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**Study of the Effect of Raw Material and Processing on Safety and Flavor of Peanut Oil**

Hui HU

Dissertation originale présentée en vue de l’obtention du grade de docteur en **s**ciences agronomiques et ingénierie biologique

Promoteurs: Prof. Marie Laure FAUCONNIER - Prof. Qiang WANG

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**Abstract**

Oil plays important role in human daily diet. Global vegetable oil production reaches 211.44 million metric tons in 2021/22. Peanut oil is the most representative oil with better flavor and rich micronutrients. The potential chemical toxicants and characteristic volatiles of peanut oil has attracted research attention. But there is still contradiction on toxicants occurrence and limitation on flavor improvement technology. The aim of this research was to investigate the effect of raw material and processing on safety and flavor of peanut oil.

Firstly, the occurrence of trans fatty acids (TFA) and fatty acid esters of 3-monochloropropane-1,2-diol (3-MCPDE) in different edible oils collected from industrialized production line in China factory were evaluated. Corn oil, soybean oil, peanut oil and palm oil were selected as representative edible oil. TFA is widely present at relatively low levels (0.37-2.61g/100g) in edible oil collected from factory in China. 3-MCPDE are only formed in the deodorization procedure during oil processing. Palm oil has the highest 3-MCPDE content (3750.5±177.3 μg/kg). No 3-MCPDE was detected in peanut oil. The chloride precursor and mitigation method of 3-MCPDE were also studied. The effect of chlorine in different peanut varieties on 3-MCPDE formation was limited. The added salt in baking could significantly promoting the 3-MCPDE formation. Fructose and lactose could remove 35.13% and 36.99% 3-MCPDE, respectively.

Secondly, the characteristic volatile compounds of low- and high-temperature pressed peanut oil were determined by using HS-SPME-GC-MS and e-nose. Seventy-one volatiles were identified in high-temperature pressed peanut oil (HPOs), mainly including pyrazines, pyrroles and ketones, of which characteristic volatiles present nutty and roasty flavor. Fifty-two volatiles were obtained from low-temperature pressed peanut oil (LPOs), mainly consisting of aldehydes, alcohols and carboxylic acids, of which characteristic volatiles show green and fresh flavor. The characteristic volatile of HPOs and LPOs have also been determined. The results indicated that the process method has a significant effect on the flavor components of peanut oil.

Thirdly, the feasibility of using microwaves (MW) pretreatment as an improvement method for cold-pressed peanut oil processing was investigated. The acid value and peroxide value of extracted oil from MW-treated peanuts were slightly increased but far below the limit in the Codex standard. Compared with the untreated sample, a significant (p < 0.05) increase in extraction yield (by 33.75%), free phytosterols content (by 32.83%), free tocopherols content (by 51.36%) and induction period (by 168.93%) of oil extracted from 5 min MW-treated peanut were observed. MW pretreatment formed pyrazines which contribute to improving the nutty and roasty flavor of oil. MW pretreatment is a feasible method to improve the oil extraction yield and obtain the cold pressed peanut oil with longer shelf life and better flavor.

Finally, the key volatile compounds and precursors of high-temperature pressed peanut oil prepared with normal- and high-oleic peanuts were studied. Sensory evaluation results indicated that normal-oleic peanut oil showed stronger characteristic flavor than high-oleic peanut oil. The compounds methylpyrazine, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine and benzaldehyde were considered as key volatiles which contribute to dark roast, roast peanutty and sweet aroma of high-temperature pressed peanut oil. The initial concentration of volatile precursors (arginine, tyrosine, lysine and glucose) in normal-oleic peanut was higher than in high-oleic peanut, which led to more characteristic volatiles forming during process and provided a stronger oil aroma of.

This research will provide data support for raw material screening and quality improvement during peanut oil industrial production.

**Keywords:** peanut oil, trans fatty acid, esters of 3-monochloropropane-1,2-diol, volatile, microwave

Résumé :

Les huiles végétales jouent un rôle important dans l'alimentation quotidienne de l'homme. La production mondiale d'huile végétale atteindra 211,44 millions de tonnes métriques en 2021/22. L'huile d'arachide est une huile végétale majeure car elle présente une saveur intéressante et est riche en micronutriments. Les composés chimiques toxiques potentiels (acides gras trans et esters d'acides gras du 3-monochloropropane-1,2-diol) et les substances volatiles caractéristiques de l'huile d'arachide ont attiré l'attention des chercheurs. Mais il persiste des points d’ombre relatifs à la présence de substances toxiques et à des limitations technologiques visant à améliorer l'arôme. L'objectif de cette recherche était d'étudier la formation de composés indésirables et la qualité organoleptique de celle-ci en lien avec les procédés technologiques de fabrication de l'huile d'arachide.

Tout d'abord, la présence de TFA et de 3-MCPDE dans différentes huiles comestibles collectées sur une ligne de production industrialisée en Chine a été évaluée. L'huile de maïs, l'huile de soja, l'huile d'arachide et l'huile de palme ont été sélectionnées comme huiles comestibles représentatives. Le TFA est largement présent à des niveaux relativement faibles (0,37-2,61g/100g) dans les huiles comestibles collectées dans les usines chinoises. Les 3-MCPDE ne sont formés que lors de la procédure de désodorisation pendant le traitement de l'huile. L'huile de palme présente la teneur en 3-MCPDE la plus élevée (3750,5±177,3 μgkg-1). Aucun 3-MCPDE n'a été détecté dans l'huile d'arachide. Le précurseur de chlorure et la méthode d'atténuation du 3-MCPDE ont également été étudiés. L'effet du chlore dans différentes variétés d'arachide sur la formation de 3-MCPDE était limité. L'ajout de sel dans la cuisson peut promouvoir de manière significative la formation de 3-MCPDE. Le fructose et le lactose peuvent éliminer 35,13% et 36,99% de 3-MCPDE, respectivement.

Deuxièmement, les composés volatils caractéristiques de l'huile d'arachide obtenue par pression à basse et à haute température ont été déterminés en utilisant l’HS-SPME-GC-MS et un nez électronique. 71 composés volatils ont été identifiés dans l'huile d'arachide pressée à basse et haute température, comprenant principalement des pyrazines, des pyrroles et des cétones, dont les composés volatils caractéristiques présentent un goût de noix et de grillé. Cinquante-deux substances volatiles ont été obtenues à partir des huiles pressées à basse pression, principalement des aldéhydes, des alcools et des acides carboxyliques, dont les substances volatiles caractéristiques présentent une saveur verte et fraîche. Les volatils caractéristiques des huiles pressées à haute pression et des huiles pressées à basse pression ont également été déterminés. Les résultats indiquent que la méthode de traitement a un effet significatif sur les composants de la saveur de l'huile d'arachide.

Troisièmement, la faisabilité de l'utilisation du prétraitement par micro-ondes comme méthode d'amélioration du traitement de l'huile d'arachide pressée à froid a été étudiée. L'indice d'acide et l'indice de peroxyde de l'huile extraite des arachides traitées aux micro-ondes ont été légèrement augmentés mais bien en dessous de la limite de la norme Codex. Par rapport à l'échantillon non traité, une augmentation significative (p < 0,05) du rendement d'extraction (de 33,75 %), de la teneur en phytostérols libres (de 32,83 %), de la teneur en tocophérols libres (de 51,36 %) et de la période d'induction (de 168,93 %) de l'huile extraite d'arachides traitées au MW pendant 5 minutes a été observée. Le prétraitement au MW a formé des pyrazines qui contribuent à améliorer le goût de noix et de grillé de l'huile. Le prétraitement au MW est une méthode réalisable pour améliorer le rendement d'extraction de l'huile et obtenir une huile d'arachide pressée à froid avec une durée de conservation plus longue et une meilleure saveur.

Enfin, les principaux composés volatils et précurseurs de l'huile d'arachide pressée à haute température préparée avec des arachides à teneur normale et élevée en acide oléique ont été étudiés. Les résultats de l'évaluation sensorielle ont indiqué que l'huile d'arachide à teneur normale en acide oléique présentait une saveur caractéristique plus forte que l'huile d'arachide à teneur élevée en acide oléique. Le méthylpyrazine, 2,5-diméthylpyrazine, 2-éthyl-5-méthylpyrazine et benzaldéhyde ont été considérés comme les principaux composés volatils qui contribuent à l'arôme de torréfaction, d'arachide torréfiée et de douceur de l'huile d'arachide pressée à haute température. La concentration initiale des précurseurs de composés volatils (arginine, tyrosine, lysine et glucose) dans l'arachide à teneur normale en acide oléique était plus élevée que dans l'arachide à teneur élevée en acide oléique, ce qui a entraîné la formation de composés volatils typiques au cours du processus et a donné un arôme d'huile plus intense.

Cette recherche fournira des données pour l’évaluation de la qualité des matières premières et l'amélioration de la qualité pendant la production industrielle d'huile d'arachide.

Mots clés : huile d'arachide, acide gras trans, esters de 3-monochloropropane-1,2-diol, volatils, micro-ondes.

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# Abbreviations

|  |  |
| --- | --- |
| Abbreviation | Full name |
| TFA | Trans fatty acid |
| 3-MCPDE | Fatty acid esters of 3-monochloropropane-1,2-diol |
| GC-MS | Gas Chromatography Mass Spectrometry |
| HPLC | High-Performance Liquid Chromatography |
| NPO | Normal peanut oil |
| HOPO | High-oleic peanut oil |
| LPO | Low-temperature pressed peanut oil |
| HPO | High-temperature pressed peanut oil |
| MW | Microwave |

# CHAPTER Ⅰ

# *General introduction*

**1. Context**

Oil supplies energy, fat soluble vitamins (vitamins A, D and E) and essential fatty acids which play important role in human daily diet (Krauss et al., 2000). Global vegetable oil production reaches 211.44 million metric tons in 2021/22. Among of them, the production of peanut oil was 6.50 million tons, among which approximately 50% was produced in China (USDA, 2022).

The safety quality of edible oil is closely related to people’s health. Trans fatty acids (TFA) and fatty acid esters of 3-monochloropropane-1,2-diol (3-MCPDE) are two kinds of processing-induced chemical toxicants which have been detected in refined edible oils. There are many researches focus on the analytical methods, occurrence, toxicities, formation mechanism and mitigation strategies of TFA and 3-MCPDE (Gao et al., 2019; Kiralan et al., 2021). Flavor is the most important sensory quality of edible oil, which is highly related to consumer preference. Compared with other edible vegetable oils, aromatic roasted peanut oil obtained by thermal processing is more popular for consumers because of its strong nutty and roasty flavor (Hu et al., 2019). Correlation of volatile compounds to peanut sensory evaluation has attracted researcher’s attention.

However, the content of TFA and 3-MCPDE in different edible oils showed diversely levels from different country (USA, Brazil, et al). For 3-MCPDE, the chlorine precursors are still contradictive. And most of the reported formation and mitigation strategies are focus on the oil processing, but ignores further cooking process. Flavor is the most important sensory quality of edible oil. Peanut oil is the most representative oil with characteristic flavor. The studies on the characteristic volatile compounds and precursors of low- and high-temperature pressed peanut oil are still lack. The industrial problems of peanut oil flavor stability have not been solved effectively.

In order to reflect the real production situation, it is necessary to monitor the occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line. The chloride precursor and mitigation method of 3-MCPDE during cooking process need to be further investigated. The characteristic volatile compounds and its precursors of low- and high-temperature pressed peanut oil need to be determined. The industrializable technology for improving peanut oil flavor need to be established.

**2. Objectives**

The overall objective of this research was to investigate the effect of raw material and processing on safety and flavor of peanut oil.

Sub-objectives are targeted:

1. To assess the TFA and 3-MCPDE occurrence in different edible oils which produced industrially;
2. To investigate the chloride precursor of 3-MCPDE and determine mitigation method during the cooking process.
3. To determine the characteristic volatile compounds of low- and high-temperature pressed peanut oil;
4. To explore an industrializable technology for improving the characteristic flavor and of low-temperature pressed peanut oil;
5. To investigate the characteristic volatile and its precursor of high-temperature pressed oil produced industrially by normal- and high-oleic peanut.

**3. Research strategy**

The first part of the thesis consists of a literature review (**Chapter 2**) summarizing the occurrence, toxicities, regulation, formation and control strategies of TFAs and 3-MCPED in edible oil. It also highlights the flavor and sensory analysis of edible oil. The effect of processing on peanut oil flavor, and changes in precursor chemistry were reviewed.

In the experiment part, **Chapter 3** was mainly conducted research on monitoring the occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line in China factory. Corn oil, soybean oil, peanut oil and palm oil were selected as representative edible oil. The chloride precursor and mitigation method of 3-MCPDE were also studied. **Chapter 4** was to evaluated the effect of pressing technology on the volatiles in peanut oil with HS-SPME-GC-MS and e-nose analysis. and to visually assess their significant differences by using PCA. The characteristic volatile compounds of low- and high-temperature pressed peanut oil were determined. **Chapter 5** was to evaluated the feasibility of using microwaves pretreatment as an improvement method for cold-pressed peanut oil processing. The changes in extraction yield, physicochemical properties, micronutrients content, oxidative stability, and flavor quality of peanut oil extracted by cold pressing after microwave pretreatment were studied. **Chapter 6** was to compared the sensory quality and the key aroma components of normal- and high-oleic peanut oil produced industrially. For a possible precursor study, the amino acids and reducing sugar profile of peanut have also been monitored during oil processing. The results of this study will provide data support for raw material screening and quality improvement during peanut oil industrial production.

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# CHAPTER II

# *Research progress on safety and flavor quality control of edible oil*

*Hui Hu1,2, Hongzhi Liu1, Aimin Shi1, Li Liu1, Qiang Wang1,\**

*1 Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences, Beijing 100193, China*

This chapter mainly reviews the research progress on safety quality and flavor quality of edible oil. For the safety quality, this chapter focus on the occurrence, toxicities, regulation, formation and control strategies of two kinds of processing-induced chemical toxicants (trans fatty acids and esters of 3-monochloropropane-1,2-diol). It also highlights the flavor and sensory analysis of edible oil, the effect of processing on the volatiles of peanut oil, and changes in precursor chemistry. The problems of existing research were summarized and the future research were prospected. The next chapter will focus on safety quality of edible oil, and carry out the research on chemical toxicants formation and control during edible oil processing.

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**1. Introduction**

Oil supplies energy, fat soluble vitamins (vitamins A, D and E) and essential fatty acids which play important role in human daily diet (Krauss et al., 2000). Global vegetable oil production reaches 211.44 million metric tons in 2021/22. Among of them, the production of peanut oil was 6.50 million tons, among which approximately 50% was produced in China (USDA, 2022). The total amount of unsaturated fatty acid is over 85% in peanut oil. The fatty acid profile of peanut oil resembles that of olive oil, which could reduce the risk of cardiovascular disease (Wang et al., 2016).

The safety quality of edible oil is closely related to people’s health. Trans fatty acids (TFA) and fatty acid esters of 3-monochloropropane-1,2-diol (3-MCPDE) are two kinds of processing-induced chemical toxicants which have been detected in refined edible oils. There are many researches focus on the analytical methods, occurrence, toxicities, formation mechanism and mitigation strategies of TFA and 3-MCPDE (Gao et al., 2019; Kiralan et al., 2021). It is an urgent problem for the food industry to reduce or remove the above chemical toxicants during oil processing and further application.

Flavor is the most important sensory quality of edible oil. Compared with other edible vegetable oils, aromatic roasted peanut oil obtained by thermal processing is more popular for consumers because of its strong nutty and roasty flavor (Hu et al., 2019). The unique flavors of thermally processed foods are commonly generated through the Strecker degradation during the Maillard reaction, which is responsible for generating various heterocyclic compounds, including pyrazines, pyrroles, pyridines, etc. (Salehi, 2020). Correlation of volatile compounds to peanut sensory evaluation has attracted researcher’s attention.

**2. Safety quality of edible oil**

**2.1. Fatty acids profile of edible oil**

The fatty acids profile of different edible oil was shown in Table 2-1 (Liu et al., 2020). Four kinds of commercial oil were collected from market in China. Soybean oil and corn oil have similar fatty acid composition with 47.4-51.7% linoleic acid, 26.38-29.67% oleic acid, and 12.45-13.76% palmitic acid. Compare to the above two oils, regular peanut oil has higher content of oleic acid (42.24%) and lower content of linoleic acid (31.37%). The oleic content of high-oleic peanut oil could reach 75-85%, which is similar with palm oil (72.71%).

Table 2-1 Fatty acids composition of edible oil

Unit: % of total fatty acid

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Peanut Oil | Soybean Oil | Corn Oil | Palm Oil |
| Myristic C14:0 | 0.05 | 0.09 | 0.04 | 0.01 |
| Pentadecanoic C15:0 | 0.01 | 0.01 | 0.01 |  |
| Palmitic C16:0 | 12.60 | 12.45 | 13.76 | 13.50 |
| Margaric C17:0 | 0.11 | 0.10 | 0.11 | 0.06 |
| Stearic C18:0 | 5.14 | 4.91 | 2.21 | 4.46 |
| Arachidic C20:0 | 2.07 | 0.44 | 0.51 | 0.49 |
| Behenic C22:0 | 3.54 | 0.61 | 0.19 | 0.14 |
| Lignoceric C24:0 | 1.57 | 0.21 | 0.18 |  |
| Palmitoleic C16:1 | 0.12 | 0.09 | 0.18 | 1.33 |
| Margaroleic C17:1 | - | - | - | 0.18 |
| Oleic C18:1 | 42.24 | 26.38 | 29.67 | 72.71 |
| Eicosenic C20:1 | 1.06 | 0.35 | 0.43 | 0.32 |
| Cetoleic C22:1 | - | - | - | - |
| Linoleic C18:2 | 31.37 | 47.40 | 51.70 | 6.07 |
| Eicosadienoic C20:2 | - | - | - | - |
| Linolenic C18:3 | 0.11 | 6.95 | 1.02 | 0.72 |
| Saturated fatty acid | 25.10 | 18.82 | 17.01 | 18.66 |
| Unsaturated fatty acid | 74.90 | 81.17 | 83.00 | 81.33 |
| Polyunsaturated fatty acid | 31.48 | 54.35 | 52.72 | 6.79 |
| Monounsaturated fatty acid | 43.42 | 26.82 | 30.28 | 74.54 |

2.2. TFAs occurrence and control strategies

The intake of TFAs causes more than 500,000 people to die in worldwide from coronary heart disease each year, and increases 21% risk of heart disease and 28% risk of mortality (WHO, 2018). The WHO issued “replacement” program to improve this global problem. This program is planning to completely eliminate the trans fats used in global food industry before 2023. All countries in the world are exploring new technologies and methods to remove TFAs in oils and fats.

The unsaturated fatty acids present in the natural oils and fats are mostly in the cis configuration, which is the two hydrogen atoms are on the same side of the carbon chain. A double bond in the fatty acid can change with some conditions from a cis (Z) to a trans (E) configuration, which is the hydrogen atoms are attached to carbons on the opposite sides of the double bond. This configuration is defined as trans (Kiralan et al., 2021).



Figure 2-1. Chemical structure of cis and trans isomers

The industrially produced trans fatty acids are generally formed by the thermal treatments including deodorization step during oil refining, partial hydrogenation and frying process. Crude oils have to undergo the refining procedure to remove the unwanted constituents from the oil with the least possible negative effect on triacylglycerols and minimal loss of the desirable constituents. Chemical and physical refining are two types of oil refining. The chemical refining process includes five procedures: degumming, neutralization, bleaching, dewaxing and deodorization. The difference between physical and chemical refining is that physical refining does not need neutralization. The processing temperature of degumming, neutralization, bleaching, dewaxing, deodorization is 70 ℃, 90 ℃, 110 ℃, 10 ℃, 260 ℃, respectively. The processing time of degumming, neutralization, bleaching, dewaxing, deodorization is 30min, 10min, 120min, 45min, 15min, respectively. Trans fatty acids generally form in the deodorization step of the refining process by reaching high temperatures (Kiralan et al., 2021). The content of trans fatty acids depends on the fatty acid composition of vegetable oil. Trans form of C18:2 and C18:3 increased in deodorization step in corn, soybean and rapeseed oil which having higher amounts of linoleic and linolenic acid (Ferrari et al., 1996). Compared with trans isomers of C18:1 and C18:2, trans isomers of C18:3 has higher levels in high-oleic safflower oil which rich in oleic acid (Ortega-Garcia et al., 2006). Čmolík (2000) reported that oleic acid was relatively stable at 270°C in deodorization of rapeseed oils which contains high content of linolenic acid. Even at low deodorization temperatures, linolenic acid is much less stable on than linoleic acid. O’Keefe (1993) indicated that the rate of 9-cis, 12-cis, 15-trans isomer formation increased from an initial value of 0.0031mg/g oil/h at 160°C to 2.4mg/g oil/h at 240°C. Trans fatty acid contents change with the type of refining in vegetable oils. Tasan (2003) studied the effects of chemical and physical refining on trans fatty acid formation. The total TFA content of oils treated with the physical method was higher than that of oils refined with chemical refining. Specifically, steam distilled sunflower oils (2.56%) had higher contents of total TFA compared to deodorized oil (0.76%).

The technological approaches for removing TFAs in oil products have attracted much attention in food industry. Interesterification is the most common ways for TFAs elimination. The fatty acids are enzymatical rearrangement during the hydrolysis of triacylglycerols and the following recreation of the bonds between the molecules (Berry et al., 2019). Fractionation is another method of fat modification. A controlled crystallization is using for melting the fat, and followed by a cooling procedure resulting in the separation of the solid—crystallized—and liquid phases by filtering the triglyceride crystals (Wassell et al., 2007). Guo (2021) reported phytosterols could exhibited anti-isomerization effects on oleic acid, linoleic acids and linolenic acids. The anti-isomerization rates of six phytosterols increased with heating time of peanut oil.

2.3. 3-MCPDE occurrence and control strategies

The compound 3-monochloropropane-1,2-diol (3-MCPD) is a member of the chemical class approximately termed ‘chloropropanols’ which defines a group of alcohols contained a 3-carbon backbone substituted with one or two chlorine atoms (Velisek, 2009). The chemical structure of 3-MCPD and its corresponding fatty acid esters are shown in Figure 2-2. Chloropropanols were firstly found in the 1980s from hydrolyzed vegetable proteins (HVP) produced by HCl hydrolysis of proteinaceous by-products. First reports on the occurrence of 3-MCPDE were published by Cerbulis (1984). Twenty years later, 3-MCPDE have received close attention after findings of elevated levels in refined vegetable oils/fats and foodstuffs (Richard, 2015).

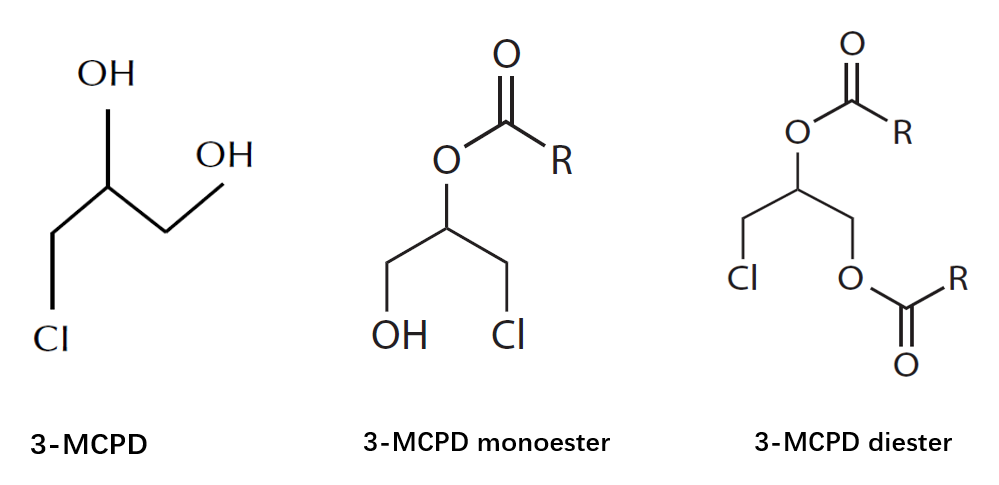


Figure 2-2. Chemical structure of 3-MCPD and its corresponding fatty acid esters

The toxicity of 3-MCPD was graded as potentially carcinogenic to humans by the International Agency for Research on Cancer (IARC, 2012). In 2013, the European Food Safety Authority estimated a tolerable daily value (TDI) of 2 μg/kg body weight (BW) for the amount of free 3-MCPD. In 2018, the European Commission has defined a maximum limit (ML) for the content of glycidol fatty acid esters in vegetable fats and oils (European Commission, 2018). Afterwards, the European Commission established for the sum of the presence of 3-monochloropropane-1,2-diol (3-MCPD) and 3-MCPDE in vegetable oils, fish oils, and oils from other marine organisms (European Commission, 2020).

Previous researches have strongly recommended that processing affects the overall MCPD ester levels in oils and foods. Refined soybean, sunflower, rapeseed, olive, and safflower oils have relatively 3–32 times of 3-MCPD esters content than their non-refined counterparts. For example, the 3-MCPDE content in refined safflower and olive oils were 2,355–3,218 μg/kg and 300–2,462 μg/kg, respectively, which were 32 and 24 times than that of their unrefined counterparts, respectively. The content of 3-MCPDE in refined soybean, rapeseed, and sunflower oils were 1,234 μg/kg, 381–670 μg/kg, and <300 μg/kg, respectively, which were 12, 4–7, and 3 times than that of their unrefined counterparts (Gao et al, 2019). The 3-MCPDE formation during frying has also been studied. Frying temperature and concentration of sodium chloride significantly affect the 3-MCPD esters formation in palm oil during deep-frying (Wong et al. 2017).

In recent years, many research on mitigating the formation of 3-monochloropropane-1,2-diol fatty acid esters (3-MCPDE) and glycidol fatty acid esters (GE) in refined vegetable oils have been reported. Free fatty acids, diacylglycerols, monoacylglycerols and chlorine are considered to be the precursors for 3-MCPDE, but many results are still contradictory. Several potential mitigation strategies including controlling the deodorization temperature, adding chelating agents, changing CPO processing conditions were also reviewed by Gao (2019). However, these possible mitigation strategies are focus on the oil processing, but ignores further cooking process.

