MS (Xu et al., 2017)
		Heart-cut MDGC	Characterization of key odorants causing a fusty/musty off-flavor in native cold-pressed rapeseed oil (Matheis & Granvogl, 2016b)
IMS–MS	Separated by drift time based on molecular charge, weight, and shape, multi-dimensional, enantiomeric separation, sensitivity, low resolution	1D GC	Identification of adulteration in canola oil (Chen et al., 2018)
		1D GC	Detection of odor fingerprint as marker of rapeseed oil refined grade (Chen et al., 2019)
TOF-MS	Sort the ions by mass-to-charge ratio, high resolution, high accuracy, high price	GC×GC	Characterization of volatiles in four vegetable oils (including rapeseed oil) by HS-GC×GC–TOF-MS (Hu et al., 2014)
MS/MS	Transitions from precursor ions to product ions, selectivity, sensitivity, high price	1D GC	Semiquantitative determination of wax ester compositions from seed oil (Iven et al., 2013)
FID	Ionization with flame jet, low maintenance requirements, widely use, detector flame oxidizes all oxidizable compounds, only sensitive for C-containing compounds, standard curve for every sample	GC×GC	Effect of heat treatment on the composition of butter samples in more detail (Adahchour et al., 2005)
		Hybrid GC×GC–MDGC	Quantitative analysis of oxygenated compounds in a thermally stressed algae-derived biofuel oil (Mitrevski & Marriott, 2012)
		1D GC	Comparison of different extraction methods of volatile compounds in French olive oils (Cavalli et al., 2003)
FPD	Photomultiplier tube to enhance the light intensity, sensitive to sulfur and phosphorous containing compounds, standard curve for every sample	1D GC	New discovery of flavor compounds in roasted sesame seeds by GC–FPD/MS and GC–FPD/FTIR (Nakamura et al., 1989)
O	Olfactory port, often simultaneously used with an FID	1D GC and 2D GC	Detection of the odor-active compounds of non-roasted and roasted rapeseed oils by GC–O (Gracka et al., 2016)
		1D GC	Characterization of key odorants causing a fusty/musty off-flavor in native cold-pressed rapeseed oil (Matheis & Granvogl, 2016b)
O–MS	Olfactory port combined with MS, analysis of key odorants, accuracy in complex matrices	1D GC	Characterization of glucosinolates and pungent odors in rapeseed oils from raw and microwaved seeds (Zhou et al., 2018)
IR	Vibrational spectroscopy, rapid, non-destructive, expertise required, complex algorithms, few reports		Classification of 112 virgin olive oil samples (Sinelli et al., 2010)

(Continues)

TABLE 3 (Continued)

Detectors/sensors	Features	Chromatographic systems	Applications
NMR	Zeeman effect, conformation of unknown aroma-active compounds, expertise required, few reports	1D GC	Determination of 2-ethyl-3,6-dimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine by GC–MS/NMR (Buttery & Ling, 1997)
Chemical sensors	Based on conductivity, easy use, stability, rapid test, high price, rough qualification and quantitation, high operating temperature—thus, artifact formation possible, drift errors	–	Detection of olive oil adulteration with rapeseed and sunflower oils (Mildner-Szkudlarz & Jelen, 2009)
Flash-GC e-nose	GC + FID, fast qualification, systematic, higher resolution than chemical sensors	1D GC	Classification of flavor rapeseed oil production areas (Zhang, Wu, et al., 2020)
zNose™	Surface acoustic wave (SAW) detector commonly, less drift errors, sensitivity, easy use, non-ionic detection	1D GC	Flavor analysis of 16 types of vegetable oils (including rapeseed oil) (Gan et al., 2005)
MS-based e-nose	Mass detector, rapid test, sensitivity, expertise required, pattern recognition and calibration models have to be developed	–	Determination of ratios of rapeseed oil and other oils (Hong et al., 2011)

Abbreviations: 1D GC, one-dimensional gas chromatography; FID, flame ionization detector; FPD, flame photometric detector; FTIR, Fourier transform infrared; GC×GC, comprehensive two-dimensional gas chromatography; IMS–MS, ion-mobility spectrometry–mass spectrometry; IR, infrared spectroscopy; MDGC, multi-dimensional gas chromatography; MS, mass spectrometry; MS/MS, tandem mass spectrometry; NMR, nuclear magnetic resonance spectroscopy; O, olfactory port; TOF-MS, time-of-flight-mass spectrometry.

ionization detection (FID) is only useful for the quantitation of major flavor compounds. However, the comparison of retention indices for the identification of volatiles should only be used in combination with authentic reference compounds to avoid any inaccurate results (Sghaier et al., 2015). Compared with FID, flame photometric detection (FPD) exhibits element (S and P) selectivity and was used for the detection of four *S*-containing compounds in roasted sesame oil for the first time (Nakamura et al., 1989). Pulsed flame ionization detection has appeared in recent years with a 100 times higher sensitivity than FPD for *S*-containing aroma compounds, which has been applied to wine for the quantitation of sulfur odor-active substances (Sha et al., 2017).

To develop more selective and sensitive identification techniques of aroma compounds, many modified MS detectors have arisen, such as ion mobility spectrometry–mass spectrometry (IMS–MS), tandem mass spectrometry (MS/MS), and TOF-MS. GC–IMS–MS with chemometric analysis built a model to predict volatiles of adulterated canola oil, in less analysis time without any pretreatment (Chen et al., 2018). MS/MS could be used for isomeric information and identification of unknown volatiles; however, only a few studies are available on the detection of the aroma of rapeseed oil with MS/MS till now. HS-GC×GC–TOF-MS showed high efficiency for acquiring whole mass spectral data to detect adulteration of four vegetable oils, including rapeseed oil (Hu et al., 2014). Besides, nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy using specialized software and complex algorithms, as well as MS-based IMS–MS, are feasible to identify enantiomeric aroma compounds (Nakamura et al., 1989).

3.2.2 | Chromatographic separation technology

Many flavor compounds, often with nearly the same structures, cause an overlap in sample extracts via one-dimensional (1D) GC separation, whereas multidimensional gas chromatography (MDGC) (more than one GC column for multiple dimensions separation using GC columns of different polarities) addresses this shortcoming and has often efficiently applied. As key odorants are often present only in trace amounts, they might also be overlapped by major (non-aroma-active) volatiles leading to a misinterpretation of the mass spectrum obtained. MDGC mainly contains the conventional heart-cut MDGC that gets a further separation for target components on the second column and comprehensive GC×GC that contains a continuous and quick modulation process for non-target analysis (Amaral & Marriott, 2019). Columns with different polarities (DB-FFAP and DB-5 are commonly used) decide the selectivity and sensitivity concerning the compounds of interest. Sghaier et al. (2015) concluded that the nonpolar–polar column order in the GC×GC system provided good separation of volatile compounds in heated rapeseed oil. As stated earlier, both MDGC and GC×GC have their emphases so that the combination of both techniques (i.e., MDGC/GC×GC) should be highlighted, as it was applied to wine and coffee to identify potent odorants, whereas it has not been applied to rapeseed oil up to now (Mitrevski & Marriott, 2012). Furthermore, a novel multidimensional system (more than two separation columns), which has particularly been introduced in the area of plant metabolomics, may show a perspective use for detecting the transformation of precursors into odorants during processing (Amaral & Marriott, 2019).

Volatiles present in different conformations are sometimes hard to determine. However, in fact, isomers with different structural and stereo features contribute to distinctive odor qualities and odor thresholds in aroma chemistry. Ortner et al. (2016) determined the ratio of 3-methylbutanoic acid to 2-methylbutanoic acid by HRGC–MS via stable isotope dilution assays (SIDAs). Matheis and Granvogl (2016b) identified isomers including (*E*,*Z*)-2,6-nonadienal and (*E*,*E*)-2,4-nonadienal, 3-hydroxy-4,5-dimethylfuran-2(5*H*)-one and 4-hydroxy-2,5-dimethylfuran-3(2*H*)-one, and 2-ethyl-3,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine using HRGC/HRGC–MS. This is of importance due to the fact that different isomers cannot only have different odor qualities but also odor thresholds, for example, a much lower threshold in water for 2-ethyl-3,5-dimethylpyrazine compared to 2-ethyl-3,6-dimethylpyrazine. Heart-cut MDGC, using an enantioselective column in the second dimension, was successfully used for the characterization of aroma-active enantiomers in rapeseed oil. Matheis and Granvogl (2016b) also made a comprehensive identification of key aroma-active compounds in cold-pressed rapeseed oil and quantitated (*R*)-2-, (*S*)-2-, and 3-methylbutanal as well as (*R*)-2-, (*S*)-2-, and 3-methylbutanoic acid by HRGC/HRGC–MS using a chiral cyclodextrine phase in the second dimension. The separation of enantiomers can also be implemented using the chiral column in the first dimension during GC×GC (Amaral & Marriott, 2019), which has also the potential to be applied in further studies on odorants in rapeseed oil.

3.2.3 | Olfactory detection technique and e-nose

A human assessor, as a particular detector, is typically combined with GC in the methodology known as GC–O.

Volatiles at low concentrations do not automatically mean that there is only a low contribution to the overall aroma of this food, which is evaluated by the combination of analytical-instrumental methods (quantitation via stable isotopically labeled internal standards based on mass spectrometry) and sensorial methods (determination of odor thresholds in a food-related matrix). Over the past decades, the molecular sensory science concept was successfully established as state-of-the-art methodology to characterize (= identification and quantitation) the key aroma compounds and to evaluate their contributions to the total aroma. It includes aroma profile analysis, AEDA, SIDA, determination of odor thresholds followed by the calculation of OAVs, and aroma recombination experiments. Recently, the key odorants of rapeseed, mustard seeds, native cold-pressed rapeseed oils eliciting the desired flavor and a musty/fusty off-flavor, and steam-treated rapeseed oils eliciting the desired flavor and a fishy off-flavor were successfully elucidated by application of the molecular sensory science concept (Matheis & Granvogl, 2016a, 2016b, 2019a, 2019b; Ortner et al., 2016).

Based on the aims of time-saving, labor-saving, and simulation of human olfactory, electronic nose (e-nose) with different sensors (especially metal-oxide-semiconductor [MOS] sensors) has the advantages of being easy to use and quick to test. Shen et al. (2001) demonstrated that the e-nose could monitor changes in volatiles associated with oil oxidation and could be used to predict peroxide value and sensory evaluations of vegetable oils.

To obtain a precise odor profile correlated with the degradation level of oil, Rusinek et al. (2020) designed a three-parameter (the maximum response, cleaning time, and response time) e-nose technique for odor description. Results showed that volatiles information provided by e-nose may help to interpret the quality of the oil in the absence of information on the corresponding raw seeds. However, chemical sensors only allow rough quantitation while working at high temperatures and are easily interfered with water vapor (Buettner, 2017). e-Nose combined with other techniques (e.g., GC) in the study of rapeseed oil could be concluded as a potential method for aroma characterization. It is noteworthy that the flash GC e-nose system with FID detector was rapid and of low cost for virgin rapeseed oil discrimination and has been proven to be useful in the classification of fragrant rapeseed oil production areas (Wang et al., 2020; Zhang, Wu, et al., 2020). Also, results obtained for volatiles detected by flash GC e-nose were verified to show a good correlation with total polar compounds during rapeseed oil frying, which is a potential rapid and convenient method to monitor the frying process (Xu et al., 2019). Although this technique cannot accurately measure the structure of volatile compounds, it shows a promising way for oil quality control. Meanwhile, further two types of e-nose systems (i.e., GC-based and MS-based e-nose systems) with different principles share the same advantage of the rapid test (Buettner, 2017); more details are shown in Table 3.

Aroma-active compounds that are present at trace or low concentrations often possess considerable odor activity due to very low odor thresholds. These trace odorants cannot be ignored and difficulties regarding their successful identification and quantitation can occur. In terms of growing trends for time-saving, simple, and automatic techniques in flavor analysis, e-nose shows broad application prospects on the one side but have to be improved to fulfill the requirement to detect also the ultra-trace amounts of important aroma-active compounds on the other side. What's more, the integrated approaches with high discriminating power, robustness results, and comprehensive profiling are of great necessity, and when it comes to time-sensitive samples, achieving the best balance between the rapid test and high resolution for aroma compounds analysis is crucial. Also, advanced software connected with aroma detection equipment for real-time analysis, data processing with various chemometric methods, and data visualization should be carried forward to communicate the complexity of the aroma information about rapeseed oil without losing its richness and depth.

3.3 | Sensory evaluation

The sensory evaluation is an integral part of the development of products that involves the evaluation of appearance, aroma, and taste as well as overall quality by a trained panel or a consumer panel. It aims to get reproducible and reliable results, so appropriate vocabularies, for example, for odor descriptors are necessary. Quantitative descriptive analysis (QDA) is efficient in revealing the key odor notes in rapeseed oil samples as described by trained panelists according to references. Virgin rapeseed oils with high quality are linked to sensory attributes such as seed-like, nutty, woody, and astringent (Brühl & Matthäus, 2008). All attributes used for sensory evaluation of rapeseed oil in former studies are listed in Table 4. These studies rated on different linear scales odor attributes and general desirability of oil samples. QDA with the intensities of each of the chosen sensory descriptors on a spider plot could show the differences of rapeseed varieties (Tynek et al., 2012), oils derived from peeled or unpeeled rapeseed (Pollner & Schieberle, 2016), or the change of flavor characteristics in rapeseed oil during roasting (Jing et al., 2020; Mao et al., 2019). By presenting aroma profiles with six odor attributes, including cabbage-like, nutty/fatty, earthy/pea-like, malty, sweaty, and seasoning-like, Matheis and Granvogl (2016a)

TABLE 4 Sensory analysis used in the evaluation of rapeseed oils

Samples	Panelists	Intensity scales	Sensory attributes	References
Cold-pressed rapeseed oil and refined rapeseed oil	10	0-10	Acidic, desirability, earthy, green, metallic, musty, oxidized, sweet	Jeleń et al., 2000
Canola oil, corn oil, and soybean oil	n.m.	0-10	Beany, burnt, buttery, corn-like, fishy, grassy, "hydrogenated odor", melon-like, nutty, paint-like, rubbery, weedy	Shen et al., 2001
Refined rapeseed oil	10	0-10	Acidic, floral, green, hay-like, oxidized, sweet	Jeleń et al., 2007
Virgin rapeseed oil	n.m.	0-5	Astringent, bitter, burnt, fusty, musty, nutty, rancid, roasty, seed-like, sprouted seeds-like, straw-like, woody, yeast-like	Brühl & Matthäus, 2008
Virgin rapeseed oil	n.m.	0-5	Asparagus-like, astringent, bitter, fusty, horseradish-like, musty, nutty, roasty/burnt, seed-like, straw-like, woody	Matthäus & Brühl, 2008
Cold-pressed rapeseed oil	n.m.	0-0.7	Acidic, bitter, burnt, grassy, melon-like Nousea fruity, musty/fusty, rancid, rapeseed-like, sunflower-like, varnish-like	Tynek et al., 2012
Virgin rapeseed oil	10	0-5	Astringent, nutty, rancid, roasty, seed-like, woody	Wei et al., 2012
High-oleic rapeseed oil	10	0-10	Astringent, burnt, nutty, rancid, roasty, seed-like, straw-like, woody	Rękas et al., 2015
Virgin rapeseed oil	10	0-10	Acidic, bread-like, burnt, butter-like, green, nutty, oily, oxidized, roasty	Gracka et al., 2016
Native cold-pressed rapeseed oil	20	0-3 (steps of 0.5)	Cabbage-like, earthy/pea-like, malty, nutty/fatty, seasoning-like, sweaty	Matheis & Granvogl, 2016a, 2016b
Raw/roasted mustard seeds and rapeseed	15	0-3 (steps of 0.5)	Cabbage-like (dimethyl trisulfide), caramel-like (4-hydroxy-2,5-dimethylfuran-3(2*H*)-one), coffee-like (2-furanmethanethiol), earthy (2,3-diethyl-5-methylpyrazine), earthy/pea-like (2-isopropyl-3-methoxypyrazine), fatty/green ((*E*)-2-nonenal), green/grassy (hexanal), malty (3-methylbutanal), popcorn-like (2-acetyl-1-pyrroline), putrid/cabbage-like/sulfury (methanethiol), roasty (acetylpyrazine)	Ortner et al., 2016
Cold-pressed rapeseed oil	17-25	0-3 (steps of 0.5)	Cabbage-like (dimethyl sulfide), cucumber-like ((*E*,*Z*)-2,6-nonadienal), fatty ((*E*,*E*)-2,4-nonadienal), green/grassy (hexanal), malty (3-methylbutanal), pea-like (2-isopropyl-3-methoxypyrazine) (50-fold above the odor threshold)	Pollner & Schieberle, 2016
Cold-pressed rapeseed oil and virgin rapeseed oil	6	0-5	Burnt, nutty, rancid, roasty, seed-like	Kraljić et al., 2018
Microwaved rapeseed oil and raw oil	10	0-3 (steps of 0.5)	Cabbage-like, coffee-like, earthy, fatty, green/grassy, pungent/sulfury, roasty	Zhou et al., 2018

(Continues)

TABLE 4 (Continued)

Samples	Panelists	Intensity scales	Sensory attributes	References
Steam-treated rapeseed oil	20	0-3 (steps of 0.5)	Cabbage-like, earthy/pea-like, fatty, fishy, sweaty, vinegar-like	Matheis & Granvogl, 2019a
Commercial fragrant rapeseed oil	12	0-5	Burnt (50 mg of octanol/L), chemical (0.1 mg of heptanol/L), fishy (0.01 mg of dimethyl trisulfide/L), green (1 mg of hexenal/L), metallic (50 mg of 1-heptene-3-one/L), nutty (10 mg of 2,5-dimethylpyrazine/L), pickled (2 mg of 4-isothiocyanato-1-butene/L), pungent (0.5 mg of allyl isothiocyanate/L)	Zhou et al., 2019
Virgin rapeseed oil	10	0-5	Green, nutty, oxidized oil-like, pungent, roasty	Wang et al., 2020

Abbreviation: n.m., not mentioned in reference.

compared the similarity between the original native cold-pressed rapeseed oil and the respective aroma recombinate to verify the successful characterization of all key aroma-active compounds. Besides, they used the same approach to study the fusty/musty off-flavor in cold-pressed rapeseed oil and confirmed trimethylamine as the only odorant related to the fishy off-flavor in steam-treated rapeseed oil (Matheis & Granvogl, 2016b, 2019a, 2019b). Matthäus and Brühl (2008) used various typical odor attributes to explain the influence of seed drying, external factors, and storage conditions on the sensory evaluation of rapeseed oil. Gracka et al. (2017) conducted a sensory panel evaluation based on color, appearance, odor, and taste of rapeseed oils through spider plots, which indicated distinctions among these oils. Sensory profile analysis, including not only aroma notes but also color and clarity, was applied to evaluate the oils obtained from cold-pressed and hot-pressed rapeseed (Kraljić et al., 2018). Malcolmson et al. (1994) and Shen et al. (2001) performed shelf life research on sensory stability of canola oils that was based on the overall aroma and odor intensity.

As a discriminative method, triangle testing is simple, cost-effective, and straightforward to determine orthonasal odor thresholds in the aroma research of rapeseed oil (Matheis & Granvogl, 2016a). Petersen et al. (2012) applied duo–trio testing and it showed a significant difference between thermally stressed and unstressed rapeseed oil samples after 22 days of storage in terms of sensory evaluation. Also, a paired comparison test was conducted by the same authors to specify the rancid perception of rapeseed oil. However, during these discriminative approaches, the order combinations should be randomized and only three to six samples should be evaluated simultaneously. All the abovementioned methods should be conducted by trained panelists, whereas preference tests could be operated by untrained consumers. Fuentes et al. (2013) analyzed the sensory quality during the storage of canola oils via a 9-cm scale evaluating appearance, aroma, taste, texture, and overall impression. Moreover, a ranking test was performed by a Korean panel to determine the most desirable canola oil relative to toasting temperature (Park et al., 1997). Traditional sensory profiling evaluation methods include the QDA and preference test, which is occasionally restricted by time, cost, and the evaluation ability of panelists. Flash profile is suitable for the exploratory stage of sensory evaluation and finding main sensory differences between products by untrained subjects ranking the products for each attribute that they individually create (Bredie et al., 2018). Free sorting, as a type of the sorting procedure approach, was used to classify 33 fragrant rapeseed oil samples by their odors, which was easy and rapid, and got rid of specific language development and a quantitative rating system (Zhang, Wu, et al., 2020). Projective

mapping (also called napping) can settle the drawback of time-consuming methods with no further sensory training and is more preferable to information-rich multisample sorting compared to the sorting procedure for perceptual mapping. This has successfully been shown for apples and cheese, which might also be useful for further research in the sensory analysis of rapeseed oils (Nestrud & Lawless, 2010).

Sensory assessment is crucial and should be done based on standardized procedures to get reliable results for a quality parameter. Non-standardized language, individual variability, expectations/bias, and differences between "expert" opinions and consumer preferences limit the accuracy of sensory analysis. All these abovementioned features can be divided into two considerations: objectivity and normalization of sensory analysis. The consistency and reproducibility of sensory evaluation results should be emphasized. For example, dimethyl trisulfide (mentioned as reference odorant in Table 4) was described with different odor attributes by Ortner et al. (2016) and Zhou et al. (2019). The selection of sensory descriptors and corresponding reference standards (including concentration) should strictly be considered.

3.4 | Chemometric approaches

The well-developed sample extractions and analytical methods are often not enough to differentiate the diverse sensory properties of samples. Thus, the requirement of multivariate methods is very helpful and sometimes even indispensable. Table 5 presents the chemometric methods used for flavor analysis in rapeseed oil. In most cases, principal component analysis (PCA) is the first stage for visualization of differences among the samples according to the scores plot. Aroma compounds responsible for the grouping of the samples are shown in the loading plots, which help researchers to find possible marker compounds of the respective oils. PCA of oil samples cannot only be obtained by analytical approaches such as GC–MS and e-nose, but also by sensory assessment to find principal descriptors, which can be used to analyze the correlation between the quality of rapeseed oil and roasting conditions (temperature and time), storage time, rapeseed varieties, and cold pressing with different pretreatments (Jeleń et al., 2000; Jing et al., 2020; Rękas et al., 2015; Wei et al., 2012). However, some researchers found that PCA results based on volatile compounds showed a significant difference compared to those results based on the sensory quality of rapeseed oil (Bonte et al., 2017; Gracka et al., 2017). The overall structure of the dataset may be revealed by generating a three-dimensional plot if the first two principal components obtained from the data matrix are not enough to account for a substantial fraction of the total variance. Zhang, Wu, et al. (2020) used a three-dimensional model of score plot of a PCA of fragrant rapeseed oils to discriminate the origin, based on flash GC e-nose analysis. Zhou et al. (2013) visualized the influence of the microwave processing times on the rapeseed oils using preferable classification by three-dimensional component plots. Similar results of classification by PCA were obtained via hierarchical cluster analysis (HCA) with a heatmap illustration to distinguish four edible oils by Hu et al. (2014). The main difference between PCA and HCA, based on the principle of these two analytical methods, is that PCA produces new variables, whereas HCA does not. Regarding the application, PCA focuses on the comprehensive evaluation of the contribution of data, whereas HCA has the advantages of being simple and intuitive. In addition, the test and selection of distance functions is not a trivial matter when HCA is applied to cluster the samples. Although PCA and HCA show the groups of datasets, these unsupervised methods might sometimes not perform very well with effective discriminating power. In general, linear correlation coefficients might render very similar interpretations of the PCA and HCA results, which may be recognized as exploratory methods. In terms of the correct result of both classification and discrimination, many supervised multivariate statistical methods should be highlighted. For example, linear discriminant analysis (LDA) helped to reveal 3-methylbutanal and 2-methylpropanal as important contributors to the prediction of sensory good or bad rapeseed oils (Bonte et al., 2017). Random forest (RF) fits many decision tree classifiers to improve the predictive accuracy and control overfitting, which has been utilized for the classification of four types of edible oils based on the 15 most important volatiles (Hu et al., 2014). When a possible strong association between volatiles and rapeseed oil flavor quality should be tested, Pearson correlation coefficients are a good tool to use. By this method, a correlation between acetaldehyde and ethanol produced by seed fermentation and the seedling growth to indicate the extent of seed deterioration was shown (Buckley & Buckley, 2009). Another regression technique, partial least squares regression (PLSR), a supervised method, can analyze the relationship between independent and dependent variables in large datasets. The PLSR model was used to clarify the relationship between total polar compounds and volatiles in fried rapeseed oils and it displayed a good prediction of the total polar compounds content with volatile compounds (Xu et al., 2019). In addition to the single dependent variable applied in PLSR, the PLSR model may also involve two multivariate matrices of sensory attributes and volatile compounds, which could explain the relationship between volatiles and sensory descriptors in rapeseed oils by a two-factor model (Zhou et al., 2019). Similar to PLSR,

TABLE 5 Chemometric methods for flavor analysis of rapeseed oil

Methods	Characteristics	Applications	References
PCA	Loading plot and scores plot, visualized, convenient, unsupervised classification	Classification of oil samples into different types and storage times based on the odor characteristics	Jeleń et al., 2000
		Identification of volatiles sensitive to the presence of olive oil, canola oil, and sunflower oil	Negroni et al., 2001
		Differentiation of oil samples varying in storage time	Jeleń et al., 2007
		Differentiation of conventional and high-oleic rapeseed oils with different lipid oxidation properties	Petersen et al., 2012
		Differentiation of oil production of various cultivars and cold pressing pretreatments	Wei et al., 2012
		Differentiation of different rapeseed varieties or oxidative properties	Petersen et al., 2013
		Differentiation of rapeseed varieties and the effect of pretreatment with dehulling and microwaving on the flavor characteristics of rapeseed oils	Zhou et al., 2013
		Differentiation of rapeseed oil samples prepared by different roasting conditions	Gracka et al., 2016
		Differentiation of rapeseed oils eliciting desired or undesired sensory properties	Bonte et al., 2017
		Differentiation of cold-pressed rapeseed oils varying in pretreatment methods	Gracka et al., 2017
		Classification of refined grades of rapeseed oils	Chen et al., 2019
		Determination of the relationship between the key volatiles derived from thermal degradation of glucosinolates and roasted rapeseed oil flavor	Mao et al., 2019
		Differentiation of rapeseed varieties and roasting conditions	Jing et al., 2020
		Determination of the variable odor profile in oil occurring during prepressing treatment of rapeseed	Rusinek et al., 2020
HCA	Unsupervised classification	Differentiation of rapeseed oil samples prepared with different frying times	Xu et al., 2019
RF	No over-fitting	Establishment of a classification model for four edible oils (soybean, peanut, rapeseed, and sunflower oils)	Hu et al., 2014
LDA	Predictive accuracy	Differentiation of sensory good and bad (musty/fusty) virgin rapeseed oils	Bonte et al., 2017
Pearson correlation analysis	Simple correlation analysis	Correlation between seedling growth and extent of seed deterioration	Buckley & Buckley, 2009
PLSR	Multivariate matrices analysis	Explanation of the relationship between samples, flavor compounds, and sensory descriptors	Zhou et al., 2019

Abbreviations: HCA, hierarchical cluster analysis; LDA, linear discriminant analysis; PCA, principal component analysis; PLSR, partial least squares analysis; RF, random forest.

principal component regression (PCR) models a response variable when there are a large number of predictor variables. However, it constructs these predictors in different ways (PCR creates components to explain the variability without considering response variables, whereas PLSR performs vice versa), which has not been reported in oil aroma analysis yet. As a nonlinear supervised method, the probabilistic neural network has allowed discrimination between qualities of beer samples or red and white wine samples successfully (Dębska & Guzowska-Świder, 2011; Santos et al., 2010). For quantitative monitoring, a support vector machine (SVM) is widely used for classification and regression analysis, implicitly mapping their inputs into high-dimensional feature spaces (Qiu & Wang, 2017; Wang et al., 2019). There is a report that SVM, RF, extreme learning machine, and PLSR were applied in the establishment of regression models to process signals of additives in fruit juices (Qiu & Wang, 2017). Besides, classification and influence matrix analysis, fuzzy rule-building expert system, soft independent modeling of class analogy, and pattern recognition by independent multicategory analysis were also reported to be applied in the classification and authentication of food (Granato et al., 2018; Mehretie et al., 2018). These supervised methods could also be applied in the flavor analysis of rapeseed oil shortly.

