



Chemical composition, sensory properties and application of Sichuan pepper (*Zanthoxylum* genus)

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ABSTRACT

This review summarized the composition of volatile and nonvolatile compounds, the sensory mechanism and the application of Sichuan pepper (*Zanthoxylum* genus) as a spice and multifunctional food, such as antibacterial, inhibition of inflammation, and antioxidant among others. The aim is to provide a better understanding and potential future in-depth research and application of Sichuan pepper.

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1. Introduction

Sichuan pepper, also known as Huajiao, belongs to *Zanthoxylum* genus in Rutaceae family. It commonly refers to at least five species of *Zanthoxylum* genus, including *Z. bungeanum*, which is native to southwest China, *Z. shinifolium*, which is native to Japan, Korea and east China, *Z. armatum* which is also known as Indian prickly ash, Nepal pepper or toothache tree [1], *Z. piperitum* [2] and *Z. simulans* [3]. The ground pericarps is used as common spice in Sichuan cuisine, and the leaves of *Z. piperitum* are also used in Japanese cuisine [4].

Sichuan pepper has strong and pleasant aroma. Over two hundreds volatiles have been identified that are responsible for its citrus, woody, spicy notes [5–12]. Due to its desirable odor quality, Sichuan pepper extract has been used in fine fragrances creation as an accent touch. Sichuan pepper is also a widely used spice in Chinese cuisine. It provides a unique flavor with tingling and numbing sensation and is commonly paired with chili pepper to create Mala flavor, which literally means numbing and spicy. Non-volatile compounds including alkylamides and polyphenols have

been identified. In some of the *Zanthoxylum* genus, like *Z. piperitum*, total amide content can be as high as 3% [13]. Sanshools and hydroxyl sanshools, from the same family as piperine and capsaicin, are commonly found alkylamides in Sichuan pepper. They are responsible for the numbing, tingling and buzzing mouth sensation after consuming Sichuan pepper flavored dishes or food products [14]. The unique sensation is different from the pungency caused by capsaicin, piperine or isothiocyanates. It is caused by modulating two-pore potassium channels instead of activating TRPA1 or TRPV1 channel [15]. The antioxidant and anti-inflammatory property of Sichuan pepper extract is largely related to its polyphenols content. Over twenty polyphenols including flavonoids, lignans and their glycosides have been identified in *Zanthoxylum* genus.

Other than its application in fragrance, culinary, antioxidant, Sichuan pepper extract has also been shown to have antimicrobial, antiviral, skin lifting, herbicide safener, drug transdermal penetration enhancing, lipid lowering capabilities, which make Sichuan pepper a promising ingredient in food, cosmetics, pharmaceutical, and agricultural industries [9,11,16–23].

2. Volatile components

Due to its great value as flavor and aroma enhancer, interests grow in figuring out the volatile components that contribute to Sichuan pepper's distinctive aroma. The volatile compounds identified up to date in Sichuan pepper is summarized in Table 1, which includes the results from the following cited research

Yoon et al. compared headspace using mulberry paper bag (HS-MPB-μ-SPE) with solid phase micro extraction (SPME) in

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Table 1
Volatile component found in *Z. bungeanum*, *Z. schinifolium* and *Z. piperitum* species.