**3. Flavor quality of edible oil**

3.1. Flavor and sensory analysis

Sensory science has been defined as the “scientific discipline used to evoke, measure, analyze, and interpret those responses to products that are perceived by the senses of sight, smell, touch, taste, and hearing” (Stone and Sidel, 2004). Within the edible oil industry, discriminative sensory flavor analysis is commonly used to better understand the molecular basis for oil flavor and communicate with acceptability of commercial products. Descriptive sensory flavor analysis is the technique of describing the complex flavor of a given product with using trained panel which utilizing a lexicon specifically developed for a given product (Lawless and Civille, 2013). Lexicons are qualitatively, quantitatively and objectively describing specific flavor attributes for a given product. Proper lexicon development and implementation is important for sensory data. A roasted peanut lexicon was published by USDA scientists Johnsen (1988). This lexicon established reference values on a 1 to 10 quantitative scale for individual attributes which detected in roasted peanuts according to three clas­sifications: (1) aromatics; (2) the basic tastes, i.e., sweet, bitter, salty, sour; and (3) feeling factors such as astringency detected via the trigeminal system. Common undesirable flavors were also defined in the lexicon of roasted peanuts.

Peanut oil is the most distinctive oil with characteristic flavor. Compared with other edible vegetable oils, aromatic roasted peanut oil obtained by thermal processing is more popular for consumers because of its strong nutty and roasty flavor (Hu et al., 2019). The unique flavors of thermally processed foods are commonly generated through the Strecker degradation during the Maillard reaction, which is responsible for generating various heterocyclic compounds, including pyrazines, pyrroles, pyridines, etc. (Salehi, 2020). The volatile components of roasted peanut are chemically complex which could be identified with gas chromatography (GC) systems. Advanced detection technologies coupled with model reconstitution experi­ments have documented numerous odor-active compounds (Chetschik et al., 2008, 2010). This was well demonstrated in a study investigating headspace volatiles of aromatic peanut oil, which revealed three classes of characteristic volatiles over the course of roasting: (1) nonheterocyclic, (2) N-heterocyclic or heterocyclic compounds containing nitrogen, and (3) O-heterocyclic or heterocyclic compounds contain­ing oxygen (Liu et al., 2011). Peanuts were roasted in a lab-scale roaster at 200 °C from 0-50 min. With specific roasting conditions, Liu report that 50 min was the optimized roasting time for “desirable nutty and roasty flavor” of the high-temperature expressed peanut oil. Nonheterocyclic compounds dominated in the early stages of roasting and gradually increased through 30 min. These compounds included various alde­hydes, ketones, alcohols and other compounds resulting from thermal degrada­tion of lipids. These volatiles are often attribute to beany, grassy and oily aromas. Total volatile content increased significantly at approximately 40 min. Primary component shift­ing from nonheterocyclic compounds to N-heterocyclic compounds followed by O-heterocyclic compounds. Furan derivatives were the most important O-heterocyclic compounds accounted for about 25% of total volatiles at peak roast.

Pyrazines are a varied class of heterocyclic nitrogen-containing compounds derived from nonenzymatic protein–sugar interactions, and these compounds have been related to roasty and nutty flavor (Baker et al., 2003). Many indi­vidual pyrazine peaks from roasted peanuts or peanut oil have been identified through GC–MS, and are often correlated to flavor of given product. However, their exact contribution to roasted peanut flavor is controversial (Chetschik et al., 2008; Neta et al., 2010; Smith and Barringer, 2014). Methanethiol, 2,3-pentanedione, 3-(methylthio)propanal, 2- and 3-methylbutanal and 2-acetyl-1-pyrroline were identified to have the highest odor activity values in roasted peanut meal with using stable isotope dilution and GC–olfactometry (GC–O) analysis (Chetschik et al., 2010). Kaneko reported the key volatiles in fresh roasted in-shell peanuts concluded a sulfur con­taining aromatic, 2-methyl-3-furanthiol, might be an important volatiles attribute to the flavor of fresh roasted in-shell peanuts (Kaneko et al., 2013).

3.2. Processing technology on peanut oil flavor

There are two main types of industrial peanut oil-processing methods: high-temperature pressing and cold pressing. The pretreatment before high-temperature pressing reaches 160-200 ℃, which brings characteristic flavor of peanut oil. The temperature of pretreatment and crushing for low-temperature pressing must lower than 70 ℃ to prevent the micronutrients loss and protein denaturation. More than 90% of peanut oil production in China is performed by the traditional technique of high-temperature pressing (Wang et al., 2016). The aromatic roasted peanut oil obtained by this method is more popular with consumers because of the strong typical flavor. However, the pretreatment of roasting and high-temperature pressing leads to the loss of micronutrients and poor oil stability. The peanut oil produced by cold pressing maintains the original quality of the peanut, and a peanut protein meal with low denaturation level could be further produced for food use. However, when compared with hot-temperature pressing, lower oil extraction yield and weaker roasted flavors of the oils were the main differences with cold-pressing. Over 100 volatile components were identified in hot-pressed peanut oil, including pyrazines, aldehydes, furans, alcohols and pyrroles (Baker et al., 2003). Chung (1993) identified 99 volatiles in heated peanut oil by GC-MS, and the total amount of all volatiles increased with increasing temperature. Matsui (1998) suggested that 2-methylbutanoate, 2,5-ethyl-3-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, (Z)-2-nonenal, (E, E)-2,4-decadienal, and (E)-β-damascenone are key odorants in commercial oil processed from roasted peanuts. Liu (2011) investigated the influence of the roasting process during peanut oil production on the volatiles in peanut oil by HS-SPME-GC-MS. N- and O-heterocyclic compounds possessed the highest relative percentage area, 61.68% and 24.57%, respectively. Twenty pyrazines were considered to be the key contributors to the intense nutty/roasty flavor of peanut oil. Hu (2014) identified and quantified 64 volatiles in high temperature pressed peanut oil by HS-GC×GC-TOFMS. Of them, 2-undecenal, 2-methoxy-4-vinylphenol, and 1-butyl-2-cyclohexen-1-ol are characteristic volatiles in peanut oil. Zhao (2013) reported that 31 potential marker volatiles were able to discrimination between sesame oils, peanut oils, and soybean oils by HS-GC/GC–TOF/MS.

3.3. Changes in precursor chemistry

The major precursors for volatiles in peanut are proteins, sugars, and lipids (Davis and Dean, 2016). Different kinds of sugars and proteins mixtures react differently, which lead to different volatiles formation. A previous study reported that aspartic acid, glutamic acid, glutamine, asparagine, histidine, and phenylalanine contributed to the characteristic peanut flavor formation, and monosaccharides are highly related to pyrazine component (Newell et al., 1967). Compared with glycine and diglycine, triglycine has the highest capability to formed pyrazines in Maillard model systems. Major pyrazines were identified as 2,5-dimethylpyrazine and trimethylpyrazine (Lu et al., 2005). Glutamine and asparagine have shown high reactivities to produce high content of pyrazines (Ho et al., 2005). The rapeseed peptides subsequently reacted with D-xylose to largely produce methylpyrazine and ethyl-2,5-dimethylpyrazine (He et al., 2019). Methylpyrazine and 2,5-dimethylpyrazine were identified in the D-glucose and L-theanine Maillard model systems but were not detectable in thermal reactions with single D-glucose or L-theanine (Guo et al., 2018). The compounds 2,6-dimethyl-3-ethyl pyrazine, 2,5-diethylpyrazine and 2-methyl-3,5-diethylpyrazine were formed in the reaction between 1,4-13C-labeled L-ascorbic acid and L-glutamic acid. The α-amino carbonyl or α-amino hydroxy compounds were found to be the precursors of pyrazines (Yu et al., 2013).

The sensory quality difference between normal- and high-oleic peanut has also been studied. There were small differences in the roasting, astringency, over-roasting, and nuttiness attributes between these two kinds of peanuts. High-oleic lines exhibiting slightly greater intensities of those attributes (Isleib et al, 2006). Variation among individual lines for several sensory attributes (dark roasted, raw/beany, roasted peanutty, sweet aromatic, sweet, bitter, wood-hulls-skins, and “off flavors” stale/cardboard, fruity/fermented and plastic/chemical) suggest the flavor of high-oleic cultivars is at least as good as the profiles of normal-oleic cultivars (Isleib et al., 2015).

**4. Problems and Prospects**

Trans fatty acids (TFA) and fatty acid esters of 3-monochloropropane-1,2-diol (3-MCPDE) are two kinds of processing-induced chemical toxicants in refined edible oils. However, the content of TFA and 3-MCPDE in different edible oils showed diversely levels from different country (USA, Brazil, et al). For 3-MCPDE, the chlorine precursors are still contradictive. And most of the reported formation and mitigation strategies are focus on the oil processing, but ignores further cooking process.

Flavor is the most important sensory quality of edible oil, which is highly related to consumer preference. Peanut oil is the most representative oil with characteristic flavor. The studies on the characteristic volatile compounds and precursors of low- and high-temperature pressed peanut oil are still lack. The industrial problems of peanut oil flavor stability have not been solved effectively.

In order to reflect the real production situation, it is necessary to monitor the occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line. The chloride precursor and mitigation method of 3-MCPDE during cooking process need to be further investigated. The characteristic volatile compounds and its precursors of low- and high-temperature pressed peanut oil need to be determined. The industrializable technology for improving peanut oil flavor need to be established.

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# CHAPTER III

# *Chemical toxicants formation and control during edible oil processing*

*Hui Hu1,2, Bo Jiao1, Qin Guo1, Hongzhi Liu1, Aimin Shi1, Li Liu1, Qiang Wang1,\**

*1 Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences, Beijing 100193, China*

The previous chapter reviews the research progress and problems on safety quality and flavor quality of edible oil. This chapter focus on two kinds of risk compositions in edible oil (trans fatty acids and esters of 3-monochloro-1,2-propanediol). The occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line in China factory was investigated. The chloride precursor and mitigation method of 3-MCPDE were also studied. The next chapter will focus on flavor quality of edible. The volatile profiles of low- and high-temperature pressed peanut oil were evaluated by using HS-SPME-GC-MS and e-nose analysis.

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**1. Introduction**

Trans fatty acids (TFA) and esters of 3-monochloro-1,2-propanediol (3-MCPDE) are two kinds of risk compositions in edible oil. Increasing epidemiologic and biochemical evidence suggests that individuals with higher dietary TFA intake are significant risk factor for cardiovascular disease, cancer and diabetes (Ashraful Islam et al., 2019). TFA are mainly formed from cis fatty acids by partial hydrogenation and thermal processing steps of oil processing. The last procedure of refining is the most important stage in the formation of trans fatty acids by reaching high temperatures (180°C–270°C) (Wolff, 1997). Because of the isomerization from cis to trans, temperature is one of the important parameters of the deodorization step in the vegetable oil refining process (Ortega-Garcia et al., 2006). Besides temperature, trans fatty acid contents change with the type of refining in vegetable oils. Tasan and Demirci reported the TFA changes during different steps of refining (2003). Total TFA of oils refined with the physical processing was higher than that of oils treated with chemical refining. 3-MCPDE are processing contaminants which formed in refined edible oils. Recently, the European Commission implemented maximum limits for the presence of free and bound 3-MCPDE in vegetable (European Commission, 2020). Previously research reported the occurrence of 3-MCPDE in several vegetable oils including canola oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, rapeseed oil, sunflower oil, walnut oil, et al (Richard, 2015). Among of them, palm oil could be considered as most susceptible to the formation of 3-MCPDE. However, all studies were published so far. The results from different country (USA, Brazil, et al) showed diversely levels.

The aim of this part was to monitor the occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line in China factory. Corn oil, soybean oil, peanut oil and palm oil were selected as representative edible oil. The chloride precursor and mitigation method of 3-MCPDE were also studied.

**2. Materials and methods**

2.1. Materials

Corn oil, soybean oil, peanut oil and palm oil processing samples were collected from the industrialized production line in China factory. The procedure and sampling point of different oil processing were shown in Table 3-1. Three independent samples were collected from each sampling point and tested within one week. All reagents used in this research were obtained from Sigma-Aldrich (St. Louis, MO, USA), including C18:1 isomer (C18:1-9 t), C18:2 isomers (C18:2-9c,12c, C18:2-9 t,12c, C18:2-9c,12 t, C18:2-9 t,12 t), C18:3 isomers (C18:3-9c,12c,15c, C18:3-9 t,12c,15c, C18:3-9c,12 t,15c, C18:3-9c,12c,15 t, C18:3-9 t,12 t,15c, C18:3-9 t,12c,15 t, C18:3-9c,12 t,15 t, C18:3-9 t,12 t,15 t), 1,2-bis-palmitoyl-3chloropropanediol-d5 (chemical purity: 97%, isotopic purity: 98.8%), etc.

Table 3-1 The procedure and sampling point of different oil processing

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Corn oil | Soybean oil | Peanut oil | Palm oil |
| Pressing | √ | × | √ | √ |
| Solvent extraction | √ | √ | × | × |
| Degumming | √ | √ | √ | × |
| Neutralization | √ | √ | × | × |
| Bleaching | √ | √ | × | √ |
| Dewaxing | √ | √ | √ | × |
| Deodorization | √ | √ | × | √ |

2.2. Trans fatty acid analysis using GC-FID

Oil samples were methylated using a methanolic KOH solution as previously described by Zhang et al. (2015), and analyzed by established methods in our lab using GC-2010 chromatograph (Shimadzu, Kyoto, Japan) equipped with an CP-SIL 88 column (100 m × 0.25 μm × 0.2 mm; Supelco, Bellefonte, PA, USA) and a flame ionization detector (FID) (Guo et al., 2015). The initial temperature of 60 °C was maintained for 5 min and then increased to 160 °C at a rate of 25 °C/min. After a time of 5 min at 160 °C, the temperature was again raised at a rate of 2 °C/min to achieve a final temperature of 225 °C. The sample was maintained at this final temperature for 15 min. The injection volume was 1 μL with a split ratio of 1:10, and helium (99.999%) was used as the carrier gas with a flow rate of 6.3 mL/min. The injector and interface temperatures were both 230 °C. The identities of TFAs contained in the samples were determined by comparing retention times to those of known standards.

2.3. 3-MCPDE analysis using GC-MS

An approximately 100-mg oil sample was accurately weighted into a 50 mL plastic centrifuge tube with a screw cap. 1 mL tetrahydrofuran and 50 μL working internal standard solution were added. The centrifuge tube was then screwed tightly and vortexed for 30 s. The transesterifications and purification of 3-MCPDE were followed the method established by our laboratory (Jiao et al., 2017). Splitless injection mode was used, and the injection volume was 1 μL. The temperature of the injector was set at 250 °C. High-purity helium (purity > 99.99%) was used as a carrier gas, and the flow rate was maintained at 1 mL min-1. The GC temperature programming was as follows: holding at 50 °C for 1 min followed by ramping up at 2 °C min-1 to 90 °C, a final ramping up at 45 °C min-1 to 250 °C and holding at 250 °C for 5 min. The total GC run time for these tests was 30 min for each sample. The quadrupole instrument was operated in selective ion-monitoring (SIM) mode. The analytes were ionised by electron impact (EI) at an ion energy of 70 eV, and the solvent delay time was maintained at 7 min. The temperatures of the transfer line, MS source and MS quadrupole were 250, 230 and 150 °C, respectively. The m/z ratios 275, 289 and 453 and m/z 278, 294 and 456 were the qualitative ions of the 3-MCPD and d5-3-MCPD derivatives, respectively, and the m/z ratios 253 and m/z 257 were the quantitative ions of the 3-MCPD and d5-3-MCPD derivatives, respectively.

2.4. Chloride determination using Ion chromatography

Ten representative peanut varieties in China were collected for 3-MCPDE formation capability evaluation. The chloride ions determination was followed the method described in Reference (). The chloride ions in the oil were extracted into ultrapure water. After moderate dilution, the solution was filtered through a 0.22 μm water filtration membrane and determined by ion chromatograph. AS-16 analytical column (4 mm × 250 mm) and AG-16 guard column (4 mm × 50 mm) was used. The analysis was using 25 mmol /L KOH as eluent (1 mL/min flow rate). The temperature of column was maintained at 30 °C. The injection volume was 10 μL.

2.5. 3-MCPDE formation capability evaluation

3-MCPDE formation ability analysis followed the method described in Reference (Pudel et al., 2011). Peanut oil was obtained by hydraulic press (Model QYZ-230, Taian, China). The cold-pressing parameters were between 22–25MPa and 60 °C inside the press temperature for 30 min. There was no further oil obtained by longer pressing time. Residue particles in the oil were removed by 4300r/min centrifugation for 10 min. 10 g of the oil sample was weighed into an appropriate open glass vial and heated in an oil bath at 240 °C for 2 h. After cooling down to room temperature, the content of 3-MCPDE was determined giving the capability of different peanut varieties to form 3-MCPDE.

2.6. Effect of salt on the 3-MCPDE formation

3 g of low-temperature pressed peanut oil was mixed with 0 and 0.5mmol NaCl in a test tube. A small amount of anhydrous sodium sulfate was added for dehydration. Then it was heated in oven at 220 °C for 2h and cooled to room temperature. The supernatant was collected for 3-MCPDE determination after 4500 r/min centrifugation for 30 min.

2.7. Effect of sugars on the 3-MCPDE formation

0.3g of fructose, maltose, sucrose, galactose, cyclodextrin, lactose, mannose, glucan and xylose were dissolved in 1mL pure water, respectively. Then it was mixed with 10 g of peanut oil and heated in oven at 220 °C for 2 h and cooled to room temperature. The supernatant was collected for 3-MCPDE determination after 4500 r/min centrifugation for 30 min.

**3. Results and discussion**

3.1 Formation of trans fatty acids during different edible oil processing

Trans fatty acid (TFA) is commonly present in edible oils. Each year, the intake of TFA causes more than 500,000 people worldwide to die from coronary heart disease. TFA also increases the risk of heart disease by 21% and mortality by 28% (WHO, 2018). The WHO issued “replacement” program in 2018 which planning to completely eliminate industrial application of TFA in worldwide by 2023. The formation of TFA during different edible oil processing were traced in the present study. Corn oil, soybean oil, peanut oil and palm oil were selected as representative oil to studied. As shown in Table 3-2, TFA was detected in four kinds of crude oil range from 0.24-0.41g/100g. The processing temperature of degumming, neutralization, bleaching, dewaxing, deodorization is 70 ℃, 90 ℃, 110 ℃, 10 ℃, 260 ℃, respectively. The content of TFA increased with the increasing processing temperature, and reached the highest content after deodorization. Among the whole processing, the most TFA (42.03%-80.10%) was formed during deodorization. Compared with other oils, soybean oil has the highest TFA content in crude oil (0.41 g/100g) and deodorized oil (2.16 g/100g). Because there is no deodorization needed in peanut oil processing, peanut oil has the lowest TFA content in final product (0.37g/100g). Similar results were reported by Ferrari (1996) that TFA are generally form in the deodorization step during the whole refining processing. Deodorized corn oil and deodorized soybean oil has 1.5% and 4.6% TFA, respectively. Hou was collected 93 edible oils consumed in China (2012). TFA (>2%) was detected in 17 (18%) samples ranging from 0.14% to 4.76%. The overall TFA content was 1.15±0.12% for soybean oil and 2.01± 0.24% for corn oil. Generally, it can be indicated that TFA is widely present at relatively low levels in edible oil collected from factory in China.

Table 3-2. Formation of trans fatty acids during different edible oil processing

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Corn oil  g/100g | Soybean oil  g/100g | Peanut oil  g/100g | Palm oil  g/100g |
| Crude oil | 0.24 | 0.41 | 0.33 | 0.37 |
| Degummed oil | 0.24 | 0.41 | 0.37 | / |
| Neutralized oil | 0.42 | 0.41 | / | / |
| Bleached oil | 0.60 | 0.43 | / | 0.40 |
| Dewaxed oil | 0.61 | 0.43 | 0.37 | / |
| Deodorized oil | 1.32 | 2.16 | / | 0.69 |

3.2 Formation of 3-MCPDE during different edible oil processing

Previous researches have strongly recommended that processing affects the overall MCPDE levels in oils and foods. Refined soybean, sunflower, rapeseed, olive, and safflower oils have relatively 3–32 times of 3-MCPDE content than their non-refined counterparts. For example, the 3-MCPDE content in refined safflower and olive oils were 2,355–3,218 μg/kg and 300–2,462 μg/kg, respectively, which were 32 and 24 times than that of their unrefined counterparts, respectively. The content of 3-MCPDE in refined soybean, rapeseed, and sunflower oils were 1,234 μg/kg, 381–670 μg/kg, and <300 μg/kg, respectively, which were 12, 4–7, and 3 times than that of their unrefined counterparts (Gao et al, 2019). In the present study, 3-MCPDE are only formed in the deodorization procedure during oil processing, which is consistent with previous studies. Palm oil has the highest 3-MCPDE content (3750.5±177.3 μg⋅kg-1). No 3-MCPDE was detected in peanut oil.

In the present study, corn oil, soybean oil, peanut oil and palm oil processing samples were collected from the industrialized production line in China factory. The crude corn oil is obtained by pressing corn germ and extracted from corn meal by using industrial hexane. The crude oil required refining process including degumming, neutralization, bleaching, dewaxing and deodorization. As can be seen from Table 2, 3-MCPDE was not detected in the crude oil, degummed oil, neutralized oil, bleached oil and dewaxed oil. A quantity of 932.6±7.8 μg⋅kg-1 3-MCPDE was detected in deodorized corn oil. Steamed-frying and pressing are two thermal processing before refining. The processing temperature of the above processing is close to 100 ℃. It can be indicated that 3-MCPDE are only formed in the deodorization procedure with 260 ℃ during corn oil processing.

Soybean oil is processed by solvent extraction and whole refining like corn oil. The processing conditions are basically the same as corn oil. As shown in Table 2, 3-MCPDE was not detected in the extraction crude oil, degummed oil, neutralized oil, bleached oil and dewaxed oil. A quantity of 201.89±12.3 μg⋅kg-1 3-MCPDE was detected in deodorized soybean oil. The soybean oil refining conditions are the same as corn oil processing. The difference on triglyceride composition and chloride content may be the main reason for the difference of 3-MCPDE content.

Peanut oil is the only kind of oil in the present study that no 3-MCPDE was detected. Although the peanut oil processing includes several thermal procedures. But the temperature of frying, pressing and degumming are all much lower than the deodorization temperature (260℃). Lack of deodorization is the main reason for the 3-MCPDE results.

In China, Crude palm oil is generally imported from Malaysia. Before exporting, crude palm oil will be pre-refined to meet the standard of edible oil. After arriving in China, crude oil will be bleached and deodorized to become final product. As shown in Table 3-3, the content of 3-MCPDE in crude palm oil, bleached oil, deodorized oil was 286.9±7.9 μg⋅kg-1, 3360.2±185.3 μg⋅kg-1, 3750.5±177.3 μg⋅kg-1, respectively. It is entirely different with soybean oil or corn oil that 3-MCPDE was detected from crude peanut oil. After bleaching, the content of 3-MCPDE in peanut oil is more than ten times higher than that of crude oil. However, the temperature of the bleaching processing is generally around 110-120 ℃ which is much lower than the deodorization temperature (260 ℃). The possible reason for this result may be because that the formation temperature of 3-MCPDE has reached during the pre-refining. After breaking the formation threshold of 3-MCPDE, the temperature required to form 3-MCPDE may decrease. The formation mechanism needs to be further studied. There is no significant difference between the content of 3-MCPDE in bleached oil increased and deodorized oil, which might be because the reaction substrate was exhausted.

Table 3-3. Formation of 3-monochloropropane-1,2-diol (3-MCPD) esters during different edible oil processing

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Corn oil  /μg⋅kg-1 | | Soybean oil  /μg⋅kg-1 | Peanut oil  /μg⋅kg-1 | Palm oil  /μg⋅kg-1 |
| Crude oil | | ＜LOD | ＜LOD | ＜LOD | 286.9±7.9 |
| Degummed oil | | ＜LOD | ＜LOD | ＜LOD | / |
| Neutralized oil | | ＜LOD | ＜LOD | / | / |
| Bleached oil | | ＜LOD | ＜LOD | / | 3360.2±185.3 |
| Dewaxed oil | | ＜LOD | ＜LOD | ＜LOD | / |
| Deodorized oil | | 932.6±7.8 | 201.89±12.3 | / | 3750.5±177.3 |

3.3 Effect of chloride ion on 3-MCPDE formation

The ability of forming 3-MCPDE from 10 peanut varieties were shown in Table 3-4. The content of inorganic and organic chlorine in peanut varieties was 135.91mg⋅kg-1 - 168.16 mg⋅kg-1. Among of them, the peanut variety 177 has the highest chloride content (168.16 mg⋅kg-1), and Huayu 22 has the lowest (135.91mg⋅kg-1). The content of 3-MCPDE was lower than LOD before simulated deodorization. After deodorization simulation, the ability of forming 3-MCPDE from different varieties was significantly different. The content of 3-MCPDE ranged from 122.52 μg⋅kg-1 to 465.58 μg⋅kg-1. Among of them, the peanut variety 177 has the highest 3-MCPDE formation capacity (465.58 μg⋅kg-1), while the peanut variety Huayu 22 has the lowest formation capacity (122.52 μg⋅kg-1). However, as shown in Figure 3-1 that the correlation between chloride concentration of ten peanut varieties and 3-MCPDE formation ability is weak (R2=0.1513). It can be indicated that the effect of chlorine in raw materials on 3-MCPDE formation was limited.