4 | IMPACT OF TREATMENTS ON RAPESEED OIL AROMA

4.1 | Storage

Good storage conditions for the seeds and oils are essential for a high quality of the final oils, including the overall aroma. In contrast, improper storage conditions may lead to an off-flavor formation in rapeseed oil.

Aroma compounds that emerged in rapeseed were confirmed as potential indicators of deterioration during the storage of the seeds, for example, ethanol and acetaldehyde (Buckley & Buckley, 2009). Moreover, 3-methylbutanal and 2-methylpropanal, which are produced by microorganisms (bacteria or fungi) (Schulz & Dickschat, 2007) were considered as promising compounds for the detection of deterioration of raw seeds by inappropriate storage conditions (Bonte et al., 2017). Recent work of Matheis and Granvogl (2016b) also verified that improper storage conditions (residual moisture and elevated temperature) could result in an increase of microbial metabolisms and generate the fusty/musty off-flavor (e.g., 2- and 3-methylbutanoic acid). Glucosinolate degradation products were also described as important indicators for the deterioration of wet seeds during storage (Bonte et al., 2017).

For rapeseed oils, a significant increase of volatiles was described in aged oils collected from supermarket shelves compared to the fresh oils, especially for 2-pentenal (44-fold increase), (*E*,*E*)-2,4-heptadienal (13-fold), and (*E*,*E*)-2,4-decadienal (12-fold) (Raghavan et al., 1994). Malcolmson et al. (1994) analyzed canola oil stored in glass bottles at 24°C without light, showing that the original aroma remained unchanged for 16 weeks. Based on the work of Snyder (1995), an increase of volatile compounds including eight aldehydes and three alkanes was observed in canola oil by comparing the original state with that after accelerated storage at 60°C for 8 and 16 days, respectively. Among them, octanal, nonanal, hexanal, and decadienal showed the highest increase.

Jeleń et al. (2000) reported that the concentrations of aldehydes increased in refined rapeseed oil after 10 days of storage time at 50°C, which was consistent with the increase in the total volatiles. However, this phenomenon was correlated with a decrease in the sensory desirability of the oil. Twenty-eight volatile components were identified in refined rapeseed oil after accelerated storage at 60°C for 0–12 days by the same group. Hexanal, 2,4-heptadienal, (*E*)-2-heptenal, and 1-penten-3-ol were the major volatiles in stored oils (Jeleń et al., 2007). Wang et al. (2005) reported on (*E*,*E*)-2,4-heptadienal, (*E*,*Z*)-2,4-heptadienal, (*E*,*E*)-2,4-decadienal, (*E*,*Z*)-2,4-decadienal, hexanal, and nonanal as the predominant aroma compounds in stored canola oil. In addition, the mushroom-like smelling 1-octen-3-one significantly contributed to the overall odor of the aged canola oil due to its low detection threshold in oil. Fuentes et al. (2013) evaluated the physicochemical and sensory quality of canola oil packaged in PET bottles demonstrating that the peroxide value and acid value of canola oil increased after 375 days of storage time. However, statistically significant differences were not observed ($p < 0.05$) in the descriptive analysis and acceptance testing for the canola oil, because an oxidized aroma and/or taste were/was not detected. Kiralan and Ramadan (2016) found an increase of hexanal, (*E*)-2-heptenal, and 3,5-octadien-2-one in canola oil stored for 12 days at 60°C using a forced-draft air oven, whereas the concentration of 6-methyl-5-hepten-2-one showed a variation. Interestingly, (*E*,*E*)-2,4-decadienal was only identified in fresh canola oil in a study performed by Snyder (1995) but disappeared after thermal oxidation, which was inconsistent with previous research. Overall, lipid oxidation mainly occurs during storage of rapeseed and rapeseed oil, which depends on humidity, temperature, oxygen, and light and forms volatile/aroma-active compounds including aldehydes, ketones, and acids. Rapeseed oil sealed and stored at low temperature without light shows a slowed generation of undesired off-flavors, for example, a rancid off-flavor mainly formed by short-chain acids.

4.2 | Dehulling

Rapeseed hull is mainly composed of non-nutritive substances such as cellulose and lignin with low contents of oil and protein. Also, the existence of abundant polyphenols in the hull makes the rapeseed meal appearing bitter and astringent, reducing its utilization value. Also, the contents of polycyclic aromatic hydrocarbons in rapeseed hull are higher than those in rapeseed kernel. Thus, the dehulling process was considered as a good way to produce oil with good quality and improve the utilization value of rapeseed meal (Liu et al., 2018).

Zhou et al. (2013) found that dimethyl disulfide, 2,4-pentadienenitrile, and *o*-xylene were present in the volatile fraction of "dehulled" rapeseed oil but absent in untreated rapeseed oil. Moreover, products of glucosinolate degradation including methallyl cyanide and 4-isothiocyanato-1-butene (pungent aroma) in rapeseed oil decreased significantly after dehulling. The smelling of cold-pressed rapeseed oil obtained from dehulled seeds was found to be milder than that of untreated oils. However, the results of Gracka et al. (2017) demonstrated that the whole seed oil revealed similar sensory aspects and volatiles compared to peeled seed oil. Pollner and Schieberle (2016) analyzed the aroma compounds in rapeseed oils obtained by cold pressing of either unpeeled or peeled seeds using the molecular sensory science concept. Thereby, dimethyl sulfide (cabbage-like) was evaluated as a potential indicator to distinguish between these two types of rapeseed oils. The results indicated that the amount of dimethyl sulfide in "peeled" rapeseed oils (424 μg/kg) was remarkably higher compared to that in the "unpeeled" rapeseed oil (4.1 μg/kg). However, quantitation of dimethyl sulfide in 10 commercially peeled or unpeeled rapeseeds oils presented significant differences, but no influence of the peeling on the dimethyl sulfide content was found. Thus, further studies to elucidate the influence of peeling on the flavor formation of rapeseed oils are needed due to the inconsistent results of previous studies.

4.3 | Roasting

As an important pretreatment method, roasting is widely applied in the processing of rapeseed oil. Roasting prior to extraction can help to improve the oil yield, and it is also essential for the production of desirable aroma and color.

Sensory experiments from Park et al. (1997) suggested that the "roasted" rapeseed oil was markedly more preferred by panelists than the "unroasted" rapeseed oil. However, Kraljić et al. (2018) found that there is no significant difference in the aroma attributes between cold-pressed rapeseed oil and oil from seed conditioned at 60°C for 30 min, probably due to the not very high temperatures applied. An increase in the roasting temperature (80 and 100°C) resulted in a decrease of the seed-like aroma and an increase of the roasted and nutty odors in the oil. Burnt smelling with low intensity was only found in the oil obtained from roasted rapeseed at 100°C. Rękas et al. (2015) also reported that unroasted high-oleic rapeseed oil was characterized by a woody, straw-like, and weak seed-like aroma. However, they found that the intensity of the seed-like odor increased with the roasting temperature of 100°C. According to Wei et al. (2012), a roasting temperature of 120°C resulted in the appearance of a nutty aroma note in the oil, whereas roasting at a temperature of 140°C led to an explicit increase of the roasted and burnt off-flavors. However, Gracka et al. (2016) reported on oily, green, and acidic odor notes that predominated in rapeseed oils obtained from unroasted and roasted rapeseed at 140 and 160°C, whereas the attributes related to the oil obtained from roasted rapeseed at 180°C were nutty, bread-like, roasted, and burnt. The reason may be the difference in moisture content of the raw material and roasting time.

Roasting of oilseeds can accelerate lipid oxidation, Maillard reaction, Strecker degradation, caramelization, and the formation of volatiles in general (Frauendorfer & Schieberle, 2008). The amounts of Strecker aldehydes in oils obtained from roasted rapeseed (at 150°C for 40 min) showed an increase compared to the unroasted seeds. In the late period of the thermal treatment experiment (40–50 min), the concentrations of the Strecker aldehydes in rapeseed oil were 20 times higher than the initial amounts (Jing et al., 2020). Kraljić et al. (2018) analyzed the volatiles in rapeseed oils obtained via cold pressing and hot pressing (60°C) and mostly found breakdown products of glucosinolates that were related to the seed-like aroma. An increase of the conditioning temperature (80 and 100°C) led to the inactivation of the myrosinase, favoring the thermal decomposition of precursor compounds present in the seeds that led to the generation of nitriles, aldehydes, pyrazines, and furans that impart a nutty and roasted aroma to the oil. In another study, esters, acids, alkanes, alcohols, aldehydes, and ketones were identified as the major volatiles in oil obtained from heated rapeseed (150°C) during the early stage (0–20 min), which showed a fluctuant behavior. In the late stage (20–60 min), new volatiles such as nitriles, pyrazines, and some nitrogen- and *S*-containing compounds occurred in significant amounts (Mao et al., 2019). Jing et al. (2020) investigated the aroma variations of virgin rapeseed oil during roasting (150°C for 50 min) and observed a clear increase of the amounts of volatiles (e.g., aldehydes, nitriles, pyrazines, and ketones) during the heat

treatment. For example, the contents of the pyrazines increased by >99% and the amounts of the aldehydes by >64%.

Gracka et al. (2016) found dimethyl sulfide, dimethyl trisulfide, octanal, phenylacetaldehyde, 2,3-butanedione, 2,3-diethyl-5-methylpyrazine, and 3-isopropyl-2-methoxypyrazine to be key aroma compounds in roasted rapeseed oil, whereas dimethyl sulfide, octanal, and hexanal were described to be the predominant aroma-active components in unroasted rapeseed oil. Raw and roasted rapeseed were also studied by Ortner et al. (2016) applying the sensomics approach. Thereby, 27 and 43 aroma-active compounds were found in raw and roasted (140°C, 60 min) rapeseed, respectively. Among these odorants, dimethyl sulfide (asparagus-like), 2-furanmethanethiol (coffee-like), and 2-isopropyl-3-methoxypyrazine (earthy, pea-like) showed the highest OAVs in raw seeds, whereas 2-furanmethanethiol (coffee-like), methanethiol (putrid, cabbage-like, sulfury), 3-methylbutanal (malty), 2-acetyl-1-pyrroline (popcorn-like), dimethyl trisulfide (cabbage-like), dimethyl sulfide (asparagus-like), 2,3-pentanedione (butter-like), 2-isopropyl-3-methoxypyrazine (earthy, pea-like), 2,3-butanedione (butter-like), 3-(methylthio)propanal (cooked potato-like), and 4-hydroxy-2,5-dimethylfuran-3(2*H*)-one (caramel-like) were present with high OAVs (74–36,000) in roasted seeds.

In general, moderate roasting of seeds helps to enhance the final aroma of the respective rapeseed oil. However, improper roasting conditions (high temperature or long roasting time) will lead to undesired side effects including darker colors, sensory defects, and the generation of contaminants (e.g., polycyclic aromatic hydrocarbons). Thus, strict control of the conditions for seed roasting is essential for the final rapeseed oil quality. Moreover, new thermal treatment methods with higher heat transfer rates and more accurate temperature control are needed to be further explored.

4.4 | Microwave

Microwave treatment is a new method to replace the conventional thermal treatment (roasting), which has received attention owing to its high efficiency, short application times, and energy-saving and which has already been applied to rapeseed oils to improve their aroma. Wei et al. (2012) showed that the predominant aroma of the untreated and microwave-treated (800 W for 5 min) rapeseed oils is woody, nutty, and seed-like, whereas the conventional thermally treated rapeseed oil had roasted and rancid odor notes. The authors concluded that the microwave treatment of rapeseed could produce a desired nutty aroma in the final oils. Further, they found that the percentage of 4-isothiocyanato-1-butene (pungent) decreased from about 67% to 55% of total volatile compounds in the cold-pressed oils after microwave treatment, whereas other glucosinolate degradation products including 5-hexenenitrile and 3-methyl-3-butenenitrile increased. A similar phenomenon was observed by Zhou et al. (2013) reporting on a decrease of the 4-isothiocyanato-1-butene content by 97% in microwave-treated (800 W for 3 min) rapeseed oils compared to the crude oils. Pyrazines appearing after 6 min of microwave treatment led to a roasted odor compared to untreated rapeseed oil. Years later, the same group studied the odorants formed from glucosinolate degradation in oils from raw and microwave-treated rapeseed (Zhou et al., 2018). Thereby, the amount of dimethyl trisulfide increased by factors between 2 and 85 in rapeseed oil after microwave treatment. Dimethyl sulfoxide and dimethyl sulfone also increased from raw oil to microwave-treated oil. The formation pathway was postulated by the rearrangement of isothiocyanate or methionine. Additionally, a clear decrease of allyl isothiocyanate, 1-isothiocyanatobutane, and 4-isothiocyanato-1-butene was observed in oil during the microwave treatment. The intensity of the cabbage-like odor attribute of microwave-treated rapeseed oils was higher than that of raw oils, whereas the intensity of the pungent aroma was lower (Zhou et al., 2018). Ren et al. (2019) also found that 4-isothiocyanato-1-butene decreased by 74%–95% and methallyl cyanide increased by 95% in the microwave-treated rapeseed oils. Pyrazines and furans also emerged in the microwave-treated oils and contributed to a roasted sensory attribute.

Kiralan and Ramadan (2016) treated canola seeds with microwaves (2.450 MHz and 0.45 kW for 2 and 4 min) and identified *p*-cymene and hexanal as predominant volatiles in the corresponding canola oils. Moreover, γ-terpinene and α-thujene were only found in the microwave-treated oils, which were rarely reported in other studies. McDowell et al. (2017) investigated the effects of microwaving and roasting on the aroma of rapeseed oil. Results showed that the raw oils were characterized by floral, fatty, green, and grassy sensory attributes, whereas the microwave-treated (800 W for 2 min) and roasted (in the oven at 180°C for 10 min) rapeseed oils elicited, beside some of the former ones, also baked, nutty, sweet, and almond-like odor notes. Interestingly, oil from microwave-treated seeds contained furfural in a higher proportion than that from roasted seeds.

Thus, microwave pretreatment is a promising method that needs more attention in the industrial production of rapeseed oil due to its convenience, high efficiency, and contributory effect on the aroma.

4.5 | Flavoring with herbs

Flavored oil is defined as an oil (e.g., rapeseed oil or olive oil) to which other ingredients including herbs, spices, fruits, or vegetables were added to enhance shelf life, improve nutritional value, and enrich odor attributes (Adams et al., 2011; Assami et al., 2016; Clodoveo et al., 2016).

Generally, two main methods are applied to flavored rapeseed oil: (i) the use of refined rapeseed oil as a solvent to extract odorants and further bioactive compounds from herbs and spices by different processing methods including but not limited to mechanical stirring, ultrasound, microwave, and heating and (ii) the addition of essential oils of herbs or spices to rapeseed oil directly. The sensory description of flavored rapeseed oils is often tightly related to that of the corresponding spices or herbs.

Adams et al. (2011) described the differences in types and amounts of volatile compounds between the herbs and the corresponding rapeseed oils flavored with dried thyme, basil, and oregano at concentrations of 3% and 6% produced at 50–90°C for up to 60 min. Thereby, larger proportions of hydrocarbon monoterpenes, such as γ-terpinene and myrcene, and oxygenated monoterpenes, particularly 1,8-cineole, were found in the flavored oils compared to those of the initial herbs, whereas phenolic and sesquiterpene compounds detected in the HS of the flavored rapeseed oils were present at remarkably lower contents compared to the original herbs. Kowalski et al. (2018) estimated how the flavoring with rosemary affected the composition of the volatiles of rapeseed oil. The study showed that the direct addition of essential oil to rapeseed oil was the most effective flavoring method and that 1,8-cineole was the dominant volatile compound. Two years later, the same group studied the influence of flavoring of rapeseed oil with marjoram on the concentrations of volatile compounds (Kowalski et al., 2020). Thereby, the major aroma compound was γ-terpinene, which showed a lower content in the flavored oil with microwave-assisted maceration compared to classic maceration with shaking. The highest content of volatiles in general, but also of γ-terpinene, and the lowest antioxidant activity were simultaneously found in the rapeseed oil flavored by the direct addition of the essential oil. Oils flavored by maceration of the herbs revealed a higher antioxidant activity but lower amounts of volatiles, which led to the conclusion that the antioxidant activity of flavored oils was more related to non-volatile bioactive components.

4.6 | Refining

The complete refining process of rapeseed oil including degumming, neutralization, bleaching, dewaxing, and deodorization removes some undesirable substances, such as phospholipids, free fatty acids, impurities, and pigments from the oil. Thus, it contributes to the improvement of the physicochemical properties and the stability of rapeseed oil but can also remove significant amounts of desired aroma compounds.

The odorants in refined rapeseed oil were studied by Guth and Grosch (1990) for the first time. 1-Octen-3-one, (*Z*)-1,5-octadien-3-one, (*Z*)-2-nonenal, (*E*)-2-nonenal, 3-methyl-2,4-nonanedione, and *trans*-4,5-epoxy-(*E*)-2-decenal were reported with the highest FD factors among 23 aroma substances detected by AEDA. Jeleń et al. (2000) found that the concentration of total volatiles in refined rapeseed oil was lower than that in oil obtained by cold pressing. However, after storage of 3, 5, and 10 days, the refined oil showed a higher concentration of volatiles. The amounts of major volatiles, namely, aldehydes, showed a similar tendency in refined and cold-pressed rapeseed oils during storage. A possible reason is that lower contents of antioxidative components were present in the refined rapeseed oil compared to cold-pressed rapeseed oil, which resulted in more volatile products of (thermal) oxidation during storage. Uriarte et al. (2011) reported on almost 30 volatiles in refined rapeseed oils, such as 2-propanone, pentanal, hexanal, (*E*)-2-butenal, 2-ethylfuran, 2-pentylfuran, and short-chain acids (two to seven carbon atoms). Chen et al. (2019) analyzed the differences in volatiles of rapeseed oil with different "levels." These levels of rapeseed oils were identified according to the Chinese National Standard GB/T 1536–2004. Fourth-level rapeseed oil with a low degree of refining had more volatile compounds, whereas in first-level rapeseed oil with a high degree of refining, only three aroma components, namely, 1-phenylethanol, acetophenone, and limonene, were detected. Thus, it can be concluded that the type and amounts of volatiles increased with a decrease in the degree of oil refining. The complete refining process can ensure the safety of rapeseed oil and avoid the formation of a rancid off-flavor, but it also leads to clear losses of desirable aroma-active and other bioactive compounds (e.g., tocopherols and sterols), which affect the sensory characteristics and the oxidation stability. Thus, moderate refining is proposed to guarantee the safety, nutritional value, and desired sensory attributes of rapeseed oil products.

4.7 | Oil heating

Rapeseed oil is often used as cooking (frying) oil at high temperatures, which produces some additional odorants. Fullana et al. (2004a) analyzed the volatiles of canola oil heated at 180 and 240°C for 15 and 7 hr. Thereby, hexanal, nonanal, 2-propenal (acrolein), and 2-decenal were the dominant aldehydes in the cooking oil fumes at 180°C; however, nonanal, heptanal, acrolein, 2-hexenal, and 2-decenal became more abundant at 240°C. As the predominant volatile compound, acrolein was found in canola oils at both temperatures. The total aldehydes showed a decrease after heat processing at 240°C for 7 hr or longer times because polymerization reactions of triacylglycerols become more dominant than their oxidation reactions (Fullana et al., 2004b). (*E*)-2-Decenal and (*E*,*E*)-2,4-heptadienal were regarded as useful indicators of oxidative changes of frying oils because they were important to distinguish oils at a very early stage of oxidation during the frying process. These compounds also correlated well with the indices of oil degradation including polymerized triacylglycerides and total polar compounds (Petersen et al., 2013). The generation of volatiles, and especially of aldehydes, in rapeseed oil increased almost linearly with the heating temperature, and they enhanced drastically when the temperature reached the fire point of the oil. In a very recent study, Kasprzak et al. (2020) also found a significant increase in the total concentration of volatiles in refined rapeseed oil after heating at 180°C for 15 min (40 mg/L of oil) compared to the unheated one (12 mg/L of oil). The amounts of volatiles in heated rapeseed oil at 180°C for 8 hr exhibited a 23-fold increase compared to the original oil. Thereby, the amounts of aldehydes and ketones increased from 2% to 22% and from 2% to 12%, respectively, of the total volatile compounds. It is noteworthy that normal rapeseed oil may not be suitable for a longer use for frying purposes or several cycles of reheating because the used oil would have higher amounts of free fatty acids and a remarkably lower smoke point, leading to higher emissions of undesirable volatile compounds during heating.

In general, canola oil with a high degree of refining is often used for heat processing, but also virgin rapeseed oil is used for cooking. Thus, additional studies on the influence of heating on the aroma of rapeseed oil with different refining degree are warranted. High-oleic rapeseed oil was reported to be an excellent alternative to other commonly used cooking oils at high temperatures (Matthäus et al., 2009). It has a very low saturated fatty acid content and a considerable proportion of oleic acid that helps to reduce cardiovascular disease. Furthermore, oleic acid has better storage and thermal stability compared to linoleic acid. In general, the suitability and stability of high-oleic rapeseed oil resulted in comparable or better results than the widely used normal rapeseed oils.

5 | CONCLUSION

The aroma of rapeseed oil is one of the most important criteria for its acceptance by consumers. One hundred thirty-seven aroma-active compounds found in rapeseed oil in previous studies based on olfactometry were collected in this review, including aldehydes, ketones, acids, esters, alcohols, phenols, pyrazines, furans, indole, pyridines, pyrrolines, thiazoles, thiophene, further *S*-containing compounds, nitriles, and alkenes. Some of these compounds require further validation (e.g., nitriles) due to a lack of recombination experiments in previous work. Roasty, fatty, cheese-like, green, fruity, pungent, citrus-like, sweaty, sweet, spicy, flowery, nutty, earthy, sulfury, and coconut-like aroma notes were found to be main odor descriptors in rapeseed oil.

Much work has been performed on analytical techniques to reveal key odorants of rapeseed oil, but much remains to be done. It is still a challenge to couple the instrumental data with the sensory data and obtain a "complete" aroma profile of rapeseed oil. Some key trace aroma-active compounds (especially related to off-flavor) need to be further identified. The future instrumental techniques will impose increasing demands on accuracy, precision, sensitivity, time-saving, portability, and real-time monitoring. Differences also exist in the expectation of sensory good rapeseed oils from different regions due to different dietary habits and preferences, which warrants further investigation. Also, data processing with various chemometric methods and data visualization needs to be carried forward to communicate the complexity of the aroma information about rapeseed oil without losing its richness and depth.

Qualitative and quantitative analysis of key odorants is the first step. Furthermore, evaluating the relationship between sensory characteristics and (amounts of) odorants of rapeseed oil will give a better understanding of how rapeseed oil aroma is influenced by the presence of aroma-active substances. This review also summarized the effects of different treatments on the aroma of rapeseed oil; however, it is still premature to conclude that it is fully understood. The formation mechanisms and control techniques of aroma components of rapeseed oil under different treatment methods and conditions remain to be investigated, which will contribute to producing more uniform rapeseed oil products with desired aroma and higher consumer acceptance.

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AUTHOR CONTRIBUTIONS

Youfeng Zhang conceptualized and visualized the study, curated the data, acquired funding, contributed in investigation, administered the project, wrote the original draft, and reviewed and edited the manuscript. YuQi Wu curated the data, contributed in investigation, wrote the original draft, and reviewed and edited the manuscript. Sirui Chen and Binbin Yang curated the data, contributed in investigation, and wrote the original draft. Hui Zhang and Xingguo Wang conceptualized the study, administered the project, and contributed in supervision. Michael Granvogl conceptualized the study, administered the project, contributed in supervision, and reviewed and edited the manuscript. Qingzhe Jin conceptualized the study, acquired funding, administered the project, contributed in supervision, and reviewed and edited the manuscript.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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Outlines

The aroma of rapeseed oil is one of the most important criteria for its acceptance by consumers. Fragrant rapeseed oil is a kind of virgin oil with a lower degree of refining, which makes it more complex in composition. Some components in oil (e.g., phospholipids, free fatty acids, phenolic compounds, etc.) would influence the distribution and volatilization of volatile substances through binding, known as “matrix effect”. Flavor analysis based on the complicated sample matrix composition in oil should receive more attention. One hundred and thirty-seven aroma-active compounds found in rapeseed oil in previous studies based on olfactometry were collected in this review, including aldehydes, ketones, acids, esters, alcohols, phenols, pyrazines, furans, pyrrolines, indoles, pyridines, thiazoles, thiophenes, further S-containing compounds, nitriles, and alkenes. Some of these compounds require further validation (e.g., nitriles) due to a lack of recombination experiments in previous work. The effects of different treatments on the aroma of rapeseed oil were also summarized, however, it is still premature to conclude that it is fully understood. The formation mechanisms and control techniques of aroma components of rapeseed oil under different treatment methods and conditions (e.g., roasting) remain to be investigated, which will contribute to producing more uniform rapeseed oil products with desired aroma and higher consumer acceptance. Glucosinolate degradation products are the major volatile flavor compounds of rapeseed oil. However, a more thorough exploration of the mechanisms of flavor compounds formation from different single glucosinolates via thermally induced degradation with different reaction conditions is still required.

First, a systematic comparison between five flavor trapping techniques including solid-phase microextraction (SPME), SPME-Arrow, headspace stir bar sorptive extraction (HSSE), direct thermal desorption (DTD), and solvent-assisted flavor evaporation (SAFE) for hot-pressed rapeseed oil was conducted. Besides, methodological validation of these five approaches for 31 aroma standards found in rapeseed oil was conducted to compare their stability, reliability, and robustness. Secondly, key odorants in representative commercial FRO samples were identified by Sensomics approach. Then, key odorants and overall aroma profiles of oils from rapeseeds roasted under different conditions were compared. At last, the thermal degradation behavior and generated volatile products of progoitrin (the main glucosinolate of rapeseed) in liquid (different pH) and solid phase systems were investigated. The possible formation pathways of major S-containing (thiophenes) and N-containing (nitriles) volatile (flavor) compounds were proposed (Figure 1).