Compound name	Odor description	<i>Z. bungeanum</i> [7,9]	<i>Z. schinifolium</i> [7,10,11,12]	<i>Z. piperitum</i> [6,8,27]
1,8-Cineole	cooling, fresh, medicinal	x	x	x
10-Epi- γ -eudesmol		x	x	
1-Terpineol	pinene, floral, lilic	x	x	x
2,4-Decadienal	fatty, green		x	
2,4-Diethylheptan-1-ol			x	
2,4-Dimethylacetophenone		x	x	
2,4-Heptadienal		x		
2,4-Hexadienal		x		
2,6-Dimethyl-2-heptenal			x	
2,6-Dimethylheptanal			x	
2-Methyl-6-methylen-octa-1,7-dien-3-one				x
2-Methyl-3-buten-2-ol		x	x	
2-Nonenal	cucumber, melon		x	
2-Oxabicyclo[2.2.2]octan-6-ol, 1,3,3-trimethyl-, 6-acetate		x	x	
2-Phenylethyl acetate	floral, rose, honey	x	x	
2-Propenal	harsh		x	
2-Propenoic acid, 3-phenyl-, methyl ester			x	
2-Tridecanone			x	
2-Undecenal	fresh, fruity, orange peel		x	
3,6- α -Farnesene		x	x	
3-Buten-2-one		x	x	
3-Methylpentadecane			x	
3-Nonanone	cucumber	x		
4-Carvomenthenol		x		
4-Methyl-1-heptanol			x	
4-Methyl-1-pentanol			x	
4-Terpinenol	peppery, woody		x	x
4-Terpinenyl acetate		x	x	
6,7-Epoxymyrcene				x
6-Methyl-1-heptanol			x	
6-Methyl-5-hepten-2-one		x		
6-Methylheptanal			x	
7-Epi- α -selinene				x
9-Epi- <i>E</i> -caryophyllene				x
Acetaldehyde	pungent, fruity	x	x	
Allo-aromadendrene		x		x
α -Armophene				x
α -Bergamotene		x		
α -Cadinol			x	
α -Calacorene		x		x
α -Copaene		x		x
α -Cubebene		x	x	x
α -Elemol			x	x
α -Farnesene	citrus, lavender herbal, bergamot, neroli, green	x		
α -Gurjunene			x	x
α -Humulene		x	x	x
α -Muulolene			x	x
α -Phellandrene	terpenic, green, peppery	x	x	
α -Pinene	pine	x	x	x
α -Selinene			x	x
α -Terpinene	woody, citrus	x	x	x
α -Terpineol	lilac, pine	x	x	x
α -Terpinyl acetate	woody	x	x	x
α -Thujene	aromatic	x	x	x
α -Thujone	cedarleaf, thujonic	x	x	
Benzeneacetic acid, methyl ester			x	
β -Bisabolene				x
β -Calacorene				x
β -Caryophyllene	spicy, clove	x	x	x
β -Cedrene				x
β -Cubebene		x		x
β -Elemene		x	x	x
β -Phellandrene		x	x	x
β -Pinene	pine	x	x	x
β -Selinene			x	
β -Thujone	cedar, thujonic, spicy woody	x	x	
Bicyclogermacrene			x	
Bois de rose ketone		x		
Borneol	camphoraceous	x	x	x
Bornyl acetate	pine	x		x
Butyl butyrate	fruity, pineapple		x	
Camphene	camphoraceous, pine	x	x	x

Table 1 (Continued)

Compound name	Odor description	<i>Z. bungeanum</i> [7,9]	<i>Z. schinifolium</i> [7,10,11,12]	<i>Z. piperitum</i> [6,8,27]
Carvone	sweet, spearmint, herbal, minty	x	x	x
Caryophyllene oxide	sweet, fresh, dry woody, spicy	x	x	x
<i>cis</i> - β -Ocimene	green, metallic	x	x	x
<i>cis</i> -Carveol		x	x	x
<i>cis</i> -Carveyl acetate		x		
<i>cis</i> -Limonene oxide				x
<i>cis</i> -Linalool oxide	floral muguet, metallic	x	x	x
<i>cis</i> - <i>p</i> -2-Menthen-1-ol		x	x	
<i>cis</i> - <i>p</i> -Mentha-2,8-dien-1-ol		x		
<i>cis</i> -Sabinene hydrate			x	x
<i>cis</i> -Sabinene hydrate acetate				x
Citronellal	floral, rose, fatty, citrus	x	x	x
Citronellol	floral, rose, citrus		x	x
Citronellyl acetate	floral, rose, citrus	x		x
Crotonaldehyde			x	
Cryptone		x		x
Cubenol				x
Decanal	aldehydic, waxy, orange peel		x	
Dihydrocarvone		x	x	
Epi- α -cadinol		x	x	
Espatuleno		x		
Ethyl pyruvate		x		
Exo-2-hydroxycinole acetate				x
Furfural alcohol	cherry			x
Geraniol	sweet, floral, fruity, rose	x	x	x
Geranyl acetate	floral, rose	x		x
Germacrene B		x		
Germacrene D		x	x	x
Germacrene D-4-ol		x	x	
Heptyl acetate	fruity, harsh	x	x	
Hexanal	green, fatty, aldehydic	x	x	
Hexyl acetate	pear	x	x	
Hotrienol		x	x	
Humulene oxide		x		
Isoamyl alcohol	banana	x	x	
Isobutanol		x	x	
Isobutyl acetate	banana	x	x	
Isobutyl butanoate				x
Isodecanal			x	
Isopiperitenone		x		
Isopulegol	minty	x		x
Limonene	citrus, orange	x	x	x
Linalool	floral muguet, citrus	x	x	x
Linalool oxide dehydrate		x		
Linalyl acetate	citrus, bergamot	x	x	x
Linalyl formate	citrus, green	x	x	
Linalyl propionate	bergamot, floral	x		
Menth-2-en-1-ol				x
Methyl 4-methylvalerate		x	x	
Methyl citronellate			x	
Myrcene	terpenic, green	x	x	x
Myrcene epoxide		x	x	
Myrtenal		x	x	x
Myrtenol		x	x	x
Myrtenyl acetate				x
Neoiso-isopulegol			x	
Nerol	floral, rose, green	x	x	
Nerol oxide		x		
Neryl acetate	floral, rose, soapy	x	x	x
Nonanal	green, cucumber	x	x	
Octanal	aldehydic, citrus orange	x	x	
Octyl acetate				x
<i>o</i> -Cymene				x
<i>p</i> , α -dimethylstyrene		x	x	
<i>p</i> -1,8-Menthadienyl-7 acetate		x		
<i>p</i> -Cymen-8-ol		x	x	
<i>p</i> -Cymene	terpenic, spicy	x	x	x
Perillene		x	x	
Phenethyl acetate	floral, rose, sweet, honey	x		
Pinocarvone		x	x	x
Piperitone	minty			x
<i>p</i> -Isopropylbenzyl alcohol		x		
<i>p</i> -Menth-1-en-9-al		x	x	