Table 3-4. 3-MCPDE contents before and after deodorization simulation

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Peanut varieties** | **3-MCPDE content in pressed oil /μg⋅kg-1** | **3-MCPDE content in deodorized oil /μg⋅kg-1** |
| 1 | Huayu 22 | ＜LOD | 122.52 |
| 2 | Huayu 25 | ＜LOD | 161.9 |
| 3 | Huayu 33 | ＜LOD | 420.12 |
| 4 | Luhua 18 | ＜LOD | 427.14 |
| 5 | Luhua 19 | ＜LOD | 300.18 |
| 6 | 2011 | ＜LOD | 394.78 |
| 7 | Jufeng | ＜LOD | 452.37 |
| 8 | 177 | ＜LOD | 465.58 |
| 9 | Fuhua 9719 | ＜LOD | 244.39 |
| 10 | 101 | ＜LOD | 368.10 |

Figure 3-1. Correlation between the concentration of inorganic chloride and 3-MCPDE formation abilities

3.4 Control strategies of 3-MCPDE formation during cooking processing

In recent years, many research on mitigating the formation of 3- monochloropropane-1,2-diol fatty acid esters (3-MCPDE) and glycidol fatty acid esters (GE) in refined vegetable oils have been reported. Several potential mitigation strategies including controlling the deodorization temperature, adding chelating agents, changing CPO processing conditions were also reviewed by Gao (2019). The present study was focus on the lack of research on mitigating the formation of 3-MCPDE during cooking procedure. The added salt in baking will provide inorganic chloride source for the reaction system. This part of inorganic chloride could provide rich substrates for the formation of 3-MCPDE. As shown in Figure 3-2, the formation of 3-MCPDE was compared between low-temperature pressing peanut oil (3-MCPDE <LOD) with 0.5mmol NaCl and without NaCl under 2 hours roasting. 3-MCPDE was produced in the oil with 0.5mmol NaCl. The yield was up to 19.2 mg⋅kg-1 which was 159 times higher than that of the group without NaCl (120.84 μg⋅kg-1). Therefore, it was suggested to minimize the amount of salt added and its co-heating time with oil-containing foods. Salt could be added at the end of baking to improve sensory quality.

Figure 3-2. The effect of salt on the formation of 3-MCPDE during baking

The cooking process is a complex system. In the presence of acid, 3-MCPDE can be hydrolyzed and become free 3-MCPD. If the free 3-MCPD is controlled by sugar reaction, the 3-MCPDE could be controlled by eliminating the generated 3-MCPDE. In the presence of acetic acid (simulated vinegar) and water, the effect of fructose, galactose, mannose, xylose, sucrose, lactose, maltose, cyclodextrin, and glucan on the content of 3-MCPDE in peanut oil were studied. Compared with the control, the 3-MCPD content in peanut oil decreased 21.40%-36.99% after adding sugar (Figure 3-3). Monosaccharide fructose and disaccharide lactose have the most obvious removal effect with 35.13% and 36.99% 3-MCPDE removed, respectively. Oligosaccharide cyclodextrin has poor removal effect with 21.40% of 3-MCPDE removed. It is speculated that the control mechanism of sugar is the 3-MCPDE hydrolyzed to form free 3-MCPDE, and then react with ketose or aldose. Thus, the content of 3-MCPDE in oil reduced (Figure 3-4).

Figure 3-3. Mitagite 3-MCPDE by adding sugar during cooking

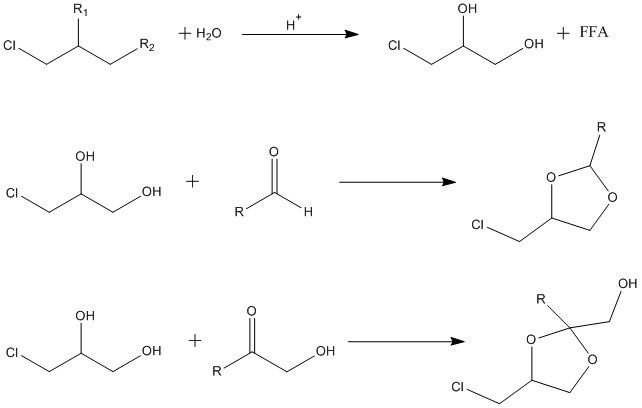


Figure 3-4. Reaction of 3-MCPDE and aldose or ketose

**4. Conclusion**

Corn oil, soybean oil, peanut oil and palm oil processing samples were collected from the industrialized production line in China factory. TFA is widely present at relatively low levels (0.37-2.61g/100g) in edible oil collected from factory in China. 3-MCPDE are only formed in the deodorization procedure with 260 ℃ during oil processing. Palm oil has the highest 3-MCPDE content (3750.5±177.3 μgkg-1). Because the lack of deodorization, peanut oil is the only kind of oil with no 3-MCPDE was detected. The effect of chlorine in raw materials on 3-MCPDE formation was limited. The added salt in baking will provide inorganic chloride source which could significantly increase the 3-MCPDE formation. Monosaccharide fructose and disaccharide lactose have the most obvious removal effect with 35.13% and 36.99% 3-MCPDE removed, respectively.

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# CHAPTER IV

# *Comparison of volatile profiles of low- and high-temperature pressed peanut oil*

*Hui Hu1,2, Hongzhi Liu1, Aimin Shi1, Li Liu1, Marie Laure Fauconnier2,\*, Qiang Wang1,\**

*1 Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences, Beijing 100193, China*

*2 Laboratory of Chemistry of Natural Molecules, Gembloux Agro-Bio Tech, Liege University,*

*Passage des Déportés 2, 5030 Gembloux, Belgium*

The previous chapter concludes that TFA and 3-MCPDE are widely present at relatively low levels in edible oil collected from factory in China. Although the 3-MCPDE may be formed during the further cooking because of the added salt, fructose and lactose have obvious removal effect on it. This chapter mainly focus on flavor quality of edible. The effect of pressing technology on the volatiles in peanut oil were evaluated. The characteristic volatile compounds of low- and high-temperature pressed peanut oil were determined. According to the results of this chapter, the next chapter will focus on improvement of characteristic volatiles in low-temperature pressed peanut oil.

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Hui Hu, Hongzhi Liu, Aimin Shi, Li Liu, Marie Laure Fauconnier\*, Qiang Wang\*. Comparison of volatile profiles in high- and low-temperature pressed peanut oils.

**1. Introduction**

The annual consumption of peanut oil in China is 2.8 million tons, which is above half of total world production. Peanut oil is becoming more popular with consumers because of its nutritional properties (Velickovska et al., 2016). It contains high content of unsaturated fatty acids, including 35-72% oleic acid, 20-45% linoleic acid, and a range of biologically active substances such as phospholipids, phytosterols, and vitamins (Wang et al., 2016). Fatty acid composition and biologically active compounds may justify further processing technologies of peanut oil production (Zhou et al., 2016).

Currently, two pressing technologies are commonly used for the peanut oil production: high-temperature pressing and low-temperature pressing. More than 90% of peanut oil in China is produced by the former technology. For high-temperature pressed peanut oil (HPO) production, the high temperature gives it strong nutty and roasty flavor which is greatly favored by consumers. However, HPO has a heavy loss of biologically active compounds because of the high temperature treatment. Only less than 10% peanut oil is produced by low-temperature pressing under 70°C, which could preserve the original nutritional substances of peanuts (Wang et al., 2016). In addition to the nutritional properties, it is of extreme importance for an edible oil to have acceptable sensory properties because the market success is mostly determined by consumer sensory perception together with quality and price (Emir et al., 2014). However, low-temperature pressed peanut oil (LPO) has the characteristic green flavor and lacks of desired nutty and roasty aroma, which affects its industrial application in China.

Flavor is one of the most important criteria in getting consumers to accept the oil (Dong et al., 2012). However, only few studies on the contribution of volatiles to the flavor of peanut oil are available. Chung (1993) identified 99 volatiles in heated peanut oil by GC-MS, and the total amount of all volatiles increased with increasing temperature. Matsui (1998) suggested that 2-methylbutanoate, 2,5-ethyl-3-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, (Z)-2-nonenal, (E, E)-2,4-decadienal, and (E)-β-damascenone are key odorants in commercial oil processed from roasted peanuts. Liu (2011) investigated the influence of the roasting process during peanut oil production on the volatiles in peanut oil by HS-SPME-GC-MS. N- and O-heterocyclic compounds possessed the highest relative percentage area, 61.68% and 24.57%, respectively. Twenty pyrazines were considered to be the key contributors to the intense nutty/roasty flavor of peanut oil. Hu (2014) identified and quantified 64 volatiles in peanut oil by HS-GC×GC-TOFMS. Of them, 2-undecenal, 2-methoxy-4-vinylphenol, and 1-butyl-2-cyclohexen-1-ol are characteristic volatiles in peanut oil. Zhao (2013) reported that 31 potential marker volatiles were able to discrimination between sesame oils, peanut oils, and soybean oils by HS-GC/GC–TOF/MS.

To differentiate the flavor attributes of peanut oils subjected to different pressing technologies, the Heracles II flash electronic nose (Alpha MOS, Toulouse, France, Figure 4-1) was employed which was integrated with GC functionalities and electronic nose (e-nose) olfactive fingerprint software. The GC system is based on the method of ultra-fast gas chromatography, capable of performing very quickly and is highly selective and sensitive. An advantage of using the Heracles II e-nose over the α-Fox and Gemini e-nose systems is that the Heracles II is able to potentially identify volatiles associated with each peanut oil sample, and this information can help to better explain differences among samples. The e-nose has been widely used to analyze sensory quality of edible oil (Marion et al., 2011; Chatterjee et al., 2012; Zhou et al., 2013).



Figure 4-1. Heracles II flash electronic nose

Although there were few published studies on the volatiles of peanut oil. The studies on the volatile profiles of low- and high-temperature pressed peanut oil are still lack. Therefore, the objective of this study was to evaluate the effect of pressing technology on the volatiles in peanut oil with HS-SPME-GC-MS and e-nose analysis, and to visually assess their significant differences by using PCA.

**2. Materials and methods**

2.1 Chemicals

All chemicals used for sample preparation and GC-MS analysis were analytical grade and HPLC grade unless otherwise stated. C6-C23 normal alkanes which used to calculate the retention indices (RI), were purchased from Shanghai Chemical Reagent Co. (Shanghai, China).

2.2 High- and Low-temperature pressed peanut oil

Four commercial high-temperature pressed peanut oil (HPOs) of different brands, namely Luhua (H1), Hujihua (H2), Longda (H3) and Fulinmen (H4) were obtained from the market in Beijing, China. Four low-temperature pressed peanut (LPOs) were studied. Among of them, three commercial LPOs namely Changshouhua (L1), Hesanyuan (L2), Luyou (L3) were obtained from the market. Due to the lack of authentic commercial cold-pressed peanut oil in China market, LPO (L4) was produced in our laboratory by using Luhua 9 as raw material.

2.3 Headspace-solid phase micro-extraction

HS-SPME is considered a rapid and convenient method for the volatile compounds analysis. The volatiles of peanut oil were extracted followed the method described in Reference with slightly modification (Liu et al., 2011). A polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber (length, 1 cm; film thickness, 65 μm) was used (Supelco, Bellefonte, PA, US). Five grams of peanut oil was weighed into a 20 mL glass vial which was sealed with an aluminum cover and a Teflon septum. It was pre-equilibrated for 20 min at 50°C in a thermostatic bath and stirred thoroughly with a magnetic stirrer. After the equilibration time, an auto SPME holder containing fiber was inserted into the vial, and the fiber was exposed to the headspace for 40 min. When the process was completed, the fiber was then inserted into the injector port of the gas chromatography-mass spectrometry (GC-MS) system. The volatiles absorbed by the fiber were thermally desorbed in the hot injection port of the GC for 2 min at 250°C.

2.4 GC-MS analysis of volatiles

GC-MS analysis was performed using a trace GC system equipped with a DB-WAX capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness) and with a trace mass spectrometer (Finnigan, San Jose, CA, US). The analysis was carried out in the splitless mode, using helium as the carrier gas (1 mL/min flow rate). The detector temperature was 280°C, respectively. The oven temperature program was 40°C for 3 min, then was raised to 120°C at a rate of 5°C/min, ramped up to 200°C at a rate of 10°C/min, and maintained isothermal for 5 min. Mass spectra were recorded in electron impact ionization mode (70 eV) scanning a mass range (m/z) from 35 to 500 amu. The ion source temperature was maintained at 200°C.

2.5 Identiﬁcation of volatiles

For identification of volatiles, the peanut oils were analyzed by GC-MS under the experimental conditions mentioned above. Then, volatiles were primarily identified by comparison of the mass spectra with data from the commercially available mass spectra NIST databases. In addition, the volatiles were identified by matching the retention indices (RI) with data found in the literature. The RI were calculated according to the formula and based on a series of n-alkanes (C6-C23). RIx = 100n + 100 (tRx−tRn)/(tRn+1−tRn), where retention time (tR) of tRn <tRx <tRn+1; n = number of atom carbon.

2.6 Heracles Ⅱ flash e-nose analysis

Five mL of oil samples were heated at 60°C inside a controlled thermostat-sampling chamber for a headspace generation time of 10 min. Five mL of volatiles were injected to the GC system with an HS100 auto-sampler from 10 mL sealed vials by means of a carrier gas (25 kPa) at a flow-rate of 0.5 mL/s for 15 s. The gas sampling syringe was heated at 200°C. The trap was initially kept at 40°C and heated to 240°C in 20 s. The GC column temperature was kept at 40°C for 5 s, programmed to 250°C at a rate of 3°C/s, and finally held at 250°C for 30 s. The FID detector was maintained at 270°C. The total acquisition time and time between subsequent analyses were 105 s and 8 min, respectively. The method of analysis was calibrated using an n-alkanes standard solution (nC6-nC16) to convert retention time in Kovat indices. The volatiles were identified by using AroChem database. The database consists of a library of chemical compounds which assists in the characterization of chemical compounds detected on the chromatograms with both chemical and sensory information. Data processing was carried out with Alpha Soft software (V12.4 software, Alpha MOS, Toulouse, France).

2.7 Statistical analysis

Significant differences among the eight peanut oil samples for each of the volatiles were determined by one-way analysis of variance (ANOVA) using an SPSS Program, version 18.0 (SPSS Inc., Chicago, IL, US, 2009). Statistical signiﬁcance was inferred at p<0.05. The data obtained from the HS-SPME/GC-MS and Heracles II e-nose system were analyzed by PCA performed by CAMO Unscrambler® X software (V.10.3, CAMO Software AS, Oslo, Norway).

**3. Results and discussion**

3.1 Volatile profile of peanut oil

3.1.1 Volatiles analyzed by GC-MS

The volatile profiles of different peanut oils are presented in Table 4-1. A total of 79 volatiles were identified. Of them, 71 volatiles were in the HPOs and 52 in the LPOs. Hexanal, 2,3-butanediol, phenethyl alcohol, acetic acid, pentanoic acid, hexanoic acid, hexanoic acid, and 2-pentylfuran were presented in both peanut oils with different concentration. Most of the volatiles identified in the present study were reported in other plant oils, including apricot kernel oil, pumpkin seed oil, flaxseed oil, rapeseed oil, sesame oil, almond oils (Dong et al., 2012; Poehlmann et al., 2013; Wei et al., 2015; Zhou et al., 2013; Matheis et al., 2016; Pollner et al., 2016; Zhou et al., 2016). As shown in Table 4-1 and 4-2, the number of peaks and total peak area of volatiles in peanut oils ranged between 30-59 and 3.48×107-8.59×107, respectively. HPO1 has the largest peak area and number of volatiles among all samples (8.59×107, 59 types). In general, high-temperature pressing enhance the characteristic aroma of peanut oil by increasing the number and quantity of volatiles. Although the number of volatiles in HPOs is more than in LPOs, the total peak area of volatiles in HPO3 and HPO4 is lower than in LPO4, LPO1, and LPO3.

Table 4-1. Volatiles of peanut oils pressed by different technologies

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | Compounds | OT/  ppb | Volatiles (%) | | | | | | | |
| H1 | H2 | H3 | H4 | L1 | L2 | L3 | L4 |
|  | **Aldehydes** |  |  |  |  |  |  |  |  |  |
| 1 | Butanal,2-methyl- | 10 | 1.83±0.02c | 2.23±0.02a | 2.17±0.04b | ND | 0.69±0.04e | 1.18±0.04d | ND | ND |
| 2 | Hexanal | 326 | 5.3±0.02g | 5.94±0.04f | 10.44±0.03e | 4.04±0.02h | 31.22±0.34b | 33.43±0.79a | 22.13±0.44c | 15.72±0.14d |
| 3 | Hexanal,5-methyl- |  | 1.55±0.02c | 2.31±0.02a | 1.4±0.05d | ND | ND | ND | 2.09±0.05b | 0.83±0.04e |
| 4 | 2-Heptenal, (*Z*)- | 1500 | ND | ND | ND | ND | 5.58±0.11a | 5.66±0.02b | 1.98±0.01d | 2.69±0.01c |
| 5 | Octanal | 51.5 | 14.1±0.05a | 2.81±0.03d | ND | 1.46±0.02f | 1.74±0.03e | 8.02±0.09b | 2.99±0.06c | 0.9±0.03g |
| 6 | 2-Octenal, (*E*)- | 900 | 0.52±0.03g | 0.65±0.03f | 1.42±0.01d | ND | 1.78±0.03c | 5.12±0.09a | 1.17±0.07e | 2.08±0.01b |
| 7 | Nonanal | 1000 | ND | ND | ND | ND | 1.96±0.03d | 3.01±0.1c | 3.66±0.07b | 5.05±0.03a |
| 8 | 2,4-Nonadienal, (*E*, *E*)- | 1.5 | ND | ND | ND | ND | 0.37±0.03a | 0.32±0.01b | 0.17±0.02c | ND |
| 9 | 2,4-Decadienal, (*E*, *E*)- | 196 | 0.68±0.03f | 1.34±0.02c | ND | 0.82±0.02e | 1.1±0.05d | 1.92±0.04b | 0.29±0.01g | 7.02±0.09a |
| 10 | 2-Undecenal |  | ND | ND | 0.4±0.03e | ND | 0.45±0.02d | 1.06±0.03a | 0.56±0.02c | 0.75±0.02b |
| 11 | Benzaldehyde |  | 2.09±0.04b | 2.17±0.02a | 1.51±0.03c | 1.36±0.02d | 0.87±0.02g | 1.17±0.04e | ND | 0.94±0.03f |
| 12 | Benzene acetaldehyde | 24 | 0.24±0.04c | 0.55±0.03a | ND | 0.37±0.02b | ND | ND | ND | ND |
|  | **Ketones** |  |  |  |  |  |  |  |  |  |
| 13 | 2-Propanone,1-hydroxy- |  | 0.68±0.03b | 0.3±0.02c | 1.05±0.03a | ND | ND | ND | ND | ND |
| 14 | 2-Propanone,1-(acetyloxy)- |  | 1.33±0.02a | 0.33±0.02c | 0.95±0.03b | ND | ND | ND | ND | ND |
| 15 | Acetoin |  | 0.29±0.01c | 0.36±0.03a | 0.28±0.01b | 0.23±0.02d | ND | ND | ND | ND |
| 16 | 2-Cyclopenten-1-one,2-hydroxy-3-methyl- |  | 0.52±0.01c | 0.42±0.01d | 1.33±0.02a | 0.89±0.03b | ND | ND | ND | ND |
|  | **Alcohols** |  |  |  |  |  |  |  |  |  |
| 17 | Propylene Glycol |  | ND | ND | 0.36±0.01a | ND | 0.22±0.02d | 0.24±0.02c | 0.31±0.03b | ND |
| 18 | 2,3-Butanediol |  | 1.07±0.04c | 0.93±0.02d | 2.78±0.02a | 0.52±0.01f | 0.94±0.02e | 2.36±0.03b | 0.42±0.01g | 0.05±0.02h |
| 19 | 1,4-Butanediol |  | 0.71±0.01d | 0.82±0.02c | ND | 2.46±0.02a | ND | ND | ND | 1.58±0.03b |
| 20 | 1-Pentanol |  | 0.56±0.01e | 0.97±0.02d | 0.51±0.04f | ND | 3.21±0.03a | ND | 3.12±0.06b | 1.51±0.03c |
| 21 | 1-Hexanol |  | 0.9±0.02d | 4.78±0.03c | ND | ND | 20.72±0.14a | ND | 18.11±0.45b | ND |
| 22 | 1-Heptanol |  | 0.66±0.02f | 0.96±0.03e | ND | 4.78±0.03a | 0.94±0.03d | ND | 1.63±0.02c | 3.2±0.15b |
| 23 | 1-Octanol |  | ND | 0.67±0.03c | ND | ND | 0.9±0.05b | ND | 1.41±0.01a | 0.61±0.02d |
| 24 | 1-Octen-3-ol |  | ND | ND | ND | ND | 1.43±0.04c | 2.34±0.02a | 1.35±0.03d | 1.9±0.05b |
| 25 | 1-Nonanol |  | ND | ND | ND | ND | 1.05±0.03c | ND | 1.08±0.04b | 4.29±0.04a |
| 26 | Benzyl alcohol |  | 0.17±0.01f | 0.24±0.02e | 0.4±0.03b | 0.31±0.02d | 0.42±0.02a | ND | 0.35±0.02c | 0.12±0.02g |
| 27 | Phenyl ethyl Alcohol | 211 | 0.55±0.02f | 0.48±0.01g | 0.58±0.02e | 0.67±0.03d | 1.44±0.03a | 0.6±0.05c | 0.75±0.01b | 0.42±0.02h |
|  | **Acids** |  |  |  |  |  |  |  |  |  |
| 28 | Acetic acid | 135 | 2.22±0.02d | 1.89±0.02e | 9.21±0.03a | 7.21±0.06b | 1.36±0.02g | 3.17±0.02c | 1.74±0.01f | 0.31±0.01h |
| 29 | Butanoic acid | 147 | ND | 0.1±0.00e | ND | ND | 0.21±0.01d | 2.89±0.01a | 0.42±0.01b | 0.38±0.01c |
| 30 | 2-Butenoic acid,3-methyl- | 24 | 0.27±0.02e | 0.29±0.02d | 0.51±0.04c | ND | 0.69±0.01b | 0.76±0.03a | ND | ND |
| 31 | Pentanoic acid |  | 0.23±0.02h | 0.56±0.02g | 0.56±0.02f | 1.29±0.03d | 1.00±0.00e | 2.99±0.06b | 2.07±0.12c | 3.26±0.02a |
| 32 | Hexanoic acid |  | 1.54±0.03h | 4.74±0.02f | 4.52±0.01g | 7.69±0.03e | 10.63±0.19c | 10.22±0.14d | 17.08±0.46b | 25.41±0.3a |
| 33 | Heptanoic acid |  | ND | ND | 0.64±0.02d | ND | 0.56±0.03e | 0.82±0.04c | 1.73±0.03b | 2.11±0.1a |
| 34 | Octanoic acid |  | ND | ND | 0.44±0.02f | 0.62±0.02e | 0.7±0.04d | 1.08±0.04c | 3.58±0.01a | 1.97±0.02b |
| 35 | Nonanoic acid |  | ND | ND | ND | ND | 0.92±0.01d | 1.95±0.03b | 2.24±0.01a | 1.44±0.06c |
|  | **Esters** |  |  |  |  |  |  |  |  |  |
| 36 | Hexyl formate |  | ND | ND | 0.78±0.02d | 1.08±0.04b | ND | 3.1±0.15a | ND | 0.74±0.03c |
| 37 | 1-Butanol,2-methyl-, acetate |  | 0.38±0.02c | ND | ND | 1.08±0.04a | ND | ND | ND | 0.48±0.02b |
| 38 | Butyrolactone |  | ND | 2.64±0.03b | 1.15±0.48d | 2.59±0.03a | ND | ND | 0.72±0.04c | ND |
| 39 | n-Caproic acid vinyl ester |  | ND | ND | 0.61±0.04d | ND | 1.35±0.03c | 0.59±0.03e | 1.43±0.03b | 2.67±0.09a |
| 40 | Pantolactone |  | 1.39±0.01a | 1.27±0.04c | 1.15±0.03d | 1.24±0.01b | ND | ND | ND | ND |
|  | **Hydrocarbons** |  |  |  |  |  |  |  |  |  |
| 41 | 1,3-Hexadiene,3-ethyl-2-methyl- |  | 0.28±0.02e | 0.29±0.03c | 0.34±0.01b | ND | 0.3±0.01d | 0.53±0.02a | ND | ND |
| 42 | 1,3-Dioxane,4,5-dimethyl- |  | 2.63±0.02a | ND | ND | 0.87±0.04c | 0.45±0.03d | ND | ND | 1.97±0.04b |
| 43 | Azulene |  | ND | ND | ND | ND | 0.26±0.02b | ND | 0.39±0.02a | ND |
| 44 | 2-Methoxy-4-vinylphenol | 50 | 4.42±0.03c | 4.65±0.03a | 3.14±0.03d | 4.63±0.02b | ND | ND | ND | ND |
| 45 | Benzyl nitrile |  | 0.32±0.02c | 0.48±0.03b | ND | 0.49±0.02a | ND | ND | ND | ND |
| 46 | Phenol |  | 0.22±0.03d | 0.28±0.02b | 0.23±0.03c | 0.76±0.01a | ND | ND | ND | ND |
| 47 | Phenol,4-ethyl- | 44 | 0.13±0.01b | ND | ND | 0.2±0.02a | ND | ND | ND | ND |
|  | **Pyrazines** |  |  |  |  |  |  |  |  |  |
| 48 | Pyrazine, methyl- | 27000 | 4.7±0.05a | 2.11±0.01d | 3.41±0.03b | 2.41±0.04c | ND | ND | ND | ND |
| 49 | Pyrazine,2,5-dimethyl- | 2600 | 3.64±0.03d | 15.09±0.86a | 10.32±0.01b | 8.77±0.04c | ND | ND | ND | ND |
| 50 | Pyrazine,2,6-dimethyl- | 8000 | 1.13±0.03c | ND | 2.84±0.03a | 2.67±0.03b | ND | ND | ND | ND |
| 51 | Pyrazine,2-ethyl-6-methyl- |  | 1.46±0.03a | 0.69±0.03d | 1.01±0.01c | 1.26±0.03b | ND | ND | ND | ND |
| 52 | Pyrazine,2-ethyl-5-methyl- | 100 | 3.2±0.03c | 4.97±0.06a | 3.41±0.03b | 3.18±0.04d | ND | ND | ND | ND |
| 53 | Pyrazine, trimethyl- | 297 | 5.46±0.02a | 4.77±0.04d | 4.92±0.01c | 5.18±0.04b | ND | ND | ND | ND |
| 54 | Pyrazine,2-ethyl-3,5-dimethyl- | 2.4 | 0.25±0.01c | ND | 1.29±0.03a | 0.73±0.03b | ND | ND | ND | ND |
| 55 | 2,3-Diethyl-5-methylpyrazine | 0.6 | 1.02±0.01a | 1.02±0.01a | 0.51±0.03b | ND | ND | ND | ND | ND |
| 56 | Pyrazine,2-ethenyl-6-methyl- |  | 0.32±0.02a | ND | 0.26±0.02b | 0.28±0.02c | ND | ND | ND | ND |
| 57 | 2-Acetyl-3-methylpyrazine | 4 | 0.41±0.02a | ND | 0.35±0.02b | ND | ND | ND | ND | ND |
| 58 | Pyrazine,2-methyl-5-(1-propenyl)-, (*E*)- |  | 0.2±0.02b | 0.22±0.01c | 0.12±0.03d | 0.29±0.02a | ND | ND | ND | ND |
|  | **furans** |  |  |  |  |  |  |  |  |  |
| 59 | 2-Methylfuran |  | 0.53±0.02b | 1.59±0.04a | 0.32±0.03d | 0.45±0.03c | ND | ND | ND | ND |
| 60 | 2-Pentylfuran |  | 1.49±0.02f | 1.81±0.04d | 1.9±0.03c | 1.36±0.02g | 2.3±0.04b | 2.55±0.03a | 1.25±0.03h | 1.55±0.03e |
| 61 | Benzofuran,2,3-dihydro- |  | 11.78±0.06b | 8.35±0.06c | 8.29±0.04c | 15.02±0.16a | ND | ND | ND | 4.46±0.78d |
| 62 | 2-Furfural |  | 1.31±0.04 | ND | ND | ND | ND | ND | ND | ND |
| 63 | 2-Furancarboxaldehyde, 5-methyl- |  | 0.77±0.03c | 0.31±0.04d | 1.27±0.01a | 0.86±0.03b | ND | ND | ND | 0.12±0.02e |
| 64 | Dihydro-2-methyl-3(2H)-Furanone |  | 1.06±0.03c | 1.3±0.03a | 1.14±0.03b | 0.71±0.04d | 0.51±0.04f | 0.55±0.03g | ND | 0.65±0.03e |
| 65 | 2(3H)-Furanone, dihydro -5-ethyl- |  | ND | 0.45±0.02c | 0.22±0.01f | ND | 0.37±0.03e | 0.43±0.02d | 0.55±0.02a | 0.59±0.03b |
| 66 | 2(3H)-Furanone, dihydro -5-pentyl- |  | 0.47±0.03c | ND | 0.5±0.03b | ND | 0.17±0.02f | 0.33±0.02d | 0.58±0.03a | 0.2±0.02e |
| 67 | 2(3H)-Furanone, dihydro -5-butyl |  | ND | ND | ND | ND | 0.07±0.02c | ND | 0.26±0.02a | 0.12±0.01b |
| 68 | 2-Furanmethanol |  | 4.41±0.04a | 2.83±0.02d | 3.61±0.04c | 3.76±0.03b | ND | ND | ND | ND |
| 69 | 2-Furanmethanol,5-methyl- |  | 0.31±0.04d | 0.16±0.02g | 0.19±0.01f | 0.32±0.02e | 1.05±0.03b | ND | 1.23±0.02a | 0.65±0.02c |
|  | **Pyrroles** |  |  |  |  |  |  |  |  |  |
| 70 | 1H-Pyrrole,1-methyl- |  | 1.68±0.02b | 0.91±0.01d | 1.12±0.04c | 1.74±0.03a | ND | ND | ND | ND |
| 71 | 2-Acetyl-1-pyrroline |  | 1.24±0.02b | 2.06±0.04a | ND | ND | ND | ND | ND | ND |
| 72 | 1H-Pyrrole-2-carboxaldehyde |  | 1.04±0.02b | 0.51±0.04d | 0.61±0.04c | 1.13±4.94a | ND | ND | ND | ND |
| 73 | 2-Pyrrolidinone |  | 0.3±0.04d | 0.55±0.03c | 0.64±0.01b | 1.08±0.04a | ND | ND | ND | ND |
| 74 | 1H-Pyrrole-2-Carboxaldehyde,1-methyl- |  | 0.3±0.02a | 0.14±0.02c | ND | 0.28±0.02b | ND | ND | ND | ND |
|  | **Other heterocycles** |  |  |  |  |  |  |  |  |  |
| 75 | 2H-Pyran-2-one, tetrahydro-6-methyl- |  | ND | 0.79±0.02b | ND | ND | ND | ND | 0.21±0.02c | 0.82±0.04a |
| 76 | 4(H)-Pyridine, *N*-acetyl- |  | 1.52±0.01a | 0.12±0.01c | 0.46±0.01b | ND | ND | ND | ND | ND |
| 77 | Salicylanilide |  | 1.96±0.07b | 2.46±0.03a | 1.97±0.02c | 0.86±0.03d | 0.08±0.01f | ND | 0.14±0.01e | ND |
| 78 | 5-Thiazoleethanol,4-methyl- |  | 0.26±0.02c | 0.34±0.03b | 0.46±0.02a | ND | ND | ND | 0.11±0.01e | 0.38±0.19d |
| 79 | Oxime-, methoxy-phenyl- |  | ND | ND | ND | ND | ND | 1.63±0.01a | 0.62±0.03b | ND |
|  | Total number of compounds |  | 59 | 55 | 54 | 46 | 39 | 30 | 38 | 40 |