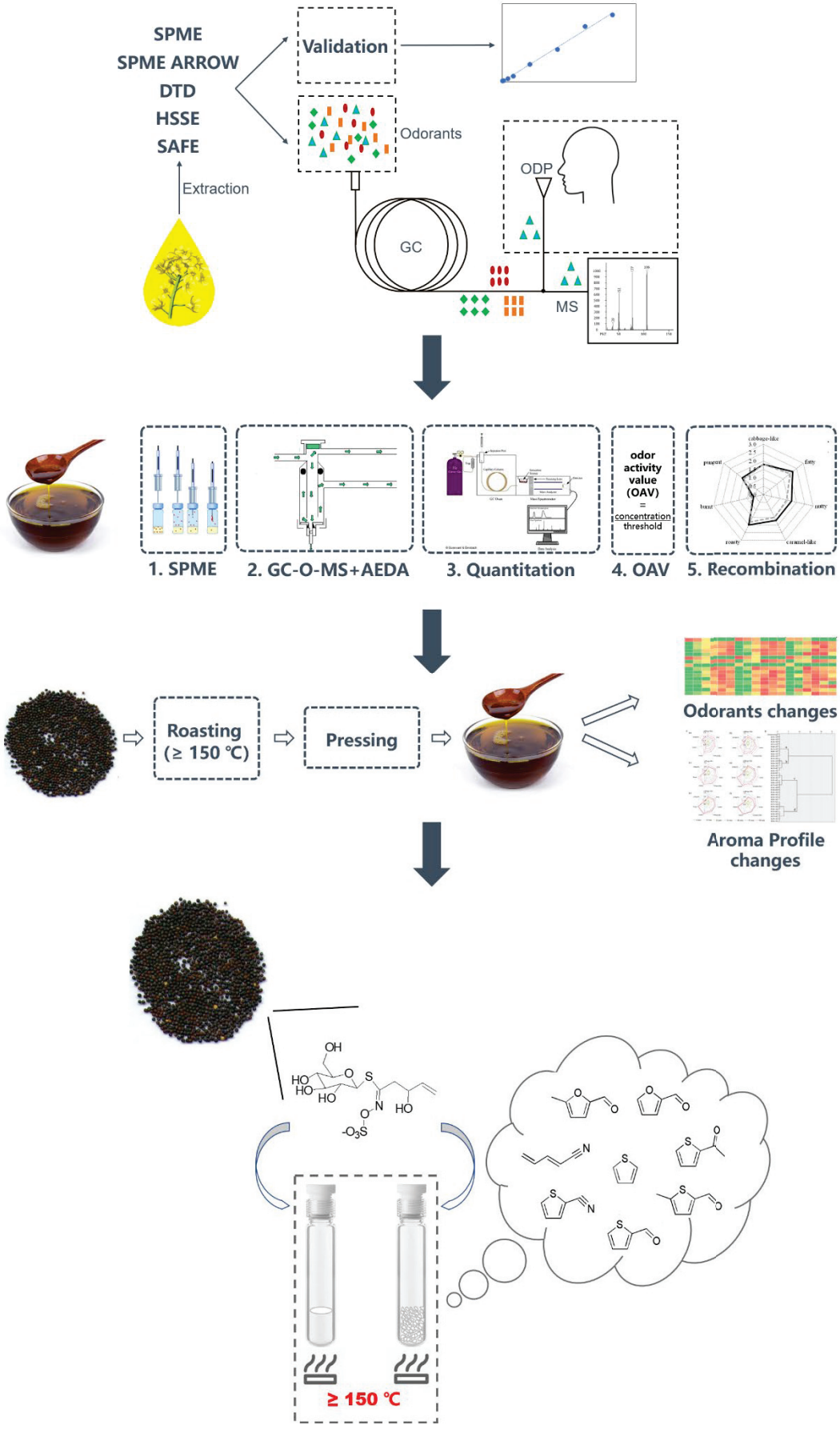

Figure 1 Schematic workflow of the thesis

II. CHAPTER

A Comparative Study on Flavor Trapping Techniques from the Viewpoint of Odorants of Hot-pressed Rapeseed Oil

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A comparative study on flavor trapping techniques from the viewpoint of odorants of hot-pressed rapeseed oil

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(*E*,*E*)-2,4-decadienal (PubChem CID: 5283349)
2,5-dimethylpyrazine (PubChem CID: 31252)
dimethyl trisulfide (PubChem CID: 19310)
2-ethyl-6-methyl-pyrazine (PubChem CID: 26332)
3-ethyl-2,5-dimethylpyrazine (PubChem CID: 25916)
hexanal (PubChem CID: 6184)
4-isothiocyanato-1-butene (PubChem CID: 76922)

ABSTRACT

Rapeseed oil, as one of the three major vegetable oils in the world, its matrix effect makes the decoding flavor a challenge. Solid-phase microextraction (SPME), SPME-Arrow, headspace stir bar sorptive extraction (HSSE), direct thermal desorption (DTD), and solvent-assisted flavor evaporation (SAFE) were compared based on the odorants in hot-pressed rapeseed oil. Besides, methodological validation for 31 aroma standards was conducted to compare reliability and robustness of these approaches. DTD showed the largest proportion of acids, while the other techniques extracted a majority of nitriles. The highest number of odorants was detected by SAFE (31), followed by HSSE (30), SPME-Arrow (30), SPME (24), and DTD (14). SPME-Arrow showed the best performance in linearity, recovery, and reproducibility followed by SPME, HSSE, DTD, and SAFE. Results reveal the advantages and limitations of diverse methodologies and provide valuable insights for the selection of extraction methods in an oil matrix and flavor decoding.

1. Introduction

It is well known that flavor plays a major role in determining the acceptance of food by consumers, which also applies to oils. As one of the most commonly consumed oil in the world, rapeseed oil is favored for its nutritional value and distinctive flavor. In the past decade, the aroma of rapeseed oil has received increasing attention (Zhang et al., 2021). Hot-pressed rapeseed oil is also highly popular with consumers due to its characteristic rich flavor caused by roasting. Only sedimentation and filtration are commonly used to remove impurities from hot-pressed rapeseed oil to reduce the flavor loss, which makes it contain more abundant volatiles than common oils (Zhang, Zhu, et al., 2020). As with some virgin oils, the composition of hot-pressed rapeseed oil is more complex than that of fully refined oil. Some components in oil (e.g., phospholipids, free fatty acids, phenolic compounds, etc.) would influence the distribution and volatilization of volatile substances through binding, known as the "matrix effect" (Genovese, Yang, Linforth, Sacchi, & Fisk, 2018). Flavor analysis based on the complicated

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sample matrix composition in oil should be paid more attention.

For further analysis of odorants in oil, an efficient extraction method is essential. Headspace techniques are commonly employed to produce genuine olfactory blueprint of food samples with little or no pre-preparation. Among these, solid-phase microextraction (SPME) is one of the most frequently used technologies for food flavor analysis due to the advantages of being fast, convenient, sensitive, automated, and reproducible. SPME has been widely used in a variety of food flavor analyses such as oil, milk, beer, and so on (Zhang, Wu, et al., 2020; High, Bremer, Kebede, & Eyres, 2019; Richter, Eyres, Silcock, & Bremer, 2017). Recently, a new approach, SPME-Arrow has been applied to food flavor analysis (e.g., wine and milk), which has been reported to contain an extraction phase 6–20 times larger than conventional SPME and showed more than 10 times the extraction efficiencies (Cha, Chin, Lee, Kim, & Jang, 2020; Manousi, Rosenberg, & Zachariadis, 2020). To date, there is only one report on using SPME-Arrow for oil flavor analysis, which just focused on pyrazines of oil (Xu et al., 2021). A good perspective could be provided by the SPME-Arrow technique in flavor analysis in the oil matrix.

The stir-bar sorptive extraction (SBSE) can also increase the volume of the adsorption phase by increasing the thickness of the adsorption phase. It is a magnetic stir bar coated with a polymer that can extract volatile compounds (Diez-Simon et al., 2020). The magnetic stir bar with different coated material can be placed in the liquid or headspace (headspace stir bar sorptive extraction, HSSE). Volatiles of olive oil have been studied by using HSSE, which could compensate for the limitations of SPME, including limited ability to extract trace aroma-active compounds and headspace saturation (Stilo, Cordero, Sgorbini, Bicchi, & Liberto, 2019). Although HSSE has rarely been employed in the rapeseed oil flavor analysis, it is still a potential flavor trapping approach for oil matrix. Fifteen years ago, a volatile analysis technique combined with dynamic headspace sampling was developed by the GERSTEL. The validation of direct thermal desorption (DTD) by using microvials in a thermal desorption unit (TDU) was also performed. DTD is a very simple method with no pre-preparation. However, a comparison of the results of DTD and other extraction methods based on food flavor has been scarcely reported in the literature so far (Lerch & Hässelbarth, 2014). Furthermore, a representative distillation technique, solvent-assisted flavor evaporation (SAFE) is used as an improvement of simultaneous distillation extraction (SDE) for the separation of volatiles from food (Engel, Bahr, & Schieberle, 1999). In this method, a high vacuum ($<10^{-3}$ Pa) is typically used, resulting in a low-temperature distillation, which is beneficial to avoid thermally induced artifact formations (e.g., Maillard or Strecker products). It is usually used in the state-of-the-art aroma analysis of the Sensomics approach (Matheis & Granvogl, 2016).

In previous studies, a series of investigations were conducted to compare different methods for trapping flavor compounds (Sghaier et al., 2016; Barba, Thomas-Danguin, & Guichard, 2017; Liu, He, & Song, 2018). Liu et al. (2018) found that SAFE presented better efficiency to extract sulfur compounds in watermelon juice than SPME. In the study of Corral, Salvador, and Flores (2015), more kinds of sulfur substances were extracted by SPME compared with SAFE. The extraction effects of different techniques differed in various matrices. We have provided a systematic literature review of recent advances and knowledge on the flavor extraction techniques of rapeseed oil (Zhang et al., 2021). Most of the studies focused on the volatiles of food which do not necessarily determine the key aroma compounds in the products. With regard to odorant, systematic comparison research on extraction methods was scarce, especially in oil matrix. Thus, odorants of hot-pressed rapeseed oil extracted by different methods with gas chromatography–olfactometry-mass (GC-O-MS) were compared, and the methodological validation (linearity, recovery, and reproducibility) of SPME, SPME-Arrow, HSSE, DTD, and SAFE-GC–MS for 31 aroma standards in rapeseed oil was conducted.

2. Materials and methods

2.1. Commercial hot-pressed rapeseed oil and chemicals

The commercial hot-pressed rapeseed oil was purchased online and chosen from a representative brand in China with high consumption. Benzaldehyde (99%), (*E*)-2-decenal (95%), 2,6-dimethylpyrazine (98%), 2-ethyl-6-methylpyrazine (98%), 3-ethyl-2,5-dimethylpyrazine (95%), 2-furanmethanol (99%), furfural (99%), (*E*,*E*)-2,4-heptadienal (90%), hexanal (99%), γ-nonalactone (97%), octanal (99%), 1-octen-3-one (96%), and phenylethyl alcohol (99%) were obtained from Sigma (St. Louis, United States). 3-Butenenitrile (97%), butyrolactone (99%), 2,5-dimethylpyrazine (99%), 2(5*H*)-furanone (96%), and 2-pentylfuran (98%) were obtained from Alfa Aesar (Heysham, United Kingdom). Dimethyl trisulfide (98%), 2-methoxy-4-vinylphenol (98%), 3-methylbutanoic acid (99%), and trimethylpyrazine (98%) were bought from J&K Chemical Corp (Beijing, China). Butanoic acid (99%), 1,2-dichlorobenzene (98%), and hexanoic acid (98%)were purchased from Carl Roth (Karlsruhe, Germany). The following reference standards were also used in this study: acetic acid (99%, VWR, Mississauga, Canada), (*E*,*E*)-2,4-decadienal (95%, Acros organics, Geel, Belgium), 2,3-dimethylpyrazine (98%, Chempur, Karlsruhe, Germany), dimethyl sulfoxide (99%, TCI, Tokyo, Japan), heptanoic acid (97%, Geyer-Chemsolute, Renningen, Germany), 5-methyl-2-furancarboxaldehyde (98%, Thermo Fisher, Waltham, United States), and (*E*)-2-octenal (96%, TCI, Tokyo, Japan).

2.2. Aroma extraction by SPME

The method was in accordance with our previous study (Zhang, Wu, et al., 2020). HS-SPME with a 2 cm long divinylbenzene/carboxen/polydimethylsiloxane fiber (DVB/CAR/PDMS, 50 μm/30 μm, Supelco Inc., Bellefonte, United States) was used. Before the first use, the fiber was conditioned at 250 °C for 30 min. For extraction, oil sample (5 g) and internal standard solution (20 μL, 1,2-dichlorobenzene, 1035 μg/mL) were added to a 20-ml headspace vial with magnetic stirring rate at 300 rpm and incubated at 70 °C for equilibrium (10 min). Extraction time and temperature were 30 min and 70 °C, respectively.

2.3. Aroma extraction by SPME-Arrow

SPME-Arrow with fiber of polydimethylsiloxane/divinyl-benzene/carboxen (PDMS/DVB/CAR, 120 μm × 20 mm, Agilent Technologies, Waldbronn, Germany) was used in this study. Five grams of oil sample and 20 μL of 1,2-dichlorobenzene solution (1035 μg/mL as internal standard) were mixed in a 20-mL capped glass vial. Volatiles were extracted for 60 min at 60 °C with 10 min of equilibrium by SPME-Arrow. Extraction parameters were optimized and are presented in the Supplementary Materials.

2.4. Aroma extraction by HSSE

Five grams of oil sample and 20 μL of internal standard solution as mentioned above were vortexed in a 20-ml headspace vial. Two Gerstel standard polydimethylsiloxane Twisters (10 mm length, 0.5 mm PDMS layer, Gerstel, Mülheim an der Ruhr, Germany) were placed in the headspace of the vial by using an externally mounted magnet. The extraction was conducted with optimized conditions as shown in the Supplementary Materials (10 min of equilibrium and 60 min of extraction at 60 °C). Twisters were then put in the TDU for desorption.

2.5. Aroma extraction by DTD

Five grams of oil sample and 20 μL of internal standard solution (1,2-dichlorobenzene, 1035 μg/mL) were mixed, and then 30 mg of sample from the mixture was taken out and weighed into a standard microvial (p/n 014756–002-00, Gerstel, Mülheim an der Ruhr, Germany). The

microvial containing the sample was placed directly into the TDU for desorption. Desorption conditions were conducted based on the reports of Lerch and Hässelbarth (2014).

2.6. Aroma extraction by SAFE

SAFE was performed according to the method described by Matheis and Granvogl (2016). Briefly, an oil sample (50 g) containing 200 μL of internal standard solution (1,2-dichlorobenzene, 1035 μg/mL) was diluted with dichloromethane (150 mL) and subjected to high vacuum distillation by SAFE (Engel et al., 1999). The special SAFE extractor (Deutsche Forschungsanstalt fur Lebensmittelchemie, Freising, Germany) was used under high vacuum (10^{-4} kPa). Flavor compounds were condensed in the flask cooled under liquid nitrogen. The extracts were desiccated over anhydrous sodium sulfate, filtered, and concentrated by using a Vigreux column (60 cm × 1 cm) to ~ 100 μL in a warm (53 °C) water bath for liquid injection of GC-O-MS. The injection volume was 1 μL.

2.7. GC-O-MS analysis

The extracts were analyzed using an Agilent 7890/5977 GC/MS (Agilent Technologies, Waldbronn, Germany) and an olfactometry detection port (ODP 3, Gerstel, Mülheim an der Ruhr, Germany). Two different chromatographic columns, J&W DB-WAX column (30 m × 0.25 mm i.d., 0.25 μm, Agilent Technologies, Waldbronn, Germany) and J&W DB-5 ms column (30 m × 0.25 mm i.d., 0.25 μm, Agilent Technologies, Waldbronn, Germany), were used for the separation of volatile compounds. The desorption and column temperature program of GC–MS was performed according to our previous study (Nedele, Bär, Mayer, Schiebelbein, & Zhang, 2022). GC-O was conducted by three experienced assessors.

2.8. Qualitative analysis of volatile compounds

The chemical identification was based on retention indices (RI), aromatic characteristics, mass spectral library, and comparison with authentic standards. RI was calculated according to a previous study (Nedele et al., 2022).

2.9. Calibration, recovery, and reproducibility

Calibration curves ($y = ax + b$) of target standards were carried out in odorless refined rapeseed oil as matrix by the equation, where the peak area ratios (y) were plotted against the concentration ratios (x) of the aroma standards to the internal standards. The liner ranges are listed in the Table 2. The recovery of aroma substance was conducted by the equation: (detected added concentration)/(theoretical added concentration) × 100%, which was used as the index of accuracy. The reproducibility was expressed as the relative standard deviation (RSD, %) for all extractions.

2.10. Statistical analysis

All experiments were performed in triplicate. Figures were constructed by using Origin 8.1 (OriginLab Corporation, Northampton, United States) and the drawing tool provided by Bardou, Mariette, Escudié, Djemiel, and Klopp (2014). Linear regression analysis of each calibration standard curve was conducted by Microsoft Excel 2019 (Microsoft Corporation, Redmond, Washington D.C., United States).

3. Results and discussion

3.1. Untargeted comparison of different volatiles trapping approaches for hot-pressed rapeseed oil

In total, volatiles from ten classes of compounds, aldehydes, ketones, acids, esters, alcohols, phenols, heterocyclic compounds, *S*-containing compounds, nitriles, and alkenes were identified in the hot-pressed rapeseed oil by the five different extraction techniques (Fig. 1). Group percentages were based on the area% of peaks provided by GC-O-MS. All methods yielded a majority of nitriles except for DTD, which accounted for at least 36% of the total volatiles. 3-Butenenitrile, 2,4-pentadienenitrile, 3-methyl-3-butenenitrile, 5-cyano-1-pentene, 5-methyl-hexanenitrile, and benzenepropanenitrile were found to be major nitriles in all volatile trapping techniques. In DTD, acids accounted for the largest proportion of the total volatile compounds (39.07%), especially fatty acids (e.g., hexanoic acid, tetradecanoic acid, and *n*-hexadecanoic acid). Also, acetic acid (vinegar-like odor) was determined with a high proportion (9.43%) in DTD. Hexanoic acid was reported to be an aroma-active compound in raw rapeseed and cold-pressed rapeseed oil with a pungent and sweaty flavor (Ortner, Granvogl, & Schieberle, 2016). Tetradecanoic acid and *n*-hexadecanoic acid are long-chain saturated fatty acids, which have been also reported to be major volatiles in the toasted canola oil (Park, Maga, Johnson, & Morini, 1995). However, they are not prone to be key aroma-active compounds in rapeseed oil (Matheis & Granvogl, 2016). *n*-Hexadecanoic acid occupied the highest proportion of the total volatiles in DTD. As the most dominant saturated fatty acid in rapeseed oil, *n*-hexadecanoic acid is more stable than polyunsaturated and monounsaturated fatty acids (Eckel, Borra, Lichtenstein, & Yin-Piazza, 2007). Different from the process of refined oil (i.e., degumming, neutralization, bleaching, and deodorization), hot-pressed rapeseed oil is a kind of virgin oil, which is processed by only degumming, sedimentation, and filtration (Jing, Guo, Wang, Zhang, & Yu, 2020). Alkali treatment in the neutralization and deodorization process can significantly reduce free fatty acids in refined oil. There is a considerable amount of free fatty acids found in hot-pressed rapeseed oil because of the lack of alkali and deodorization treatment, which is also the reason why hot-pressed rapeseed oil has a higher acid value than refined oil (Liang et al., 2023; Zhang, Zhu, et al., 2020). In DTD, the extraction temperature was 90 °C and the sample was purged continuously with He air (1.3 mL/min), which might cause the massive volatilization of free fatty saturated acid like *n*-hexadecanoic acid. Long-chain fatty acids released from the oil can contaminate the column and affect subsequent test results. Moreover, most of these free fatty acids do not contribute significantly to the aroma of oil. The literature on DTD for oil analysis is remarkably limited. An extraction temperature of 90 °C was used in the determination of volatiles in oil (Lerch & Hässelbarth, 2014). Lower temperature (80 °C) has also been tried before, based on the research of Cavalli, Fernandez, Lizzani-Cuvelier, and Loiseau (2003), and it took more time to achieve the same extraction results, resulting in excessive use of liquid nitrogen. In addition, a considerable amount of free fatty acids was still detected. Based on the results of the present study, DTD could not be the most suitable odorants extraction approach for hot-pressed oil. The second most abundant fraction was heterocyclic compounds (mainly pyrazines and furans) extracted by SPME, SPME-Arrow, HSSE, and SAFE, which mainly contribute to the nutty, caramel-like, roasted, and burnt flavor of the oil. For these five extraction methods, the main pyrazines were 2,5-dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine.

SPME and SPME-Arrow showed similar percentages for aldehydes, ketones, alcohols, heterocyclic compounds, and nitriles. The numbers of these five classes of compounds identified by SPME and SPME-Arrow were same (8 aldehydes, 2 ketones, 2 alcohols, 14 heterocyclic compounds, and 8 nitriles). SPME-Arrow extracted the highest content of phenols among these five approaches, especially for the 4-ethenyl-2,6-dimethoxy-phenol. 4-Ethenyl-2,6-dimethoxyphenol (also known as

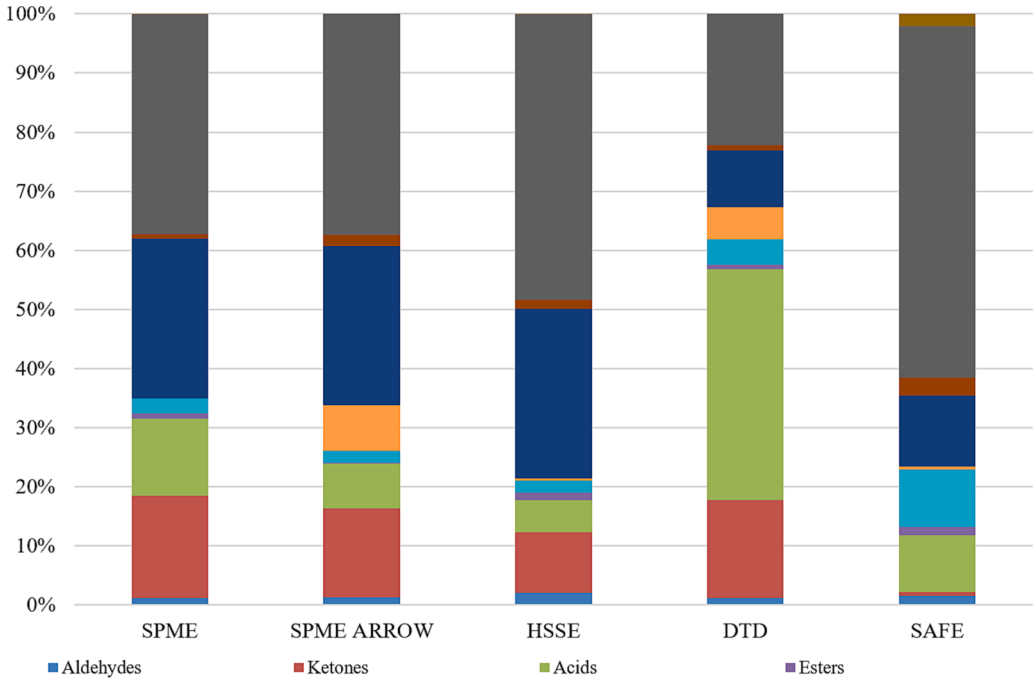

Fig. 1. Main groups of volatiles in hot-pressed rapeseed oil by different volatiles trapping methods.

canolol) is a specific phenolic compound found in rapeseed oil, which is generated by thermally induced decarboxylation from sinapic acid (abundant in rapeseed) (Kraljić et al., 2018). Roasting the seeds increases the amount of canolol, as has been demonstrated for rapeseed (Gracka, Jeleń, Majcher, Siger, & Kaczmarek, 2016). However, canolol is usually determined by High Performance Liquid Chromatography due to its high boiling point (Yao et al., 2020). To the best of our knowledge, only one paper reported the canolol as a volatile compound in the strong fragrant rapeseed oil through SPME-GC–MS (DVB/CAR/PDMS fiber, adsorbed for 20 min at 80 °C) (Tan et al., 2022). In this study, canolol was detected by all extraction methods except for SPME, which could be attributed to the different extraction conditions and phases. No aroma activity of this compound in rapeseed oil has been reported in the current literature. Canolol was found as an aroma component with phenolic and leather-like odor in brown sugar via GC-O-MS (Chen et al., 2021). Zhang, Wang, et al. (2020) compared SPME-Arrow with five different fibers and SPME (50/30 μm, 2 cm, DVB/CAR/PDMS) for the analysis of odorants in Chinese liquor (Baijiu), and results indicated that the SPME-Arrow with DVB/CAR/PDMS (120 μm) fiber also presented the best extraction result for the phenols. There is also no obvious difference in the number of volatiles extracted by SPME-Arrow and SPME. The results presented in this report are in agreement with the previous study.

The proportions of aldehydes, ketones, acids, esters, alcohols, phenols, heterocyclic compounds, *S*-containing compounds, nitriles, and alkenes captured by HSSE were 2.02%, 10.26%, 5.41%, 1.32%, 0.64%, 0.35%, 30.11%, 1.51%, 48.31%, and 0.08%, respectively. The acids proportion of HSSE was the lowest compared to other methods, but its peak area was higher than SPME and SPME-Arrow, which can be fully attributed to the greater thickness of PDMS film in SBSE. HSSE and SPME were compared for the volatiles in olive oil from the study of Cavalli et al. (2003), and they also found that HSSE showed better extraction efficiency. The PDMS stir bar performed better for hydrophobic compounds with medium volatility, while most volatiles in heated rapeseed oil are polar (Jeleń, Mildner-Szkudlarz, Jasińska, & Wąsowicz, 2007). In another study, SPME with PDMS fiber could not detect fishy odor compounds (*E*,*Z*)-2,6-nonadienal, 1-penten-3-one, and 1-octen-3-one compared to other fibers (DVB/CAR/PDMS and PDMS/DVB). SPME with DVB/CAR/PDMS had a higher polarity than PDMS stir bar (Sghaier et al., 2016).

SAFE extracts showed the highest proportions of alcohols (8.15%), *S*-containing compounds (3.10%), nitriles (59.36%), and alkenes (2.15%), compared to other techniques. In the research on hop-derived odorants in beer, SAFE showed the highest affinity for volatile alcohols, which was four times higher than HSSE (Richter et al., 2017). Although the composition of the samples differed significantly, Barba et al. (2017) found similar results in fruit juice, where SAFE presented a higher extraction efficiency for alcohol compounds, and HSSE performed better in volatile hydrocarbons. Additionally, some acids in beer with high polarity and volatility were also detected via SAFE (e.g., acetic acid, butanoic acid, and propanoic acid) in the report of Richter et al. (2017). They suggested that SAFE significantly affects the overall volatile profile owing to its bias toward acids and alcohols, and therefore they do not recommend SAFE for the targeted analysis of hop-derived volatile compounds in beer.

The results of analyses of hot-pressed rapeseed oil obtained by these five methods were highly correlated. It is widely acknowledged that there is no perfect extraction technique for the volatiles analysis and each method demonstrated biases according to extraction conditions, compound polarity, and volatility. The matrix property and aroma profile of food should be considered as important references for the selection of flavor trapping techniques.

3.2. Comparison of odorants from hot-pressed rapeseed oil via different extraction methods

Thirty-five odorants were screened by five flavor extraction techniques. Eight classes of aroma compounds were identified in the hot-pressed rapeseed oil, including 11 heterocyclic compounds, 9 aldehydes, 4 *S*-containing compounds, 3 nitriles, 4 acids, 2 phenols, 1 alcohol, and 1 ester (Table 1).