Table 1 (Continued)

Compound name	Odor description	<i>Z. bungeanum</i> [7,9]	<i>Z. schinifolium</i> [7,10,11,12]	<i>Z. piperitum</i> [6,8,27]
<i>p</i> -Mentha-1(7),2,8-triene		x		
<i>p</i> -Mentha-1,3,8-triene		x	x	
<i>p</i> -Mentha-1,8(10)-dien-9-ol		x		
<i>p</i> -Mentha-1,8-dien-4-ol		x	x	
Prenol	banana	x		
Pseudolimonene				x
Rosefuran	caramel, green, minty	x		
Sabinene	terpinenic, citrus, pine	x	x	x
Spathulenol			x	x
Terpinolene	citrus, lime	x	x	x
<i>Trans</i> -Alloocimene	green, metallic	x	x	x
<i>trans</i> -Anethole	sweet, anise, licorice			x
<i>trans</i> - β -Ocimene				x
<i>trans</i> -Carveol		x	x	x
<i>trans</i> - β -Farnesene		x		
<i>trans</i> -Limonene oxide			x	
<i>trans</i> -Linalool oxide	floral muguet, metallic	x	x	
<i>trans</i> -Myrtanol			x	
<i>trans</i> -Nerolidol		x	x	
<i>trans</i> -Ocimene epoxide		x		
<i>trans</i> -Pinocarveol		x	x	
<i>trans</i> -Piperitol		x		
<i>trans</i> - <i>p</i> -Mentha-2,8-dien-1-ol		x		x
<i>trans</i> -Sabinene hydrate		x	x	x
<i>trans</i> -Sabinene hydrate acetate		x		x
<i>trans</i> -Sabinol				x
Tricyclene				x
Valencene				x
Verbenol			x	
Viridiflorene				x
Z-Murola-4(14),5-diene				x
γ -Bisabolene				x
γ -Murolene				x
γ -Cadinene		x	x	x
γ -Gurjunene		x		
γ -Terpinene	terpenic	x	x	x
δ -2-Carene				x
δ -3-Carene	terpenic, lavenderous	x	x	x
δ -Cadinene		x	x	x
δ -Cadinol			x	x
δ -Elemene				x

extracting aroma compounds from *Z. piperitum*. Results showed that Tenax TA as adsorbent with petroleum ether as solvent provided the best combination in HS-MPB- μ -SPE method, 13 components were identified with limonene, eucalyptol and ocimene as the major components. Sixteen components were identified with HS-SPME-GC/MS method, in which limonene, eucalyptol, ocimene and linalool are the major components. This study developed a method using mulberry paper bag in conventional solvent extraction procedures to extract volatile components of *Z. piperitum*. The study claimed HS-MPB- μ -SPE to be a more simplified and cleaner sample preparation method compare to conventional solvent extraction or solid phase extraction method [24].