a) Data are mean±SD of three replicates. b) different letters in superscript within the same row indicate significant differences among the oil samples tested (Turkey’s test, *p*<0.05). c) ND means not detected or percentage of the compound is lower than 0.01%

Volatiles in eight peanut oil samples were classified according to their characteristic group, such as aldehydes, ketones, alcohols, carboxylic acids, esters, alkanes, pyrazines, furans, pyrroles, and other heterocycles (Table 4-2). Apparently, the percentages of aldehydes, alcohols, and carboxylic acids in LPOs is higher than in HPOs, whereas pyrazines, furans, pyrroles, ketones, and other heterocycles in HPOs are higher than in LPOs. Specifically, pyrazines, pyrroles, and ketones were only found in HPOs. It can be indicated that pressing temperature is one of the most important factors influencing the volatile profile of peanut oil.

Aldehydes found in peanuts are associated with harsh green note (Poehlmann et al., 2013). The level of aldehydes in LPOs (35.04-60.89%) is greater than in HPOs (8.06-26.31%) (Table 4-2), which is consistent with previous research results (Chetschik et al., 2008; Liu et al., 2011; Wei et al., 2015). This may be because the Strecker aldehydes are not end products and could react to form other compounds (Balagiannis et al., 2009; Smith et al., 2014). Although oxidation aldehydes increase with the increasing processing temperature, it was expected that the total levels of aldehydes would decrease. In peanut oils, oxidation aldehydes were signiﬁcantly correlated with the oxidative status of the oil (Bendini et al., 2011). Of the oxidation aldehydes, hexanal is main contributor to the flavor of raw peanut (Emir et al., 2014). The content of Hexanal is ranged from 15.72% to 33.43% in LPOs, while it only ranged from 5.3% to 10.44% in HPOs. The high amount of hexanal in peanut oils suggest that hexanal was enzymatically produced during biosynthesis in fresh peanut (Kalua et al., 2007). Hexanal decrease with increasing temperature, which supported that hexanal level was highest in raw peanut and decreased with roasting. Hexanal is the primary oxidation product of linoleic acid. Nonanal is derived from oleic acid (Fullana et al., 2004). The ratio of hexanal/nonanal is used as primary indicator of oxidation in most studies (Vichi et al., 2007). Interestingly, nonanal was detected in a relative higher amount in LPOs, but not been identiﬁed in HPOs at all. Same results could be found in hot-pressed and cold-pressed flaxseed oils (Wei et al., 2015). The higher concentrations of 2-methylbutanal, benzaldehyde, and phenyl acetaldehyde in HPOs are supposed to be Strecker degradation products of amino acids, such as leucine and phenylalanine (Chetschik et al., 2010). Ketones were only found in HPOs (1.12-3.61%). It can be determined that temperature is a key factor for ketone formation in peanut oils.

Table 4-2. Volatile profile of peanut oil samples pressed by different technologies

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Classes | Relative content (%) and peak area (×107) | | | | | | | | | | | | | | | |
| H1 | | H2 | | H3 | | H4 | | L1 | | L2 | | L3 | | L4 | |
| Aldehydes | 26.31±0.08 | 2.26±0.03 | 18.00±0.04 | 1.3±0.03 | 17.34±0.11 | 0.89±0.07 | 8.06±0.05 | 0.37±0.02 | 45.76±0.31 | 2.65±0.12 | 60.89±0.29 | 2.18±0.13 | 35.04±0.15 | 2.00±0.09 | 35.98±0.33 | 2.32± 0.11 |
| Ketones | 2.82±0.03 | 0.24±0.02 | 1.41±0.02 | 0.1±0.01 | 3.61±0.07 | 0.19±0.04 | 1.12±0.04 | 0.05±0.01 | ND | ND | ND | ND | ND | ND | ND | ND |
| Alcohols | 4.62±0.07 | 0.4±0.03 | 9.85±0.16 | 0.71±0.09 | 4.63±0.04 | 0.24±0.01 | 8.74±0.05 | 0.4±0.02 | 31.27±0.19 | 1.92±0.07 | 5.54±0.10 | 0.19±0.04 | 28.53±0.31 | 1.62±0.11 | 13.68±0.14 | 0.88±0.05 |
| Acids | 4.26±0.11 | 0.37±0.04 | 7.58±0.12 | 0.55±0.04 | 15.88±0.12 | 0.82±0.04 | 16.81±0.10 | 0.77±0.04 | 16.07±0.07 | 0.99±0.04 | 23.88±0.52 | 0.78±0.21 | 28.86±0.43 | 1.64±0.17 | 34.88±0.37 | 2.25±0.011 |
| Esters | 1.77±0.10 | 0.15±0.07 | 3.91±0.06 | 0.28±0.02 | 3.69±0.03 | 0.19±0.01 | 5.98±0.05 | 0.27±0.02 | 1.35±0.03 | 0.08±0.01 | 3.69±0.04 | 0.13±0.01 | 2.15±0.04 | 0.12±0.01 | 3.89±0.05 | 0.25±0.02 |
| Hydrocarbons | 8.00±0.19 | 0.69±0.07 | 5.7±0.10 | 0.41±0.04 | 3.71±0.03 | 0.19±0.01 | 6.95±0.03 | 0.32±0.01 | 1.01±0.04 | 0.06±0.01 | 0.53±0.02 | 0.02±0.01 | 0.39±0.01 | 0.02±0.01 | 1.97±0.04 | 0.13±0.01 |
| Pyrazines | 21.79±0.23 | 1.87±0.10 | 28.87±0.39 | 2.09±0.13 | 28.44±0.18 | 1.46±0.07 | 24.75±0.12 | 1.13±0.05 | ND | ND | ND | ND | ND | ND | ND | ND |
| Furans | 22.13±0.16 | 1.90±0.06 | 16.8±0.21 | 1.21±0.10 | 17.44±0.15 | 0.9±0.06 | 22.5±0.09 | 1.03±0.04 | 4.47±0.05 | 0.28±0.02 | 3.86±0.05 | 0.13±0.02 | 3.87±0.03 | 0.22±0.01 | 8.34±0.17 | 0.54±0.06 |
| Pyrroles | 4.56±0.08 | 0.39±0.05 | 4.17±0.15 | 0.3±0.04 | 2.37±0.04 | 0.12±0.02 | 4.22±0.04 | 0.19±0.02 | ND | ND | ND | ND | ND | ND | ND | ND |
| Others | 3.74±0.03 | 0.32±0.01 | 3.71±0.09 | 0.27±0.04 | 2.89±0.03 | 0.15±0.01 | 0.86±0.01 | 0.04±0.01 | 0.08±0.02 | 0.01±0.00 | 1.63±0.02 | 0.05±0.01 | 1.08±0.03 | 0.06±0.01 | 1.20±0.03 | 0.08±0.01 |
| Total | 100 | 8.59±0.19 | 100 | 7.22±0.22 | 100 | 5.15±0.17 | 100 | 4.57±0.11 | 100 | 5.99±0.15 | 100 | 3.48±0.37 | 100 | 5.69±0.40 | 100 | 6.45±0.51 |

a) Data are mean±SD of three replicates. b) different letters in superscript within the same row indicate significant differences among the oil samples tested (Turkey’s test, *p*<0.05). c) NDmeans not detected or percentage of the compound is lower than 0.01% or the peak area of the compound is lower than 0.01

The decomposition and metabolism of fatty acids will also produce volatiles including alcohols, acids and esters. Alcohols are mainly produced by lipoxygenase pathway (Beltrán et al., 2011). 1-Hexanol, 1-pentanol, 1-heptanol, and 2,3-butanediol were detected in peanut oils, while its amount varied in peanut oils depend on different pressing techniques. Carboxylic acids are linked to sour and pungent notes in peanut oil (Liu et al., 2011). Acetic acid, pentanoic acid and hexanoic acid were identiﬁed in all peanut oil samples. LPOs has lower content of acetic acid than HPOs. Conversely, LPOs has higher level of hexanoic acid, pentanoic acid and butanoic acid compared with HPOs. Acetic acid and butanoic acid were reported as odor active odorants in raw peanuts, and they were significantly reduced during roasting (Chetschik et al., 2008; Chetschik et al., 2010). Esters contribute to the positive fruity aroma of peanut oils. Five esters were detected in the peanut oil samples. The level of hexyl formate in LPO2 was much higher than those in other samples. It may be produced from the esteriﬁcation of formic and hexanol. Two alkanes were found in peanut oil samples. But they are not considered to be the important contributors to the ﬂavors of oils because of their high odor threshold values (Liu et al., 2011).

The relatively high amounts of heterocycles including pyrazines, pyrroles and furans are derived from the Maillard reaction and Strecker degradation (Wei et al., 2015). Pyrazines are considered important volatiles of peanut oil, pumpkin seed oil, and sunflower oil (Bendini et al., 2011; Liu et al., 2011; Poehlmann et al., 2013). Pyrazines were the highest contributors to the volatile profile of all HPOs (21.79-28.87%). But no pyrazine was detected in the LPOs. It can be inferred that these volatile compounds are further generated during high temperature roasting or pressing. Methylpyrazine, 2,5-dimethylpyrazine, and tri-methylpyrazine were the most abundant pyrazines in HPOs. 2,5-dimethyl-pyrazine, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, 2-ethyl-5-methylpyrazine, 2-ethenyl-6-methylpyrazine, 2-acetyl-3-methyl pyrazine, and (E)-2-methyl-5-(1-propenyl)-pyrazine have previously been reported as key contributors to roasted peanut aroma (Chetschik et al., 2008).

The higher concentrations of pyrroles were also only detected in HPOs. 2-Acetyl-1-pyrroline is degradation product of the proline and the main contributor to the roasty note of roasted peanuts and pumpkin seed oil (Chetschik et al., 2008; Poehlmann et al., 2013). A remarkable amount of 2-acetyl-1-pyrroline was detected in HPO1 and HPO2, which is consistent with the previous study that it presents a pronounced increase after roasting (Vichi et al., 2007). Furthermore, 1-methyl-1H-pyrrole and 1H-pyrrole-2-carboxaldehyde were also identified in high amount in all HPOs.

Furans generally contribute to caramel-like, sweet, fruity, and nutty flavor in foods. The level of furans in HPOs (16.80-22.50%) is higher than in LPOs (3.86-8.34%). Furans was formed at high temperature roasting process. This result is consistent with previous study (Vranová et al., 2009). Among all furanones, dihydro-2-methyl-3(2H)-furanone has only ever been identified in the flavor of aromatic peanut oil. 2,3-Dihydrobenzofuran accounted for 8.29-15.02% in HPOs and 4.46% in LPO4, respectively. 2-Methylfuran exhibited a pleasant aroma and detected in all HPOs. This is consistent with the previous report that 2-methylfuran was observed at the last stage of peanut roasting (Liu et al., 2011).

3.1.2 Principal component analysis of GC-MS data

With the aim of determining the characteristic volatiles in different peanut oil samples, the data listed in Table 4-1 were submitted to PCA analysis. As shown in Figure 4-2, the ﬁrst two principal components accounted for 62% and 15% of the total variance, respectively. Figure 4-2a shows the scatter plot of the PCA scores representing the differences among eight peanut oils. Figure 4-2b represents the corresponding loadings plot that established the relative importance of each volatile and the relationships between volatiles and peanut oil type.

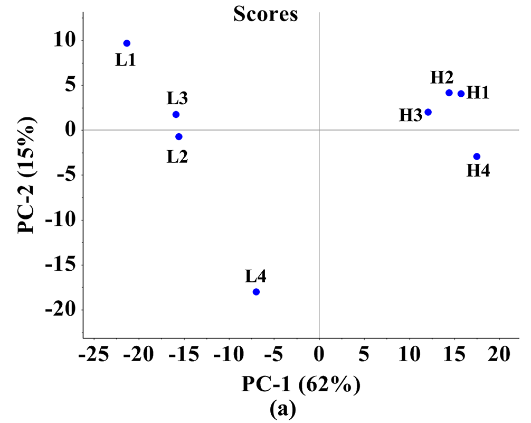
 

Figure 4-2. Score plot (a) and lodding pot (b) of PCA applied to eight peanut oil samples of GC-MS data

As is commonly known, the approximate position of the peanut oil near certain volatile vector(s) allows the conclusion that the oil characterized by the volatile(s) is particularly expressed (Bendini et al., 2011). Of all peanut oils, HPOs located in the positive region of PC1 were clearly isolated from the other samples. The compounds 61, 49, 53, 44, 52, 48, 55, 57 were associated with HPOs (Figure 4-2b and Table 4-1). This indicated that 2,3-dihydro-benzofuran (61), 2,5-dimethylpyrazine (49), trimethylpyrazine (53), 2-methoxy-4-vinylphenol (44), 2-ethyl-5-methylpyrazine (52), methyl pyrazine (48), 2,3-diethyl-5-methylpyrazine (55), 2-acetyl-3-methylpyrazine (57), and 2-ethyl-3,5-dimethylpyrazine (54) have major influence on the aroma of HPOs. These compounds are considered the characteristic volatiles in HPOs. The LPOs lied in the negative region of PC1 and were related to volatiles 2, 21, 32, 4, 7 and 6. This indicated that hexanal (2), 1-hexanol (21), hexanoic acid (32), (Z)-2-heptenal (4), nonanal (7), and (E)-2-octenal (6) were the characteristic volatiles for LPOs (Figure 4-2b and Table 4-1).

3.2 Flavor attributes analysis by e-nose system

The Heracles II e-nose system was used to discriminate flavor attributes of characteristic volatiles of peanut oils. The system was equipped with two columns MXT-5/MXT-1701 (L = 10 m, ID = 180 μm). The chromatogram obtained from peanut oils are shown in Figure 4-4. It was found that there are significant differences between the peak intensity of HPOs and LPOs. For a better visualization of the data, PCA analysis was performed. The PCA bi-plot of data collected from the Heracles II e-nose accounted for 90.54% of the variability, with PC1 and PC2 representing 72.67% and 17.87%, respectively (Figure 4-3).

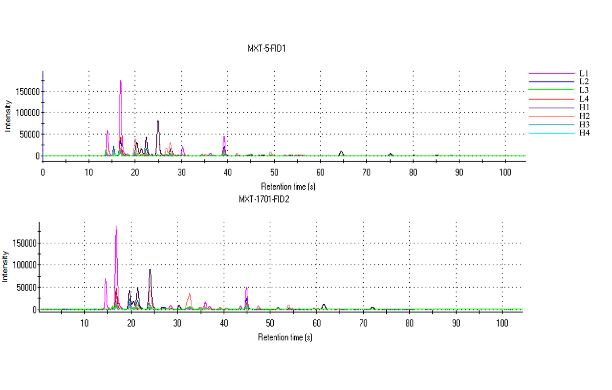
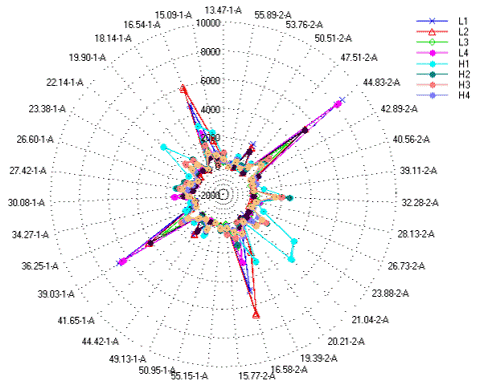
 

Figure 4-3. Superimposed chromatograms (a) and radar plot (b) of eight peanut oil samples on the 2 Heracles II columns

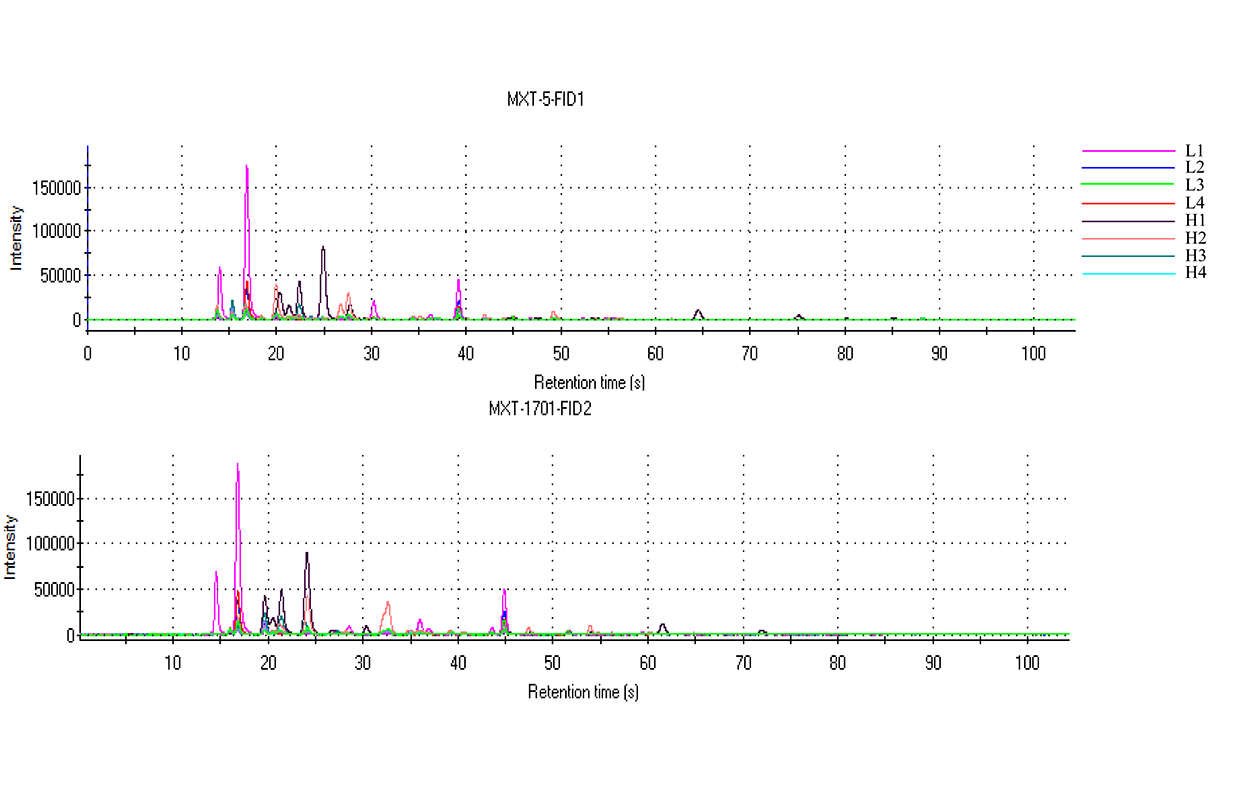


Figure 4-4. Chromatogram of HPOs and LPOs

From the PCA score plot, the principal component score distributions indicated the degree of similarities between different samples. The same peanut oil samples with repeated tests were closely located as a group. The difference between groups distributed in different locations were more clearly visualized by PCA plots (Figure 4-5). All HPOs are distributed along the left horizontal axis which is negative with PC1. LPOs are distributed along the right horizontal axis which is positive with PC1 (Figure 4-5a). The results indicated that pressing temperature have a great influence on the characteristic volatile and aroma of peanut oil. This difference could be identified by e-nose combined with PCA analysis.

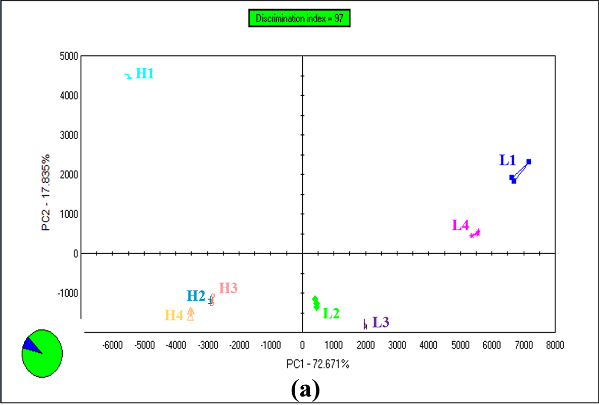
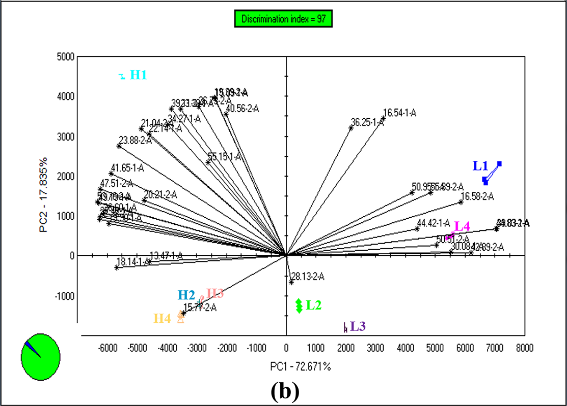
 

Figure 4-5. Score plot (a) and loading pot (b) of PCA applied to eight peanut oil samples by Heracles II e-nose analysis

The PCA loading plot shows the difference of volatile compounds of peanut oil samples (Figure 4-5b). As shown in Table 4-3, several characteristic compounds were potentially identified using Kovats indices. 2-methylbutanal (32.28-2-A, 9) was identified at high level in all peanut oils. The aldehydes hexanal (39.03-1-A, 14), (Z)-2-heptenal (44.42-1-A, 16) and nonanal (30.08-1-A, 10) are important volatiles contribute to green note of LPOs. The ester methyl-acetate (19.90-1-A, 5) and heterocyclic including 2-methylfuran (23.88-2-A, 6), 2-ethyl-5-methylpyrazine (47.51-2-A, 15), 2-ethyl-3,5-dimethylpyrazine (49.13-1-A, 17), 2,3-diethyl-5-methylpyrazine (55.15-1-A, 19) are present high levels in HOPs and low levels in LPOs. Heterocyclic compounds are important volatiles in HPOs which responsible for characteristic nutty and roasty aroma. The results of e-nose with PCA analysis are consistent with HS-SPME-GC-MS data, which both indicate that 2-ethyl-5-methylpyrazine, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, 2-methylfuran are characteristic volatiles of HPOs. Among of them, 2-ethyl-5-methylpyrazine (Didzbalis et al., 2004), 2-ethyl-3,5-dimethylpyrazine (Schirack et al., 2006; Chetschik et al., 2008; Kaneko et al., 2013), 2,3-diethyl-5-methylpyrazine (Kiefl et al., 2013; Poehlmann et al., 2013), and 2-methylfuran (Hertzschünemann et al., 2013; Petisca et al., 2013) have been reported as key volatiles in roasted peanuts and various edible vegetable oils contribute to nutty and roasty aroma. The characteristic aroma of these heterocyclic volatiles could explain the big difference of flavor between HPOs and LPOs.