In this study, heterocyclic compounds containing 6 pyrazines, 4 furans, and 1 pyrrole were identified, which are mostly generated during the Maillard reaction in thermal processing. They mainly contribute to the roasted odor (Zhang et al., 2021). Aldehydes are commonly found in

Table 1
Aroma-active compounds in hot-pressed rapeseed oil extracted by five methods.

No.	Compound	RI[a] on		Odor description	Identification[b]	Extraction methods
		DB-WAX	DB-5 ms			
1	dimethyl disulfide	1066	*n. d.*[b]	cabbage-like, sulfury	MS, RI, O	SPME-Arrow, HSSE, SAFE
2	hexanal	1075	803	fatty, green	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
3	3-butenenitrile	1181	*n. d.*	metallic, pungent	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
4	2-pentylfuran	1227	1010	fatty	S, MS, RI, O	SPME-Arrow, SAFE
5	3-methyl-3-butenenitrile	1265	*n. d.*	pungent	MS, RI, O	SAFE
6	octanal	1284	*n. d.*	fatty, citrus-like	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
7	2,5-dimethylpyrazine	1315	920	nutty, roasty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
8	2,6-dimethylpyrazine	1324	907	nutty, roasty	S, MS, RI, O	SPME, SPME-Arrow, HSSE
9	2,3-dimethylpyrazine	1338	914	nutty, roasty	S, MS, RI, O	HSSE
10	dimethyl trisulfide	1360	968	cabbage-like, sulfury	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
11	2-ethyl-6-methylpyrazine	1377	993	nutty, roasty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
12	trimethylpyrazine	1393	1005	cocoa-like, earthy, nutty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
13	(*E*)-2-octenal	1421	1057	fatty, green	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
14	3-ethyl-2,5-dimethylpyrazine	1435	1078	burnt, earthy, nutty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
15	acetic acid	1451	*n. d.*	sour	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
16	4-isothiocyanato-1-butene	1461	986	pungent	MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
17	(*E,E*)-2,4-heptadienal	1479	1007	fatty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
18	benzaldehyde	1499	955	almond-like, caramel-like	S, MS, RI, O	SAFE
19	5-methyl-2-furancarboxaldehyde	1574	965	almond-like, caramel-like	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
20	dimethyl sulfoxide	1584	972	cheese-like	S, MS, RI, O	SPME-Arrow, HSSE, SAFE
21	butanoic acid	1606	821	sour, cheese-like	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
22	(*E*)-2-decenal	1633	1260	fatty, nutty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
23	butyrolactone	1645	929	caramel-like, sweet	S, MS, RI, O	SPME-Arrow, HSSE, DTD, SAFE
24	2-furanmethanol	1658	832	burnt	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
25	(*E,E*)-2,4-nonadienal	1686	1221	fatty	MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
26	2(5H)-Furanone	1732	918	roasty	S, MS, RI, O	HSSE, DTD, SAFE
27	(*E*)-2-undecenal	1745	1361	soapy-like, metallic	MS, RI, O	SAFE
28	(*E,E*)-2,4-decadienal	1796	1317	fatty, deep-fried	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
29	hexanoic acid	1824	997	sweaty	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
30	phenylethyl alcohol	1896	1118	flowery, honey-like	S, MS, RI, O	SPME, SPME-Arrow, HSSE, SAFE
31	heptanoic acid	1949	1088	sour, sweaty, pungent	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD
32	benzenepropanenitrile	2020	1245	pungent	MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
33	1-methyl-1H-pyrrole-2-carboxaldehyde	2081	1021	popcorn, roasted meat	MS, RI, O	SPME-Arrow, HSSE, SAFE
34	2-methoxy-4-vinylphenol	2195	1313	smoky, clove-like	S, MS, RI, O	SPME, SPME-Arrow, HSSE, DTD, SAFE
35	4-ethenyl-2,6-dimethoxyphenol	2551	1574	medicinal	MS, RI, O	SPME-Arrow

[a] Retention Index (RI) was calculated by using the DB-WAX column; b: identification methods include NIST 14 MS spectra (MS), RI, standards (S), and odor attributes (O).

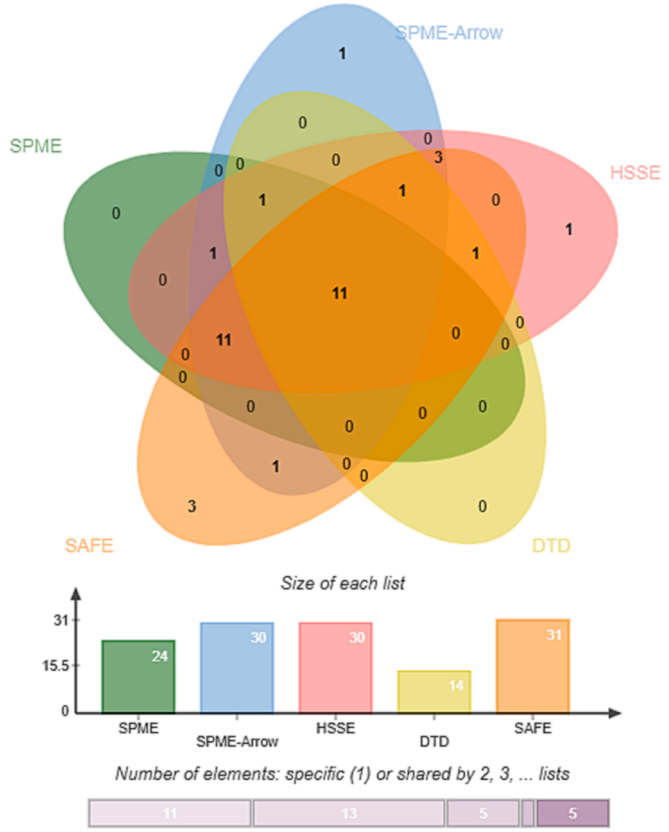

Fig. 2. Venn diagram in HSSE, SPME, SPME-Arrow, DTD, and SAFE methods from odorants in hot-pressed rapeseed oil.

vegetable oils generated from lipid oxidation, and they account for a high proportion of total volatiles in cold-pressed rapeseed oils (Mao, Zhao, Huyan, Liu, & Yu, 2019). Nine aroma-active aldehydes were identified in hot-pressed rapeseed oil in this study. Most of them were responsible for the fatty aroma, but some were related to the green and nutty odor. *S*-containing aroma-active compounds including dimethyl disulfide, dimethyl trisulfide, dimethyl sulfoxide, and 4-isothiocyanato-1-butene were also detected, imparting a sulfury, cabbage-like, and pungent aroma to the oil. Nitriles are a specific type of volatiles found in rapeseed oil, mainly formed by the thermal degradation of glucosinolate (Liang et al., 2023). 3-Butenenitrile, 3-methyl-3-butenenitrile, and benzenepropanenitrile were identified in the sample, which have a pungent fragrance. Also, 4 acids (sour and sweaty) namely, acetic acid, butanoic acid, hexanoic acid, and heptanoic acid, which mainly belong to products from lipid hydrolysis and oxidation, were detected among the odorants of rapeseed oil. In addition, the results showed that 2-methoxy-4-vinylphenol, butyrolactone, and phenylethyl alcohol were aroma-active compounds. 2-Methoxy-4-vinylphenol contributed to clove-like, smoky, and woody flavor, which has been reported to be derived from canolol in rapeseed oil by Kraljić et al. (2018). Caramel-like and sweet smelling butyrolactone was also reported in commercial fragrant rapeseed oils via GC-O combined with monolithic material sorptive extraction (MMSE) by Zhou et al. (2019). Phenylethyl alcohol (flowery and honey-like) was reported to be an important aroma-active component in cold-pressed rapeseed oil, which is generated from the Ehrlich pathway (Matheis & Granvogl, 2016).

As seen in Fig. 2, SAFE had the highest number of odorants (31), followed by HSSE and SPME-Arrow with 30 and 30, respectively. The number of aroma compounds extracted by DTD was the lowest (14). The higher number of odorants captured by SAFE could be ascribed to the higher sample amount used (50 g). Besides, 3 aroma-active substances were detected by only SAFE (3-methyl-3-butenenitrile, benzaldehyde, and (*E*)-2-undecenal). 3-Methyl-3-butenenitrile and benzaldehyde were also reported to be aroma active in fragrant *Brassica napus* and *Brassica juncea* oils via SAFE by Jia et al. (2020). However, a 30 mg of sample was used for extraction by DTD, and the TDU program was just processed for 15 min, and this might be the reason why the DTD showed the least number of odorants. Eleven aroma substances were detected by all five approaches (2,5-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, acetic acid, dimethyl trisulfide, 4-isothiocyanato-1-butene, 5-methyl-2-furancarboxaldehyde, (*E*)-2-decenal, 2-furanmethanol, benzenepropanenitrile, hexanoic acid, and 2-methoxy-4-vinylphenol). Unexpectedly, HSSE showed high performance in the extraction and enrichment of odorants although it has only one type of coating. Cavalli et al. (2003) compared HSSE and SPME for the extraction of volatiles from French olive oils. The PDMS-coated stir bar had a higher concentration capability than all SPME fibers (DVB/CAR/PDMS 50/30 μm, CAR/PDMS 85 μm, CW/DVB 70 μm, and PDMS 100 μm). SPME with DVB/CAR/PDMS fiber and HSSE were reported to be "comparable" for the volatiles selectivity. They attributed these results to the high amount of PDMS film, which is 55 μL versus 0.5 μL for DVB/CAR/PDMS from SPME. In this paper, all of the odorants detected by SPME were also found in HSSE. SPME extracted 24 aroma compounds, which were also presented in odorants extracted by SPME-Arrow. 4-Ethenyl-2,6-dimethoxyphenol (medicinal) was only found to be aroma-active in SPME-Arrow. No studies have been found regarding the comparison between SPME and SPME-Arrow for extraction of odorants from oils. The price of SPME-Arrow is 4 times more than that of normal SPME, and it needs a special injection port to fit its fiber. Considering extraction efficiency and cost in combination, SPME-Arrow seems to be not as cost-effective.

3.3. Comparison of linearity, recovery, and reproducibility of HSSE, SPME, SPME-Arrow, DTD, and SAFE used for odorants determination in rapeseed oil

Thirty-one standards were used to compare of linearity, recovery, and reproducibility of these five methods. Among them, a total of 27 standards were selected based on the results of this study. Additionally, 1-octen-3-one, furfural, 3-methylbutanoic acid, and γ-nonalactone were also selected because they were also reported as odorants in hot-pressed rapeseed oil in previous studies (Zhang et al., 2021).

As shown in Table 2, SPME-Arrow had the best linearity compared with the other four methods. All standard curves from SPME-Arrow showed correlation coefficients higher than 0.990. The correlation coefficients from SPME also indicated good linearity over the range of concentrations tested. Only 1 of these 31 aroma compounds from SPME had a correlation coefficient below 0.99, which was 0.9880 (γ-nonalactone). The correlation coefficients from DTD ranged from 0.8152 to 0.9996, with the highest number of correlation coefficients below 0.99 (7). Four and three aroma compounds had correlation coefficients below 0.99 from HSSE and SAFE, respectively. Based on the calibration equation and correlation coefficient results, SPME-Arrow is most appropriate for the quantification of aroma compounds of rapeseed oil, followed by SPME.

Table 3 provides recovery and reproducibility results from different methods. For recovery values, SPME-Arrow showed the best performance among these methods, with all values obtained from SPME-Arrow were in the range of 80%–120%. The recovery values of SPME, HSSE, DTD, and SAFE were 74%–117%, 72%–153%, 62%–117%, and 69%–163%, respectively. The numbers of compounds with recovery values outside the range of 80%–120% for SPME, HSSE, DTD, and SAFE were 3, 4, 5, and 7, respectively. Ruvalcaba, Durán-Guerrero, Barroso, and Castro (2020) calculated the recovery values of 37 volatiles in beer using HSSE, and results indicated that seven were outside the acceptable range (80%-120%). Nešpor, Karabín, Hanko, and Dostálek (2018) reported better recovery results for the same volatiles in beer using SPME,

Table 2
Comparison of linearity of SPME, SPME-Arrow, HSSE, DTD, and SAFE.

Compound	Quantifier ion (*m*/*z*)	Linear range (μg/kg)	SPME		SPME-Arrow		HSSE		DTD		SAFE	
			Calibration equation	Correlation coefficient	Calibration equation	Correlation coefficient	Calibration equation	Calibration equation	Calibration equation	Correlation coefficient	Calibration equation	Correlation coefficient
hexanal	44	3.6–3600	y = 0.3251x + 0.005	0.9962	y = 0.2238x + 0.0111	0.9980	y = 0.4383x + 0.0495	0.9855	y = 1.0336x + 0.1734	0.8958	y = 0.6572x + 0.0064	0.9951
3-butenenitrile	41	28.5–28544	y = 1.2578x −0.1374	0.9946	y = 0.2314x −0.0369	0.9950	y = 0.3048x + 0.0086	0.9939	y = 2.9608x + 0.0417	0.9965	y = 0.9635x + 0.0431	0.9976
2-pentylfuran	81	0.6–592	y = 1.0181x + 0.0195	0.9949	y = 1.3654x + 0.0077	0.9933	y = 1.7036x + 0.0221	0.9936	y = 2.2837x + 0.0321	0.9954	y = 1.6224x + 0.0149	0.9986
octanal	43	1.0–952	y = 0.1618x + 0.0037	0.9926	y = 0.1447x + 0.0011	0.9956	y = 0.1095x + 0.0053	0.9939	y = 0.0939x + 0.0107	0.8152	y = 0.0848x + 0.0084	0.9619
1-octen-3-one	55	0.8–800	y = 1.2506x + 0.0017	0.9952	y = 0.6865x + 0.0007	0.9980	y = 1.3489x −0.0016	0.9948	y = 1.3663x + 0.0008	0.9979	y = 0.9596x −0.0002	0.9967
2,5-dimethylpyrazine	108	9.3–9296	y = 1.5006x−0.0122	0.9976	y = 0.6826x −0.003	0.9982	y = 0.7989x −0.0216	0.9963	y = 0.9274x −0.017	0.9988	y = 0.7326x −0.0307	0.9906
2,6-dimethylpyrazine	108	10–10000	y = 2.4599x−0.0224	0.9983	y = 1.3787x −0.004	0.9981	y = 1.9168x −0.0077	0.9978	y = 2.9164x −0.1941	0.9915	y = 1.6638x −0.0551	0.9963
2,3-dimethylpyrazine	67	4.4–4384	y = 1.4888x−0.0098	0.9973	y = 0.8504x + 0.0008	0.9984	y = 1.0873x −0.0076	0.9990	y = 1.4944x + 0.0041	0.9975	y = 0.9959x −0.0097	0.9982
dimethyl trisulfide	126	5.3–5304	y = 0.2451x−0.0056	0.9940	y = 0.3129x −0.0052	0.9927	y = 0.8208x −0.0231	0.9937	y = 1.1673x −0.0446	0.9908	y = 1.0338x −0.0105	0.9981
2-ethyl-6-methylpyrazine	121	5.4–5424	y = 0.9844x−0.0102	0.9968	y = 0.8955x −0.0029	0.9928	y = 1.4789x −0.0259	0.9966	y = 0.7163x + 0.01	0.9932	y = 0.7431x −0.0065	0.9985
trimethylpyrazine	42	5.3–5280	y = 1.1986x−0.0168	0.9966	y = 0.9187x + 0.0061	0.9978	y = 1.2536x −0.0413	0.9918	y = 1.3161x −0.0019	0.9933	y = 0.0483x −0.0006	0.9924
(*E*)-2-octenal	41	1.0–1000	y = 0.5479x + 0.0047	0.9969	y = 0.0885x + 0.0014	0.9966	y = 0.4091x −0.0012	0.9914	y = 0.3044x −0.0008	0.9556	y = 0.1834x + 0.0002	0.9971
acetic acid	43	9.8–9776	y = 1.3338x−0.0172	0.9913	y = 0.3416x + 0.0212	0.9983	y = 0.0737x + 0.0049	0.9885	y = 1.8336x + 0.0891	0.9924	y = 0.3177x + 0.014	0.9940
3-ethyl-2,5-dimethylpyrazine	135	9.5–9496	y = 0.4855x−0.0209	0.9938	y = 0.7596x + 0.0035	0.9970	y = 0.8042x −0.0154	0.9954	y = 0.4482x −0.0172	0.9913	y = 0.2229x −0.0034	0.9975
furfural	96	10.7–10696	y = 4.9242x−0.031	0.9994	y = 0.563x + 0.0226	0.9968	y = 0.5325x −0.0061	0.9973	y = 1.9552x −0.0041	0.9908	y = 1.0221x −0.036	0.9922
(*E*,*E*)-2,4-heptadienal	81	9.9–9864	y = 3.7966x−0.1729	0.9944	y = 0.4613x + 0.0423	0.9939	y = 1.1003x −0.0113	0.9994	y = 1.0889x −0.0225	0.9982	y = 0.6029x + 0.0064	0.9964
benzaldehyde	106	5.0–5040	y = 3.67x + 0.0256	0.9976	y = 0.9682x + 0.0453	0.9901	y = 0.6904x −0.0055	0.9987	y = 1.2081x −0.0072	0.9996	y = 0.884x−0.0077	0.9919
5-methyl-2-furancarboxaldehyde	110	3.2–3160	y = 3.6512x−0.0246	0.9973	y = 0.8252x + 0.0142	0.9930	y = 0.8189x −0.0106	0.9928	y = 1.1427x −0.0064	0.9920	y = 0.823x −0.003	0.9997
dimethyl sulfoxide	63	1.7–1656	y = 1.9151x−0.0086	0.9958	y = 0.9257x−0.0043	0.9921	y = 1.1348x−0.0106	0.9913	y = 1.4159x−0.0054	0.9956	y = 0.3105x−0.0013	0.9918
butanoic acid	60	1.0–1040	y = 0.7723x + 0.0294	0.9969	y = 0.4963x + 0.0007	0.9954	y = 0.2578x + 5E-06	0.9976	y = 1.5323x + 0.0039	0.9901	y = 0.9644x−0.0012	0.9974
(*E*)-2-decenal	43	1.0–1040	y = 0.4965x + 0.0105	0.9902	y = 0.2553x + 0.0021	0.9915	y = 0.2562x + 0.0032	0.9918	y = 0.0898x + 0.0045	0.8844	y = 0.0373x + 0.0006	0.9934
butyrolactone	42	7.3–7280	y = 0.6185x−0.0055	0.9908	y = 0.1988x−0.0019	0.9945	y = 0.3932x−0.0002	0.9989	y = 0.824x + 0.0294	0.9917	y = 0.4827x−0.008	0.9904
3-methylbutanoic acid	60	1.0–928	y = 0.433x−0.0034	0.9900	y = 0.51x−0.0005	0.9919	y = 0.3679x + 0.0008	0.9989	y = 1.8862x−0.0083	0.9837	y = 0.9096x−0.0026	0.9975
2-furanmethanol	98	8.1–8072	y = 0.4539x−0.0051	0.9915	y = 0.1939x−0.0027	0.9917	y = 0.1583x−0.002	0.9962	y = 0.734x + 0.0069	0.9977	y = 0.4552x−0.0135	0.9912
2(5H)-furanone	55	9.0–8928	y = 2.267x−0.0824	0.9947	y = 0.3666x−0.0131	0.9935	y = 0.2204x−0.0103	0.9937	y = 0.5x + 0.0024	0.9983	y = 0.3636x−0.0073	0.9989
(*E*,*E*)-2,4-decadienal	81	9.5–9496	y = 1.3192x−0.0398	0.9911	y = 3.0373x−0.1377	0.9936	y = 0.8864x−0.0726	0.9893	y = 0.1228x−0.005	0.9941	y = 0.0731x−0.0003	0.9950

(*continued on next page*)

Table 2 (*continued*)

Compound	Quantifier ion (*m/z*)	Linear range (μg/kg)	SPME		SPME-Arrow		HSSE		DTD		SAFE	
			Calibration equation	Correlation coefficient	Calibration equation	Correlation coefficient	Calibration equation	Calibration equation	Calibration equation	Correlation coefficient	Calibration equation	Correlation coefficient
Phenylethyl alcohol	91	4.7–4704	y = 1.8245x−0.0161	0.9976	y = 2.1618x + 0.0185	0.9909	y = 2.0608x−0.0658	0.9927	y = 0.5904x−0.002	0.9991	y = 0.5859x−0.0049	0.9949
hexanoic acid	60	4.0–4024	y = 0.5524x + 0.0435	0.9951	y = 0.686x + 0.0253	0.9978	y = 0.2229x + 0.0005	0.9957	y = 0.3115x + 0.0586	0.8827	y = 0.3185x−0.0003	0.9958
heptanoic acid	60	1.1–1080	y = 0.5729x + 0.0212	0.9919	y = 1.4437x + 0.0005	0.9979	y = 0.1549x−0.0015	0.9828	y = 0.1087x + 0.0046	0.9443	y = 0.1156x−0.0004	0.9811
γ-nonalactone	85	1.1–1128	y = 1.4576x + 0.021	0.9880	y = 9.9122x−0.0594	0.9956	y = 2.3996x−0.0141	0.9932	y = 0.1391x + 0.0034	0.9945	y = 0.1109x + 0.0003	0.9985
2-methoxy-4-vinylphenol	135	3.6–3600	y = 0.5795x + 0.0123	0.9915	y = 4.652x−0.1607	0.9940	y = 0.7873x−0.0247	0.9929	y = 0.0444x + 0.0037	0.9946	y = 0.0044x + 0.0009	0.9493

which was consistent with the present study.

With correction through internal standard, ranges of RSD values calculated for SPME, SPME-Arrow, HSSE, DTD, and SAFE were 0.4%–8.3%, 0.2%–8%, 1.7%–12.7%, 3.8%–12.2%, and 1.4%–17.1%, respectively. SPME-Arrow showed the best results in terms of robustness. Similarly, Manousi et al. (2020) found that SPME-Arrow presented more reproducible results compared to the conventional SPME in the analysis of total volatile compounds in milk (RSD: 12.5% for conventional SPME and 6.2% for SPME-Arrow). Similar results have been reported by Richter et al. (2017). SPME-Arrow was reported to have higher mechanical robustness and a longer lifetime than normal SPME (Westland, 2023). SPME, HSSE, SBSE, and SAFE were compared for analysis of hop-derived odorants in beer. RSD was used for variability comparison. SPME was also found to be the most robust, followed by HSSE, SBSE, and SAFE without internal standard corrections. The highest variability of volatiles was found in SAFE, which was attributed to the multiple extraction procedures and the enrichment process through Kuderna-Danish. Although the SAFE can extract smaller polar substances as well as larger nonpolar substances, its reproducibility and efficiency made it less desirable than the other extraction methods (High et al., 2019).

As mentioned above, SPME-Arrow is much more expensive than conventional SPME with an additional injection port. HSSE and DTD also require specific thermal desorption and cooled injection system, and the magnetic stir bar must be cleaned after each use, which takes 2 h on average. Moreover, for virgin oil that has not been fully refined, DTD can lead to the reduction in the column lifetime due to contamination from a large amount of free fatty acid. Compared to the other four techniques, SAFE is time-consuming (at least 3 h per sample), requires considerable amounts of sample and solvent (50 g and 150 mL, respectively), and cannot be fully automated. In molecular sensory science, SAFE combined with stable isotope dilution assays can achieve accurate quantification of odorants in foods, but the high price of stable isotope standards also limits the widespread use in flavor analysis. SPME does not require an additional TDU as desorption can be performed directly in the injection port of GC–MS (Arceusz, Occhipinti, Capuzzo, & Maffei, 2013). The most efficient method for flavor extraction of hot-pressed rapeseed oil, taking into account the cost/performance ratio, is SPME.

4. Conclusion

Different methods showed biases due to the matrix effect, odorants polarity, and volatility. DTD extracts presented the highest proportion of acids mainly due to the higher temperature and continuous He-purging. SPME and SPME-Arrow presented similar percentages in the aldehydes, ketones, alcohols, heterocyclic compounds, and nitriles owing to the same fiber types. The acids proportion from HSSE was the lowest as a result of the only non-polar PDMS coating. For the qualification of odorants in hot-pressed rapeseed oil, SAFE gave the best performance, mainly due to the high sample volumes, but it performed worse than other methods in terms of linearity, recovery, and reproducibility. Unlike fruits, vegetables, and drinks, oil can be dissolved in the solvents used by SAFE (e.g., dichloromethane). Moreover, multiple extraction steps including concentration process are involved in SAFE, which could affect the extraction and enrichment efficacy. SPME-Arrow gave good performances in not only odorant extraction but also robustness, which is considered most suitable for quantifying odorants in hot-pressed rapeseed oil. Considering the cost/performance ratio, SPME is still an efficient method for aroma extraction. Multi-method combination of aroma extraction techniques could also be an option for oil matrix aroma analysis.

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Table 3
Comparison of recovery and reproducibility of SPME, SPME-Arrow, HSSE, DTD, and SAFE.

Compound	SPME		SPME-Arrow		HSSE		DTD		SAFE	
	Recovery (%)	RSD[a] (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
hexanal	113	6.7	113	4.6	93	4.6	117	3.9	82	9.3
3-butenenitrile	89	0.8	107	2.5	80	7.6	80	5.4	154	2.5
2-pentylfuran	88	2.0	110	4.0	104	9.4	104	9.3	114	15.4
octanal	110	1.0	118	0.4	116	6.2	109	5.3	81	15.5
1-octen-3-one	84	0.5	93	4.9	98	10.5	82	8.2	103	16.8
2,5-dimethylpyrazine	106	0.4	96	3.1	99	10.0	97	6.2	107	14.3
2,6-dimethylpyrazine	81	3.5	95	2.9	96	6.2	92	6.8	114	14.0
2,3-dimethylpyrazine	86	1.5	98	1.7	95	12.7	101	9.0	116	13.6
dimethyl trisulfide	100	6.2	98	3.4	114	8.8	77	9.1	95	17.1
2-ethyl-6-methylpyrazine	88	5.3	97	3.4	104	5.9	102	6.6	114	12.6
trimethylpyrazine	117	1.5	97	0.2	83	5.4	88	5.4	95	5.4
(*E*)-2-octenal	81	5.4	87	8.0	84	7.3	102	4.3	80	8.2
acetic acid	95	3.1	93	2.3	83	7.4	71	7.4	75	2.6
3-ethyl-2,5-dimethylpyrazine	101	3.8	96	3.1	106	5.1	85	5.4	111	8.8
furfural	83	3.6	100	2.2	85	8.6	78	7.3	83	11.9
(*E*,*E*)-2,4-heptadienal	78	2.7	118	2.6	99	5.8	82	4.2	94	5.6
benzaldehyde	74	2.8	108	2.6	100	4.3	92	8.7	101	10.7
5-methyl-2-furancarboxaldehyde	88	2.4	100	3.0	100	6.8	82	5.2	107	5.1
dimethyl sulfoxide	99	0.8	97	1.7	93	11.5	77	6.4	160	3.3
butanoic acid	84	3.8	93	2.6	72	4.7	82	5.0	120	3.3
(*E*)-2-decenal	79	1.0	119	5.2	112	6.1	97	10.8	69	6.9
butyrolactone	106	3.8	94	1.9	80	7.7	91	5.6	84	4.2
3-methylbutanoic acid	109	6.4	88	2.8	81	5.1	62	4.3	103	4.2
2-furanmethanol	102	1.5	88	2.8	96	6.8	90	5.5	110	4.7
2(5H)-furanone	93	2.9	85	2.1	107	8.9	83	6.2	118	3.3
(*E*,*E*)-2,4-decadienal	91	0.7	98	2.1	153	9.9	111	6.8	135	1.4
Phenylethyl alcohol	112	2.7	95	2.3	123	4.8	86	3.8	87	4.1
hexanoic acid	91	1.0	93	1.9	94	5.7	84	9.7	106	4.7
heptanoic acid	100	7.0	95	2.2	97	8.4	86	12.2	119	6.4
γ-nonalactone	87	8.3	97	1.3	77	10.5	117	6.2	74	3.1
2-methoxy-4-vinylphenol	85	3.4	87	1.2	118	1.7	82	8.7	163	3.6

[a] RSD, relative standard deviation.