An ultrasonic nebulization extraction-heating gas flow transfer coupled with headspace single drop microextraction (UNE-HGFT-HS-SDME) method was developed which offers a cheaper, low solvent, faster solution in analyzing *Z. bungeanum* essential oil composition [25]. Thirty-two compounds were identified by this method with limonene to be the most abundant component. The essential oil profile extracted by UNE-HGFT-HS-SDME was compared with essential oil respectively obtained by hydro distillation method and UNE-HS-SDME method. Results showed that profile obtained by UNE-HGFT-HS-SDME method was comparable to the essential oil profile obtained by hydro distillation method.

Similarly, a microwave distillation and simultaneous single drop micro extraction headspace GC-MS method was developed and compared with hydro distillation method in extracted *Z. bungeanum* essential oil composition [26]. Fifty-two compounds were identified by the microwave distillation method while 31

compounds were identified by hydro distillation method with limonene being the most abundant component in both methods. Number of identified compounds was the only standard in comparing the effectiveness of extraction methods in this study. The odor impacts of extracted components were not evaluated. Also how resemble the ratio of extracted components to human perceived aroma when Sichuan peppercorn is consumed was not taken into consideration in this study.

A study conducted by Jiang and Kubota studied the chemical composition differences of green, ripe and dried pericarps of *Z. piperitum* by GC-MS and used GC-Olfactometry to figure out what compounds driving the differences in aroma profiles. 57, 79 and 83 volatiles compounds were detected respectively in green, ripe and dried *Z. piperitum* pericarps. Results show that monoterpenes mostly limonene, β -phellandrene and myrcene are responsible for the strong green and pine leaf notes in the green fruit, while oxygenated terpenes are the main drive of aroma profile in ripe fruit with citronellal and geranial responsible for the potent citrus note. The dried fruits of *Z. piperitum* were perceived to have mild flavor compare to ripe fruits due to compositional change during the heat treatment process. [27].

Another study conducted by Jiang et al. studied volatile composition of *Z. piperitum* leaves by dynamic headspace (DHS) followed by thermal desorption (TD) GC-MS. In this study, 36 volatiles were identified in crushed *Z. piperitum* leaves [28]. This study demonstrated that prepared samples, in this case, mechanically disturbed leaves and crushed leaves, will increase the number of emitted volatiles compare to intact leaves.

Table 2
Alkylamides found in *Zanthoxylum* genus [31–34].

Name	Chemical Structure	Molecular Formula	Molecular Weight
α -Sanshool		C ₁₆ H ₂₅ NO	247.38
β -Sanshool		C ₁₆ H ₂₅ NO	247.38
γ -Sanshool		C ₁₈ H ₂₇ NO	273.42
δ -Sanshool		C ₁₈ H ₂₇ NO	273.42
Hydroxyl- α -sanshool		C ₁₆ H ₂₅ NO ₂	263.19
Dihydroxy- α -sanshool		C ₁₆ H ₂₅ NO ₃	263.19
Hydroxyl- β -sanshool		C ₁₆ H ₂₅ NO ₂	263.19
Dihydroxy- β -sanshool		C ₁₆ H ₂₅ NO ₃	263.19
Hydroxyl- γ -sanshool		C ₁₈ H ₂₇ NO ₂	289.419
Hydroxy- γ -isosanshool		C ₁₈ H ₂₇ NO ₂	289.419
Hydroxyl- ϵ -sanshool		C ₁₆ H ₂₅ NO ₂	263.19
Hydroxyl- ζ -sanshool		C ₁₈ H ₂₇ NO ₂	289.42
Bungeanool		C ₁₈ H ₂₉ NO ₂	291.44
Isobungeanool		C ₁₈ H ₂₉ NO ₂	291.44
(2 <i>E</i> ,7 <i>E</i> ,9 <i>E</i>)- <i>N</i> -(2-hydroxy-2-methylpropyl)-6,11-dioxo-2,7,9-dodecatrienamide		C ₁₆ H ₂₃ O ₄	294.17
(2 <i>E</i> ,6 <i>E</i> ,8 <i>E</i>)- <i>N</i> -(2-hydroxy-2-methylpropyl)-10-oxo-2,6,8-decatrienamide		C ₁₄ H ₂₁ O ₃	252.16