Table 4-3. Characterization of volatiles in eight peanut oil samples based on their Kovats Index

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| NO. | TR MXT-5(s) | RI MXT-5 | TR MXT-1701(s) | RI MXT-1701 | Possible identification | Descriptor | OT (mg/m3) | Peak area | | | | | | | |
| H1 | H2 | H3 | H4 | L1 | L2 | L3 | L4 |
| 1 | 13.47 | 402 | 16.58 | 490 | Acetaldehyde | Etheral fresh fruity, pungent | 0.09 (air) | 651 | 881 | 955 | 474 | 314 | 241 | 361 | 396 |
| 2 | 15.09 | 438 | 19.39 | 557 | Ethanol | Alcoholic ethanol, pungent, sweet | 30 (oil) | 2396 | 208 | 129 | 794 | 911 | 219 | 420 | 357 |
| 3 | 16.54 | 468 | 16.62 | 491 | 2-Methylbutanal | - | 3.80 (air) | 3092 | 1773 | 1681 | 1095 | 4618 | 2238 | 814 | 2531 |
| 4 | 18.14 | 507 | 20.25 | 576 | Propanal | Etheral plastic, pungent, solvent | 0.12 (air) | 77 | 130 | 93 | 85 | ND | ND | ND | ND |
| 5 | 19.90 | 543 | 21.04 | 599 | Methyl acetate | Blackcurrant, etheral fruity | 2.00 (oil) | 1196 | 1251 | 1153 | 768 | 262 | 233 | 202 | 269 |
| 6 | 22.14 | 597 | 23.88 | 633 | 2-Methylfuran | Burnt chocolate, metallic | 27.5 (oil) | 3338 | 545 | 1407 | 863 | 230 | 855 | 400 | 784 |
| 7 | 23.38 | 614 | 26.73 | 680 | Ethyl Acetate | Acidic butter | 5.47 (oil) | 755 | ND | ND | ND | ND | ND | 19 | ND |
| 8 | 24.74 | 630 | 28.13 | 696 | Methyl propanoate | Etheral fruity rum | 0.35 (air) | 402 | 356 | 286 | 328 | 160 | 616 | 386 | 583 |
| 9 | 27.42 | 665 | 32.28 | 748 | 2-Methylbutanal | Almond, cocoa, green, malty | 0.01 (oil) | 1353 | 1308 | 1084 | 891 | 182 | 228 | 147 | 237 |
| 10 | 30.08 | 699 | 34.82 | 776 | Pentanal | Almond, green herbaceous, malty | 0.24 (oil) | 465 | 496 | 498 | 420 | 743 | 747 | 777 | 1398 |
| 11 | 34.32 | 747 | 40.56 | 842 | Pyridine | Cold meat, fat, fishy, rancid | 2.85 (oil) | 371 | 125 | 91 | 72 | 18 | 21 | ND | 121 |
| 12 | 36.25 | 767 | 42.89 | 871 | Pentanol | Anise balsamic fruity | 0.47 (oil) | 803 | 261 | 115 | 76 | 696 | 146 | 666 | 438 |
| 13 | 36.75 | 775 | 39.11 | 829 | 2-Methylthiophene | Sulfurous | - | 809 | 140 | 123 | 86 | 106 | 63 | 64 | 56 |
| 14 | 39.03 | 802 | 44.83 | 893 | Hexanal | Acorn, green, fatty, fishy, fruity | 0.12 (oil) | 1123 | 1399 | 1512 | 988 | 6556 | 2937 | 4067 | 6371 |
| 15 | 41.65 | 831 | 47.51 | 928 | 2,3-Diethyl-5-methylpyrazine | Nutty, roasty, sweet | 0.5 (oil) | 790 | 306 | 452 | 384 | ND | ND | 70 | 94 |
| 16 | 44.42 | 867 | 51.21 | 975 | (*E*)-2-hexenal | Almond, apple, fruity, green | 0.42 (oil) | 240 | 327 | 182 | 88 | 1467 | 153 | 1081 | 145 |
| 17 | 49.13 | 922 | 53.76 | 1008 | 2-Ethyl-5-methylpyrazine | Nutty, roasted, grassy | 0.89 (air) | 1083 | 816 | 765 | 660 | 80 | 31 | 85 | 38 |
| 18 | 50.95 | 946 | 55.89 | 1038 | 2-Acetyl-1-pyrroline | Cured ham, nutty, roasty, sweet | 0.1(air) | 78 | 77 | 73 | ND | 168 | 110 | 85 | 92 |
| 19 | 55.15 | 1002 | 59.97 | 1110 | 2-Ethyl-3,5-dimethylpyrazine | Fruity, roasty, sweet | 7.5(oil) | 498 | 457 | 382 | 343 | 323 | 219 | 263 | 426 |

a) ND means not detected or peak area of the compound is lower than 0.01.

**4. Conclusion**

Significant differences in volatiles were found between high- and low-temperature pressed peanut oil. With SPME-GC-MS analysis, 71 volatiles were identified in HPOS and 52 volatiles in LPOs. Pyrazines, pyrrole and ketones are characteristic volatiles in HPOs. Aldehydes, alcohols and carboxylic acids are major volatiles in LPOs. The results of e-nose with PCA analysis are consistent with HS-SPME-GC-MS data, which both indicate that 2-ethyl-5-methylpyrazine, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine and 2-methylfuran are characteristic volatiles for HPOs. The above volatiles contribute to strong nutty and roasty aroma of HPOs. Hexanal, 1-hexanol, hexanoic acid, (Z)-2-heptenal, nonanal, and (E)-2-octenal are characteristic volatiles which attribute the green flavor for LPOs. The results of this study could provide data to support the flavor improvement of industrial peanut oil production.

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# CHAPTER V

# *The Effect of Microwave Pretreatment on Micronutrient Contents, Oxidative Stability and Flavor Quality of Peanut Oil*

*Hui Hu1,2, Hongzhi Liu1, Aimin Shi1, Li Liu1, Marie Laure Fauconnier2,\*, Qiang Wang1,\**

*1 Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences, Beijing 100193, China*

*2 Laboratory of Chemistry of Natural Molecules, Gembloux Agro-Bio Tech, Liege University,*

*Passage des Déportés 2, 5030 Gembloux, Belgium*

The characteristic volatile compounds of low- and high-temperature pressed peanut oil were determined in the previous chapter. This chapter will focus on improvement of characteristic volatiles in low-temperature pressed peanut oil. The feasibility of using microwaves pretreatment as flavor improvement method for cold-pressed peanut oil processing was evaluated. The changes in extraction yield, physicochemical properties, micronutrients content, oxidative stability, and flavor quality of peanut oil extracted by cold pressing after microwave pretreatment were studied. The next chapter will focus on formation of characteristic volatiles in high-temperature pressed peanut oil.

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**1. Introduction**

Peanut is one of the most important oil crops in the world and is also an important source of protein. The worldwide production of peanuts reached 43.98 million tons (FAO, 2018). Oil and food production are the two main uses of peanuts (Wang et al., 2016). In 2017/18, the worldwide production of peanut oil was 5.92 million tons, among which approximately 50% were produced in China (USDA, 2018).

Peanuts are a nutrient-dense food that is rich in unsaturated fatty acids, fiber, vitamins, minerals, and many other bioactive substances. Clinical trials have suggested that compared with participants who did not eat nuts, those who consumed peanuts seven or more times per week had a 20% lower death rate (Bao et al., 2013). The total amount of unsaturated fatty acid is over 85% in peanut oil. The fatty acid profile of peanut oil resembles that of olive oil, which could reduce the risk of cardiovascular disease (Wang et al., 2016). Peanut oil is also rich in sterols (900–4344 mg/kg) and tocopherols (137-934 mg/kg) which have effects in enhancing immunity, reducing the incidence of cardiovascular diseases, lowing serum cholesterol, preventing cancer, and improving the oxidative stability of oil (Akhtar et al., 2014; Wong et al., 2014; Shahzad et al., 2017).

There are two main types of industrial peanut oil-processing methods: high-temperature pressing and cold pressing. More than 90% of peanut oil production in China is performed by the traditional technique of high-temperature pressing (Wang et al., 2016). The aromatic roasted peanut oil obtained by this method is more popular with consumers because of the strong typical flavor. However, the pretreatment of roasting and high-temperature pressing leads to the loss of micronutrients and poor oil stability. The peanut oil produced by cold pressing maintains the original quality of the peanut, and a peanut protein meal with low denaturation level could be further produced for food use. However, when compared with hot-temperature pressing, lower oil extraction yield and weaker roasted flavors of the oils were the main differences with cold-pressing. In order to reduce this, a new pretreatment is required to replace the traditional treatment before cold pressing.

In the last two decades, new technologies for improving oil recovery have attracted research attention. The feasibility of using microwaves (MW) before or during oil processing has been widely studied and has confirmed its efficiency on improving the extraction yield, nutritional value, physicochemical and sensorial properties of oil (Koubaa et al., 2016). Higher oil extraction yield was observed with MW pretreatment on rapeseed, palm, soybean, rice bran, cottonseed, Moringa oleifera seeds, black seed, chia seed, and Chilean hazelnuts (Uquiche et al., 2008; Azadmard-Damirchi et al., 2010; Terigar et al., 2011; Cheng et al., 2011; Taghvaei et al., 2014; Zhong et al., 2018; Mazaheri et al., 2019; Özcan et al., 2019). Three minutes of MW pretreatment on rapeseed with 9% moisture content increased oil extraction yield by 16-19%, and the damage to the lipoprotein membrane was distinctly seen in scanning electron micrographs, which improved the oil extraction efficiency (Wroniak et al., 2016). The effect of MW treatment on the physicochemical quality of oil has been investigated in recent years. After 10 min MW pretreatment, the peroxide value (PV) of rapeseed increased from 0.99-1.14 meq O2/kg to 2.23–2.27 meq O2/kg, which is within the Codex Alimentarius limits (PV < 15 meq O2/kg) (Rekas et al., 2017). The acid value (AV) of extracted oil from MW-treated hazelnuts increased from 1.56 mg KOH/g oil to 1.83 mg KOH/g, which was attributed to triacylglycerols hydrolysis (Uquiche et al., 2008). As a contrary result, MW pretreatment caused a significant decrease in the AV of black seed oil (4.85–3.03 mg KOH/g), which can be attributed to lipase inactivation due to the thermal pretreatment (Mazaheri et al., 2019). The effect of MW on micronutrients content and oxidative stability of oil has been reported in other research (Wroniak et al., 2016; Rekas et al., 2017). Rapeseed with moisture levels of 9-15% had individual and total tocopherols in the extracted oils which first increased, then decreased according to the period of microwave radiation. With 7 min MW treatment of rapeseed with 9% moisture, the phytosterols and polyphenols in extracted oil reached maximum values (922.48 mg/100g and 96.91 TA.100g), which were 18.04% and 176.88% higher, respectively, than the untreated sample. On the contrary, the reduction of tocopherol contents compared with the control group was observed in oil extracted from MW-treated chia seed (Özcan et al., 2019). The induction period of extracted oil increased from 7.46 h to 22.80 h due to the increased micronutrients with antioxidant activity (Yang et al., 2013). The effect of MW treatment on the flavor quality of oil has been investigated. The pyrazine compounds in the rapeseed oil appeared after 6 min of microwave pretreatment, this may be the main reason for giving a pleasant roasting flavor when compared to crude oils (Zhou et al., 2013).

Studies on the microwave treatment effect on the quality of peanut oil are still lacking. The object of this study was to investigate the changes in extraction yield, physicochemical properties, micronutrients content, oxidative stability, and flavor quality of peanut oil extracted by cold pressing after microwave pretreatment. The results of this study will be used to evaluate the feasibility of using microwaves pretreatment as an improvement method for cold-pressed peanut oil processing.

**2. Materials and methods**

2.1. Materials

Peanut samples (LUHUA11, Shandong Province) were purchased from the local market (Beijing, China). Tocopherols, Sterol and Pyrazines standards were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). C6-C23 n-alkanes standards were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Chromatographic-grade methanol and acetonitrile were purchased from Thermo Fisher Scientific Inc. (Waltham, MA, USA). Other chemicals and reagents used in this study were of analytical or chromatographic grade and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Microwave Pretreatment

For each microwave (MW) pretreatment of peanuts, 500 g of shelled peanuts were placed in a 18 cm diameter petri dish inside the microwave oven (Model: MG720KG3-NA1). The samples were pretreated at a frequency of 2450 MHz (med-high setting, 700 W) for 1–5 min with 1 min intervals. The peanut sample without MW pretreatment (0 min irradiation time) was used as the control sample. The MW-pretreated samples were cooled to room temperature for the following cold-pressing.

2.3. Cold Pressing

Peanut oil was obtained by hydraulic press (Model QYZ-230, Taian, China). The cold-pressing parameters were between 22–25MPa and 60 °C inside the press temperature for 30 min. There was no further oil obtained by longer pressing time. Residue particles in the oil were removed by 4300r/min centrifugation for 10 min. The collected oil samples were stored at 4 °C for the following experiments.

Determination of oil content in peanut and peanut meal was according to the ISO method 659 (2009). Oil extraction yield was calculated on the basis of the following formula (Swetman and Head, 1998):

|  |  |
| --- | --- |
|  | (1) |

where, Y = oil yield, RS = the ratio of non-lipid components in seed to oil content in seeds, RC = the ratio of non-lipid components in cake to the residual oil content in cake.

2.4. Physicochemical Properties and Oxidative Stability

Determination of acid value and peroxide value were according to AOCS Official Method Cd 3a-63 and Cd 8b-90, respectively (2017). The color measurements were using Lovibond PFXi-880/AT in a 1-in (25.4mm) cell. The oxidative stability index (OSI) of the oil samples was determined using Rancimat (Metrohm model 743, Metrohm KEBO Lab AB, Herisau, Switzerland) according to the method described by Azadmard-Damirchi (2010). Oil samples were respectively weighed (2.5 g) into the reaction vessel and heated to 110 °C with an air flow of 20 l/h. The induction period (IP) was expressed in hours (h).

2.5. Determination of Free Tocopherols and Phytosterols by High-Performance Liquid Chromatography (HPLC)

2.5.1. Saponification of Extracted Oil Samples

The weighed oil sample (5 g) was mixed with 50 mL of 1M potassium hydroxide in 95% ethanol in a flask. Then the 5 mL 0.57 M ascorbic acid solution was added. The flasks were shaken in a water bath at 80 °C for 30 min and cooled to room temperature. Then the solution was transferred to a separating funnel. Fifty milliliters of purified water and 100 mL hexane were added into the system. The separating funnel was vigorously shaken to ensure the unsaponifiables (tocopherols and phytosterols) were fully extracted by the hexane phase. The hexane was removed at 50 °C using a vacuum rotary evaporator. The obtained residual was re-dissolved in 2 mL ethanol for HPLC analysis.

2.5.2. HPLC Analysis of Free Tocopherols and Phytosterols

Quantification of free tocopherols and phytosterols was done using a 1250 Series HPLC system (Waters, Milford, CT, USA) equipped with a UV detector (2487, Waters, Milford, CT, USA) and a C18 reversed-phase column (250 × 4.6 mm; 5 μm). The injection volume and column temperature were 20 μL and 30 °C, respectively. Tocopherols were detected at 300nm wavelength. The mobile phase was a mixture of methanol and high-purity water (98:2, v/v). The flow rate of the mobile phase was set at 1 mL·min−1. Phytosterols were detected at the 210 nm wavelength. The isocratic mobile phase (acetonitrile: high-purity water = 98:2, v/v) was set at a flow rate of 1.5 mL·min−1. Each component was quantified using an external standard method with pure standards of tocopherols and phytosterols. Waters Breeze software (Waters, Milford, CT, USA) was used to calculate the peak areas.

2.6. Volatile Compounds Analysis

2.6.1. Headspace-Solid Phase Micro-Extraction

SPME fibre (65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber, Supelco, Bellefonte, PA, USA) was used for flavor extraction. The fiber was previously conditioned at 250 °C for 1 h before each use. Five grams of the weighed oil sample was placed into a 20 mL glass vial which was sealed with an aluminum cover and a Teflon septum. The samples were heated at 50 °C for 20 min in a thermostatic bath with a magnetic stirrer and extracted for 40 min using an auto SPME holder containing fiber. Subsequently, the fiber was injected into the gas chromatography-mass spectrometry (GC-MS) system (Shimazu QP2010 SE, Kyoto, Japan). The volatiles absorbed by the fiber were thermally desorbed in the hot injection port of the GC for 2 min at 250 °C.

2.6.2. Gas Chromatography Mass Spectrometry (GC-MS) Analysis

The GC system was equipped with a DB-WAX capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness) and a trace mass spectrometer (Finnigan, San Jose, CA, US). The splitless injection mode was used. The helium was used as the carrier gas at flow rate of 1 mL/min. The injector and detector temperature were set at 250 °C and 280 °C, respectively. The oven temperature was initially set at 40 °C for 3 min, then raised to 120° C at 5 °C/min, subsequently programmed to 200 °C at 10 °C/min, and held for 5 min. Mass spectra were recorded by electron impact ionization mode (70 eV) scanning within the mass range from 35 to 500 amu. The ion source temperature was maintained at 200 °C.

2.6.3. Identiﬁcation

Volatiles were primarily identified by comparison of the mass spectra with data from the mass spectra NIST database. In addition, the volatiles were identified by matching the retention indices (RI) data in the literature (Chung et al., 1993) and comparing with commercial standards. Based on the series of n-alkanes (C6-C23), RI were calculated according to the following formula.

|  |  |
| --- | --- |
| RIx = 100n + 100 (tRx−tRn)/(tRn+1−tRn) | (2) |

Where, retention time (tR) of tRn < tRx < tRn + 1; n = number of atom carbon.

2.7. Statistical Analysis

The experiments were performed in triplicate. The least significant difference (LSD) method was used to determine the significant difference between mean values. A confidence level was set at p < 0.05 and the software SPSS (IBM SPSS 22.0, Chicago, IL, USA) was used for statistical analysis.

**3. Results and discussion**

3.1 Effect of microwave pretreatment on oil extraction yield

Oil extraction yield is one of the key indexes to evaluate the production efficiency of oil from oilseeds. MW treated and untreated peanut samples were cold-pressed to study the effect of MW pretreatment on oil extraction yield. The initial oil content of peanut was 48.90±0.30%. The oil extraction yield of untreated peanut was 57.21 ± 1.51%. As can be seen from Figure 5-1, the increasing microwave pretreatment time significantly (p < 0.05) increased the oil extraction yield. For the 1, 2, 3 min MW-treated peanut, the oil extraction yield increased to 64.93 ± 0.58%, 68.16 ± 0.59% and 73.93 ± 0.21%, respectively. Five minutes of MW treatment reached the maximum oil extraction yield (76.52 ± 0.10%), which was 33.75% greater compared to the control. The results are consistent with previous studies of the MW pretreatment effect on the extraction yield of rapeseed oil, palm oil, soybean oil, rice bran oil, cottonseed oil, and Chilean hazelnuts oil (Uquiche et al., 2008; Azadmard-Damirchi et al., 2010; Terigar et al., 2011; Cheng et al., 2011; Yang et al., 2013; Taghvaei et al., 2014; Ramos et al., 2017; Rekas et al., 2017; Zhong et al., 2018). With 2-10 min MW pretreatment on 10.5% moisture rapeseed, the oil extraction efficiency by cold pressing gradually increased from 39.21% to 53.73% (Rekas et al., 2017). The oil extraction efficiency by solvent extraction increased with longer irradiation time (up to 3.5 min), and the optimum extraction conditions resulted in a cottonseed oil extraction efficiency of 32.6% (Taghvaei et al., 2014). MW pretreatment to oilseeds improved the oil yield of both extraction methods (mechanical pressing and solvent extraction). Microscopic studies on the MW-treated oilseed structure changes showed the MW resulted in protein denaturation which could cause damages in the lipoprotein membrane surrounding individual lipid bodies. These changes promote the passage of oil from the cell membrane, which leads to improving the oil release efficiency during the extraction procedure (Uquiche et al., 2008; Ramos et al., 2017; Zhong et al., 2018).

Figure 5-1. Effect of microwave pretreatment on the oil extraction yield. Different characters (a-e) on top of the line indicate significant (p < 0.05) differences among samples with different treatment times.

3.2 Effect of microwave pretreatment on physicochemical properties of peanut oil

Color plays a very important role in the sensory properties of oil. As shown in Table 5-1, the MW treatment significantly (p < 0.05) affected the Lovibond color of extracted peanut oils. With the increasing MW treatment time, the color of extracted oil gradually changed from light yellow (R 0.00/ Y 1.20, Control) to light brown (R 0.40/ Y 3.47, 5 min MW treatment). Darkening of oils produced from roasted seeds was also reported by other researchers (Anjum et al., 2006; Yoshida et al., 2003; Rekas et al., 2017). The changes in color may be due to the formation of phospholipid non-enzymatic browning products. MW pretreatment not only resulted in the darkening of oil but also led to an increased browning index (Rekas et al., 2017), which was consistent with the result of oil extracted from roasted pine nut (Cai et al., 2013). High correlation between the browning reaction markers (absorbance, fluorescence, and pyrrolyzed phospholipid content) could indicate that the brown compounds in the roasted seed oil are due to the occurrence of a Maillard type browning reaction of phospholipids (Shrestha and De Meulenaer, 2014).

Acid Value (AV) is a measure of the free fatty acids concentration in oil, which could be used to evaluate the freshness of oilseed, crude oil and product oil. As can be seen from Table 5-1, the AV of extracted oil from untreated peanut was 0.31 ± 0.02 mg KOH/g oil. As the peanuts were being MW treated, the AV of extracted oil was significantly (p < 0.05) increased. With 5 min MW treatment, the extracted oil reached the maximum AV (0.47 ± 0.00 mg KOH/g oil). Although it was 0.16 mg KOH/g higher than the control, it was still far below the limit in the Codex standard which allows for the presence of AV up to 4 mg KOH/g in cold-pressed and virgin oils. With the MW pretreatment, the decreased triacylglycerols (TAG) and increased free fatty acids were observed (Yoshida et al., 2003). It is indicated that the increasing AV of extracted oil from MW-treated peanut may be due to the hydrolysis of TAG, as reported by other researchers (Anjum et al., 2006; Uquiche et al., 2008; Zheng et al., 2014).

Peroxide value (PV) measures the quantity of peroxides in the oil, which serves as an indicator index of the primary oxidation product formation. Very low PV (0.54 ± 0.08 meq O2/kg oil) was determined in the oil extracted from the control sample (Table 5-1). The PV of the oil significantly (p < 0.05) increased with the increasing MW treatment time. The peanuts were MW treated for 5 min and the extracted oil reached the maximum PV (5.30 ± 0.08 meq O2/kg oil), which was also within the Codex standard of cold-pressed and virgin oils (PV < 15 meq O2/kg oil). Similar results were observed in the MW pretreatment of rapeseed, Chilean hazelnuts and sunflower seed (Anjum et al., 2006; Uquiche et al.,2008; Rekas et al., 2017). The effect of MW pretreatment on PV changes of extracted oil during the storage has also been studied. Even the initial PV of extracted oil from MW-treated rapeseed (0.85 mmol/kg) was higher than the initial PV of oil from untreated rapeseed (0.70 mmol/kg), but when stored for 32d, the PV of MW-treated oil (12.83 mmol/kg) was lower than the PV of untreated oil (20.22 mmol/kg) (Zhou et al., 2017). It can be inferred that MW pretreatment samples produced lower secondary oxidation products than the untreated samples. This result was consistent with previous research (Shrestha and De Meulenaer, 2014; Zheng et al., 2014).

Table 5-1. Effect of microwave pretreatment on physicochemical properties of oil.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **MW Time**  **(min)** | **Color**  **(Red Units)** | **Color**  **(Yellow Units)** | **Acid Value**  **(mg KOH/g Oil）** | **Peroxide Value**  **(meq O2/kg Oil)** |
| 0 | 0.00 ± 0.00 f | 1.20 ± 0.10 c | 0.31 ± 0.02 d | 0.54 ± 0.08 e |
| 1 | 0.10 ± 0.00 e | 1.40 ± 0.00 c | 0.41 ± 0.01 c | 0.64 ± 0.00 e |
| 2 | 0.20 ± 0.00 d | 2.37 ± 0.44 b | 0.43 ± 0.03 bc | 2.58 ± 0.08 d |
| 3 | 0.23 ± 0.03 c | 2.67 ± 0.24 b | 0.45 ± 0.01 ab | 3.86 ± 0.16 c |
| 4 | 0.30 ± 0.00 b | 2.67 ± 0.24 b | 0.46 ± 0.02 ab | 5.10 ± 0.00 b |
| 5 | 0.40 ± 0.00 a | 3.47 ± 0.38 a | 0.47 ± 0.00 a | 5.30 ± 0.08 a |

Values represent means ± standard deviation of triplicate tests. Values in the columns with different superscripts a–f are significantly different from each other according to least significant difference tests (*p* < 0.05).