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CRediT authorship contribution statement

Youfeng Zhang: Conceptualization, Methodology, Visualization, Validation, Writing – original draft. **Felix Stöppelmann:** Visualization, Investigation. **Lin Zhu:** Visualization, Investigation. **Jiaqi Liang:** Validation, Writing – review & editing. **Marina Rigling:** Methodology, Investigation. **Xingguo Wang:** Conceptualization, Supervision. **Qingzhe Jin:** Conceptualization, Supervision. **Yanyan Zhang:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2023.136617.

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III. CHAPTER

Comparative Characterization of Key Odorants and Aroma Profiles of Fragrant Rapeseed Oil under Different Roasting Conditions

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Comparative characterization of key odorants and aroma profiles of fragrant rapeseed oil under different roasting conditions

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ABSTRACT

Fragrant rapeseed oil (FRO) produced by typical roasting process is popular for its characteristic aroma. Accordingly, key aroma-active compounds were characterized in FRO by the Sensomics approach and then correlated to the crucial roasting parameters revealed by aroma profile analysis and hierarchical cluster analysis. Nineteen key odorants in FRO were identified and quantified, among which dimethyl trisulfide (OAV, odor active value, 323, cabbage-like, sulfury) and 4-isothiocyanato-1-butene (OAV, 88, pungent) were the most important aroma-active compounds in FRO and showed first rising and then decline trends as the increased roasting temperature and time. The oil under high-temperature-short time and low-temperature-long time conditions imparted similar aroma profiles. On the basis of sensory evaluation, roasting at 160, 170, 180, 190, and 200 °C should not exceed 50, 40, 30, 30, and 30 min, respectively to satisfy consumer preference. All findings provide a reference on industrial FRO production in terms of not only aroma but also sustainability.

1. Introduction

Rapeseed oil is one of the third most-produced vegetable oil in the world, which is appreciated for its characteristic flavor and high nutritional value (Zhang et al., 2021). Fragrant rapeseed oil (FRO) is a special edible oil in China produced by hot pressing. The FRO is highly sought after in the Chinese market, which is also an indispensable cooking oil in Chinese Sichuan cuisine (one of the most popular cuisines in the world). Currently, the annual consumption of FRO in China exceeds 1.5 million tons, and the market size is about 3 billion dollars, more than 30 % of the total rapeseed oil market size in China. The FRO market is expected to increase at an annual rate of around 10 % in the following years (Jia et al., 2020; Yu et al., 2022; Yang et al., 2022).

Aroma is an important characteristic of FRO, which is also a key indicator for evaluating the quality of FRO. The aroma substances of cold-pressed rapeseed oil and roasted rapeseed were characterized by the Sensomics approach, which is a useful tool to decode the key odorants in foods and aroma changes during food processing (Matheis ÃÄ Granvogl, 2016; Ortner et al., 2016). In our previous study, volatile profiles of 33 representative commercial FROs in China were obtained via headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS) and flash gas chromatography electronic nose. Also, these 33-representative commercial FROs were classified into three groups by the sensory free sorting method (Zhang et al., 2020a). The key aroma compounds in these three different aroma types of FRO together with their relationship to the roasting process require further exploration.

Roasting prior to pressing is a crucial step in FRO processing, which

Abbreviations: FRO, fragrant rapeseed oil; OAV, odor active value; HS-SPME-GC-MS, headspace-solid phase microextraction-gas chromatography-mass spectrometry; GLS, glucosinolate; HS-SPME-GC-O-MS, headspace-solid phase microextraction-gas chromatography-olfactometry-mass spectrometry; AEDA, aroma extract dilution analysis; HCA, hierarchical cluster analysis; DVB/CAR/PDMS, divinylbenzene/carboxen/polydimethylsiloxane; FD, flavor dilution; LOD, limit of detection; LOQ, limit of quantification.

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can not only improve the oil yield but also bring the characteristic and strong flavor. Park et al. (1997) pointed out that the oil from roasted rapeseed was remarkably more appreciated than the unroasted rapeseed oil according to the sensory experiments from Korean panelists. Roasting can accelerate glucosinolate (GLS) degradation, fat oxidation, Maillard reaction, Strecker degradation, and caramelization reaction in seeds, producing a large amount of volatile substances. The temperature of roasting seeds during FRO processing is generally more than 150 °C, and some manufacturers even use 200 °C for roasting (Zhang et al., 2020a, b). At present, some studies have been conducted regarding the effect of roasting on the aroma of rapeseed oil (Kraljić et al., 2018; Mao et al., 2019; Jing et al., 2020). However, most of the flavor studies on hot-pressed rapeseed oil such as FRO remain at the level of volatile substances rather than that of aroma compounds. There have been few reports that study the effects of high roasting temperature (>150 °C) on the aroma profiles of rapeseed oil. Under drastic roasting conditions, the volatiles changes in rapeseed oil, especially the odorants that play a key role in aroma profiles are expected but not well understood so far.

In this paper, the Sensomics approach was used, including headspace-solid phase microextraction-gas chromatography–olfactometry-mass spectrometry (HS-SPME-GC-O-MS) combined with aroma extract dilution analysis (AEDA), and odor activity values (OAVs) calculations to determine key aroma substances of three representative FRO samples with distinguishing sensorial properties based our previous research (Zhang et al., 2020a). Then, an aroma recombination experiment was conducted to verify key aroma substances. Furthermore, comparative characterization of key odorants and aroma profiles of oil from roasted rapeseed under varied temperature–time conditions (150–200 °C, 0–60 min) was studied by application of aroma profile analysis and hierarchical cluster analysis (HCA). The research results would provide a data basis and guidance for the control of FRO aroma quality during the production processing.

2. Materials and methods

2.1. Commercial FRO

Three representative FRO samples (No. 11 from Hunan Province, No. 15 from Jiangsu Province, and No. 23 from Sichuan Province) were respectively selected from the three different aroma types according to our previous study (Zhang et al., 2020a), which elicited the typical aroma of the corresponding group. Thirty-three representative commercial rapeseed oils were classified into these three different aroma types by using free sorting method (Zhang et al., 2020a), capturing more than two-thirds of the estimated market share of FRO in China. All samples were obtained by internet suppliers.

2.2. Chemicals

The following reference standards were obtained from Sigma (St. Louis, United States): acetic acid (99.7 %), benzaldehyde (99.5 %), butanoic acid (99 %), 3-butenenitrile (98 %), (*E*,*E*)-2,4-decadienal (89 %), (*E*)-2-decenal (93 %), 1,2-dichlorobenzene (99 %), 2,5-dimethylpyrazine (98 %), dimethyl trisulfide (98.5 %), 2-ethyl-6-methylpyrazine (95 %), 2-furanmethanol (98 %), (*E*,*E*)-2,4-heptadienal (88 %), heptanoic acid (99 %), hexanal (98 %), 5-methyl-2-furancarboxaldehyde (98.5 %), (*E*,*E*)-2,4-nonadienal (89 %), nonanal (99.5 %), octanal (98 %), (*E*)-2-octenal (97 %), 1-octen-3-one (97 %), 2-phenylethanol (99 %), 2-pentylfuran (98 %), and trimethylpyrazine (99 %). 3-Ethyl-2,5-dimethylpyrazine (99 %) and 4-isothiocyanato-1-butene (95 %) were bought from JĀK Chemical Corp (Beijing, China).

2.3. Preparation of roasted rapeseed oil

Five kilograms of rapeseed (*Brassica napus* L.) from Hubei Province (main producing area in China) were roasted in the Type V roasting machine (Jintanmaisi, Changzhou, China) at 150, 160, 170, 180, 190, and 200 °C for 10, 20, 30, 40, 50, and 60 min, respectively. Roasted rapeseed samples were pressed by a CA59G screw expeller (IBG Monforts, Mönchengladbach, Germany). Pressed rapeseed oils were centrifuged at 3396 × g for 15 min for purification. Each roasting and pressing were replicated twice.

2.4. AEDA by GC-O-MS

Three representative FRO samples were analyzed using a GC–MS (QP-2010, Shimadzu, Shimane, Japan) equipped with an olfactory port and a DB-WAX column (30 m × 0.25 mm × 0.25 μm) based on our previous studies with small modifications (Xu et al., 2022a–c). The volatile extracts were obtained by HS-SPME with a 50 μm/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco Inc., Bellefonte, United States) according to our previously optimized method (Zhang et al., 2020a), which was diluted via an increase of the GC inlet split ratio from 3:1 to 9:1, 27:1, 81:1, 243:1, and 729:1, respectively. The flavor dilution (FD) factor was expressed as the highest dilution where an odorant could be perceived by 3 experienced assessors.

2.5. Quantitation of the odorants and calculation of OAVs

Five grams of oil samples and 20 μL internal standard solution (1,2-dichlorobenzene, 1120 μg/mL) were vortexed in a 20 mL vial. A GC–MS apparatus combined with a TSQ Quantum XLS (Thermo, Waltham, United States) was employed to analyze volatile substances. The HS-SPME-GC–MS method was referred to our previous work (Zhang et al., 2020a). The odorants were quantified by the external standard method with mass spectra using selected ion monitoring (SIM) mode based on our previous study (Xu et al., 2022a). OAV value is the ratio of volatiles content to their thresholds in odorless refined rapeseed oil from Wilmar (Shanghai, China).

2.6. Determination of orthonasal odor thresholds

Determination of orthonasal odor thresholds of odorants was conducted via triangle tests by a sensory panel consisting of 20 trained assessors. The specific method has been described previously (Matheis ĀÄ Granvogl, 2016).

2.7. Aroma profile analysis

Sensory evaluation of thirty-three representative commercial rapeseed oils and literature research about odor attributes of FRO were conducted (Zhang et al., 2020a, 2021). Seven odor attributes (cabbage-like, fatty, nutty, caramel-like, roasty, burnt, and pungent) were selected based on discussion of sensory panel. Aroma profile analysis was performed by rating the intensities of selected odor attributes on a seven-point linear scale from 0 (not perceivable) to 3 (strongly perceivable) by the same sensory panel in section 2.6.

2.8. Aroma recombination

For aroma recombination, odorless refined rapeseed oil was used as a matrix. All odorants with OAV ≥ 1 were added to the odorless rapeseed oil in the contents detected in the original FRO samples. The recombinant and original FRO sample were evaluated by the trained sensory panel (section 2.6).

2.9. Statistical analysis

Results were analyzed by using Origin 8.1 (OriginLab Corporation, Northampton, United Stated). HCA was performed in this work using SPSS 20.0 (IBM Corp., Armonk, United States).

3. Results and discussion

3.1. Decoding key sensorial molecular base of three commercial FRO by means of Sensomics

3.1.1. Qualitative analysis of aroma compounds in FRO by HS-SPME-GC-O-MS combined with AEDA

The volatile substances were extracted and separated through HS-SPME, and then GC-O-MS and AEDA were employed to determine the odorants in FRO, as shown in Table 1. Totally, twenty-four aroma-active volatile compounds including 9 aldehydes, 1 ketone, 3 acids, 1 alcohol, 2 sulfur compounds, 1 nitrile, 3 furans, and 4 pyrazines were detected in the three FRO samples. Among them, 18, 19, and 20 aroma compounds were perceived and identified in No. 11, No. 15, and No. 23 rapeseed oil, respectively. By application of AEDA with increasing GC inlet split ratios, the odorants with the highest FD factor were 4-isothiocyanato-1-butene (pungent) and dimethyl trisulfide (cabbage-like, sulfury). FD factors of 4-isothiocyanato-1-butene in No. 11, No. 15, and No. 23 rapeseed oils were 9, 243, and 729, respectively. Dimethyl trisulfide in No. 15 and No. 23 rapeseed oils showed FD factors of 243 and 729, respectively, however, it was not perceived in the No. 11 sample. 3-Butenenitrile (metallic, pungent), 2,5-dimethylpyrazine (nutty, roasty), 2-ethyl-6-methylpyrazine (nutty, roasty), and (*E*,*E*)-2,4-decadienal (fatty, deep-fried) also had relatively high FD factors. FD factors of 2,5-dimethylpyrazine in No. 15 and No. 23 samples were both 243, and FD factors of 3-butenenitrile, 2-ethyl-6-methylpyrazine, and (*E*,*E*)-2,4-decadienal also reached 243 in No. 23 sample. So far, no AEDA studies on commercial FRO have been reported to our knowledge. Only Jia et al. (2020) used AEDA and solvent-assisted flavor evaporation (SAFE) to analyze odorants in home-made roasted *Brassica napus* and *Brassica juncea* oils. They found that 5-hexenenitrile, 2,5-dimethylpyrazine, 2-ethylpyrazine, dimethyl trisulfide, 4-isothiocyanato-1-butene, 3-ethyl-2,5-dimethylpyrazine, 3,5-octadien-2-one, 5-(methylsulfanyl)pentanenitrile, 3-phenylpropanenitrile, and nonanoic acid presented high FD factors in *Brassica napus* black and yellow seed oils. Four of these compounds (2,5-dimethylpyrazine, dimethyl trisulfide, 4-isothiocyanato-1-butene, and 3-ethyl-2,5-dimethylpyrazine) were also found in this study. 5-(Methylsulfanyl)pentanenitrile and 3-phenylpropanenitrile were found to be new aroma-active nitriles in *Brassica napus* and *Brassica juncea* oils, respectively, which were not perceived in the present study. Differences in the cultivar, processing condition, and extraction method might be the main cause of discrepancies.

3.1.2. Quantitative analysis and OAVs calculation of the aroma compounds in FRO.

Validation parameters for the methodological results are displayed in Table 2. The correlation coefficients of 24 aroma compounds ranged from 0.9805 to 0.9999. The limit of detection (LOD) and limit of quantification (LOQ) of the method were calculated as 0.003–0.163 and 0.010–0.542 mg/kg. Recovery rates of 24 odorants were in the range of 81.6 %-108.2 %, which indicated that the developed external method was valid to quantify the odorants in FRO.

Concentrations of aroma compounds in the three FRO samples are shown in Table 3. By application of the established external method, 18, 19, and 20 aroma substances were quantified in the No. 11, 15, and 23 samples, respectively. Among them, 3-butenenitrile of the No. 23 sample had the highest content (15.112 mg/kg), whereas the contents of 3-butenenitrile in No. 11 and No. 15 were 0.427 and 9.205 mg/kg, respectively. (*E*,*E*)-2,4-Decadienal content was the second-highest, which were 0.279, 2.517, and 5.654 mg/kg in No. 11, No. 15, and No. 23, respectively. The maximum concentrations of 2,5-dimethylpyrazine and acetic acid were also above 3 mg/kg. Their contents in No. 11, No. 15, and No. 23 were 1.934, 3.510, 4.812, and 1.896, 3.010, 3.800 mg/kg, respectively. In addition, aroma compounds above 1 mg/kg included hexanal, 2-ethyl-6-methylpyrazine, nonanal, trimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 4-isothiocyanato-1-butene, (*E*,*E*)-2,4-heptadienal, and 2-furanmethanol.

The OAVs were calculated based on the quantitative data of aroma compounds, which are shown in Table 3. OAV is the ratio of concentration of the aroma substance in rapeseed oil to threshold value of the substance in odorless oil, which reflects the aroma intensity. The highest OAV was found in dimethyl trisulfide (323, cabbage-like, sulfury) in No. 23 sample, and it also contributed the most to the aroma of No. 15 sample, with an OAV of 35. However, dimethyl trisulfide was not

Table 1
Aroma-active compounds in three commercial FRO samples identified after HS-SPME-GC-O-MS.

No.	Compounds	RI[a]	Flavor dilution (FD) factors			Odor description	Identification[b]
			11	15	23		
1	hexanal	1075	27	27	27	fatty, green	MS, RI, O, S
2	3-butenenitrile	1181	9	81	243	metallic, pungent	MS, RI, O, S
3	2-pentylfuran	1227	1	-[c]	–	fatty	MS, RI, O, S
4	octanal	1284	3	1	–	fatty, citrus-like	MS, RI, O, S
5	1-octen-3-one	1296	–	–	9	earthy	MS, RI, O, S
6	2,5-dimethylpyrazine	1316	81	243	243	nutty, roasty	MS, RI, O, S
7	dimethyl trisulfide	1360	–	243	729	cabbage-like, sulfury	MS, RI, O, S
8	2-ethyl-6-methylpyrazine	1377	91	27	243	nutty, roasty	MS, RI, O, S
9	nonanal	1389	27	–	9	fatty, citrus-like	MS, RI, O, S
10	trimethylpyrazine	1393	9	9	81	cocoa-like, earthy, nutty	MS, RI, O, S
11	(*E*)-2-octenal	1421	9	81	3	fatty, green	MS, RI, O, S
12	3-ethyl-2,5-dimethylpyrazine	1435	27	81	81	burnt, earthy, nutty	MS, RI, O, S
13	acetic acid	1451	9	27	27	sour	MS, RI, O, S
14	4-isothiocyanato-1-butene	1461	9	243	729	pungent	MS, RI, O, S
15	(*E*,*E*)-2,4-heptadienal	1479	27	27	81	fatty	MS, RI, O, S
16	benzaldehyde	1499	–	1	1	almond-like, caramel-like	MS, RI, O, S
17	5-methyl-2-furancarboxaldehyde	1515	1	3	27	almond-like, caramel-like	MS, RI, O, S
18	butanoic acid	1606	–	1	1	sour, cheese-like	MS, RI, O, S
19	(*E*)-2-decenal,	1633	9	27	3	fatty, nutty	MS, RI, O, S
20	2-furanmethanol	1658	–	3	27	burnt	MS, RI, O, S
21	(*E*,*E*)-2,4-nonadienal	1686	3	–	–	fatty	MS, RI, O, S
22	(*E*,*E*)-2,4-decadienal	1796	27	81	243	fatty, deep-fried	MS, RI, O, S
23	2-phenylethanol	1896	1	–	–	nutty	MS, RI, O, S
24	heptanoic acid	1949	–	3	1	sour, sweaty, pungent	MS, RI, O, S

[a] Retention Index (RI) was calculated by using the DB-WAX column;
[b] identification methods include NIST 14 MS spectra (MS), RI, standards (S), and odor attributes (O);
[c] -, not smelled.

Table 2
Methodological validation of aroma compounds identified in the FRO.

No.	Compounds	ions (*m/z*)	calibration equation	correlation coefficient	recovery rate (%)	LOQ (mg/kg)	LOD (mg/kg)
1	hexanal	44	y = 0.2321× + 0.0009	0.9985	96.5	0.182	0.055
2	3-butenenitrile	41	y = 0.5262× − 0.0015	0.9935	102.1	0.105	0.031
3	2-pentylfuran	81	y = 0.5896× + 0.0103	0.9987	92.1	0.041	0.012
4	octanal	43	y = 0.2729× + 0.0078	0.9993	84.3	0.187	0.056
5	1-octen-3-one	55	y = 0.5579× + 0.0087	0.9995	100.4	0.082	0.025
6	2,5-dimethylpyrazine	108	y = 1.0732× + 0.0165	0.9971	86.7	0.010	0.003
7	dimethyl trisulfide	126	y = 5.9552× − 0.0079	0.9976	108.2	0.013	0.004
8	2-ethyl-6-methylpyrazine	121	y = 0.8007× + 0.0019	0.9971	89.4	0.021	0.006
9	nonanal	57	y = 0.3953× + 0.0146	0.9950	85.1	0.288	0.086
10	trimethylpyrazine	42	y = 3.2413× − 0.0152	0.9977	89.0	0.080	0.024
11	(*E*)-2-octenal	41	y = 0.7797× − 0.0141	0.9805	83.4	0.047	0.014
12	3-ethyl-2,5-dimethylpyrazine	135	y = 0.3953× + 0.0146	0.9991	98.3	0.055	0.017
13	acetic acid	43	y = 0.1758× + 0.0035	0.9966	96.9	0.270	0.081
14	4-isothiocyanato-1-butene	72	y = 1.1472× + 0.142	0.9834	95.1	0.542	0.163
15	(*E*,*E*)-2,4-heptadienal	81	y = 1.8695× + 0.0416	0.9962	84.2	0.462	0.139
16	benzaldehyde	106	y = 9.5953× − 0.0285	0.9999	102.0	0.048	0.014
17	5-methyl-2-furancarboxaldehyde	110	y = 8.4636× − 0.0042	0.9986	84.8	0.011	0.003
18	butanoic acid	60	y = 0.4541× − 0.0026	0.9991	98.1	0.118	0.035
19	(*E*)-2-decenal,	43	y = 0.9755× − 0.0141	0.9981	81.6	0.080	0.024
20	2-furanmethanol	98	y = 0.7536× + 0.0216	0.9946	80.7	0.178	0.053
21	(*E*,*E*)-2,4-nonadienal	81	y = 0.9907× − 0.0007	0.9958	80.2	0.082	0.024
22	(*E*,*E*)-2,4-decadienal	81	y = 0.5359× + 0.0119	0.9876	97.8	0.016	0.005
23	2-phenylethanol	91	y = 1.6257× + 0.0051	0.9992	105.4	0.012	0.003
24	heptanoic acid	60	y = 0.7386× − 0.0004	0.9942	99.8	0.055	0.017

Table 3
Concentrations and OAVs of the odorants in three commercial FRO samples.

No.	Compounds	Concentration (mg/kg)			Threshold (mg/kg)	OAV		
		11	15	23		11	15	23
1	hexanal	0.889 ± 0.122	1.033 ± 0.248	1.200 ± 0.161	0.124	7	8	10
2	3-butenenitrile	0.427 ± 0.104	9.205 ± 0.462	15.112 ± 4.605	0.897	< 1	10	17
3	2-pentylfuran	0.151 ± 0.038	-[a]	–	0.175	< 1	< 1	< 1
4	octanal	0.201 ± 0.047	0.190 ± 0.037	–	0.280	< 1	< 1	< 1
5	1-octen-3-one	–	–	0.153 ± 0.048	0.088	< 1	< 1	2
6	2,5-dimethylpyrazine	1.934 ± 0.105	3.510 ± 0.153	4.812 ± 1.415	0.120	16	29	40
7	dimethyl trisulfide	–	0.069 ± 0.022	0.646 ± 0.030	0.002	< 1	35	323
8	2-ethyl-6-methylpyrazine	0.240 ± 0.050	0.860 ± 0.231	1.693 ± 0.472	0.049	5	18	35
9	nonanal	1.413 ± 0.183	–	1.215 ± 0.258	0.430	3	< 1	3
10	trimethylpyrazine	0.301 ± 0.049	0.606 ± 0.112	1.077 ± 0.321	0.110	3	5	10
11	(*E*)-2-octenal	0.198 ± 0.045	0.257 ± 0.082	0.142 ± 0.025	0.022	9	12	6
12	3-ethyl-2,5-dimethylpyrazine	0.903 ± 0.296	1.109 ± 0.378	1.520 ± 0.273	0.090	10	12	17
13	acetic acid	1.896 ± 0.412	3.010 ± 0.521	3.800 ± 0.430	0.386	5	8	10
14	4-isothiocyanato-1-butene	0.121 ± 0.009	0.943 ± 0.090	2.453 ± 0.535	0.028	4	34	88
15	(*E*,*E*)-2,4-heptadienal	1.413 ± 0.155	0.903 ± 0.036	1.458 ± 0.509	0.481	3	2	3
16	benzaldehyde	–	0.045 ± 0.007	0.063 ± 0.002	0.075	< 1	< 1	< 1
17	5-methyl-2-furancarboxaldehyde	0.122 ± 0.016	0.390 ± 0.095	0.834 ± 0.015	0.118	1	3	7
18	butanoic acid	–	0.101 ± 0.003	0.174 ± 0.021	0.158	< 1	< 1	1
19	(*E*)-2-decenal,	0.183 ± 0.060	0.311 ± 0.060	0.381 ± 0.017	0.155	1	2	2
20	2-furanmethanol	–	0.278 ± 0.085	1.423 ± 0.086	0.514	< 1	< 1	3
21	(*E*,*E*)-2,4-nonadienal	0.085 ± 0.003	–	–	0.022	4	< 1	< 1
22	(*E*,*E*)-2,4-decadienal	0.279 ± 0.046	2.517 ± 0.305	5.654 ± 1.770	0.179	2	14	32
23	2-phenylethanol	0.016 ± 0.003	–	–	0.167	< 1	< 1	< 1
24	heptanoic acid	0.081 ± 0.025	0.297 ± 0.083	0.062 ± 0.021	1.087	< 1	< 1	< 1

[a] not detected.

detected in sample No. 11, and the substance with the largest aroma contribution in sample No. 11 was 2,5-dimethylpyrazine, which had an OAV of 16. Dimethyl trisulfide was found in 18 of 30 commercial FROs in the research of Zhou et al (2019), which was affected by the roasting temperature and sulfur amino acids. Zhang et al. (2020a) detected dimethyl trisulfide in 4 of 33 commercial FROs. Different genetic types of raw material and processing conditions might explain the distinction. Moreover, the difference may result from the various LODs of applied instruments and methods.

4-Isothiocyanato-1-butene presented the second-highest OAV (88 in No. 23). 4-Isothiocyanato-1-butene and 3-Butenenitrile were found to be the key aroma substance of FRO (No. 15 and 23), both of which are degradation products of GLS in rapeseed, and they can be decomposed by 3-butenyl glucosinolate in a case. (Shahidi et al., 1994; Bones ĀÄ Rossiter, 2006).

In this study, most substances with higher OAV values had higher FD factors in AEDA, such as dimethyl trisulfide, 4-isothiocyanato-1-butene, (*E*,*E*)-2,4-decadienal, etc. However, there were also particular cases. For example, FD factor of (*E*,*E*)-2,4-heptadienal in No. 15 was 27, and its OAV was only 2. The FD factor of 2-ethyl-6-methylpyrazine in sample No. 15 was also 27, with an OAV of 18. It could be concluded that AEDA results and OAV calculations had some differences in the analysis of aroma substances. The analysts might affect the AEDA analysis of aroma substances.