One study conducted by Yang [7] was looking at the aroma compounds of two species of *Zanthoxylum*: *Z. bungeanum* and *Z. simulans*. Essential oil is obtained by hydrodistillation. 120 compounds were found respectively in both *Zanthoxylum* species. Linalool, limonene, and sabinene are major components of essential oil from *Z. simulans*, and they make up 56% of the essential oil. Linalyl acetate, linalool and limonene are major components of essential

oil from *Z. bungeanum*, and they make up 40% of the oil. Aroma character impact (ACI) values are calculated to determine compounds with high aroma impact. For both species, Linalool is the primary odor contributor. For *Z. bungeanum*, eucalyptol, α -terpineol and geraniol are also important odor contributor. A study conducted by Behrendt et al. showed that linalool, geraniol and eucalyptol are agonists (despite weak and with low efficacy) of TRPM8 recep-

tor (menthol receptor), which can produce cooling sensation [29]. Solvent extraction method was used to obtain taste responsible components, which suffer from degradation in hydrodistillation process. Hydroxyl- α -sanshool was reported to be the primary compound that responsible for numbing sensation [7].

3. Non-volatile components

3.1. Alkylamides

Alkylamides in Sichuan pepper are listed in Table 2. Hydroxyl- α -sanshool is the most abundant component in *Z. bungeanum* oil and *Z. schinifolium* oil, which greatly contributes to the pungency of Sichuan pepper upon consumption. Based on its alkylamide composition, hydroxyl- γ -sanshool and bungeanool are suggested to be used in distinguishing *Z. bungeanum* and *Z. schinifolium* [30].

Mizutani et al. first identified hydroxyl- γ -isosanshool, bungeanool and isobungeanool besides hydroxyl- α , β and γ sanshool in *Z. bungeanum*. In the study, the pericarps were extracted by chloroform and the extract was fractionated with column chromatography over silica gel and then further purified with HPLC. The structures of the newly identified alkylamides were determined with NMR [31].

2',3'-Dihydroxy- α -sanshool and 2',3'-dihydroxy- β -sanshool were identified by Jang et al. from seeds of *Z. piperitum* [32]. The plant material was extracted with methanol and dichloromethane and the extract was separated by reversed-phase vacuum flash chromatography and HPLC. Five fatty acid amides were isolated including α -, β - and ε -hydroxyl sanshool and the two newly identified sanshools. Structures of unknown were determined with NMR.

Two new alkylamides, (2E,7E,9E)-N-(2-hydroxy-2-methylpropyl)-6,11-dioxo-2,7,9-dodecatrienamide and (2E,6E,8E)-N-(2-hydroxy-2-methylpropyl)-10-oxo-2,6,8-decatrienamide, were identified in *Z. bungeanum* by Huang et al [33]. Pericarps of *Z. bungeanum* were extracted with MeOH and then the extract was fractionated with silica gel column. Each fraction was analyzed with HR-ESI-MS and molecular formula was determined. Structures of unknown were determined with NMR.

3.2. Polyphenols

Multiple methods have been used in analyzing non-volatile fraction of Sichuan pepper. Ultra performance liquid chromatography-diode array detection electrospray ionization-mass spectrometry (UPLC-DAD-ESI-QTOP-MS/MS) was developed as a rapid method and successfully used in quantifying asarinin, sesamin, fargesin, kobusin and armatamide in *Z. armatum* species [35]. The method was also used in identifying 12 compounds including flavonoids, lignans, coumarin and amides from *Z. armatum* leaf (Table 3) [1]. Ten flavonoid glycosides, including isovitexin, vitexin, hyperoside, isoquercitrin, rutin, foeniculin, trifolin, quercitrin, astragalin and afzelin, were reported to be found in Leaves of *Z. bungeanum*, which makes the leaves a good source of natural antioxidant [36].

4. Sensory mechanism

Because of increasing interests of taste compounds from Sichuan pepper in commercial and academic fields, many studies have been focusing on understanding the sensory mechanism of pungent compounds, which pose a unique tingling and numbing sensation, extracted from Sichuan pepper.