3.3 Effect of microwave pretreatment on the free phytosterols and tocopherols content of peanut oil

Phytosterols are not only generally recognized as providing significant lowering of serum low-density lipoprotein (LDL) cholesterol in humans, but has also shown protection against various chronic ailments like cardiovascular disease, hepatoprotective, diabetes, and cancer (Wong et al., 2014; Shahzad et al., 2017). The main phytosterol sources are vegetable oils. The free-form sterols have higher efficacies (in human subjects) than sterol esters (Wong, 2014). The effect of MW pretreatment on free phytosterols content in extracted oil is shown in Table 5-2. The free phytosterols content of oil from untreated peanut was 273.55±2.51 mg/100g. The content of free phytosterols significantly (p < 0.05) increased with increasing MW treatment time. With 5 min of MW treatment, the free phytosterols in the extracted oil reached the maximum content (363.35 ± 4.22 mg/100g), which was 32.83% higher than the control. Previous research reported that 4–8 min of MW treatment of rapeseed could increase phytosterols by 57.73–140.96 mg/100g in the oil extracted by cold pressing, which was 10.18–18.36% higher than the control (Azadmard-Damirchi et al., 2010; Yang et al., 2013; Rekas et al., 2017). Comparing with the MW effect on rapeseed, MW pretreatment on peanuts has more obvious improvement in the percentage of free phytosterols content enhancement in extracted oil to the initial content in the control sample.

Tocopherols are natural antioxidants that inhibit lipid oxidation in oil. There are significant differences within the tocopherols profile among different peanut cultivars. The content of four types of tocopherols (α-, γ-, δ- and β-) in peanut oils are 18–57%, 36–78%, ND-6% and ND-2%, respectively (Akhtar et al., 2014). The free form of tocopherols has higher bioaccessibility than the esterified form, because it is easier to incorporate into mixed micelles (Yang et al., 2015). The free tocopherols profile of extracted oil is shown in Table 5-2. β-tocopherol was not detected in the oil samples in this study. The extracted oil from untreated peanuts has 18.42 ± 0.29 mg/100g free tocopherols including 13.87 ± 0.27 mg/100g α-tocopherol, 3.97 γ-tocopherol and 0.58 ± 0.02 mg/100g δ-tocopherol. MW pretreatment of peanut significantly (p < 0.05) increased the concentration of all types of free tocopherols in oils. With 5 min of MW treatment, the α-, γ- and δ-tocopherol in extracted oil all reached the maximum content (21.36 ± 0.24 mg/100g, 5.66 ± 0.04 mg/100g and 0.86 ± 0.02 mg/100g, respectively). The total free tocopherols content in extracted oil from 5 min of MW-treated peanut was 27.88 ± 0.27 mg/100g, which was 51.36% higher than the control. The damages in the lipoprotein membrane surrounding individual lipid bodies and the promoting passage of oil from cell membrane may contribute to the release of tocopherols and improving their content in the extracted oil. Contrary to our results, decreasing tocopherols content of oil from 6–30 min MW roasted peanut was reported (Yoshida et al., 2003). The tocopherols content in extracted oil from MW-treated rapeseed increased to maximum at 6 min radiation for dehulled seeds and 4 min radiation for whole seeds, and then decreased with longer treatment time. Total tocopherols in oil from MW treated rapeseed was increased to 1.08–2.61 mg/100g, which was 1.5–4% higher than control (Rekas et al., 2017). Similar results were reported by Yang (2013). With an initial moisture level of 13–15%, the tocopherols content in oil from treated rapeseed increased to maximum at 4–5 min MW exposure period. Total tocopherols in oil from MW treated rapeseed increased to 3.09-6.06 mg/100g, which was 6.50–14.02% higher than the control. The lipoprotein membrane damages may contribute to the release of tocopherols and improving their content in the extracted oil. However, it can be inferred from the reported results (Yoshida et al., 2003; Rekas et al., 2017) that the tocopherols could probably decompose with relatively long microwave pretreatments. It can be inferred that the tocopherols content in extracted oil from treated peanut possibly decreased with MW pretreatment longer than 5 min.

Table 5-2. Effect of microwave pretreatment on free phytosterols and tocopherols content (mg/100g) in oil.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **MH Time**  **(min)** | **Phytosterols** | **Tocopherols** | | | | |
| **Total** | **α-Tocopherol** | **γ-Tocopherol** | | **δ-Tocopherol** | **Total** |
| 0 | 273.55 ± 2.51 f | 13.87 ± 0.27 e | 3.97 ± 0.06 e | 0.58 ± 0.02 c | | 18.42 ± 0.29 e |
| 1 | 298.49 ± 3.26 e | 13.93 ± 0.17 e | 4.00 ± 0.07 e | 0.60 ± 0.04 c | | 18.53 ± 0.22 e |
| 2 | 310.33 ± 5.21 d | 15.82 ± 0.06 d | 4.37 ± 0.03 d | 0.60 ± 0.04 c | | 20.79 ± 0.08 d |
| 3 | 325.13 ± 6.76 c | 16.79 ± 0.22 c | 4.58 ± 0.08 c | 0.66 ± 0.01 b | | 22.03 ± 0.25 c |
| 4 | 339.16 ± 3.73 b | 20.38 ± 0.03 b | 5.05 ± 0.11 b | 0.69 ± 0.03 b | | 26.12 ± 0.12 b |
| 5 | 363.35 ± 4.22 a | 21.36 ± 0.24 a | 5.66 ± 0.04 a | 0.86 ± 0.02 a | | 27.88 ± 0.27 a |

Values represent means ± standard deviation of triplicate tests. Values in the columns with different superscripts a–f are significantly different (*p* < 0.05).

3.4 Effect of microwave pretreatment on oxidative stability of peanut oil

The oxidative stability of vegetable oil is defined as the resistance to oxidation during processing and storage (Choe and Min, 2006). The induction period (IP) is an important parameter in identifying the oxidative stability of oil. As shown in Figure 5-2, MW pretreatment on peanut significantly (p < 0.05) increases the IP of extracted oil. Oil extracted from untreated peanut has the lowest IP (6.34 ± 0.10 h). With 1, 2, 3, 4, 5 min MW pretreatment on peanut, the IP of extracted oil increased to 11.24 ± 0.08 h, 13.96 ± 0.68 h, 15.38 ± 0.59 h, 16.50 ± 0.23 h and 17.05 ± 0.31 h, respectively. These results concur with previous research (Uquiche et al., 2008; Azadmard-Damirchi et al., 2010; Yang et al., 2013; Wroniak et al., 2016; Rekas et al., 2017). The oxidative stability of vegetable oils is influenced by many factors, mainly fatty acid composition, antioxidants and minor compounds (Azadmard-Damirchi et al., 2010). As mentioned before, the darkening of extracted oil from MW-treated peanut may be due to the formation of phospholipid non-enzymatic browning products, which are known to have strong antioxidant activity (Shrestha and De Meulenaer, 2014). Tocopherols and phytosterols have also been reported to contribute to the increased oxidative and shelf life of vegetable oils (Przybylski and Eskin, 2006; Tuberoso et al., 2007). Five minutes of MW treatment on peanut could inactivate 65% lipoxygenase activity and 78% lipase activity (Ramesh et al., 1995). The inactivation of oxidative enzymes may possibly contribute to the higher oxidative stability of oil. With MW pretreatment on peanuts, increased tocopherols and phytosterols content, possible phospholipid non-enzymatic browning products and inactivation of oxidative enzymes are responsible for the improvement of the oxidative stability of extracted oil. Longer shelf life will provide stronger market competitiveness for oil products.

Figure 5-2. Effect of microwave pretreatment on the oxidative stability of oil. Different characters (a–e) on top of the line indicate significant (p < 0.05) differences among samples with different treatment times.

3.5 Effect of microwave pretreatment on volatile compounds of peanut oil

Flavor is the most important sensory quality of oil. Because of the strong nutty and roasty flavor, aromatic roasted oil is more popular with consumers than cold-pressed peanut oil. Pyrazines accounting for 50% relative percentage area were the highest contributors to the volatile profile of aromatic roasted peanut oil (Liu et al., 2011). As can be seen from Table 5-3, most of the pyrazines showed a nutty and roasty flavor. Their contribution to the whole flavor of oil will be based on their odor threshold values. 2,5-dimethyl-pyrazine is highly correlated to a roasted peanut flavor and aroma (Baker et al., 2003). A total of 101 volatile compounds in pretreated and untreated samples were identified by HS-SPME/GC-MS. The key pyrazine compounds in extracted oil from MW treated and untreated peanut by cold pressing re shown in Table 5-3. There were no pyrazines detected in the extracted oil from untreated and 1 min MW-treated peanut. With 2 min MW treatment on peanuts, 0.47 ± 0.02% trimethyl-pyrazine was detected in the volatile profile of the extracted oil. The relative content and peak area of pyrazines in extracted oil significantly (p < 0.05) increased in the period of 3–5 min of MW treatment. This observation was consistent with the previous research results, which found pyrazines in extracted oil significantly increased after 6 min of MW treatment on rapeseed (Zhou et al., 2013). With 4, 5 min MW treatment on peanuts, the relative content and peak area of pyrazines in extracted oil reached the maximum (33.37 ± 0.24% and 31.56 ± 0.31 × 107, respectively). The relative content and peak area of 2,5-dimethyl-pyrazine in extracted oil reached the maximum (5.56 ± 0.12%, 4.34 ± 0.06 × 107, respectively) with 4, 5 min MW treatment on peanuts, respectively. Pyrazines are heterocyclic nitrogen-containing compounds derived from nonenzymatic protein–sugar interactions (Davis and Dean, 2017). The formation of pyrazines in peanuts required at least 30 min roasting, and could reach a temperature of about 180 °C. Forty to 50 min roasting of peanuts leads to the formation of large amounts of pyrazine compounds (Ramesh et al., 1995). With 5 min of MW treatment, the peanut temperature could reach 125–130 °C (Schirack et al., 2006). Compared with roasting, MW could promote the formation of pyrazines by a shorter period of thermal treatment under a relatively low temperature, which could be considered the most suitable way to improve the flavor of cold-pressed peanut oil. The MW pretreatment solved the bottleneck of cold-pressed peanut oil in industrial application and promotion. As a high-quality vegetable oil, flavored cold-pressed peanut oil provided a new choice for consumers.

Table 5-3. Key pyrazine compounds identified using HS-SPME and GC-MS in extracted oil from MW treated and untreated peanut by cold pressing.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Compounds** | **Odor description** | **Microwave pretreatment time** | | | | | | | | | |
| **0 min** | **1 min** | **2 min** | **3 min** | | | **4 min** | | **5 min** | |
|  | **Peak Area (×107)** | **Relative Content (%)** | **Peak Area (×107)** | **Relative Content (%)** | **Peak Area (×107)** | **Relative Content (%)** | **Peak Area (×107)** | **Relative Content (%)** | **Peak Area (×107)** | **Relative Content (%)** |
| 2-Methyl-pyrazine | Nutty, roasted | ND | ND | ND | 1.07 ± 0.01 | | 2.27 ± 0.02 | 2.92 ± 0.03 | 3.84 ± 0.03 | 3.56 ± 0.02 | 3.47 ± 0.01 |
| 2,5-Dimethyl-pyrazine | Roasted | ND | ND | ND | 2.33 ± 0.01 | | 4.97 ± 0.03 | 4.23 ± 0.10 | 5.56 ± 0.12 | 4.34 ± 0.06 | 4.23 ± 0.07 |
| 2,6-Dmethyl-pyrazine | Nutty, roasted, sweet | ND | ND | ND | 0.77 ± 0.01 | | 1.64 ± 0.03 | 2.07 ± 0.09 | 2.72 ± 0.10 | 2.43 ± 0.02 | 2.36 ± 0.03 |
| 2-Ethyl-pyrazine | Peanut-butter, nutty, woody, buttery | ND | ND | ND | 0.42 ± 0.01 | | 0.90 ± 0.02 | 0.95 ± 0.03 | 1.25 ± 0.04 | 1.05 ± 0.04 | 1.02 ± 0.03 |
| 2,3-Dimethyl-pyrazine | Nutty, green | ND | ND | ND | ND | | ND | 1.02 ± 0.01 | 1.35 ± 0.01 | 1.05 ± 0.01 | 1.02 ± 0.01 |
| 2-Ethyl-6-methyl-pyrazine | Nutty | ND | ND | ND | ND | | ND | 1.18 ± 0.02 | 1.55 ± 0.03 | 1.48 ± 0.04 | 1.44 ± 0.03 |
| 2-Ethyl-5-methyl-pyrazine | Nutty, roasted, grassy | ND | ND | ND | ND | | ND | 2.30 ± 0.04 | 3.03 ± 0.05 | 2.60 ± 0.02 | 2.53 ± 0.01 |
| Trimethyl-pyrazine | Nutty, roasted, grassy | ND | ND | 0.47 ± 0.02 | 1.31 ± 0.06 | 1.44 ± 0.04 | 3.06 ± 0.07 | 2.93 ± 0.02 | 3.86 ± 0.03 | 3.34 ± 0.18 | 3.25 ± 0.11 |
| 2,5-Dimethyl-3-ethyl-pyrazine | Nutty, roasted, earthy | ND | ND | ND | 1.68 ± 0.02 | | 3.59 ± 0.04 | 3.51 ± 0.11 | 4.61 ± 0.13 | 3.82 ± 0.13 | 3.72 ± 0.07 |
| 2,3-Dimethyl-5-ethyl-pyrazine | Nutty, roasted | ND | ND | ND | 0.29 ± 0.01 | | 0.63 ± 0.01 | 0.81 ± 0.04 | 1.07 ± 0.05 | 1.02 ± 0.02 | 0.99 ± 0.01 |
| 2-Ethenyl-6-methyl-pyrazine |  | ND | ND | ND | 0.22 ± 0.01 | | 0.46 ± 0.02 | 0.33 ± 0.02 | 0.43 ± 0.02 | 0.44 ± 0.01 | 0.43 ± 0.01 |
| 3,5-Diethyl-2-methyl-pyrazine |  | ND | ND | ND | ND | | ND | 0.81 ± 0.04 | 1.07 ± 0.06 | 1.00 ± 0.07 | 0.97 ± 0.04 |
| 2-Methyl-6-(1-propenyl)-, (E)- pyrazine |  | ND | ND | ND | 0.48 ± 0.02 | | 1.02 ± 0.04 | 0.79 ± 0.09 | 1.04 ± 0.10 | 1.06 ± 0.05 | 1.04 ± 0.04 |
| Acetyl-pyrazine |  | ND | ND | ND | ND | | ND | ND | ND | 1.88 ± 0.07 | 1.83 ± 0.08 |
| 2-Acetyl-3-methyl-pyrazine | Nutty, vegetable | ND | ND | ND | ND | | ND | 1.52 ± 0.08 | 1.99 ± 0.10 | 2.50 ± 0.12 | 2.44 ± 0.06 |
| Total |  |  |  | 0.47 ± 0.02 | 1.31 ± 0.06 | 8.70 ± 0.06 | 18.54 ± 0.13 | 25.37 ±0 .20 | 33.37 ± 0.24 | 31.56 ± 0.31 | 30.74 ± 0.20 |

Compounds have been identified by comparison with commercial standards. Odor threshold and description in oil provided from Ref. (Liu et al., 2011). Values represent means ± SD (n = 3). ND, not detected

**4. Conclusion**

Peanut microwave pretreatment prior to cold pressing was effective for improving the extraction yield, micronutrients content, oxidative stability, and flavor quality of oil. Although the acid value (AV) and peroxide value (PV) of extracted oil from MW-treated peanuts were increased, the values were both far below the limit in the Codex standard for cold-pressed and virgin oils. Comparing with the untreated sample, 5 min MW pretreatment on peanuts significantly increased the oil extraction yield, phytosterols content, tocopherols content, and the induction period of the oil extracted by cold pressing. MW pretreatment on the peanut also formed the pyrazine which contributed to improving the nutty and roasty flavor of the cold-pressed oil. In conclusion, MW pretreatment is a feasible method to improve the oil extraction yield and to obtain the cold pressed peanut oil with longer shelf life and better flavor. The economics and energy requirements for the industrial-scale continuous microwave-assisted system need to be further investigated.

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# CHAPTER VI

# *Study on Key Aroma Compounds and its Precursors of Peanut Oil Prepared with Normal- and High-Oleic Peanuts*

*Hui Hu1,2, Aimin Shi1, Hongzhi Liu1, Li Liu1, Marie Laure Fauconnier2,\*, Qiang Wang1,\**

*1 Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences, Beijing 100193, China*

*2 Laboratory of Chemistry of Natural Molecules, Gembloux Agro-Bio Tech, Liege University,*

*Passage des Déportés 2, 5030 Gembloux, Belgium*

The previous chapter concludes that microwave pretreatment is a feasible method to improve the oil extraction yield and to obtain the low temperature pressed peanut oil with longer shelf life and better flavor. This chapter will focus on the formation of characteristic volatiles in high-temperature pressed peanut oil. The key aroma components of normal- and high-oleic peanut oil produced industrially were determined. For a possible precursor study, the amino acids and reducing sugar profile of peanut have also been monitored during oil processing. The results of this study will provide data support for raw material screening and sensory quality improvement during high temperature pressed peanut oil industrial production.

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**1. Introduction**

Peanut is one of the most important oil crops in the world. Worldwide, the production of peanuts reached 49.62 million tons in 2020/21, and the production of peanut oil was 6.43 million tons, among which approximately 50% was produced in China (USDA, 2021). The total amount of unsaturated fatty acid is over 85% in peanut oil. The fatty acid profile of peanut oil resembles that of olive oil, which could reduce the risk of cardiovascular disease (Wang et al., 2016).

The flavor, nutritional quality, and shelf-life of peanut and its products are related to the relative proportion of various fatty acids (Derbyshire, 2014). With more than 72% oleic acids, high-oleic peanut is well recognized by processors for its low oxidative and ability to extend the shelf life of products (Yu et al., 2020). Wang Qiang research group reported that high-oleic peanut oil could attenuate diet-induced Metabolic Syndrome, associated with modulating gut microbiota (Zhao et al., 2019). The breeding of high-oleic acid peanut in China has developed rapidly in recent years. Since the first high-oleic natural mutant discovered in 1987, over 190 high oleic peanut cultivars have been developed in China (Norden et al., 1987). More and more peanut processing companies are trying to use high-oleic acid peanut in oil processing. More than five brands of high-oleic peanut oil have entered the market in China in the last three years. All these products use high-oleic runner peanut raw materials from the USA. However, the consumer feedback showed that the aroma of high-oleic peanut oil was not as good as that of normal-oleic peanut oil.

Compared with other edible vegetable oils, aromatic roasted peanut oil obtained by thermal processing is more popular for consumers because of its strong nutty and roasty flavor (Hu et al., 2019). The unique flavors of thermally processed foods are commonly generated through the Strecker degradation during the Maillard reaction, which is responsible for generating various heterocyclic compounds, including pyrazines, pyrroles, pyridines, etc. (Salehi, 2020). Correlation of volatile compounds to peanut sensory evaluation has attracted researcher’s attention. A previous study reported that aspartic acid, glutamic acid, glutamine, asparagine, histidine, and phenylalanine contributed to the characteristic peanut flavor formation, and monosaccharides are highly related to pyrazine component (Newell et al., 1967). Pyrazine compounds are responsible for the roasted flavor and aroma during peanut roasting (Baker et al., 2003). Over 100 volatile components were identified in hot-pressed peanut oil, including pyrazines, aldehydes, furans, alcohols and pyrroles. Pyrazines are considered to be the major volatile compounds responsible for the typical roasted/nutty flavor of hot-pressed peanut oil (Qian et al., 2019). The compounds 2/3-methyl-1H-pyrrole, 5-methyl-2-furancarboxaldehyde, benzeneacetaldehyde, 2,3 dimethyl-1H-pyrrole, 2,5 dimethyl pyrazine, 5-methyl-2-furanmethanol, and maltol were considered the most important volatile components which positively correlated with the peanutty and roasted aroma (Dimitrios et al., 2016).

The major precursors for volatiles in peanut are proteins, sugars, and lipids (Davis and Dean, 2016). Different kinds of sugars and proteins mixtures react differently, which lead to different volatiles formation. Compared with glycine and diglycine, triglycine has the highest capability to formed pyrazines in Maillard model systems. Major pyrazines were identified as 2,5-dimethylpyrazine and trimethylpyrazine (Lu et al., 2005). Glutamine and asparagine have shown high reactivities to produce high content of pyrazines (Ho et al., 2005). The rapeseed peptides subsequently reacted with D-xylose to largely produce methylpyrazine and ethyl-2,5-dimethylpyrazine (He et al., 2019). Methylpyrazine and 2,5-dimethylpyrazine were identified in the D-glucose and L-theanine Maillard model systems but were not detectable in thermal reactions with single D-glucose or L-theanine (Guo et al., 2018). The compounds 2,6-dimethyl-3-ethyl pyrazine, 2,5-diethylpyrazine and 2-methyl-3,5-diethylpyrazine were formed in the reaction between 1,4-13C-labeled L-ascorbic acid and L-glutamic acid. The α-amino carbonyl or α-amino hydroxy compounds were found to be the precursors of pyrazines (Yu et al., 2013).

The sensory quality difference between normal- and high-oleic peanut has also been studied. There were small differences in the roasting, astringency, over-roasting, and nuttiness attributes between these two kinds of peanuts. High-oleic lines exhibiting slightly greater intensities of those attributes (Isleib et al, 2006). Variation among individual lines for several sensory attributes (dark roasted, raw/beany, roasted peanutty, sweet aromatic, sweet, bitter, wood-hulls-skins, and “off flavors” stale/cardboard, fruity/fermented and plastic/chemical) suggest the flavor of high-oleic cultivars is at least as good as the profiles of normal-oleic cultivars (Isleib et al., 2015).

Studies of characteristic volatile compounds and precursors of normal- and high-oleic peanut oil are still lacking. The object of this study was to compare the sensory quality and the key aroma components of normal- and high-oleic peanut oil produced industrially. For a possible precursor study, the amino acids and reducing sugar profile of peanut have also been monitored during oil processing. The results of this study will provide data support for raw material screening and sensory quality improvement during high temperature pressed peanut oil industrial production.

**2. Materials and methods**

2.1. Materials

Normal- and high-oleic peanut raw materials and oil processing samples (roasted peanut, peanut oil, and peanut meal) were collected from the industrialized production line in factory (Jinsheng Cereals & Oils Group, Shandong Province, China). The varieties of normal- and high-oleic peanut are Baisha 1016 (China) and high-oleic runner (USA), respectively. The peanut raw material was roasted at 150 °C for 45 min. After this, roasted peanuts were pressed at 120 °C to obtain peanut oil. All reagents used in this research were obtained from Sigma-Aldrich (St. Louis, MO, USA), including methyl-pyrazine, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 1-methyl-1H-pyrrole, furfural, benzaldehyde, 2-furanmethanol, hexanal, pentanal, 1,2,3-trichloropropane, etc.

2.2. Sensory Evaluation

Sensory evaluation was performed at room temperature. Twelve panelists (7:5 male: female) participated to sensory evaluation. All of the panelists are well-trained researchers with a minimum of 300 h experience in sensory evaluation. Details on the methods, lexicon and attribute definitions have been previously published (Johnsen et al., 1988; Sanders et al., 1989; Schirack et al., 2006). The sensory attributes used were roast peanutty aroma, dark roast aroma, sweet aroma, raw/beany aroma, woody/hulls/skins aroma, and a 9-point scale was used (1 = very weak, 9 = very strong). The lexicon of flavor sensory attributes is shown in Table 6-1.

Table 6-1. Flavor sensory attributes as obtained from the expert panel.

|  |  |
| --- | --- |
| **Sensory Attribute** | **Description a** |
| Roast Peanutty | The aromatic associated with medium-roast peanuts having a fragrant character such as methyl pyrazine |
|
| Dark Roast | The aromatic associated with dark roasted peanuts having a very browned or toasted character |
|
| Sweet Aromatic | The aromatics associated with sweet material such as caramel, vanilla or molasses |
|
| Raw/Beany | The aromatics associated with light roast peanuts having a legume like character |
|
| Woody/Hulls/Skins | The aromatics associated with base peanut character (absence of fragrant top notes) related to dry wood, peanut hulls and skins |
|
|

a Lexicon and method defined in the literature (Johnsen et al., 1988; Sanders et al., 1989; Schirack et al., 2006).

2.3. Volatile Compounds Analysis

Volatile compounds in normal- and high-oleic peanut and oil processing samples were analyzed by headspace-solid phase micro-extraction (HS-SPME). SPME fiber (50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane, Stableflex, Supelco Co., Bellefonte, PA, USA) was utilized for flavor extraction. The fiber was previously conditioned at 270 °C for 30 min before the first measurement. The sample (5 g) were weighed into a 20 mL glass vial which was sealed with an aluminum cover and a Teflon septum. A 25 μL aliquot of 1,2,3-trichloropropane (0.25 mg/mL in methanol) as internal standard was added. It was pre-equilibrated for 10 min at 55 °C in shaken incubator. After the equilibration time, an auto SPME holder containing fiber was inserted into the vial, and the fiber was exposed to the headspace for 40 min. The volatiles absorbed by the fiber were thermally desorbed in the hot injection port of the GC for 150 s at 260 °C. GC-MS analysis was performed using GC system (Agilent 7890B, Agilent Technologies, Santa Clara, CA, USA) and mass selective detector (Agilent 5977B) equipped with a VF-WAX column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Agilent CP9205, Agilent Technologies, Santa Clara, CA, USA). The analysis was carried out in the splitless mode, using helium as the carrier gas (1 mL/min flow rate). The detector temperature was 250 °C. The oven temperature program was initially set at 40 °C for 5 min, and programmed at 5 °C/min to 250 °C which was held for 5 min. Mass spectra were recorded in electron impact ionization mode (70 eV) scanning a mass range (m/z) from 35 to 500 amu. The ion source temperature was maintained at 230 °C. For the identification of volatiles, the peanut oils were analyzed by GC-MS under the experimental conditions mentioned above. Volatiles were primarily identified by comparison of the mass spectra with data from the commercially available mass spectra NIST databases. In addition, the volatiles were identified by matching the retention indices (RI) with data found in the literature (Liu et al., 2011) and comparing them with commercial standards. Based on the series of n-alkanes (C7-C30), RI were calculated according to the following formula:

RIx = 100n + 100 (tRx − tRn)/(tRn + 1 − tRn) (1)

where retention time (tR) of tRn < tRx < tRn + 1; n = number of atom carbon.

2.4. GC-MS-O Analysis of Volatile Compounds

GC-MS-O analysis was performed using GC system (Agilent 7890B, Agilent Technologies, Santa Clara, CA, USA) and mass selective detector (Agilent 5973B) equipped with Olfactory detection port (ODP3, Gerstel, Germany). The GC-MS system parameters were the same as in 2.3. The connector temperature of the olfactometer was 150 °C. The end effluent of capillary, respectively, flows into the MS and olfactometer at a split ratio of 1:1. The odor strength was set up to a 5-point scale (1 = very weak, 5 = very strong).