It could be determined that the key aroma substances in these three FRO samples were hexanal, 3-butenenitrile, 1-octene-3-one, 2,5-dimethylpyrazine, dimethyl trisulfide, 2-ethyl-6-methylpyrazine, nonanal, trimethylpyrazine, (*E*)-2-octenal, 3-ethyl-2,5-dimethylpyrazine, acetic acid, 4-isothiocyanato-1-butene, (*E*,*E*)-2,4-heptadienal, 5-methyl-2-furancarboxaldehyde, butanoic acid, (*E*)-2-decenal, 2-furanmethanol, (*E*,*E*)-2,4-nonadienal, and (*E*,*E*)-2,4-decadienal based on the results of GC-O-MS combined with AEDA and OAVs (≥1). The key aroma aldehydes, ketones, and acids are mainly derived from lipid oxidation. Among them, nonanal and (*E*)-2-decenal can be generated by auto-oxidation of oleic acid. The auto-oxidation of linoleic acid can generate hexanal and 2,4-decadienal. 2,4-Decadienal can produce (*E*)-2-octenal and hexanal in the *retro*-aldol reaction mediated by moisture. The auto-oxidation of linolenic acid can generate (*E*,*E*)-2,4-heptadienal. 1-Octen-3-one is mainly produced from linoleic acid via the *β*-splitting pathway. Acetic acid is the end product of fatty acid oxidation (Ho ĀÄHartman, 1994). For key aroma pyrazines, carbohydrate in oilseed can form dicarbonyl compounds during the heat treatment process, which then reacts with polypeptides or free amino acids to produce α-amino ketones, and finally condensed to form pyrazines (Umano et al., 1995). Aldol condensation and subsequent cyclization can also generate pyrazines (Sacchetti et al., 2016). Furan aroma substances can be formed by lipid oxidation, carbohydrate degradation, and Maillard reaction (Zhang et al., 2021). The number of key aroma compounds in No. 11, No. 15, and No. 25 samples were 14, 14, and 18, respectively. These three FRO samples shared 13 key aroma compounds.

Attributed to the importance of key aroma compounds to the sensorial property of FRO, research on the aroma substances of FRO has gradually attracted attention in recent years. The nitriles including 2-butenenitrile, octanenitrile, and 5-(methylthio)-pentanenitrile were considered the main contributors to spicy odor in virgin rapeseed oil by calculating the OAV in the research of Jing et al. (2020). However, these nitriles were just semi-quantified with 2-octanol as an internal standard. OAVs were calculated by using these semi-quantitative data, which makes it hard to provide direct evidence for the characterization of key odorants. Su et al. (2019) used HS-SPME-GC-O-MS and the time-intensity method to find 16 characteristic flavor substances of FRO, including 5 pyrazines, 3 nitriles, 4 aldehydes, 1 olefin, 1 ester, 1 acid, and 1 sulfur compound. Zhou et al. (2019) used GC-O-MS and a new extraction method (monolithic material adsorption extraction, MMSE) to analyze the odorants in a commercial FRO. 2,5-Dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, dimethyl trisulfide, 4-isothiocyanato-1-butene, butyrolactone, and benzonitrile were determined to be key aroma compounds by calculating OAVs in their study. The former four compounds were also identified to be key aroma substances in this paper.

3.1.3. *Aroma profile analysis and reconstitution analysis*

Aroma substance standards with corresponding contents were added to the odorless rapeseed oil for aroma recombination. The sensory panel selected 7 aroma attributes (cabbage-like, fatty, nutty, caramel-like, roasty, burnt, and pungent). On the basis of the odor properties of assigned key odorants, cabbage-like odor was mainly produced by dimethyl trisulfide, while aldehyde substances were mainly related to fatty smelling. The nutty sensory attribute was from pyrazines and aldehydes, and furans mainly produced the caramel-like fragrance. The roasty odor mainly resulted from pyrazine compounds. 3-Butenenitrile, 4-isothiocyanato-1-butene, and some acids had a pungent odor.

Aroma profiles of FRO and the corresponding recombinant are shown in Fig. 1. The results showed that the strongest fragrant characteristic in sample No. 11 is fatty (2.0), followed by roasty attribute (1.8). Correspondingly, sample No. 11 had the highest nonanal and (*E*,*E*)-2,4-nonadienal contents, which mainly presented fatty smelling. It also showed the highest OAV level of 2,5-dimethylpyrazine, contributing to the roasty smelling. All aroma attributes in sample No. 15 were stronger than that of No. 11′s. All aroma intensity scores of sample No. 23 were the highest among these three samples. Sample No. 23 also had the highest contents of key aroma compounds except for nonanal, (*E*)-2-octenal, (*E*,*E*)-2,4-nonadienal among these three samples. Results indicated a good correspondence between aroma profiles and key odorants levels.

Three aroma profiles of FRO samples and the corresponding recombinants all showed high similarity, proving that the key aroma substances of FRO have been well identified and quantified. However, there were minor differences in individual aroma properties. Key aroma substances in FRO constituted the main aroma profile of FRO. The

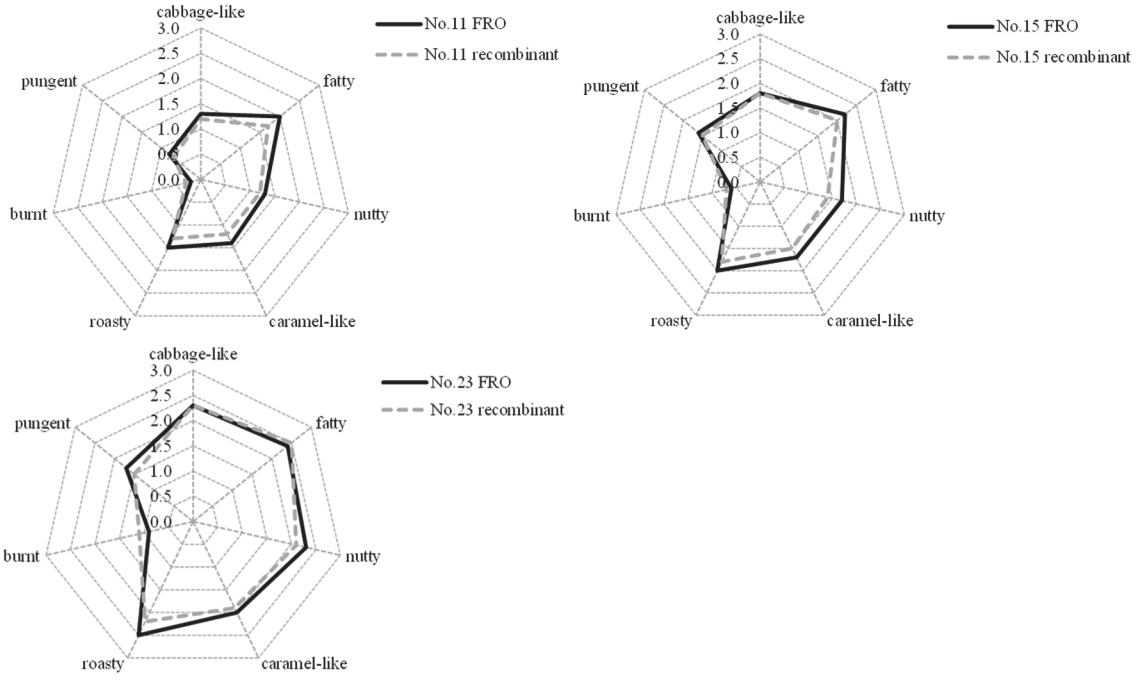

Fig. 1. Aroma profiles of three commercial FRO (solid line) and the corresponding recombinant (dotted line).

existence of other aroma substances and their synergistic effects with key aroma substances could also produce differences in the aroma profile of original and recombinant samples.

3.2. Influence of roasting conditions on sensory property of FRO

3.2.1. Changes in key odorants of rapeseed oil in different roasted conditions

To understand the relationship between key odorants generation to intervention points of roasting seed, this section focused on changes in 16 key odorants of oil from roasted rapeseed under different conditions, including hexanal, 3-butenenitrile, 2,5-dimethylpyrazine, dimethyl trisulfide, 2-ethyl-6-methylpyrazine, nonanal, trimethylpyrazine, (*E*)-2-octenal, 3-ethyl-2,5-dimethylpyrazine, acetic acid, 4-isothiocyanato-1-butene, (*E*,*E*)-2,4-heptadienal, 5-Methyl 2-furancarboxaldehyde, (*E*)-2-decenal, 2-furanmethanol, and (*E*,*E*)-2,4-decadienal (Fig. 2). 1-Octen-3-one, butanoic acid, and (*E*,*E*)-2,4-nonadienal were not detected in our home-made FRO samples. Variety of raw materials might be one of the main reasons for this.

Aroma-active aldehydes such as hexanal, nonanal, (*E*)-2-octenal, (*E*,*E*)-2,4-decadienal contribute to the fatty and green flavor of the oil, which mainly belong to lipid oxidation products. Hexanal, nonanal, and (*E*)-2-octenal were found in cold-pressed rapeseed oil (control group) and the early roasting stage (0–20 min). After that, their contents gradually declined with prolonging roasting time. As the roasting became more vigorous and lasted longer, (*E*,*E*)-2,4-heptadienal, (*E*)-2-decenal, and (*E*,*E*)-2,4-decadienal showed first rising and then decline trends, where the maximum values were 5.05, 1.13 and 6.37 mg/kg at 200 °C-40 min, 200 °C-60 min, and 200 °C-40 min, respectively. According to the results of a previous study, (*E*,*E*)-2,4-decadienal could be degraded into 2-octenal and hexanal through *retro*-aldol condensation reactions (Josephson ĀÄLindsay, 1987). (*E*,*E*)-2,4-Decadienal can also take part in the Maillard reaction, which may lead to a decrease in its content (Napolitano et al., 2008). Acetic acid appeared in rapeseed oil after 40 min at 150 °C. The content of acetic acid firstly increased with the increase of roasting temperature and time and reached a maximum of 8.15 mg/kg at 190 °C for 50 min. Then it began to decrease, which dropped to 3.29 mg/kg under extreme conditions of roasting in this study (200 °C for 60 min). These lipid oxidation products' contents reached the peaks under different conditions, which might be resulted from the different fatty acid composition and generation pathways. Increasing temperature would accelerate the lipid oxidation, subsequently promoting the generation of the most lipid oxidation products. It could also lead to the further degradation, reaction, and volatilization of lipid oxidation products, causing a decrease in the contents (Pazhouhanmehr et al., 2016; Schaich, 2005).

For GLS degradation products, 3-butenenitrile wasn't found during the early roasting stage (0–10 min). At 150 °C for 30 min, 3-butenenitrile was determined to be 0.45 mg/kg, and its content increased continuously with the increased time. The maximum level was found to be 21.55 mg/kg at 200 °C for 40 min. The concentrations of nitriles in rapeseed oil increased with a rise in roasting temperature (Kraljić et al., 2018). In the study reported by Mao et al. 2019, the low-molecular-weight nitriles were generated from GLS during rapeseed roasting, which also increased significantly after thermal treatment (Mao et al., 2019). Jing et al. (2020) found that the nitriles contents of rapeseed oil remarkably increased after roasting for 40 min at 150 °C. These results showed that thermal treatment can significantly promote the thermal degradation of GLS as well as the generation of nitriles. A lowered myrosinase activity, and thus, a reduced degradation of GLS after thermal processing might also contribute to the rise of nitriles (Wei et al., 2012). 4-Isothiocyanato-1-butene was detected in cold-pressed rapeseed oil with a content of 0.28 mg/kg. As the roasting process progressed, the concentration increased initially and then decreased. The maximum value appeared at 190 °C for 50 min, reaching 2.63 mg/kg. Jing et al. (2020) studied the flavor variations of oil from roasted rapeseed (150 °C for 50 min) by using a semi-quantitative approach. They found that concentration of 4-Isothiocyanato-1-butene was remarkably higher in the late stage of roasting by comparison with the initial concentration. 4-Isothiocyanato-1-butene was reported to be the major volatile compound of rapeseed oil with cold pressing in the research of Kraljić et al. (2018), occupying 56 % of total volatile compounds. After heating seeds at 60 °C, the proportion of 4-isothiocyanato-1-butene increased and reached over 68 %, whereas it decreased under a higher temperature (100 °C). They attributed the increase to the long-time contact of GLS and myrosinase. Factors influencing the formation mechanisms of 4-isothiocyanato-1-butene during roasting need to be further investigated. In addition, dimethyl trisulfide was not detected in the early stage but appeared at 150 °C/30 min and 160 °C/30 min, which were 0.13 and 0.21 mg/kg, respectively. Moreover, it was also found when the seeds were roasted at 170, 180, 190, and 200 °C for 20 min, and the contents were 0.09, 0.14, 0.16, and 0.21 mg/kg, respectively. Dimethyl trisulfide might be derived from the sulfur-containing amino acid methionine. Methionine can generate methional, methanethiol, and dimethyl disulfide, and finally, produce dimethyl sulfide and dimethyl trisulfide via a disproportionation reaction (Matheis ĀÄ Granvogl, 2016). The changes in dimethyl trisulfide showed a similar tendency to that of 3-butenenitrile.

2,5-Dimethylpyrazine, 2-ethyl-6-methylpyrazine, trimethylpyrazine, and 3-ethyl-2,5-dimethylpyrazine were not determined during 0–10 min at each temperature. They increased as the roasting temperature and time were raised, peaked at 170, 180, 190, and 200 °C, respectively, with contents of 9.07, 2.44, 2.63, and 3.37 mg/kg, and then diminished with the higher temperature or longer time. For another class of heterocyclic compounds, furans had similar variation trends. 5-methyl-2-furancarboxaldehyde had a minimum value of 0.02 mg/kg in cold-pressed rapeseed oil and achieved a maximum value of 1.99 mg/kg at 190 °C/40 min. The maximum level of 2-furanmethanol was 6.49 mg/kg, which was measured at 200 °C for 30 min. Heterocyclic substances are an important class of odorants that are derived during the Maillard

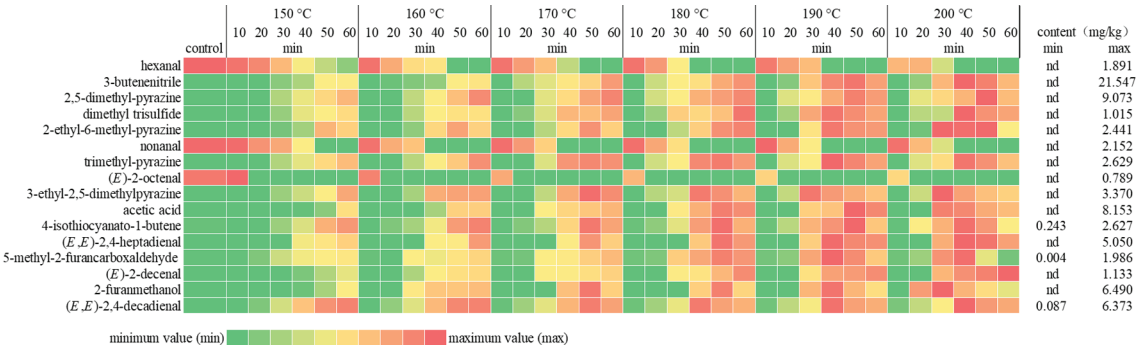

Fig. 2. Changes in key aroma compounds of oils from rapeseed roasted under different conditions.

reaction, carbohydrate degradation, and Strecker degradation, often related to roasty odor. Heterocyclic substances contents are positively correlated with applied thermal treatment temperature and time (Kraljić et al., 2018; Mao et al., 2019). However, with the further increase in roasting temperature and time, the vigorous condition might result in cracking and polymerization reactions of aroma compounds. Additionally, some aroma substances were volatilized and lost as the roasting process progressed.

3.2.2. *Changes in aroma profile of rapeseed oil in different roasted conditions*

Wei et al. (2012) reported that rapeseed roasted at 120 °C led to a nutty odor in the oil. The roasty and burnt flavors increased obviously at a roasting temperature of 120 °C. According to R kas et al. (2015), a woody, straw-like, and weak seed-like aroma were presented in the cold-pressed high-oleic rapeseed oil. An increase in the intensity of the seed-like odor note was observed at 100 °C. Oily, green, and acidic odor attributes were detected to be the major aroma in cold-pressed rapeseed oil and oils with roasting at 140 and 160 °C for 5, 10, and 15 min in the previous literature (Gracka et al., 2016). Also, nutty, bread-like, roasted, and burnt attributes were shown in the roasted rapeseed oil at 180 °C. In the present study, a wider range of roasting conditions was considered to systematically study their effects on the aroma profiles of rapeseed oils.

As can be seen from Fig. 3A, cold-pressed rapeseed oil mainly presented cabbage-like, fatty, and pungent flavor, with scores of 0.9, 0.5, and 0.5 points, respectively, and other odor attributes were very weak. Only 6 of 16 target odorants were detected in cold-pressed rapeseed oil (Hexanal, nonanal, (*E*)-2-octenal, 4-isothiocyanato-1-butene, 5-methyl-2-furancarboxaldehyde, and (*E*,*E*)-2,4-decadienal). Among them, the contents of 4-isothiocyanato-1-butene (0.28 mg/kg), 5-methyl-2-furancarboxaldehyde (0.02 mg/kg), and (*E*,*E*)-2,4-decadienal (0.09 mg/kg) in cold-pressed rapeseed oil were relatively low. In the early stage of roasting (10–20 min), the overall flavor intensity of rapeseed oil samples was low, and the cabbage-like, fatty, and pungent flavor were major sensory attributes of the oil. As the roasting temperature and time continuously increased, fatty, cabbage-like, and pungent smelling became more prominent with increasing contents of aroma-active aldehydes and *S*-containing Compounds (e.g., (*E*,*E*)-2,4-decadienal, dimethyl trisulfide, and 4-isothiocyanato-1-butene). At 150 °C/40 min and 160 °C/30 min, the rapeseed oil developed a marked nutty, caramel-like, and roasty flavor. 2,5-Dimethylpyrazine, 2-ethyl-6-methylpyrazine, trimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 5-methyl-2-furancarboxaldehyde, and 2-furanmethanol were also detected under these two conditions. Then the overall flavor strengthened with the further increase in roasting temperature and time, and the total content of odorants amounted accordingly. At 160 °C/60 min, 170 °C/50 min, and 180 °C/40 min, roasty, nutty, caramel-like, and burnt fragrance began to dominate the overall flavor. Under these conditions, the pyrazines and furans responsible for roasty, nutty, caramel-like, and burnt odor also accounted for the highest proportion. The rapeseed oils had a very strong burnt aroma under stronger conditions, which might be hard to be accepted by consumers. Therefore, based on sensory evaluation, roasting seeds at 160, 170, 180, 190, and 200 °C should not exceed 50, 40, 30, 30, and 30 min, respectively to avoid the unaccepted intense burnt aroma.

The aroma wheel scores of rapeseed oil under the different roasting conditions were analyzed by HCA, and a dendrogram was constructed, which is shown in Fig. 3B. It can be seen from the figure that the rapeseed oil samples under different roasting conditions had obvious clustering trends. Objects can be divided into 4 groups (a, b, c, and d) when taking 5 average distance thresholds into account. Group a contained samples from the early stage (mainly 0–20 min). Group b mainly contained samples from roasted seeds for 20–30 min. Oil samples from the intermediate roasting stage (30–40 min) and late roasting stage with relatively low temperature (150–160 °C for 50–60 min) were mainly clustered in group d. Group c mainly included samples at the later stage of roasting (40–60 min). The results indicated that aroma profiles of samples under different roasting conditions could be effectively distinguished by HCA, and roasting conditions including temperature and time were important factors affecting the sensory properties of roasted rapeseed oil. At the early stage (10 min), the temperature had a small influence on aroma profiles. More importantly, the results also indicated

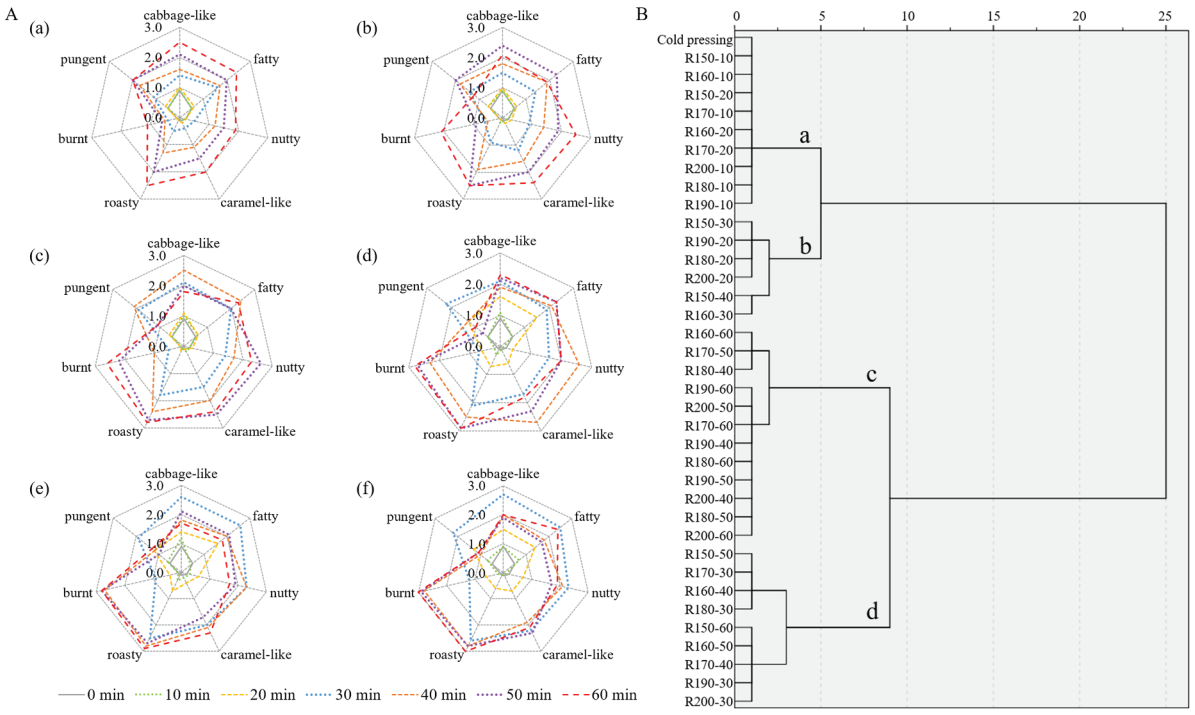

Fig. 3. A: Aroma profiles of rapeseed oils under different roasting conditions (a) 150 °C, (b) 160 °C, (c) 170 °C, (d) 180 °C, (e) 190 °C, (f) 200 °C; **B:** HCA of aroma profiles of rapeseed oils under different roasting conditions (e.g., R15010: roasted at 150 °C for 10 min).

that oils under relative high-temperature-short time and low-temperature-long time conditions could have similar aroma profiles (e.g., 200 °C-30 min and 150 °C-60 min), which provided a reference for finding a balance between oil aroma and energy cost for industrial FRO production.

4. Conclusion

Nineteen key aroma-active compounds in three representative commercial FRO imparting characteristic aroma notes were identified and quantified by means of the Sensomics approach, which included 7 aldehydes, 1 ketone, 2 acids, 1 nitrile, 4 pyrazines, 2 furans, and 2 sulfur compounds. Under the designed set-up with broad roasting parameters, most of the aroma substances except hexanal, nonanal, and (*E*)-2-octenal showed first rising and then decline trends as the roasting process progressed under temperatures no<150 °C. The dynamic certain changes of the key odorants could bring distinguishable variation on the overall sensory property of oil, revealed by the aroma profiles analysis and HCA. Remarkably, under dedicated control of roasting processing, roasted rapeseed oils under high-temperature-short time and low-temperature-long time conditions could exhibit similar pleasant aroma profiles, which could provide a reference for industrial FRO production achieving not only target modulation of the aroma but also sustainable production in the near future. Also, thermally induced contaminants (e.g., polycyclic aromatic hydrocarbons) during the roasting of rapeseed should be receive more attention in the coming studies.

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CRediT authorship contribution statement

Youfeng Zhang: Conceptualization, Writing – original draft, Methodology, Visualization, Validation. **Cheng Zhen:** Visualization, Investigation. **Bixi Zhao:** Visualization, Investigation. **Shengmin Zhou:** Visualization, Investigation. **Yuanrong Jiang:** Visualization, Investigation. **Xingguo Wang:** Conceptualization, Project administration, Supervision. **Qingzhe Jin:** Conceptualization, Project administration, Supervision, Writing – review ĀÄediting. **Yanyan Zhang:** Conceptualization, Project administration, Supervision, Writing – review ĀÄediting.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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This manuscript is dedicated to the memory of my mentor, Prof. Dr. Michael Granvogl (1974-2022).

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IV. CHAPTER

Characterization of Thermally Induced Flavor Compounds from the Glucosinolate Progoitrin in Different Matrices via GC-TOF-MS

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Characterization of Thermally Induced Flavor Compounds from the Glucosinolate Progoitrin in Different Matrices via GC-TOF-MS

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ABSTRACT: As important flavor precursors, glucosinolates are ubiquitous in the plant family of Brassicaceae. Glucosinolate degradation products are the major volatile flavor compounds of rapeseed oil, accounting for up to 80% of the total volatiles. However, up to now, little attention has been paid to the volatile flavor products of the nonenzymatic thermal degradation of glucosinolates. One of the most important factors that determine the flavor of hot-pressed rapeseed oil is the roasting process, where the thermal degradation of glucosinolates mainly occurs. The thermal degradation behavior and volatile products of progoitrin (the main glucosinolate of rapeseed) in different matrices (phosphate buffer at a pH value of 5.0, 7.0, or 9.0, sea sand, and rapeseed powder) at different temperatures (150−200 °C) and times (0−60 min) were studied using HPLC and GC-TOF-MS. Thereby, the degradation rate of progoitrin decreased in the following order: pH 9.0 > sea sand > rapeseed powder > pH 7.0 > pH 5.0. Further, a higher degradation was observed with increasing temperature and time. Under the applied conditions in this study, 2,4-pentadienenitrile was the major nitrile and thiophenes were the major sulfur-containing volatile compounds formed. Possible formation pathways of main sulfur-containing and nitrogen-containing volatiles were proposed.

KEYWORDS: *progoitrin, glucosinolate, thermal degradation, volatiles, GC-TOF-MS*

INTRODUCTION

Glucosinolates (GSLs) are sulfur (S)- and nitrogen (N)-containing secondary plant metabolites that widely occur in *Brassica* oilseeds such as rapeseed and black mustard seed. Isothiocyanates and nitriles are naturally generated via enzymatic hydrolysis of glucosinolates when the plant cells are ruptured, which are associated with pungent and spicy flavor. The chemical and thermal degradation of glucosinolates is very common during the processing of *Brassica* crops (cooking, boiling, or roasting).[1−4] In addition, isothiocyanates were reported to exert beneficial effects on human health.[5]

As one of the major producers of rapeseed oil in the world, China manufactured 6.04 million metric tons of rapeseed oil in 2019/20.[6] Usually, rapeseed high in erucic acid is also high in glucosinolate contents. In our previous study, the erucic acid content and the amount of volatile glucosinolate degradation products in fragrant rapeseed oil revealed a positive correlation.[7] The "2020 Chinese National Rapeseed Harvest Quality Survey Report" showed that the average content of erucic acid in rapeseed in China's seven major producing provinces was 15.8%, while rapeseed with a low content of erucic acid (<3.0%) represented less than one-third of the samples.[8] Up to now, rapeseed with high contents of erucic acid and glucosinolates still predominates in China.