2.5. Amino Acid Profile Analysis

Amino acids determination followed the method described in Reference (Paul et al, 2016). The amino acid profile was measured using ion exchange chromatography. The sample (100 mg) was hydrolyzed with 10 mL 6 N HCl containing 0.1% phenol, followed by nitrogen flushing for 1 min and closing the hydrolysis bottle. Bottles were heated at 110 °C for 24 h in an oven and cooled with ice. After this, 30 mL of citrate buffer at pH 2.2 was poured (with continuous stirring) into bottles while they were still on ice. Then pH was adjusted between 0.5 and 1 using 7.5 N NaOH and then readjusted to 2.2 using 1 N NaOH. This solution was added in a 100 mL volumetric flask already containing 1 mL solution of 500 μM norleucine in citrate buffer at 2.2 pH. The volume of this flask was made 100 mL by adding citrate buffer at 2.2 pH. This solution was stirred and filtered through a 0.2 μm filter. The filtered solution was used to measure amino acids separately using Biochrom 20 plus amino acid analyzer (Biochrom Limited, Cambridge, UK).

2.6. Soluble Reducing Sugar Profile Analysis

Soluble reducing sugars determination followed the method described in Reference (Tahir et al., 2011). Defatted sample (0.5 g) was weighted in centrifuge tube. Soluble reducing sugars were extracted with 10 mL 70% ethanol under ultrasonic condition for 20 min. The supernatant was collected after 2000 r/min centrifugation for 10 min. The ethanol extraction and centrifuge procedure were repeated with the residue. Two parts of supernatant were filtered and vacuum rotary evaporated under 50 °C. The volume was made constant at 1 mL with 70% ethanol for analysis. The detection was performed on HPLC (Agilent 1260 Infinity, Agilent Technologies, Santa Clara, CA, USA) with diode array detector (G4212B). Spherisorb column (4.6 mm × 250 mm, 5 μm, Waters, Milford, MA, USA) was used. The mobile phase was 70% acetonitrile at a flow rate of 1 mL/min. The results were expressed as gram sugar per kilogram samples.

2.7. Statistical Analysis

The experiments were performed in triplicate. The least significant difference (LSD) method was used to determine the significant difference between mean values. A confidence level was set at p < 0.05, and the software SPSS (IBM SPSS 22.0, Chicago, IL, USA) was used for statistical analysis.

**3. Results and discussion**

3.1 Sensory evaluation of peanut oil processing samples

Flavor is the most important quality of peanut products. The sensory evaluation results of peanut raw materials and thermal processed samples are shown in Figure 6-1. There are significant differences in sensory attributes between the raw material and thermal processed sample. Raw/beany and woody are the main flavors of peanut raw material. Normal-oleic peanut has a slightly stronger sweet aromatic (3.15) than high oleic peanut (2.40). Flavor attributes of high-oleic raw peanuts have been reported to be very similar to the normal oleic cultivars (Isleib et al., 2006). After roasting, raw/beany and woody flavor attributes significantly reduced. Dark roast, roast peanutty and sweet aromas make a great contribution to the roasted peanut flavor. Under the same processing conditions, roasted normal-oleic peanut has stronger roast (4.28), peanutty (4.80) and sweet (4.65) flavors, which were 16.33%, 20.75% and 29.17% higher than those of roasted high-oleic peanut, respectively. Roasted high-oleic peanuts have a stronger raw/beany (3.6) and woody (3.45) aroma than roasted normal-oleic peanuts (3 for raw/beany, 2.4 for woody). After high temperature press, the dark roast, roast peanutty and sweet aroma of samples continuously increased. Normal-oleic peanut oil has stronger roast (6.00), peanutty (7.2) and sweet (5.85) flavors, which were 21.21%, 29.73% and 18.18% higher than those of roasted high oleic peanut, respectively. The raw/beany and woody aromas of normal- and high-oleic peanut oil were all around 2 with no difference. Statistically significant variation among 59 roasted peanuts was reported (Isleib et al., 2015). High oleic peanut cultivars showed a wide range of several sensory attributes (dark roasted, raw/beany, roasted peanutty, sweet aromatic, wood-hulls-skins, and “off flavors” stale/cardboard). The upper limit of positive sensory attributes for the high-oleic peanuts was greater than the normal cultivars. The differences in sensory quality between normal- and high oleic peanut products maybe caused by the composition and relative concentration of characteristic key volatile components.

Figure 6-1. Sensory evaluation result of normal- and high-oleic peanut and oil processing samples.

3.2 Comparison of volatile components between normal- and high oleic peanut oil

As shown in Table 6-2, a total of 93 volatile components were identified in normal- and high-oleic peanut oil (NPO and HOPO), including 20 aldehydes, 17 alcohols, 10 alkanes, 8 acids, 5 ketones, 5 alkenes, 2 esters, 7 Pyrazines, 3 Pyridines, 3 Pyrroles, 11 furans and 2 pyrans. Most of the identified volatile components have been reported (Liu et al., 2011; Qian et al., 2019). Several py-razines, pyridines, pyrroles, furans and pyrans were firstly reported in the present study, including 2-methoxy-3-(1-methylethyl)-pyrazine, 1-(2-pyridinyl)-ethanone, 1-methyl-1H-pyrrole, 2-methyl-furan, 5-methyldihydro-2(3H)-furanone, 4-methyldihydro-2(3H)-furanone, 5-pentyldihydro-2(3H)-furanone, 3-hydroxydihydro-4,4-dimethyl-2(3H)-furanone, tetrahydro-2H-pyran-2-one and 3-hydroxy-2-methyl-4H-pyran-4-one. The composition and relative content of N-heterocyclic, O-heterocyclic and nonheterocyclic between normal- and high-oleic pea-nut oil were significantly different. The HOPO contains 39.40% N-heterocyclic, which is twice that of NPO. Among them, 35.14% 1-methyl-1H-Pyrrole in HOPO is three times that of NPO. Pyrroles were formed in the Maillard reaction and highly correlated to roast flavor and aroma (Nursten, 2005). Pyrazines are diverse heterocyclic nitrogen-containing compounds derived from nonenzymatic protein–sugar interactions. These volatile compounds contribute to the roasted/nutty flavor (Davis and Dean, 2016). The pyrazine content of NPO and HOPO were 3.16% and 4.17%, respectively. O-heterocyclic accounting for 7.44% and 4.24% volatile components of NPO and HOPO, respectively. Ten furans in HOPO account for 6.78% of volatile components, which is twice the amount in HOPO. Furan derivatives have been identified as the second largest volatiles in roasted peanut oil (Vranov and Ciesarov, 2009). They were considered to contribute to the thermally processed food flavor, including caramel-like, sweet, fruity, and nutty. Nonheterocyclic compounds were derived from lipid decomposition (Ho and Shahidi, 2005). Aldehyde compounds were the most important nonheterocyclic compounds which appear as green, painty, metallic, beany and rancid and are also responsible for the undesirable flavors of oils (Kalua et al., 2007). The NPO contains 39.36% aldehydes which is 1.61 times that of HOPO. Hexanal accounts for 17.29% and 5.74% of total volatiles in NPO and HOPO, respectively. High oleic acid improves the oxidative stability of peanut products and reduces the formation of aldehydes.

Table 6-2. Composition and relative content of volatile components in normal- and high-oleic peanut oil.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  |  | **Normal-Oleic Peanut Oil** | **High-Oleic Peanut Oil** |
| **Order** | **Retention Index** | **Volatile Compound** | **Volatile Compound (%)** | **Volatile Compound (%)** |
|  |  | **N-heterocyclic** |  |  |
|  |  | Pyrazines |  |  |
| 1 | 1265 | Pyrazine, methyl- | 0.57 | 0.79 |
| 2 | 1319 | Pyrazine, 2,5-dimethyl- | 1.27 | 1.73 |
| 3 | 1334 | Pyrazine, ethyl- | 0.24 | 0.22 |
| 4 | 1344 | Pyrazine, 2,3-dimethyl- | 0.08 | 0.03 |
| 5 | 1389 | Pyrazine, 2-ethyl-5-methyl | 0.75 | 1.20 |
| 6 | 1434 | Pyrazine, 2-methoxy-3-(1-methylethyl) | 0.14 |  |
| 7 | 1440 | Pyrazine, 3-ethyl-2,5-diemethyl | 0.09 | 0.19 |
|  |  | Pyridines |  |  |
| 8 | 1178 | Pyridine | 0.11 |  |
| 9 | 1577 | Pyridine, 3-methoxy- | 0.49 |  |
| 10 | 1599 | Ethanone, 1-(2-pyridinyl) | 0.10 | 0.09 |
|  |  | Pyrroles |  |  |
| 11 | 1140 | 1H-Pyrrole, 1-methyl- | 12.94 | 35.14 |
| 12 | 1976 | Ethanone, 1-(1H-pyrrol-2-yl) | 0.13 |  |
| 13 | 2032 | 1H-Pyrrole-2-caboxaldehyde | 0.05 |  |
|  |  | Total | 16.98 | 39.40 |
|  |  | **O-heterocyclic** |  |  |
|  |  | Furans |  |  |
| 14 | 1233 | Furan, 2-methyl- | 0.17 |  |
| 15 | 1235 | Furan, 2-pentyl- | 2.39 | 1.12 |
| 16 | 1608 | 2(3H)-Furanone, dihydro-5-methyl |  | 0.18 |
| 17 | 1614 | 2(3H)-Furanone, dihydro-4-methyl | 1.04 | 1.05 |
| 18 | 1629 | 2(3H)-Furanone, dihydro- | 0.53 | 0.74 |
| 19 | 1665 | 2-Furanmethanol | 0.91 | 0.22 |
| 20 | 1697 | Furan, 2-pentyl- | 0.14 |  |
| 21 | 1730 | 2,5-Furandione, 3,4-dimethyl | 0.09 |  |
| 22 | 2027 | 2(3H)-Furanone, dihydro-5-pentyl | 0.07 |  |
| 23 | 2042 | 2(3H)-Furanone, dihydro-3-hydroxy-4,4-dimethyl | 0.41 |  |
| 24 | 2407 | 2,3-dihydro-benzofuran | 1.03 |  |
|  |  | Pyrans |  |  |
| 25 | 1804 | 2H-Pyran-2-one, tetrahydro- |  | 0.06 |
| 26 | 1968 | 4H-Pyran-4-one, 3-hydroxy-2-methyl- | 0.67 | 0.87 |
|  |  | Total | 7.44 | 4.24 |
|  |  | **Nonheterocyclic** |  |  |
|  |  | Aldehydes |  |  |
| 27 | <1000 | Butanal, 2-methyl- | 1.19 | 1.12 |
| 28 | <1000 | Butanal, 3-methyl- | 1.16 | 0.88 |
| 29 | <1000 | Pentanal | 2.87 | 0.48 |
| 30 | 1078 | Hexanal | 17.29 | 5.74 |
| 31 | 1185 | Heptanal | 0.76 | 1.89 |
| 32 | 1218 | 2-Hexenal, (E) | 0.48 | 0.13 |
| 33 | 1290 | Octanal | 1.08 | 3.75 |
| 34 | 1324 | 2-Heptenal, (Z) | 4.94 | 1.06 |
| 35 | 1395 | Nonanal | 1.33 | 4.95 |
| 36 | 1429 | 2-Octenal, (E) | 0.63 |  |
| 37 | 1468 | Furfural | 1.27 | 0.76 |
| 38 | 1518 | Benzaldehyde | 2.69 | 2.77 |
| 39 | 1531 | 2-Nonenal, (E) | 0.47 |  |
| 40 | 1643 | benzeneacetaldehyde | 1.15 | 0.10 |
| 41 | 1704 | Benzaldehyde, 4-ethyl- | 0.12 | 0.09 |
| 42 | 1762 | 2,4-Decadienal | 0.56 |  |
| 43 | 1783 | 3-Phenylbutanal | 0.13 |  |
| 44 | 1806 | 2,4-Decadienal, (E,E)- | 1.21 |  |
| 45 | 1829 | 2-Propenal, 3-phenyl | 0.05 |  |
| 46 | 2405 | Benzaldehyde, 4-methyl |  | 0.70 |
|  |  | Alcohols |  |  |
| 47 | <1000 | 2-Propanol |  | 0.33 |
| 48 | <1000 | Ethanol | 0.44 |  |
| 49 | <1000 | 2-Butanol |  | 0.05 |
| 50 | 1092 | 1-Propanol, 2-methyl- | 0.06 | 0.31 |
| 51 | 1207 | 1-Butanol, 3-methyl |  | 2.16 |
| 52 | 1256 | 1-Pentanol | 4.08 | 2.16 |
| 53 | 1359 | 1-Hexanol | 5.79 | 2.29 |
| 54 | 1453 | 1-Octen-3-ol | 2.33 | 0.36 |
| 55 | 1558 | 1-Octanol | 0.46 | 2.45 |
| 56 | 1582 | 2,3-Butanediol | 0.08 |  |
| 57 | 1618 | Ethanol, 2-(2-ethoxyethoxy) | 0.18 | 0.26 |
| 58 | 1659 | 1-Nonanol |  | 0.62 |
| 59 | 1791 | Ethanol, 2-(2-butoxyethoxy)- | 0.15 |  |
| 60 | 1912 | Phenylethyl Alcohol | 1.33 | 2.89 |
| 61 | 2018 | Phenol | 0.08 | 0.07 |
| 62 | 2184 | Phenol, 2-(1-methylpropyl)- | 0.19 |  |
| 63 | 2309 | 5-Thiazoleethanol, 4-methyl | 0.35 |  |
|  |  | Alkanes |  |  |
| 64 | <1000 | Pentane | 6.34 |  |
| 65 | <1000 | Heptane | 1.01 | 1.59 |
| 66 | <1000 | Octane | 1.92 | 2.00 |
| 67 | <1000 | Heptane, 2,4-dimethyl |  | 0.65 |
| 68 | <1000 | 2-Propanone |  | 1.35 |
| 69 | <1000 | Octane, 4-methyl |  | 0.43 |
| 70 | <1000 | Heptane, 2,2,4,6,6-pentamethyl- | 0.51 | 4.52 |
| 71 | <1000 | Decane | 0.03 | 2.29 |
| 72 | 1197 | Dodecane |  | 1.07 |
| 73 | 1401 | Tetradecane | 0.80 |  |
|  |  | Acids |  |  |
| 74 | 1496 | Acetic acid | 1.58 | 0.73 |
| 75 | 1769 | Pentanoic acid | 0.35 | 0.11 |
| 76 | 1875 | Hexanoic acid | 1.87 | 0.96 |
| 77 | 1981 | Heptanoic acid | 0.44 | 0.49 |
| 78 | 2087 | Octanoic acid | 0.46 | 0.28 |
| 79 | 2164 | Benzoic acid | 0.55 |  |
| 80 | 2192 | Nonanoic acid | 0.99 | 0.50 |
| 81 | 2298 | Decanoic acid | 0.07 |  |
|  |  | Ketones |  |  |
| 82 | 1129 | 3-Penten-2-one, 4-methyl- | 0.50 |  |
| 83 | 1182 | 2-Heptanone | 0.49 |  |
| 84 | 1286 | 2-Octanone | 0.14 | 0.20 |
| 85 | 1340 | 6-Methyl-5-hepten-2-one | 0.06 | 0.06 |
| 86 | 1407 | 3-Octen-2-one | 0.33 |  |
|  |  | Alkenes |  |  |
| 87 | <1000 | 2-Octene, (Z) | 0.49 |  |
| 88 | <1000 | 2-Octene, (E) | 0.23 |  |
| 89 | <1000 | Alpha-Pinene | 0.27 |  |
| 90 | 1096 | Undecane |  | 0.42 |
| 91 | 1195 | Limonene | 0.70 | 0.24 |
|  |  | Esters |  |  |
| 92 | 1071 | Acetic acid, butyl ester |  | 0.12 |
| 93 | 1635 | Decanoic acid, ethyl ester | 0.55 |  |
|  |  | Total | 75.58 | 56.37 |

3.3 GC-O analysis of key volatile components of high-temperature pressed peanut oil

The contribution of volatile components to the whole flavor of peanut oil was based on their relative concentration, odor classification and odor strength. Quantitative determination and odor strength evaluation are used for characteristic volatile components study. The correlation between characteristics volatile compounds and sensory characteristics has been studied. The compounds 2,5-dimethylpyrazine (correlated with nutty and roasted odors) and 1-methyl-1H-pyrrol (correlated with sweet and woody odor) are two of the most reported volatile components in roasted peanut products. The compounds 2/3-methyl-1H-pyrrole, 5-methyl-2-furancarboxaldehyde, benzeneacetaldehyde, 2,3-dimethyl-1H-pyrrole, 2,5-dimethylpyrazine, 5-methyl-2-furanmethanol and maltol are positively correlated to peanutty and roast aroma (Dimitrios, 2016). Having the second highest relative concentration of furan derivatives, 2-furaldehyde contributes to the sweet and caramel-like aromas of heated foods (Flament, 2002). As a Strecker degradation product of phenylalanine amino acid, benzaldehyde provided an almond-like aroma (Ho et al., 2007).

As shown in Table 6-3, several pyrazines, pyrroles, furans and aldehydes were screened out as possible key volatiles, which contribute to the nutty, roasty and sweet flavors of peanut oil. Among all pyrazines, 2,5-dimethylpyrazine was most highly correlated to roasted peanut flavor and aroma. Comparing with 1-methy-1H-pyrrole, 3 pyrazine showed stronger nutty odor with GC-MS-O evaluation in the present study. 2,5-dimethylpyrazine has the strongest nutty odor (3.67). The nutty odor strength of methylpyrazine and 2-ethyl-5-methylpyrazine are 3.00 and 2.67. Although the 1-methyl-1H-pyrrole has the highest relative concentration (6.29 mg/kg in NPO, 7.28 mg/kg in HOPO), its nutty odor strength is only 1.33. A similar result was reported in which the correlation coefficient of 1-methyl-1H-pyrrole to nutty flavor was relatively low (Dimitrios, 2016). It can be determined that methylpyrazine, 2,5-dimethylpyrazine and 2-ethyl-5-methylpyrazine are key volatiles that contribute to the nutty and roast flavor of peanut oil. The NPO contains 0.28 ± 0.02 mg/kg methylpyrazine, 0.62 ± 0.05 mg/kg 2,5-dimethylpyrazine and 0.37 ± 0.03 mg/kg 2-ethyl-5-methylpyrazine, which are 75%, 72% and 48% higher than those of HOPO, respectively. The sensory comparison between normal- and high-oleic peanut has been reported. Compared with normal-oleic peanut, four high-oleic breeding lines (derived by the Florida high-oleic gene) showed a stronger roasted peanut sensory attribute (Pattee and Knauft, 1995). High-oleic peanuts contribute higher roast (1.83 vs. 1.57, p < 0.05) and nutty (2.69 vs. 2.53, p < 0.05) aromas than normal-oleic peanuts among 14 peanut genetic entries (5 high-oleic, 9 normal-oleic). Roasted high-oleic peanuts have a wider roasted peanutty (3.92–5.15) odor range than roasted normal-oleic peanut (4.26–4.89) (Isleib et al., 2006).

The compounds 1-methyl-1H-pyrrole, furfural, benzaldehyde, 2-furanmethanol and 3-hydroxyl-2-methyl-4H-pyran-one contribute to the sweet aroma of peanut oil (Table 6-3). Among of them, benzaldehyde and 3-hydroxyl-2-methyl-4H-pyran-one are considered to be the key volatiles with 2.33 and 2.00 sweet aroma strength, respectively. Compared with normal-oleic peanut oil, high-oleic peanut oil has a higher relative concentration of furfural (0.62 vs. 0.00), benzaldehyde (1.30 vs. 0.57), 2-furanmethanol (0.44 vs. 0.05) and 3-hydroxyl-2-methyl-4H-pyran-one (0.32 vs. 0.18), which lead to a stronger sweet aroma. This is consistent with the previous sensory evaluation result. There is no significant difference on sweet aroma between high-oleic roasted (2.44) and normal-oleic roasted pea-nuts (2.39) (Isleib et al., 2006). Sweet aromatic strength ranged from 2.41 to 3.24 fiu for high-oleics peanuts and 2.71 to 3.24 fiu for normal-oleic (Isleib et al., 2015). Hexanal is one of the primary oxidation products of linoleic acid, which contributes the green and grassy flavors to the oil. The relative content of hexanal in normal-oleic peanut oil was much higher (8.40 vs. 1.19) than in high-oleic peanut oil. This is attributed to the oxidative stability of high-oleic oil. However, the green odor strength of hexanal is very weak (1.00).

The variety and origin of collected peanut greatly influenced the sensory comparison results between normal- and high-oleic peanut samples. In the present study, with the same processing condition, normal-oleic peanut oil has a higher relative concentration of key volatile components, which contribute to stronger roasted, nutty and sweet aromas. The differences in peanut oil flavor maybe caused by the composition of volatile precursors in raw material.

Table 6-3. Odor strength and relative concentration of key volatile components in normal- and high-oleic peanut oil.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  | **Normal-Oleic Peanut Oil** | **High-Oleic**  **Peanut Oil** |
| **Retention Time** | **Key Volatile Compounds** | **Odor Description** | **Odor Strength** | **Concentration(mg/kg)** | **Concentration(mg/kg)** |
| 7.4–7.5 | Pentanal | Nutty | 1.33 ± 0.58 | 1.39 ± 0.08 | 0.10 ± 0.01 |
| 10.3–10.6 | Hexanal | Green, Beany | 1.00 ± 0.00 | 8.40 ± 0.74 | 1.19 ± 0.06 |
| 12.1–12.7 | 1H-Pyrrole, 1-methyl- | Nutty, Sweet | 1.33 ± 0.58 | 6.29 ± 0.69 | 7.28 ± 0.42 |
| 14.9–15.1 | Furan, 2-pentyl- | Green, Earthy, Beany | 1.00 ± 0.00 | 1.16 ± 0.10 | 0.23 ± 0.01 |
| 16.0–16.2 | Pyrazine, methyl- | Nutty, Roasted, Cocoa | 3.00 ± 0.00 | 0.28 ± 0.02 | 0.16 ± 0.02 |
| 17.6–17.8 | Pyrazine, 2,5-dimethyl- | Nutty, Roasted, Cocoa | 3.67 ± 0.58 | 0.62 ± 0.05 | 0.36 ± 0.01 |
| 19.8–20.0 | Pyrazine, 2-ethyl-5-methyl | Nutty, Roasted, Grassy | 2.67 ± 0.58 | 0.37 ± 0.03 | 0.25 ± 0.00 |
| 21.3–21.5 | Furfural | Sweet | 1.67 ± 0.58 | 0.62 ± 0.05 |  |
| 22.8–23.0 | Benzaldehyde | Sweet | 2.33 ± 0.58 | 1.30 ± 0.09 | 0.57 ± 0.01 |
| 25.8–26.0 | 2-Furanmethanol | Sweet | 1.67 ± 0.58 | 0.44 ± 0.05 | 0.05 ± 0.00 |
| 32.4–32.6 | 4H-Pyran-4-one, 3-hydroxy-2-methyl- | Sweet | 2.00 ± 0.00 | 0.32 ± 0.01 | 0.18 ± 0.01 |

3.4 Amino acids and reducing sugars profile of normal- and high oleic peanut oil processing samples

Proteins and sugars are considered the major precursors for volatiles in peanuts. Reactivities of amino acids in Maillard model systems have drawn much attention. Dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine were largely synthesized in an aspartic acid–ascorbic acid model system (Yu et al., 2012). Similarly, nine pyrazines were identified in the L-glutamic acid and 1,4-13C-labeled-ascorbic acid Maillard model system, and the total content of pyrazines was 63.52 mg/mol. 2,5-dimethylpyrazine (34.42 mg/mol) and ethyl-5-methylpyrazine (21.17 mg/mol) were the major pyrazines formed in the model system (Yu et al., 2013). The structure of the N-terminal amino acid determined the overall formation of pyrazines, and the C-terminal amino acid showed less influence. The production of 2,5(6)-dimethylpyrazine and trimethylpyrazine was very high in the case of glycine, alanine or serine, whereas it was low for proline, valine or leucine (Van Lancker et al., 2012).

The Maillard reaction between characteristic amino acids and sugars has also been studied. A quantity of 17,280 μg pyrazines was formed in a leucine (0.5 mol/L)-rhamnose (2.0 mol/L) model system, and 2-isoamyl-6-methylpyrazine (780 μg) was highly branched (Ara et al., 2017). Eight pyrazines (0.805 mg/g of ribose) were synthesized in cysteine-ribose Maillard model system. 5H-5-methyl-6,7-dihydrocyclopentapyrazine (0.042 mg/g of ribose) was identified as a distinctive volatile component among all the pyrazines (Chen et al., 2000). Volatile compounds formed by the reaction of 2-deoxyglucose with glutamine, glutamic acid, asparagine and aspartic acid were studied (Lu et al., 1997). Compared with other amino acids-involved model systems, 2-deoxyglucose and asparagine generated the highest content of methylpyrazine. Results also indicated the importance of the 2-hydroxy group on glucose molecules for the effective generation of flavor compounds. A reactive Maillard reaction intermediate derived from xylose and phenylalanine was synthesized by using a stepwise increase of heating temperature. The Maillard Reaction intermediate reacted with cysteine to form various pyrazines (Cui et al., 2017).