Glucosinolate degradation products are the major volatile flavor substances of rapeseed oil, which can account for up to 80% of the total volatiles.[7,9] Thermal degradation of glucosinolates is the main degradation pathway in the production of hot-pressed rapeseed oil during the industrial roasting process due to the fast inactivation of myrosinase at high temperatures (150−200 °C) for more than 30 min, which generates volatile nitriles, isothiocyanates, and other volatile substances.[7,10] Several isothiocyanates and nitriles were previously reported to be aroma-active compounds in rapeseed oil.[11] However, at present, there are only a few studies on the thermal degradation of glucosinolates in rapeseed during roasting, especially for the thermally induced generation of volatile flavor compounds of individual glucosinolates at high temperatures (>150 °C).[10,12] Hanschen et al.[2,13] studied the thermal degradation products of aliphatic glucosinolates treated at 100 and 130 °C and proposed pathways, however, without a special emphasis on the volatiles. Ortner and Granvogl[14] identified aroma-active compounds generated by thermal degradation of the glucosinolate sinigrin (2-propenyl/allyl glucosinolate) at 140 °C for 30 min in different matrices using gas chromatography-olfactometry and aroma extract dilution analysis. As the main glucosinolate of the seed of *Brassica napus*, progoitrin ((*R*)-2-hydroxybut-3-enylglucosinolate) is an important precursor of characteristic flavor compounds in rapeseed oil. Up to now, only a few studies have evaluated the thermal degradation of progoitrin. Lanzani et al.[15] found that progoitrin was totally degraded after heat treatment at 100 °C for 3 h. However, only 35% of progoitrin

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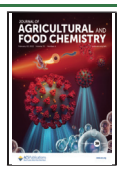

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was degraded in aqueous solution at 100 °C after 5 h in the study of MacLeod and Rossiter.[16] Thus, a more detailed investigation on the thermal degradation of progoitrin is needed due to inconsistent results of previous reports. Also, these studies did not involve the formation of volatile flavor compounds formed at high temperatures (>150 °C).

Thus, this paper aims at (i) studying the degradation behavior of progoitrin in various matrices under different conditions, (ii) identifying the volatile flavor compounds by headspace-solid phase microextraction-gas chromatography-time-of-flight-mass spectrometry (HS-SPME-GC-TOF-MS), and (iii) proposing the possible generation pathways of the major volatiles generated from progoitrin by thermal degradation to provide data and theoretical basis for the modulation of volatile glucosinolate degradation compounds of hot-pressed rapeseed oil to obtain oils with the desired flavors.

MATERIALS AND METHODS

Chemicals and Materials. Progoitrin potassium salt (≥98%) was purchased from Zzstandard (Shanghai, China), and sinigrin potassium salt (≥98%) was obtained from ANPEL (Shanghai, China). Acetic acid (98%), 2-acetylpyridine (98%), 2-acetylthiophene (98%), benzaldehyde (98%), benzothiazole (98%), 2,3-butanedione (98%), 1,3-dimethylbenzene (98%), 2-ethyl-1-hexanol (98%), 2-furancarboxaldehyde (98%), 1-heptanol (98%), 2-heptanone (98%), 5-methyl-2-furancarboxaldehyde (98%), 6-methyl-5-hepten-2-one (98%), 5-methyl-2-thiophenecarboxaldehyde (98%), 1-octanol (98%), styrene (98%), thiophene (98%), 2-thiophenecarbonitrile (98%), 2-thiophenecarboxaldehyde (98%), and 2-thiophenepropanenitrile (98%) standards were purchased from Sigma-Aldrich (Bellefonte, PA). 1,2-Dichlorobenzene (98%) standard and high-performance liquid chromatography (HPLC) grade solvents (acetonitrile and methanol) were obtained from J&K Scientific (Beijing, China). *n*-Alkanes (C_8−C_{40}) were purchased from Sigma-Aldrich. The ultrapure water used in this work was provided using a Milli-Q system from Millipore (Billerica, MA). Other solvents and reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China). Rapeseed (*B. napus*) Kangyou 61 was used in this study.

Thermal Treatment of Progoitrin. For heat processing, progoitrin (1.4 μmol/g) was weighed into screw cap glass tubes (10 mL) containing different matrices (1 g): phosphate buffer (0.067 mol/L) at a pH value of 5.0, 7.0, or 9.0, sea sand, or rapeseed powder. Microwave heating was used to inactivate enzymes in the rapeseed matrix. Moreover, a mixture of methanol/water (7/3, v/v; 75 °C) was used to remove glucosinolates from rapeseed meal. For solid matrices, progoitrin was dissolved in methanol and then added to the matrices. After that, the solvent was blown down with nitrogen to ensure uniform dispersion. Afterward, all of these mixtures were heated in pressure-resistant hermetical glass tubes at different temperatures (150, 160, 170, 180, 190, or 200 °C) for 5, 10, 15, 20, 30, 40, 50, or 60 min. After thermal treatment, the mixture was quickly cooled by an ice-water bath and analyzed directly. Three parallel experiments were carried out.

Analysis of Progoitrin. The extraction and determination of progoitrin from different matrices were conducted according to Hanschen et al.[2] and Mao et al.[10] Briefly, the sample (200 mg) was extracted three times using methanol/water (7/3, v/v; 75 °C) in the presence of sinigrin (1 μmol) as the internal standard. Then, the extract was applied to a DEAE-Sephadex A-25 ion exchanger and desulfated using aryl sulfatase. Desulfo-progoitrin was determined using an HPLC instrument (Shimadzu, Kyoto, Japan), equipped with an LC-10 AD model pump, an SPD-10A ultraviolet (UV) detector, and a C18 column (5 μm, 4.6 × 250 mm; Hanbon Science and Technology, Jiangsu, China). The wavelength was set at 229 nm and the column temperature was 30 °C. The mobile phase A was acetonitrile/water (20/80, v/v), and the mobile phase B was water. The flow rate was 1 mL/min with an elution program as follows: 5% A (0−4 min), increased linearly to 15% A in 7 min, and then increased linearly to 100% A in 25 min. Sinigrin was used as the internal standard to calculate the concentration of progoitrin via relative response factors. The content of progoitrin was expressed as μmol/g of the matrix.

Volatile Analysis by HS-SPME-GC-TOF-MS. One gram of sample was placed into a 20 mL headspace glass vial and incubated at 40 °C for equilibrium. The solid phase microextraction (SPME) fiber was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm; Supelco, Bellefonte, PA). Prior to each usage, the fiber was conditioned at 250 °C for 30 min. Then, it was exposed to the sample headspace under the following conditions: an incubation time of 10 min, an extraction time of 30 min, and an extraction temperature of 40 °C. After extraction, the SPME fiber was inserted into the GC-MS injector for desorption at 250 °C for 5 min. Gas chromatography (Agilent series 7890B; Agilent Technologies, Palo Alto, CA) coupled with time-of-flight mass spectrometry (Pegasus BT LECO, St. Joseph, MI) was employed for analyzing the volatiles. A DB-5ms column (30 m × 0.25 mm ID, 0.25 μm film thickness; Agilent Technologies, Palo Alto, CA) was used to separate the volatiles. The oven temperature was held at 40 °C for 2 min and then increased to 250 °C at the rate of 10 °C/min and held for 5 min. The temperatures of the GC-MS transfer line and ion source were set at 280 and 210 °C, respectively. High-purity helium (99.9995%) was used as the carrier gas at a constant flow of 1 mL/min. The mass spectrometer was operated in electron ionization mode (70 eV). The acquisition delay was 90 s, and ions were collected in the mass range of 33−450 amu at an acquisition rate of 10 spectra/s. A semiquantification of the volatile compounds was performed using 1,2-dichlorobenzene as the internal standard. Therefore, it was ensured that the internal standard was not present in the samples. Twenty compounds were identified via retention indices (RIs) and mass spectrometry in comparison to authentic reference compounds. The remaining compounds were identified using their RIs and mass spectra that were compared to Wiley 9 mass spectral library (Chichester, U.K.) (Supporting Information). RIs were calculated using a homologous series of C_8−C_{40} *n*-alkanes.

Statistical Analysis. Results were reported as mean ± standard deviation from three replicates of each experiment and were compared by one-way analysis of variance (ANOVA) using Origin 8.1 (OriginLab Corporation, Northampton, MA) and IBM SPSS Statistics for Windows, version 20.0 (IBM Corp., Armonk, NY), and the post hoc analysis was performed using Duncan's multiple range tests.

RESULTS AND DISCUSSION

Influence of Temperature and Matrix on the Thermal Degradation of Progoitrin. The effects of temperature and matrix (buffer solution with pH values of 5.0, 7.0, or 9.0, sea sand, and rapeseed powder) on the thermal degradation of progoitrin are shown in Figure 1. Line charts showed a decrease in progoitrin content with an increase in the temperature and time for all matrices. Progoitrin in the buffer solution with a pH value of 5.0 (Figure 1A) exhibited the strongest thermostability. At 150 °C, the progoitrin content decreased from 1.42 to 0.66 μmol/g with the time ranging from 0 to 60 min. Full degradation of progoitrin was seen at 170 °C after 60 min and at 200 °C after 20 min. In the buffer solution with a pH value of 7.0 (Figure 1B), progoitrin was degraded by 35% after 30 min and by 93% after 60 min at 150 °C. The degree of degradation increased with the increase of temperature, and complete degradation of progoitrin was observed after 50 min at 170 °C. Progoitrin in the buffer solution with a pH value of 9.0 (Figure 1C) showed the lowest thermal stability with >90% of progoitrin degradation within 5 min at 150 °C. At higher temperatures, progoitrin was completely degraded within 10 min or even in a shorter time. The thermal stability of progoitrin under neutral pH

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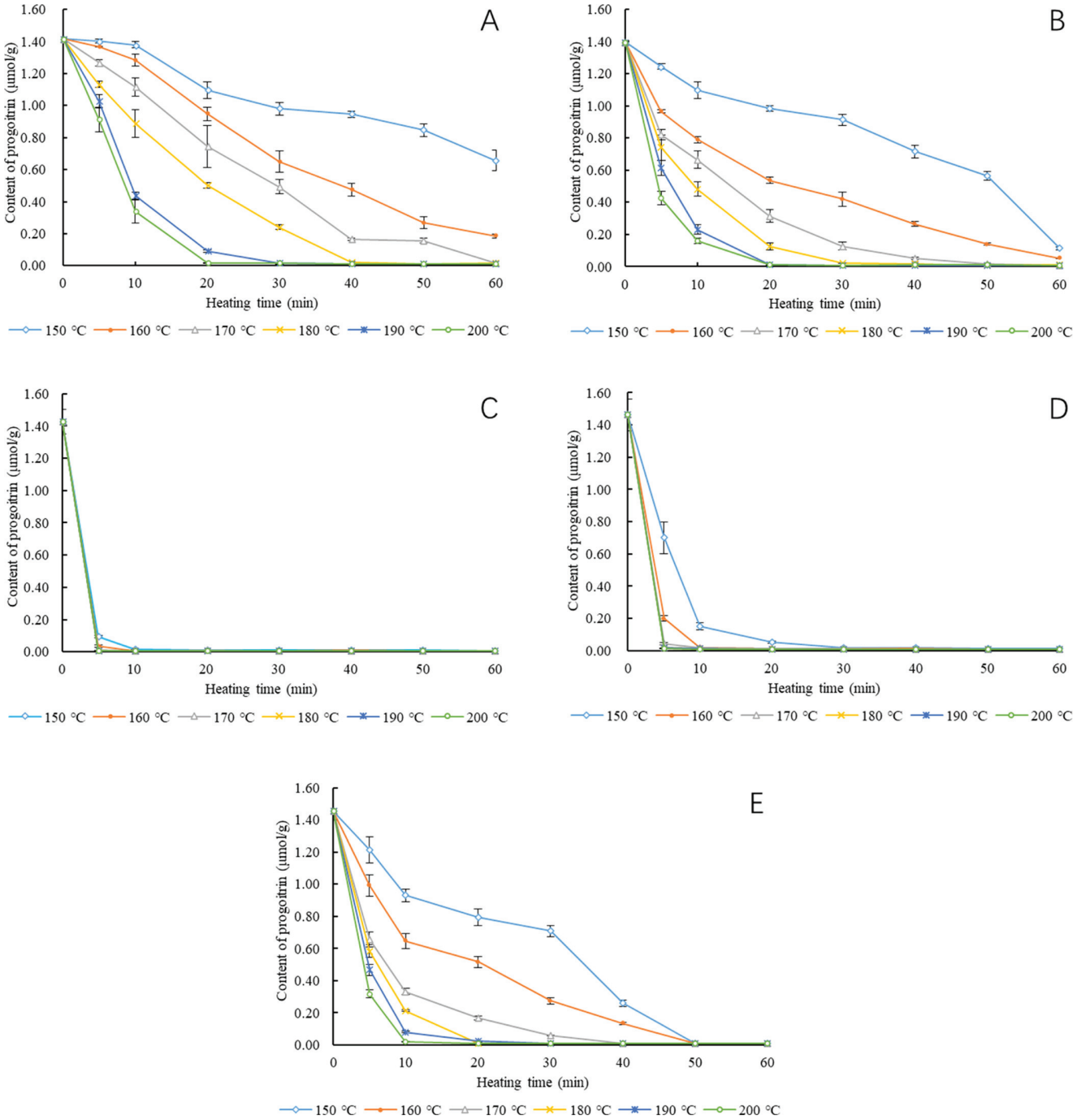

Figure 1. Effects of matrices and conditions on the content of progoitrin (A) pH 5.0, (B) pH 7.0, (C) pH 9.0, (D) sea sand, and (E) rapeseed powder.

value in sea sand (Figure 1D) and in rapeseed powder (Figure 1E) was between those of the basic and acidic conditions.

Hanschen et al.[2] studied the thermally induced degradation of sinigrin under different conditions. The stability of sinigrin tended to be lower at pH 8.0 than at pH 5.3, with 93% of the original amounts degraded after 30 min at 130 °C. Under dry conditions at 130 °C, the thermal stability of sinigrin was between those found at aqueous conditions at pH 5.3 and pH 8.0. They also investigated the influence of the pH value on the thermal degradation of glucosinolates in broccoli sprouts after cooking for 80 min at 100 °C. Results showed that glucosinolates were more labile toward heat treatment under basic conditions compared to neutral and slightly acidic conditions.[17] Results obtained in the present study are in line with these findings. Based on the structure and thermal degradation behavior of progoitrin, it was deduced that the bimolecular nucleophilic substitution reaction (S_N2) occurred during thermal degradation under basic conditions (Figure 2). For C-1 of the glucosyl moiety, the charge is transferred from the carbon atom to the adjacent oxygen and sulfur atoms due to the high electronegativity of oxygen and sulfur atoms, and thus, the electron cloud tends to shift toward the oxygen and

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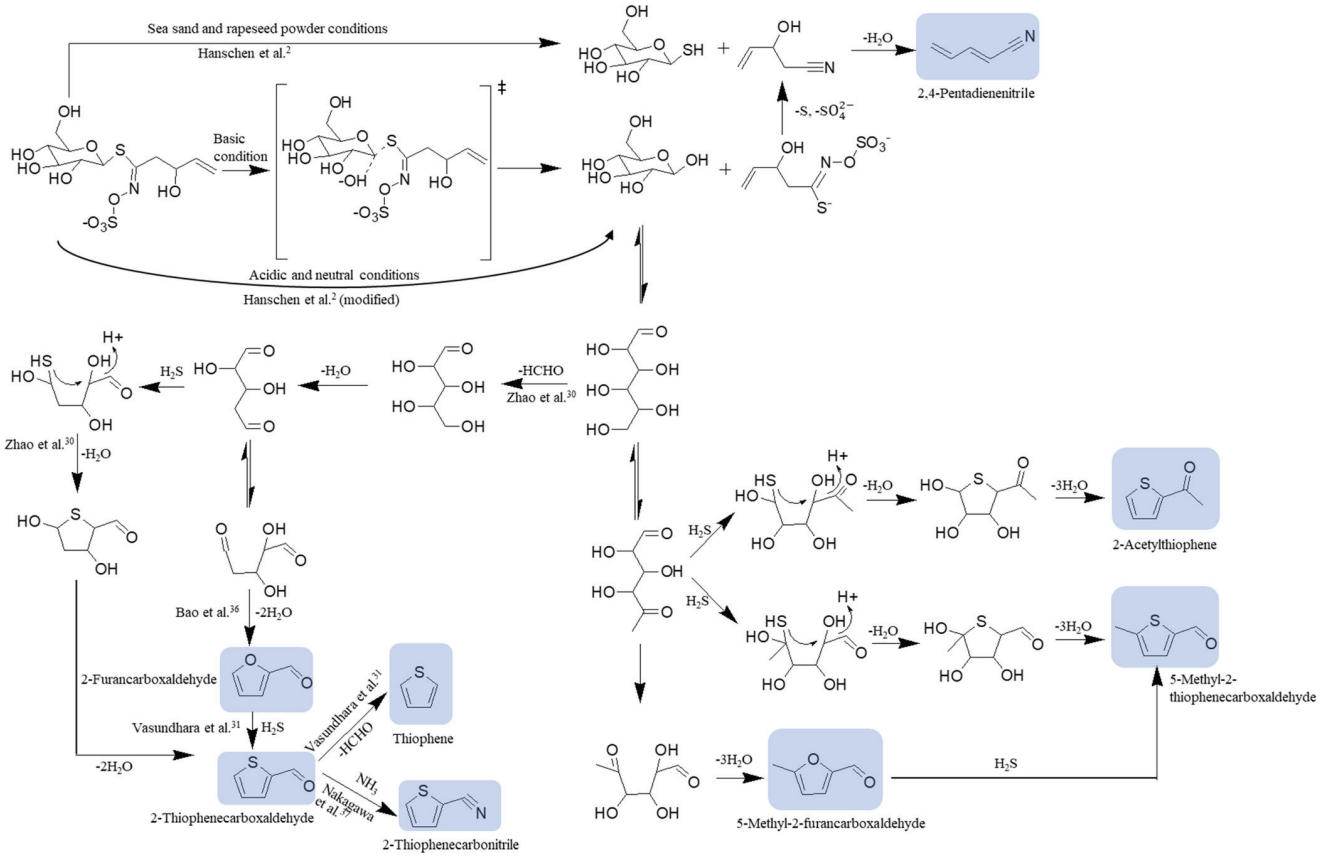

Figure 2. Possible formation pathways of major thermal degradation products of progoitrin.

sulfur atoms. These atoms cause positively charged C1 of the glucosyl moiety. Under aqueous conditions, the hydroxide ions attack the C1 with a back side through S_N2 to form a transition state. In the transition state, the hydroxide ions lead to the charge transfer, which results in the increase of charge density of sulfur and decrease of charge density of oxygen. The breaking of the S−C1 bond and formation of the O−C1 bond happen simultaneously. The reactivity of S_N2 depends on the strength of the nucleophile. Thus, high amounts of hydroxide ions lead to the rapid degradation of glucosinolates under basic conditions due to their high nucleophilicity. When the nucleophile is used as the solvent, S_N2 follows the first-order kinetics. However, the study of Gronowitz et al.[18] showed different results from the present study. They studied the thermal degradation of a glucosinolate mixture (65−70% of progoitrin and 15% of gluconapin) in distilled water at 100 °C for 5 h, resulting in a 64% degradation of the initial glucosinolate contents. Also, they evaluated the degradation of the mixture at 100 °C at pH values of 5, 8, or 10 for 30 min. Thereby, 13, 58, and 15% of the original glucosinolate contents were left. MacLeod and Rossiter[16] assessed the thermal degradation of progoitrin in aqueous solution at 100 °C for 5 h with a 35% degradation of the original progoitrin content. The differences among these results are possibly due to differences in the reaction conditions (e.g., temperature and time).

In the present study, the thermostability of progoitrin heated in sea sand was slightly stronger than that in buffer solution at pH 9.0 but weaker than that in all of the other matrices. Thereby, 48, 14, and 3% progoitrin were left after 5 min of heat treatment at 150, 160, or 170 °C, respectively. However, progoitrin was fully degraded after 5 min at temperatures ≥180 °C. Progoitrin in rapeseed powder was slightly less stable compared to neutral pH conditions. Thereby, the degree of degradation was also enhanced with the increase of temperature and time. At 150 °C, complete degradation of progoitrin was observed after 50 min of heat processing, and at 200 °C, the remaining progoitrin was 22% after 5 min and almost all progoitrin was fully degraded after 10 min. Oliviero et al.[19] reported that the thermal degradation rate constants of glucosinolates in broccoli at 120 °C decreased with the increase of water content (13% > 34% > 56% > 68% > 82%). The glucosinolate in the driest matrix showed the highest degradation rate constant at 120 °C, which resulted from the higher activation energy of the driest sample. Based on the study of Hanschen et al.,[2] more degradation of sinigrin was observed in broccoli sprouts powder than in dry conditions at 130 °C. After 45 min, 78.8% sinigrin was degraded in broccoli sprouts powder. However, Mao et al.[10] found that after roasting for 60 min at 150 °C, the progoitrin content in Zhongyou 821 rapeseed (from Shaanxi province of China) decreased by 28.6% and in Huifeng No. 3 rapeseed (from Gansu province of China) by 85.9%, associated with the rapeseed variety. Thus, the matrix effect is an important factor for these differences.[5]

Influence of Matrices and Conditions on the Generation of Thermal Degradation Products of Progoitrin. A total of 33 volatile flavor compounds were identified during the thermal degradation of progoitrin in different matrices. Among them, the basic conditions produced

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Table 1. Volatile Flavor Products after Thermal Treatment of Progoitrin in Different Matrices[a]

RI[b]	RI[c]	compound	molecular formula	volatiles detected in the matrix[d] pH 5.0	pH 7.0	pH 9.0	sea sand
595	611	2,3-butanedione	$C_4H_6O_2$	+	+	+	–
610	614	acetic acid	$C_2H_4O_2$	–	–	–	tr
666	674	(*Z*)-2-butenal	C_4H_6O	+	+	+	+
675	682	thiophene	C_4H_4S	+	+	+	+
746	748	dimethyl disulfide	$C_2H_6S_2$	tr	tr	–	–
[e]	780	2,4-pentadienenitrile	C_5H_5N	+	+	+	+
790	792	2-hexanone	$C_6H_{12}O$	+	+	+	–
833	839	2-furancarboxaldehyde	$C_5H_4O_2$	+	+	+	+
836	843	2,4-dimethyl-1-heptene	C_9H_{18}	+	+	+	–
866	872	1,3-dimethylbenzene	C_8H_{10}	+	+	+	–
891	891	2-heptanone	$C_7H_{14}O$	+	+	+	+
893	894	styrene	C_8H_8	+	+	+	–
913	908	2-methyl-2-cyclopenten-1-one	C_6H_8O	–	–	+	–
–	951	1,5-hexadien-3-ol	$C_6H_{10}O$	+	+	-	+
962	964	benzaldehyde	C_7H_6O	+	+	+	–
965	969	5-methyl-2-furancarboxaldehyde	$C_6H_6O_2$	–	–	–	+
970	971	1-heptanol	$C_7H_{16}O$	+	+	+	–
986	987	6-methyl-5-hepten-2-one	$C_8H_{14}O$	+	+	+	–
–	999	2-thiophenecarbonitrile	C_5H_3NS	+	+	+	+
1008	1006	2-thiophenecarboxaldehyde	C_5H_4OS	+	+	+	+
1019	1020	2-ethyl-1-hexanol	$C_8H_{18}O$	+	+	+	+
–	1026	2(*5H*)-thiophenone	C_4H_4OS	–	+	–	–
1035	1034	2-acetylpyridine	C_7H_7NO	–	–	+	–
1059	1052	3-methyl-3*H*-1,2-dithiole	$C_4H_6S_2$	tr	tr	+	–
1071	1071	1-octanol	$C_8H_{18}O$	+	+	+	+
1088	1086	2-acetylthiophene	C_6H_6OS	–	–	+	–
1118	1096	5-methyl-2-thiophenecarboxaldehyde	C_6H_6OS	+	–	+	–
–	1108	2,5-dihydrothiophene sulfone	$C_4H_6O_2S$	–	+	–	–
1185	1186	1-(2-thienyl)-1-propanone	C_7H_8OS	–	–	+	–
1214	1217	thieno[3,2-*b*]thiophene	$C_6H_4S_2$	–	–	+	–
1229	1235	benzothiazole	C_7H_5NS	+	+	+	+
–	1269	2-thiophenepropanenitrile	C_7H_7NS	–	–	+	–
–	1270	4-cyanothiophenol	C_7H_5NS	–	–	+	–

[a]Twenty compounds were identified via retention indices (RIs) and mass spectrometry in comparison to authentic reference compounds. The remaining compounds were identified using their RIs and mass spectra that were compared to Wiley 9 mass spectral library (Chichester, U.K.) (Supporting Information). [b]RI from Wiley 9 mass spectra library. [c]Retention index (RI) determined on the DB-5ms stationary phase. [d]+, Volatiles detectable by GC-TOF-MS; –, volatiles not detectable by GC-TOF-MS; tr, trace amount detected (<0.1 μg/kg). [e]Not found in the reference (Wiley 9 mass spectra library).

the largest number of volatiles (27), followed by neutral conditions (23) and acidic conditions (21), while sea sand conditions revealed the lowest number of volatile flavor compounds (Table 1). The volatile products of progoitrin under rapeseed powder conditions were not included in the discussion due to the significant effect of the matrix. Rapeseed powder itself can generate a large amount of volatile compounds under high-temperature heating treatment. Ortner and Granvogl[14] investigated the aroma-active compounds of the thermal degradation of sinigrin in phosphate buffer at pH values of 5.0, 7.0, or 9.0, and sea sand. The quantities of the aroma-active compounds in different matrices decreased by the following order: pH 9 > pH 7 > pH 5 > sea sand. The findings in the present study were consistent with the results of Ortner and Granvogl.[14]

As the major degradation products of progoitrin in the present study, a total of 16 N-containing and S-containing compounds were found, 14 of which were first identified in the thermal degradation substances of glucosinolates (2-acetylpyridine, 2-acetylthiophene, benzothiazole, 4-cyanothiophenol, 2,5-dihydrothiophene sulfone, 3-methyl-3*H*-1,2-dithiole, 3-methyl-2-thiophenecarboxaldehyde, 5-methyl-2-thiophenecarboxaldehyde, thieno[3,2-*b*]thiophene, 1-(2-thienyl)-1-propanone, 2-thiophenecarbonitrile, 2-thiophenecarboxaldehyde, 2-thiophenepropanenitrile, and 2(5*H*)-thiophenone). The effects of temperature and time on N-containing and S-containing degradation products are shown in Figure 3. 2,4-Pentadienenitrile was the main N-containing compound, which was present in all matrices. It was found to be a common volatile compound in rapeseed oil, especially in hot-pressed rapeseed oil, which demonstrated that 2,4-pentadienenitrile was a thermal degradation product of glucosinolates to some extent.[7,20] Also, it has been reported that nitriles are the predominant thermally induced degradation products of glucosinolates.[21,22] Aliphatic glucosinolates can be thermally decomposed to produce the corresponding nitriles and isothiocyanates.[17] Gronowitz et al.[18] reported that (*R*)-l-cyano-2-hydroxy-3-butene was the main thermal (100 °C) degradation nitrile of progoitrin. MacLeod and Rossiter[16] also found that progoitrin was thermally (100 °C) decomposed to