The amino acids and reducing sugars profile of peanut samples during the oil processing were investigated in the present study. As shown in Table 6-4, there is no significant difference in amino acids between high-oleic peanuts and normal-oleic peanuts. Arginine, tyrosine and lysine were continuously decreased during the thermal processing. Among of them, arginine has the highest relative concentration in peanut raw materials. During the roasting procedure, the relative concentration of arginine in normal-oleic peanut decreased from 2.63 g/100 g to 1.13 g/100 g, which is also the highest loss of all the amino acids. The relative concentration of arginine in high-oleic peanuts decreased from 2.51 g/100 g to 1.08 g/100 g. There was no tyrosine detected in roasted peanut and oil samples, which indicates that all the tyrosine was reacted in the roasting procedure. As shown in Table 6-5, glucose was the only sugar which was continuously consumed during the thermal processing. The relative concentration of glucose in normal-oleic peanuts decreased from 0.18 mg/g to 0.12 mg/g during the thermal procedure. The content of glucose in high-oleic peanuts decreased from 0.07 mg/g to 0.03 mg/g during peanut oil processing. The relative concentration of arginine, tyrosine, lysine and glucose in peanut samples had a significant negative correlation with characteristic pyrazines, which indicated these compositions could be precursors of key volatile components. The initial relative concentration and process consumption of characteristic precursors (arginine, tyrosine, lysine and glucose) in normal-oleic peanuts was higher than in high-oleic peanuts, which led to the formation of more specific volatile components. This is consistent with sensory evaluation results for normal- and high-oleic peanut oil. Similarly, a quantity of 2229.66 mg/mol pyrazines were formed with the Maillard model system between 0.5 mol/L tyrosine and 0.5 mol/L glucose under 130 °C for 2.5 h. 2,5-Dimethylpyrazine and 2-ethyl-3-methylpyrazine were the majority of 15 formed pyrazines (Yu et al., 2012). The effects of high-intensity ultrasound on Maillard reaction in a model system of D-xylose and L-lysine were studied (Yu et al., 2017). 2-Methylpyrazine, 2,5-Dimethylpyrazine, 2,3-Dimethylpyrazine and 2,3,5-Trimethylpyrazine were formed in the thermal model. The ultrasonic-assisted Maillard model system could produce 3-ethyl-2,5-dimethylpyrazine, butyl amine and maltol, which were absent from thermal model. The capacity of glucose for pyrazine formation during the Maillard reaction was reported (Ni et al., 2021). The glucose produced by Maillard reaction generated 56.7 ng/g 2-methylpyrazine, which is 18.62–32.17% higher than the fructose, ribose and xylose produced by Maillard reaction.

Table 6-4. Amino acids profile of normal- and high-oleic peanut oil processing samples (g/100 g).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **Normal-Oleic Peanut** | **Roasted Normal-oleic Peanut** | **Normal-Oleic Peanut Meal** | **High Oleic Peanut** | **Roasted High-Oleic Peanut** | **High-Oleic Peanut Meal** |
| Aspartic acid | 2.83 ± 0.11 a | 2.80 ± 0.14 a | 3.37 ± 0.24 a | 2.65 ± 0.13 a | 2.75 ± 0.08 a | 3.10 ± 0.03 a |
| Threonine | 0.66 ± 0.07 a | 0.67 ± 0.04 a | 0.75 ± 0.04 a | 0.64 ± 0.05 a | 0.65 ± 0.07 a | 0.71 ± 0.05 a |
| Serine | 1.37 ± 0.06 a | 1.38 ± 0.07 a | 1.53 ± 0.03 a | 1.25 ± 0.09 a | 1.29 ± 0.12 a | 1.44 ± 0.09 a |
| Glutamic acid | 4.63 ± 0.12 ab | 4.65 ± 0.02 ab | 5.45 ± 0.31 a | 4.37 ± 0.16 b | 4.52 ± 0.15 ab | 5.08 ± 0.16 ab |
| Proline | 1.06 ± 0.05 a | 1.07 ± 0.06 a | 1.16 ± 0.14 a | 0.97 ± 0.04 a | 1.02 ± 0.04 a | 1.09 ± 0.05 a |
| Glycine | 1.22 ± 0.06 a | 1.22 ± 0.09 a | 1.42 ± 0.09 a | 1.43 ± 0.07 a | 1.45 ± 0.05 a | 1.55 ± 0.08 a |
| Alanine | 0.92 ± 0.08 a | 0.93 ± 0.05 a | 1.06 ± 0.07 a | 0.86 ± 0.00 a | 0.91 ± 0.07 a | 0.99 ± 0.03 a |
| Cystine | 0.35 ± 0.02 a | 0.35 ± 0.01 a | 0.39 ± 0.02 a | 0.35 ± 0.04 a | 0.35 ± 0.02 a | 0.40 ± 0.01 a |
| Valine | 1.05 ± 0.04 a | 1.04 ± 0.07 a | 1.23 ± 0.14 a | 1.05 ± 0.07 a | 1.09 ± 0.05 a | 1.21 ± 0.07 a |
| Isoleucine | 0.75 ± 0.05 a | 0.74 ± 0.06 a | 0.95 ± 0.08 a | 0.74 ± 0.05 a | 0.79 ± 0.11 a | 0.86 ± 0.05 a |
| Leucine | 1.55 ± 0.11 a | 1.55 ± 0.09 a | 1.87 ± 0.09 a | 1.57 ± 0.08 a | 1.56 ± 0.13 a | 1.72 ± 0.12 a |
| Tyrosine | 0.96 ± 0.07 a | 0.00 ± 0.00 b | 0.00 ± 0.00 b | 0.90 ± 0.00 a | 0.00 ± 0.00 b | 0.00 ± 0.00 b |
| Phenylalanine | 1.23 ± 0.14 a | 0.95 ± 0.04 a | 1.14 ± 0.04 a | 1.15 ± 0.07 a | 1.01 ± 0.07 a | 1.35 ± 0.08 a |
| Histidine | 0.71 ± 0.05 b | 1.25 ± 0.13 a | 1.43 ± 0.05 a | 0.70 ± 0.03 b | 1.25 ± 0.09 a | 0.80 ± 0.00 b |
| Lysine | 1.02 ± 0.07 a | 0.70 ± 0.03 b | 0.69 ± 0.03 b | 1.00 ± 0.04 a | 0.74 ± 0.03 b | 0.73 ± 0.04 b |
| Arginine | 2.63 ± 0.16 a | 1.13 ± 0.05 b | 1.09 ± 0.08 b | 2.51 ± 0.07 a | 1.08 ± 0.07 b | 1.07 ± 0.01 b |

Volume in a row with different superscripts were significantly different (*p* < 0.5).

Table 6-5. Sugars profile of normal- and high-oleic peanut oil processing samples (g/kg).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **Normal-Oleic Peanut** | **Roasted Normal-Oleic Peanut** | **Normal-Oleic Peanut Meal** | **High-Oleic Peanut** | **Roasted High-Oleic Peanut** | **High-Oleic Peanut Meal** |
| Fructose | 0.26 ± 0.06 b | 0.81 ± 0.09 a | 0.94 ± 0.05 a | 0.24 ± 0.10 b | 0.62 ± 0.04 ab | 0.57 ± 0.05 ab |
| Glucose | 0.18 ± 0.06 a | 0.14 ± 0.03 a | 0.12 ± 0.04 a | 0.07 ± 0.01 a | 0.04 ± 0.01 a | 0.03 ± 0.02 a |
| Sucrose | 50.99 ± 1.37 b | 58.36 ± 3.18 ab | 68.57 ± 0.81 a | 56.73 ± 3.51 ab | 64.15 ± 3.29 ab | 60.19 ± 1.27 ab |
| Maltose | 3.06 ± 0.16 bc | 4.31 ± 0.20 ab | 4.83 ± 0.34 a | 1.87 ± 0.23 d | 3.27 ± 0.34 bc | 2.64 ± 0.12 cd |
| Starchyose | 0.69 ± 0.06 b | 2.36 ± 0.37 ab | 3.27 ± 0.45 ab | 2.57 ± 0.23 ab | 4.53 ± 0.63 a | 3.05 ± 0.99 ab |
| Raffinose | 2.30 ± 0.02 b | 3.59 ± 0.12 a | 3.66 ± 0.05 a | 2.42 ± 0.15 b | 2.64 ± 0.17 b | 2.89 ± 0.07 b |

Volumes in a row with different superscripts were significantly different (*p* < 0.5).

**4. Conclusion**

Significant differences in sensory attributes were found between peanut raw materials and thermal processed samples. Sensory evaluation results showed that normal-oleic peanut oil has a stronger dark roast, roast peanutty and sweet aroma than high-oleic peanut oil under the same processing conditions. Methylpyrazine, 2,5-dimethylpyrazine and 2-ethyl-5-methylpyrazine are considered to be the key volatiles contributing to the nutty and roasty flavor of peanut oil. Benzaldehyde and 3-hydroxyl-2-methyl-4H-pyran-one play important roles in the sweet aroma of peanut oil. The initial concentration of characteristic precursors (arginine, tyrosine, lysine and glucose) in normal-oleic peanuts was higher than in high-oleic peanuts, which led to the formation of more specific volatile components and contributed to the stronger, specific aroma of the oil. The formation mechanism of key volatiles in peanut oil needs to be further investigated. The results of this study could provide data to support the screening of suitable high-oleic peanut varieties for industrial oil processing and improve the characteristic flavor of peanut oil.

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# CHAPTER VII

# *General discussion and perspective*

**1. General discussion**

**1.1. Summary of the thesis**

The aim of this research was to investigate the effect of raw material and processing on safety and flavor of peanut oil. For the safety quality, the occurrence of TFA and 3-MCPDE in corn oil, soybean oil, peanut oil, and palm oil which collected from industrialized production line in China factory were evaluated. The chloride precursor and mitigation method of 3-MCPDE were also studied. For the flavor quality, it was confirmed that microwave pretreatment is a feasible method to improve the oil extraction yield and obtain the low-temperature pressed peanut oil with longer shelf life and better flavor. The characteristic volatiles and its possible precursors of high-temperature pressed peanut oil were highlighted.

**1.2. Chemical toxicants formation and control during edible oil processing**

Trans fatty acids (TFA) and esters of 3-monochloro-1,2-propanediol (3-MCPDE) are two kinds of risk compositions in edible oil. The occurrence of TFA and 3-MCPDE in different edible oils collected from industrialized production line in China factory.

The occurrence of TFA in edible oil from different countries are diversely. The content of TFA in the vegetable oils collected from China (Hou et al., 2012), Swiss (Richter et al., 2009), Malaysia (Tang, 2002), India (Amrutha Kala, 2012) were 0.14-4.76%, 0.03-10.5%, 0-3.83%, 0.3-5.8%, respectively. Compared to the previous studies, the content of TFA in edible oil collected from factory in China is relatively low levels (0.37-2.61g/100g), which could be indicated that most oil factory in China have been able to reduce TFA during processing. However, products rich in partial hydrogenated vegetable oils have higher levels of TFA. The content of TFA in margarine collected from Slovenia (Abramovic et al., 2018), Pakistan (Anwar et al., 2006), Swiss (Richter et al., 2009), Saudi Arabia (Bakeet et al., 2013) were 0.11-6.37%, 2.45-21.10%, 0.15-29.3%, 0.2-8.3%, respectively.

Previous researches have strongly recommended that processing affects the overall MCPD ester levels in oils and foods. Refined soybean, sunflower, rapeseed, olive, and safflower oils have relatively 3–32 times of 3-MCPD esters content than their non-refined counterparts. For example, the 3-MCPDE content in refined safflower and olive oils were 2,355–3,218 μg/kg and 300–2,462 μg/kg, respectively, which were 32 and 24 times than that of their unrefined counterparts, respectively. The content of 3-MCPDE in refined soybean, rapeseed, and sunflower oils were 1,234 μg/kg, 381–670 μg/kg, and <300 μg/kg, respectively, which were 12, 4–7, and 3 times than that of their unrefined counterparts (Gao et al, 2019). In the present study, 3-MCPDE are only formed in the deodorization procedure during oil processing, which is consistent with previous studies. Palm oil has the highest 3-MCPDE content (3750.5±177.3 μg⋅kg-1). No 3-MCPDE was detected in peanut oil.

In recent years, many research on mitigating the formation of 3- monochloropropane-1,2-diol fatty acid esters (3-MCPDE) and glycidol fatty acid esters (GE) in refined vegetable oils have been reported. Several potential mitigation strategies including controlling the deodorization temperature, adding chelating agents, changing CPO processing conditions were also reviewed by Gao (2019). The present study was focus on the lack of research on mitigating the formation of 3-MCPDE during cooking procedure. The added salt in baking will provide inorganic chloride source, which could greatly promote formation of 3-MCPDE. It was suggested to minimize the amount of salt added into oil-containing foods during high-temperature cooking. Monosaccharide fructose and disaccharide lactose have the most obvious removal effect with 35.13% and 36.99% 3-MCPDE removed, respectively. Using fructose instead of traditional sugar in food industry is worth applying.

**1.3. Improvement of characteristic volatiles in low-temperature pressed peanut oil**

The peanut oil produced by cold pressing maintains the original quality of the peanut, and a peanut protein meal with low denaturation level could be further produced for food use. However, lower oil extraction yield and weaker roasted flavors are disadvantages of low temperature pressed peanut oil.

The feasibility of using microwaves (MW) before or during oil processing has been widely studied and has confirmed its efficiency on improving the extraction yield, nutritional value, physicochemical and sensorial properties of oil (Koubaa et al., 2016). Application of MW pretreatment on rapeseed increased the oil extraction yield (obtained by ME) by 10%, phytosterols content by 15%, tocopherols content by 55%, and oxidation induction time by 7 times (Azadmard-Damirchi et al.,2010). A significant influence of MW pre-treatments on volatile compounds of rapeseed oil was reported by Zhou (2013). Compared with untreated sample, MW pretreatment could efficiently produce pyrazine compounds and reduce 97% 4-isothiocyanate-1-butene, which is a negative volatile. In addition to these advantages, MW treatment could reduce the changes in flavor and nutrients during cooking process compared to traditional heating (Vadivambal & Jayas, 2010).

In the present study, a significant (p < 0.05) increase in extraction yield (by 33.75%), free phytosterols content (by 32.83%), free tocopherols content (by 51.36%) and induction period (by 168.93%) of oil extracted from 5 min mircrowave-treated peanut were observed. With microwave pretreatment on peanuts, increased tocopherols and phytosterols content, possible phospholipid non-enzymatic browning products and inactivation of oxidative enzymes are responsible for the improvement of the oxidative stability of extracted oil. Longer shelf life and richer micronutrients will provide stronger market competitiveness for oil products.

Compared with roasting, microwave pretreatment could promote the formation of pyrazines by a shorter period of thermal treatment under a relatively low temperature, which could be considered the most suitable way to improve the flavor of cold-pressed peanut oil. The microwave pretreatment perfect solved the bottleneck problems of cold-pressed peanut oil in industrial application and promotion. Economic evaluation is required for using MW at industrial scale. The application of microwave pretreatment in essential oil processing is worth studying.

**1.4. Formation of characteristic volatiles in high-temperature pressed peanut oil**

High-oleic acid peanut oil has developed rapidly in China in recent years due to its high oxidative stability and nutritional properties. In the last five years, over 190 high oleic peanut cultivars have been developed in China. More and more peanut processing companies are trying to use high-oleic acid peanut in oil processing. However, the consumer feedback showed that the aroma of high-oleic peanut oil was not as good as that of normal-oleic peanut oil.

Previous studies have shown that there were small differences in the roasting, astringency, over-roasting, and nuttiness attributes between these two kinds of peanuts. High-oleic lines exhibiting slightly greater intensities of those attributes (Isleib et al, 2006). Variation among individual lines for several sensory attributes suggest the flavor of high-oleic cultivars is at least as good as the profiles of normal-oleic cultivars (Isleib et al., 2015). However, the sensory evaluation results indicated that normal-oleic peanut oil showed stronger characteristic flavor than high-oleic peanut oil. The differences in sensory quality between normal- and high oleic peanut products maybe caused by the collected raw materials and processing conditions, which both affects composition and relative concentration of characteristic key volatile components.

In the present study, the compounds methylpyrazine, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine and benzaldehyde were considered as key volatiles which contribute to dark roast, roast peanutty and sweet aroma of peanut oil. With the same processing condition, normal-oleic peanut oil has a higher relative concentration of key volatile components, which contribute to stronger roasted, nutty and sweet aromas. The results further confirm the previous prediction that the variety and origin of collected peanut greatly influenced the sensory comparison results between normal- and high-oleic peanut samples.

Proteins and sugars are considered the major precursors for volatiles in peanuts. In the present study, glucose and amino acids arginine, tyrosine, lysine, were considered as the possible precursors of characteristic volatiles of high-temperature pressed peanut oil. Tyrosine and lysine have been both reported to be involved in the formation of 2,5-dimethylpyrazine (Yu et al., 2012; Yu et al., 2017). However, arginine was first found to be involved in characteristic volatile formation.

The most accepted possible pathway of pyrazine formation is the condensation of α-amino carbonyls o yield dihydropyrazines followed by the oxidation (Figure 7-1). The oxidation step is no longer necessary when the hydroxyl group on either carbon atom adjacent to those attached to the amino or carbonyl groups. A dehydration step further involves the loss of hydroxyl group from the dihydropyrazine and yield the pyrazine (Low et al., 2007). The possible mechanism for the formation of 2,5-dimethylpyrazine by arginine and glucose could be speculated, and the most reasonably formation pathway is shown in Figure 7-2, which is similar to the previous research (Poisson et al., 2009). Arginine provides amino group after the deamination reaction. Glucose supplying carbonyl group or ketone group to generate intermediates through the Strecker-type degradation. Finally, 2,5-dimethylpyrazine is formed through dehydration and reduction reaction.

The present research will provide data support for raw material screening and sensory quality improvement during high-temperature pressed peanut oil industrial production. The peanut variety with high content of oleic, arginine, tyrosine, lysine, and glucose could greatly promote production of peanut oil with good flavor and longer shelf life.

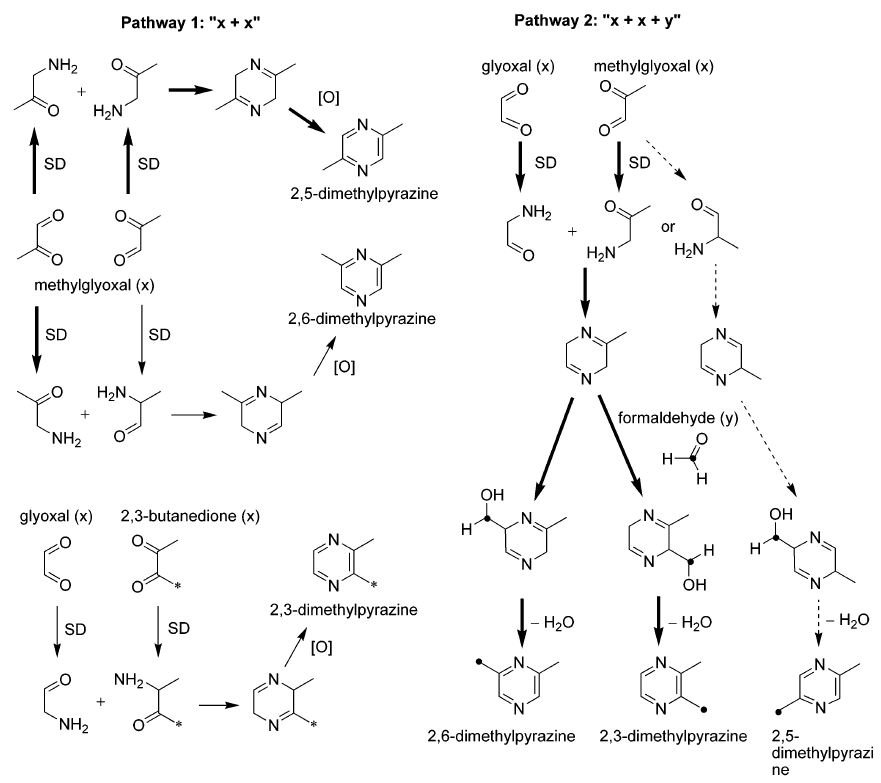


Figure 7-1. Two possible mechanisms for dimethylpyrazine formation, where x denotes R-dicarbonyl precursors and y denotes aldehydes that may react with the dihydropyrazine intermediate (Low et al., 2007)

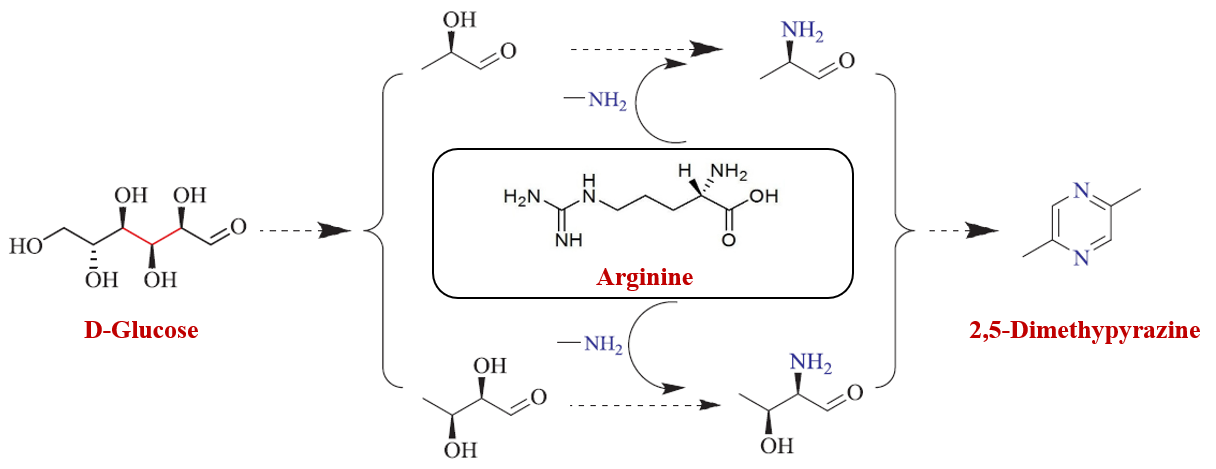


Figure 7-2. 2,5-Dimethylpyrazine formation pathway prediction

**2. Perspectives**

This thesis studied the formation and control of processing quality of peanut oil. The results will provide data support for raw material screening and quality improvement during peanut oil industrial production. However, there are still a lot of work needs to be discussed and explored. Three directions could be considered for future work:

1) The microwave pretreatment perfect solved the bottleneck problems of cold-pressed peanut oil in industrial application and promotion. However, the microwave pretreatment has been only applied in oil processing by using laboratory or pilot-scale equipment. Up to now, no correlational research has been conducted in industrial equipment. The application development and energy requirements for the industrial-scale microwave-assisted system need to be further investigated. Continuous production efficiency, uneven heating and high energy consumption are all possible problems needs to be solved in industrial application.

2) The glucose and amino acids arginine, tyrosine, lysine, were considered as the possible precursors of characteristic volatiles of high-temperature pressed peanut oil. The ability of above precursors to form characteristic volatiles needs to be further evaluated through model thermal reaction system. The possible formation mechanism of 2,5-Dimethylpyrazine was speculated, but still needs further investigation. Carbon Module Labeling is suggested as a powerful tool for identifying intermediate MR products and speculating MR pathway.

3) There are nearly 200 high-oleic peanut varieties in China, and this number is growing rapidly. In order to obtain peanut products with better flavor and longer shelf life, it is necessary to screen special high-oleic peanut varieties with high content of precursors of the characteristic volatile for industrial processing.

4) After roasting and pressing, high-temperature pressed peanut oil requires degumming and dewaxing which is a continuous cooling procedure. After that, peanut oil will be filled in commercial bottle or stored in oil tanks. It is a big challenge for the oil industry to maximum retain the roasty and nutty flavor during refining and storage. Increasing cooling efficiency and nitrogen charging are worth trying to reduce the loss of characteristic volatiles such as pyrazine. This could also slow down the oil oxidation rate and reduce the production of oxidation product which leads to negative flavor.

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# Author’s publications directly linked to this thesis

**I. Articles:**

1. **Hui Hu**, Aimin Shi, Hongzhi Liu, Li Liu, Marie Laure Fauconnier\*, Qiang Wang\*. Study on Key Aroma Compounds and its Precursors of Peanut Oil Prepared with Normal- and High-Oleic Peanuts. ***Foods***, 2021, 10(12), 3036 (Marked as “**Feature Paper**” by Journal)- **Chapter VI**
2. **Hui Hu**, Hongzhi Liu, Aimin Shi, Li Liu, Marie Laure Fauconnier, Qiang Wang\*. The Effect of Microwave Pretreatment on Micronutrient Contents, Oxidative Stability and Flavor Quality of Peanut Oil. ***Molecules***. 2019, 24(62)- **Chapter V**
3. **Hui Hu**, Marie Laure Fauconnier\*, Qiang Wang\*, et al. Comparison of volatile profiles in high- and low-temperature pressed peanut oils. **Under writing** - **Chapter IV**
4. **Hui Hu**, Bo Jiao, Qin Guo, Qiang Wang\*, et al. Chemical toxicants formation and control during edible oil processing. **Under writing** - **Chapter III**
5. **Hui Hu**, Hongzhi Liu, Li Liu, Qiang Wang\*. Research Progress on processing quality control of edible oil. **Under writing** - **Chapter II**

# Author’s publications related to this thesis

**I. Articles:**

1. Yalong Guo, **Hui Hu** (**Co-First Author**), Qiang Wang\*, et al. A novel process for peanut tofu gel: its texture, microstructure and protein behavioral changes affected by processing conditions. ***LWT - Food Science and Technology***. 2018, 96:140-146
2. Jiao Bo, **Hui Hu**, Aimin Shi, Hongzhi Liu, Li Liu, Qiang Wang\*, Wusheng Fu, Benu Adhikari. An improved method for the measurement of 3-monochloropropanediol esters by matrix solid-phase dispersion supported liquid–liquid extraction. ***International Journal of Food Science and Technology***. 2017, 52(11): 2404-2411 – related to **Chapter III**
3. Liu Yue, **Hui Hu**, Hongzhi Liu, Qiang Wang\*. Recent Advances in the Developing of Instant Flavor Peanut Powder: Generation, Regulation, and Challenges. *Foods*, 11(11), 1544 - related to **Chapter II**

**II. Books:**

1. Qiang Wang (editor), **Hui Hu** (co edit), et al. Peanut Processing Characteristics and Quality Evaluation. Springer, 2018.
2. Qiang Wang (editor), **Hui Hu** (co edit), et al. Peanuts: Processing Technology and Product Development. Academic Press, 2016.

**III. Patents:**

1. Qiang Wang, **Hui Hu**, Yunhua Liu, Lei Deng, Aimin Shi, Hongzhi Liu, Li Liu. Flavor extract of low-temperature-pressed peanut cake and method for using the same. US patent, No. 10645963 B2. – related to **Chapter V**
2. Qiang Wang, **Hui Hu**, Xiaoyong Xia, Aimin Shi, Hongzhi Liu, Li Liu, Bo Jiao. Method for simultaneously detecting four isomers of resveratrol in peanut. US patent, No. 10024827 B1.