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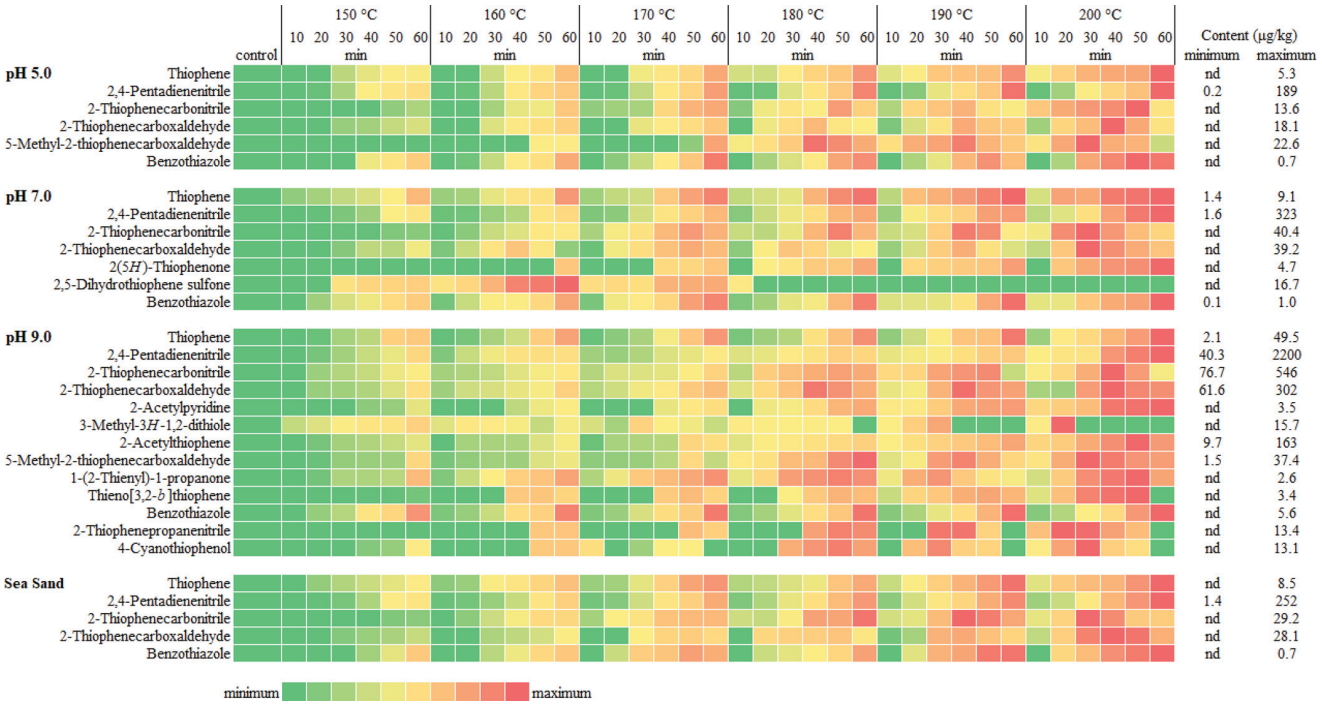

Figure 3. Effects of matrices and conditions on the volatile S-containing and N-containing products (nd: not detectable).

generate L-cyano-2-hydroxy-3-butene during gas chromatography. However, in the present study, L-cyano-2-hydroxy-3-butene was not found in any matrix. This difference might result from the applied conditions (e.g., temperature). Mao et al.[10] studied the volatiles of oil from progoitrin-rich rapeseed during roasting at 150 °C. They found 17 volatile nitriles, which also did not include L-cyano-2-hydroxy-3-butene. The results indicated that under the applied conditions in this study, 2,4-pentadienenitrile was the major nitrile formed from progoitrin during thermal degradation at high temperatures compared to L-cyano-2-hydroxy-3-butene. It could be inferred that during the thermal treatment, progoitrin was first degraded to L-cyano-2-hydroxy-3-butene, which might be unstable due to the presence of the hydroxyl group and a double bond. The elimination of the hydroxyl group and formation of a double bond at C-2 occurs at elevated temperatures (≥150 °C).[10] In this study, the highest content of 2,4-pentadienenitrile was found under basic conditions (40.3−2200 μg/kg), followed by neutral (1.6−323 μg/kg) and sea sand (1.4−252 μg/kg) conditions, while the lowest content was present under acidic conditions (0.2−189 μg/kg). In all matrices, the 2,4-pentadienenitrile concentration increased with the increase of temperature and time. In the study of Gronowitz et al.,[18] basic conditions achieved greater L-cyano-2-hydroxy-3-butene yields than neutral and acidic conditions during the thermal degradation of progoitrin. Hanschen et al.[2] also reported that more nitriles (e.g., 3-butenylnitrile) were formed under basic conditions compared to acidic conditions in the thermally induced degradation of sinigrin. 2-Acetylpyridine was only present under basic conditions and its content increased with temperature and time in the range between not detectable (nd) and 3.5 μg/kg. It was reported to be an aroma compound (nutty and roasty) in cold-pressed rapeseed oil but finally did not contribute to the overall aroma of rapeseed oil according to the odor activity value.[23]

For S-containing compounds, dimethyl disulfide was found in phosphate buffer at pH values of 5.0 and 7.0. Although it has a very low content, due to its low odor threshold in oil (44 μg/kg), it can have a high contribution to flavor. Consequently, it was reported as an aroma-active compound in rapeseed oil in previous studies.[4,11] Dimethyl disulfide can be generated from methionine through disproportionation.[24] Jin et al.[25] studied the thermally induced degradation of 1-isothiocyanato-4-(methylsulfinyl)butane (sulforaphane) in aqueous solution, which was the breakdown product of 4-methylsulfinylbutyl-glucosinolate (glucoraphanin). Dimethyl disulfide was also detected as the thermal degradation product in their study. Allyl methyl sulfide, diallyl sulfide, and diallyl disulfide were found to be aroma-active thermal degradation compounds of sinigrin based on the study of Ortner and Granvogl.[14] Diallyl sulfide and diallyl disulfide were formed by the thermal treatment of allyl isothiocyanate for 1 h at 100 °C according to the results of Chen and Ho.[26] Allyl isothiocyanate is known to originate from the breakdown of sinigrin, contributing to the pungent flavor.[2] Interestingly, Ortner and Granvogl[14] did not find this aroma-active compound in their study. No isothiocyanate was found in the present study either. MacLeod et al.[21] reported that isothiocyanates appeared at a higher temperature (150 °C) during the heat treatment of sinigrin, benzylglucosinolate, and 2-phenethylglucosinolate. However, when it comes to the plant system, nitriles were reported to be the predominant thermal breakdown products, and isothiocyanates were only determined at a relatively low temperature of 100 °C and disappeared at higher temperatures.[13] In the processing of rapeseed, contents of isothiocyanates were higher at a low-temperature treatment (<100 °C), which was considered to be mainly derived from the reaction of enzymatic hydrolysis of glucosinolates.[4,9] Overall, further studies to elucidate the formation of isothiocyanates in the thermal degradation of glucosinolates are desirable.

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Thiophenes are another class of volatile S-containing compounds, also detected in the applied matrices in the present study, revealing a total of 9 thiophenes (2-acetylthiophene, 5-methyl-2-thiophenecarboxaldehyde, thieno[3,2-*b*]thiophene, 1-(2-thienyl)-1-propanone, thiophene, 2-thiophenecarbonitrile, 2-thiophenecarboxaldehyde, 2-thiophenepropanenitrile, and 2(5*H*)-thiophenone) as thermally induced breakdown products of progoitrin. 2-Thiophenepropanenitrile was present in phosphate buffer at pH values of 5.0, 7.0, and 9.0, and sea sand conditions as the main thiophene; the concentration was nd−13.6, nd−40.4, 76.7−546, and nd−29.2 μg/kg. In addition, thiophene was detected in all matrices, responsible for the roasty flavor. The content of thiophene in phosphate buffer at pH values of 5.0, 7.0, and 9.0, and sea sand conditions was nd−5.3, 1.4−9.1, 2.1−49.5, and nd−8.5 μg/kg, which increased with the temperature and time during thermal processing. 2-Thiophenecarboxaldehyde was found in all matrices with the content of nd−18.1, nd−39.2, 61.6−302, and nd−28.1 μg/kg for pH 5.0, 7.0, and 9.0, and sea sand conditions. 5-Methyl-2-thiophenecarboxaldehyde was found at pH values of 5.0 and 9.0. Both 2-thiophenecarboxaldehyde and 5-methyl-2-thiophenecarboxaldehyde increased with the increase of heating time and temperature at the initial stage and then experienced a slight decrease at higher temperatures with longer time, which might be due to the decomposition or polymerization under harsh reaction conditions. 2(5*H*)-Thiophenone (nd−4.7 μg/kg) was only found at a pH value of 7.0. In contrast, 2-acetylthiophene (9.7−163 μg/kg), thieno[3,2-*b*]thiophene (nd−3.4 μg/kg), 1-(2-thienyl)-1-propanone (nd−2.5 μg/kg), and 2-thiophenepropanenitrile (nd−13.4 μg/kg) were only detected at a pH value of 9.0. Thiophenes were identified in many systems such as meat (beef, chicken meat, pork), coffee, peanut, popcorn, onion, black tea, and so on.[27] Thiophene, 2-thiophenecarboxaldehyde, 5-methyl-2-thiophenecarboxaldehyde, and thieno[3,2-*b*]-thiophene were found in the peptide−xylose Maillard reaction model system according to the results of Xu et al.[28] The generation of thiophenes was also reported in the Maillard reaction model system including carbohydrates and different sources of sulfur (e.g., cysteine and glutathione).[29] Zhao et al.[30] suggested two possible formation pathways of thieno[3,2-*b*]thiophene in a glutathione−glucose reaction with fat. To date, there have been few reports on the formation of thiophenes from glucosinolates. Only one manuscript reported that thiophene (onion-like), 2-methyltetrahydrothiophen-3-one (garlic-like), 2-thiophenecarboxaldehyde (earthy, burnt), and 2-acetylthiophene (roasty, sulfury) were found to be aroma-active products of the thermal degradation of sinigrin.[14] In the pathway proposed by Vasundhara et al.,[31] thiophene could be generated by the reaction of 2-furancarbaldehyde and hydrogen sulfide. Thiophene derived from a thermal reaction model system of D-glucose−hydrogen sulfide−ammonia was also reported by Shibamoto and Russell.[32] Lanzani et al.[15,33] reported that the thermal degradation products of progoitrin after 3 h at 100 °C were 2,3-pentadienoic acid, 1-amino-butadiene, and 1-amino-2-hydroxybut-3-ene, which were not found in the present study; different reaction conditions could be one of the reasons. In addition, these S-containing (e.g., hydrogen sulfide) and N-containing (e.g., ammonia) compounds might provide sources of sulfur and nitrogen to further react with D-glucose to generate thiophenes.

2-Furancarboxaldehyde and (*Z*)-2-butenal were found in all matrices, and 5-methyl-2-furancarboxaldehyde was detected under sea sand conditions. They were suggested to originate from glucose.[34,35] 2,3-Butanedione was present in phosphate buffer at pH values of 5.0, 7.0, and 9.0 with the butter-like smell, which was also reported in the thermal degradation of sinigrin.[14] It is known to be formed via an Aldol reaction of acetaldehyde and hydroxyacetaldehyde, which are products of carbohydrate degradation. There were some volatile alkenes, ketones, alcohols, and aromatic compounds with carbon numbers >6, which might result from rearrangement or polymerization reactions at high temperatures.

Possible Formation Pathways of Main Thermal Degradation Products of Progoitrin. Figure 2 presents possible formation pathways of the main thermal degradation products of progoitrin. As it can be seen, progoitrin might mainly experience an S_N2 reaction, which could explain the rapid thermal degradation of progoitrin under basic conditions. Progoitrin is degraded to yield glucose and thiohydroxymate-*O*-sulfonate that spontaneously loses sulfate and rearranges to the corresponding nitrile (L-cyano-2-hydroxy-3-butene) in aqueous matrices. Hanschen et al.[2] suggested that aliphatic glucosinolates degrade to 1-thio-β-D-glucose and the corresponding nitrile under dry conditions. 1-Cyano-2-hydroxy-3-butene loses the hydroxyl group to form 2,4-pentadienenitrile. As mentioned above, hydrogen sulfide (H_2S) and ammonia (NH_3) were found to be thermal degradation products of progoitrin heat-processed at 100 °C for 3 h based on the studies of Lanzani et al.[15,33] Moreover, as products of aliphatic glucosinolates, aliphatic isothiocyanates can generate an unstable *O*-thiocarbamic acid, which is degraded quickly to form carbonyl sulfide and the corresponding amine, and further form H_2S and carbon dioxide.[5] Glucose undergoes a reaction to form a carbohydrate module with a C-5 glucose fragment, which reacts with H_2S by cyclization to form 2-thiophenecarboxaldehyde.[30] The C-5 glucose fragment can also form 2-furancarbaldehyde by a cyclization reaction and then produce 2-thiophenecarboxaldehyde and thiophene via a reaction with H_2S.[31,36] Nakagawa et al.[37] reported that aldehydes could react with NH_3 via dehydration and oxidation to form nitriles. Therefore, 2-thiophenecarboxaldehyde might form 2-thiophenecarbonitrile by reacting with NH_3. In addition, H_2S might react with the carbonyl group at C1 of glucose and then form 2-acetylthiophene and 5-methyl-2-thiophenecarboxaldehyde by dehydration and cyclization. Besides, 5-methyl-2-furancarboxaldehyde might also be formed from glucose by cyclization and then form 5-methyl-2-thiophenecarboxaldehyde by reacting with H_2S, according to the study of Vasundhara et al.[31]

In summary, the results of the present study could provide data and theoretical basis for the flavor control of glucosinolate-containing raw material (e.g., rapeseed and mustard seed) under thermal treatment at elevated temperatures (>150 °C). Further isotopic labeling studies are desirable to verify the pathways of the thermal degradation of progoitrin and other glucosinolates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.1c04415.

Mass spectra of the compounds in the sample and corresponding standards for identification purposes (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HPLC, high-performance liquid chromatography; HS-SPME-GC-TOF-MS, headspace-solid phase microextraction-gas chromatography-time-of-flight-mass spectrometry; LOD, limit of detection

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Concluding Remarks and Outlook

1. Scientific Progress

This thesis provided a useful decision tool for flavor decoding in oil matrix. The relationship between the roasting process and the flavor formation of hot-pressed rapeseed oil was analyzed and clarified, whereby the main odorants and aroma profiles were given. The pyrolysis mechanism of 2-hydroxy-3-butenyl glucosinolate (an important flavor precursor in rapeseed) was addressed.

A systematic comparison of five flavor trapping techniques for decoding flavor in oil matrix was conducted in the first part. In DTD, acids accounted for the largest proportion of the total volatile compounds (39%), especially for fatty acids (e.g., hexanoic acid, myristic acid, and n-hexadecanoic acid), which might due to a considerable amount of released free fatty acid under high temperature. SPME and SPME-Arrow showed similar percentages in the aldehydes, ketones, alcohols, heterocyclic compounds, and nitriles. The acids proportion from HSSE was the lowest compared with other methods, but its peak area was higher than ones extacted by SPME and SPME-Arrow, which can be completely attributed to the higher thickness of PDMS film in SBSE. SAFE extracts showed the highest proportions in alcohols (8.15%), *S*-containing compounds (3.11%), nitriles (59.33%), and alkenes (2.15%), compared with other techniques. In the aroma analysis of FRO, SAFE had the highest number of odorants (32), followed by HSSE (30), SPME-Arrow (29), SPME (25), and DTD (14). Thirty-one standards were used for the comparison of linearity, recovery, and repeatability of these five methods. SPME-Arrow showed the best performance in linearity, recovery, and repeatability followed by SPME, HSSE, DTD, and SAFE. The most efficient flavor extraction method for hot-pressed rapeseed oil, taking into account the cost/performance ratio, could be SPME.

In the second part, the Sensomics approach was performed including HS-SPME-GC-O-MS, AEDA, OAVs calculations, and aroma recombination to determine key odorants of representative FRO. Key odorants based on the results of GC-O-MS combined with AEDA and OAVs ($\geq$ 1) were hexanal, 3-butenenitrile, 1-octene-3-one, 2,5-dimethylpyrazine, dimethyl trisulfide, 2-ethyl-6-methylpyrazine, nonanal, trimethylpyrazine, (*E*)-2-octenal, 3-ethyl-2,5-dimethylpyrazine, acetic acid, 4-isothiocyanato-1-butene, (*E*,*E*)-2,4-heptadienal, 5-methyl-2-furancarboxaldehyde, butanoic acid, (*E*)-2-decenal, 2-furanmethanol, (*E*,*E*)-2,4-nonadienal, and (*E*,*E*)-2,4-decadienal. 3-Butenenitrile and 4-isothiocyanato-1-butene belong to glucosinolate degradation products, which were a special kind of odorants existing in rapeseed

oil. The nutty sensory attribute was from pyrazines and aldehydes, and furans mainly produced the caramel-like fragrance. The roasty odor mainly resulted from pyrazine compounds. 3-Butenenitrile and 4-isothiocyanato-1-butene mainly contributed to a pungent odor. Dimethyl trisulfide (OAV, odor activity value, 323, cabbage-like, sulfury) and 4-isothiocyanato-1-butene (OAV, 88, pungent) were the most important aroma-active compounds in FRO.

Then, a comparative characterization of key odorants and aroma profiles of oil from roasted rapeseed under varied temperature-time conditions (150-200 ºC, 0-60 min) was conducted. Under the designed set-up with broad roasting parameters, most of the aroma substances except hexanal, nonanal, and (*E*)-2-octenal showed first rising and then decline trends as the roasting process progressed under temperatures no less than 150 ºC. In the early stage of roasting (10-20 min), the overall flavor intensity of rapeseed oil samples was low, and the cabbage-like, fatty, and pungent flavor were major sensory attributes of the oil. As the roasting temperature and time continuously increased, fatty, cabbage-like, and pungent smelling became more intense with increasing contents of aroma-active aldehydes and *S*-containing compounds (e.g., (*E*,*E*)-2,4-decadienal, dimethyl trisulfide, and 4-isothiocyanato-1-butene). At 160 ºC/60 min, 170 ºC/50 min, and 180 ºC/40 min, roasty, nutty, caramel-like, and burnt fragrance began to dominate the overall flavor.

At last, the thermal degradation behavior and products of the progoitrin ((*R*)-2-hydroxybut-3-enylglucosinolate as a main glucosinolate of rapeseed) were studied in various matrices under designed conditions. As the major degradation products of progoitrin in the present study, a total of 16 *N*-containing and *S*-containing compounds were found. 2,4-Pentadienenitrile was the major nitrile formed from progoitrin compared to l-cyano-2-hydroxy-3-butene under the applied conditions in this study. It is speculated that progoitrin was first degraded to l-cyano-2-hydroxy-3-butene which might be unstable due to the presence of the hydroxyl group and a double bond. The elimination of the hydroxyl group and formation of a double bond at C-2 occurs at elevated temperatures (≥ 150 °C). The degradation rate of progoitrin decreased in the following order: pH 9.0 > sea sand > rapeseed powder > pH 7.0 > pH 5.0. Progoitrin might mainly experience an S_N2 reaction, which could explain the rapid thermal degradation of progoitrin under basic conditions. The degradation product of progoitrin, hydrogen sulfide can be used as a source of sulfur, which could be further combined with glucose to generate thiophenes. Possible formation pathways of the main thermal degradation products of progoitrin were proposed.

2. Application options

FRO is a kind of hot-pressed rapeseed oil that suffers no additional refining process except for sedimentation or filtration. The lower degree of refining helps to retain more aroma and bioactive components. Logically, the compositions of hot-pressed rapeseed oil are more complex than that of fully refined oil. As a kind of so-called “solvent”, oil including some components (e.g., phospholipids, free fatty acids, phenolic compounds, etc.) would influence the distribution and volatilization of volatile substances through binding, known as “matrix effect”, which makes the decoding flavor a challenge. The results of Chapter II provided a good reference for the flavor quality monitoring of virgin oil in the industry. Taking cost/performance ratio into account, SPME is still an efficient flavor extraction method.

In practical production, the temperature of roasting seeds during FRO processing is generally more than 150 ºC, and some manufacturers even use 200 ºC for roasting. In Chapter III, drastic roasting conditions were used. Under dedicated control of roasting processing, roasted rapeseed oils under high-temperature-short time and low-temperature-long time conditions could exhibit similar pleasant aroma profiles, which could provide a reference for industrial FRO production achieving not only target modulation of the aroma but also sustainable production in the near future.

Thermal degradation is the main glucosinolates degradation pathway in the production of hot-pressed rapeseed oil during the roasting process (at least 150 °C) in the industry due to the fast inactivation of myrosinase at high temperatures, which generates volatile nitriles, isothiocyanates, and other volatile substances. The *Brassica napus* seed is the most predominantly used material for the industrial production of rapeseed oil, and progoitrin is the main glucosinolate of *Brassica napus* seed. Results of Chapter IV provided data and theoretical basis for the modulation of volatile glucosinolate degradation compounds of hot-pressed rapeseed oil in industrial production to obtain oils with the desired flavors.

3. Outlook

3.1 Development of technology to obtain a “complete” aroma profile of rapeseed oil

Much work has been performed on analytical techniques to reveal key odorants of rapeseed oil, but much remains to be done. It is still a challenge to couple the instrumental data with the sensory data and obtain a “complete” aroma profile of rapeseed oil. Some key trace aroma-active compounds (especially related to off-flavor) need to be further identified. Multi-method combination of flavor capturing techniques might also be an option of aroma analysis for oil matrix. The future instrumental techniques will impose increasing demands on accuracy,

precision, sensitivity, time-saving, portability, and real-time monitoring. Differences also exist in the consumer expectation of “good” sensory rapeseed oils from different regions due to different dietary habits and preferences, which warrants further investigation. Also, data processing with various chemometric methods and data visualization needs to be carried forward to communicate the complexity of the aroma information about rapeseed oil without losing its richness and depth.

3.2 Further research on aroma release and aroma interaction with oil matrix

The key aroma substances of FRO constitute the main aroma profile of FRO, but the existence of some non-key aroma compounds and their synergistic effect with key odorants might also produce differences between aroma profiles of the original sample and the corresponding recombinant. In addition, the difference between the matrix compositions of the original sample and the corresponding recombinant would also affect the release and perception of aroma substances, resulting in their specific aroma profiles. More and more studies have shown that the aroma characteristics of food are not formed by the simple addition of various odorants, and the interaction law of different aroma substances in rapeseed oil needs to be further studied.

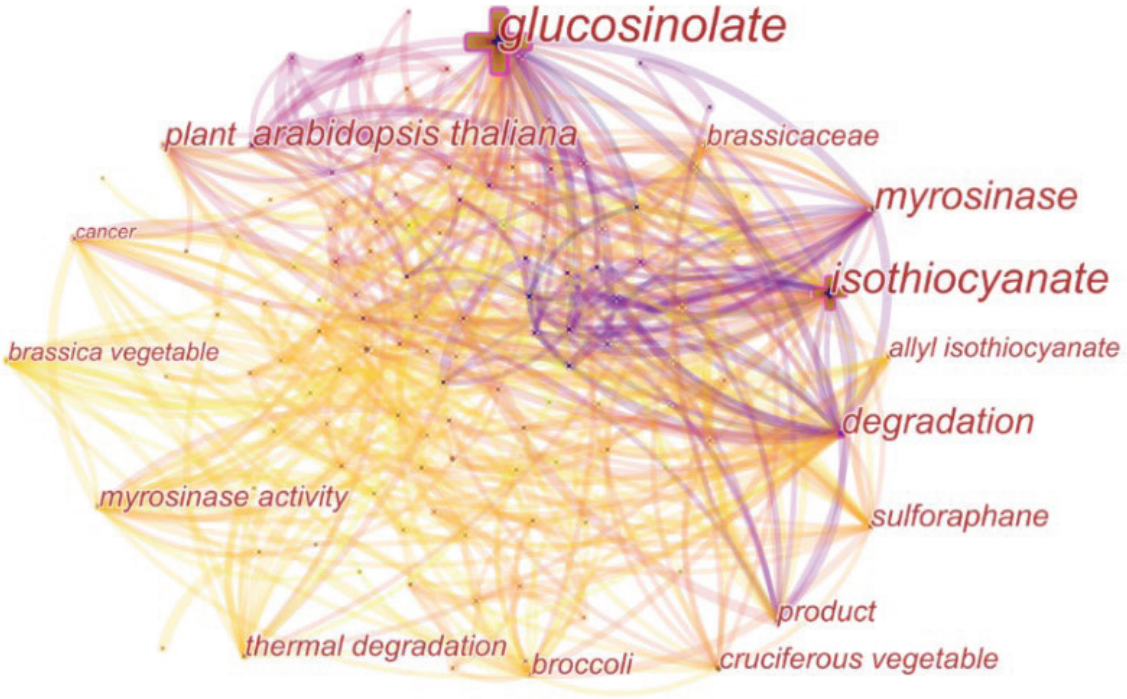
3.3 Further validation of the aroma changes in actual production

Comparative characterization of key odorants and aroma profiles of oil from roasted rapeseed under varied temperature-time conditions (150-200 ºC, 0-60 min) was studied by application of aroma profile analysis and HCA. However, the material was studied at the laboratory scale, which is lower than 10% of the lowest actual scale of production. Further validation of the actual production needs to be conducted.

3.4 Further validation of the thermal degradation pathway of glucosinolate

Enzymatic degradation of glucosinolates has been intensively reviewed during the last decade, while nonenzymatic and thermal degradation also need to be considered [1]. So far, it was believed that isothiocyanates were mainly formed upon enzymatic hydrolysis of glucosinolates through myrosinase [2]. However, relatively large quantities of both isothiocyanates and nitrile have been observed when heating glucosinolates on a gas chromatography column at high temperatures (200ºC), and isothiocyanates formation was thought to be favored by greater heat [3]. On the contrary, another study revealed that relative isothiocyanate contents decreased with increasing thermal impact. In contrast to the nitriles, isothiocyanates are also considered to be thermolabile and degrade in aqueous solution [4]. Effects of thermal treatment on glucosinolates and the formation and fate of their breakdown products are still far away from

being sufficiently understood because of the various impact parameters (e.g., water content, matrix, metal ion, ascorbic acid, pH value, and temperature) [4, 5]. A more thorough exploration of the mechanisms of isothiocyanates formation from different single glucosinolates via thermally induced degradation with different reaction conditions is still required. The thermal degradation pathway of progoitrin was proposed in my previous work, which is based on the degradation products under the applied conditions [6]. Further isotopic labeling studies are desirable to verify the pathways of the thermal degradation of progoitrin and other glucosinolates. Moreover, the glucosinolates degradation matrix used in my previous work only employed the phase state and pH, more influencing factors should be considered to make the



models closer to the real plant system.

Figure 2 Keyword co-occurrence network map

DTD is a volatile capturing technique that involves placing sample into a small vial within a thermal desorption tube. The sample is heated in a thermal desorption unit under a flow of inert gas, then volatile compounds are trapped by a cooled injection system and finally determined by GC-MS. DTD requires little sample preparation and can be conducted automatically by a dynamic headspace sampling system. Remarkably, during sample introduction, we have full control over the temperature program and pneumatic program via this method, which can simulate the behavior of the sample at high temperature (up to 450 ºC) [7]. DTD is considered be used as a reactor of glucosinolate thermal degradation for the first time, allowing the reaction to occur directly at the injection port. The reaction and product collection can be proceeded

simultaneously, avoiding the loss caused by multiple transfers and extraction of the products. Precise control of conditions and real-time analysis of volatile pyrolysis products would be also achieved.

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