A few alkylamides are responsible for the unique taste of Sichuan pepper. Sugai et al. successfully isolated six alkylamides from *Z. piperitum* and characterized their pungent qualities. The six isolated alkylamides included α -, β -, γ -, δ -sanshool and hydroxyl

α and β -sanshool [38,39]. Each purified fractions were evaluated in 5% sucrose solution. α -sanshool and hydroxyl- α -sanshool were described to impart a tingling, numbing characteristic. β -sanshool and hydroxyl- β -sanshool were described to impart numbing and bitter sensory characteristics. γ -sanshool and δ -sanshool, the all-trans isomer of γ -sanshool, were described to have burning, numbing and fresh characteristics. Hydroxyl- α -sanshool was reported to account for most of pungency perception of Sichuan peppercorn.

Synthesis of compounds contains functional groups of sanshool and bungeanool showed that the structure of those compounds largely affects their pungency level. Galopin et al. proposed a model to predict the pungency of synthesized cinnamamides. They found the molecules only show noticeable pungency when they have *N*-isobutyl carboxamide and the $(\text{CH}=\text{Z}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{E}-\text{CH})$ motif in their structures and optional structure feature including hydroxyl group and *N*-alkyl group [40].

Conflicting theories have been proposed to explain sensory mechanism of sanshools. A study conducted by Koo et al. showed evidence on activation of TRPV1 and TRPA1 channels from hydroxyl- α -sanshool. TRPV1 is associated with burning and painful sensations caused by capsaicin and TRPA1 is activated by pungent stimulants including cinnamyldehyde and isothiocyanate which presents in mustard and horse radish. The author attributed the causing of a numbing, tingling sensation to the activation of both TRPV1 and TRPV1 at the same time [41]. Study conducted by Sugai et al. also showed sanshools including α -, β -, γ -, δ -, hydroxyl- α , and hydroxyl- β sanshool were able to activate TRPA1 ion channel [38]. Study conducted by Koo et al. [41] confirmed that hydroxyl- α -sanshool can activate both TRPA1 and TRPV1 and further illustrated how alkyl structure influences the activation of those two channels. By synthesizing molecules derived from hydroxy- α -sanshool, this research showed the activation of TRPV1 is nonselective toward the structural saturation of alkylamides, however alkene's presence in alkyl chain greatly affect the activation of TRPA1 receptor. In the study, the influence of hydroxyl- α -sanshool was simulated by green Sichuan pepper oil extract which contains 76% of hydroxyl- α -sanshool, 21% hydroxyl- β -sanshool and 3% unidentified components. Hydroxy- β -sanshool was assumed to have no excitement influence on sensory neuron, which is contradicted with other study showing although hydroxyl- β -sanshool is not the major contributor to the pungency sensation of Sichuan pepper, it is able to inhibit KCNK3 channel [42,43].

On the other hand, study conducted by Bautista et al. proposed that Sichuan peppercorn excites sensory neurons by modulating two-pore potassium channels. The studies showed the chemesthetic sensations of sanshool instead of being mediated by activating TRPA1 or TRPV1 are caused by the activation of KCNK channels by blocking outward K^+ current. This study further narrowed the activation effect of sanshool on KCNK channels down to 3 subtypes, which includes KCNK3 (TASK-1), KCNK9 (TASK-3) and KCNK18 (TREK). In the study conducted by Koo et al., pluronic acid was used to increase the solubility of sanshool was tested to be an activator of TRPA1 channel, which may contribute to a false positive result of sanshool being an activator of TRPA1 [41,42]. Albin et al. studied sensory mechanism of sanshools by whether the induced tingling sensation can be cross-desensitized by capsaicin or mustard oil. Results showed to be negative and suggested that TRPV1 and TRPA1 are not involved in inducing tingling sensation [15]. From a psychophysical standpoint, study conducted by Albin et al. examined the effect of repeated alkylamide stimulation. Results showed that the tingling sensation was largely related to the length of interstimulus interval: sensitizing pattern occurred with short interstimulus intervals while desensitizing pattern occurred with long interstimulus intervals [15]. The results contradicted from pre-

Table 3
Polyphenols found in *Zanthoxylum* genus.

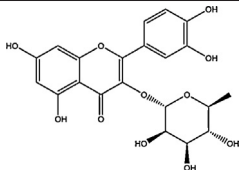
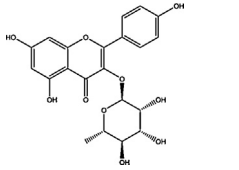
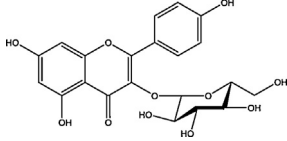
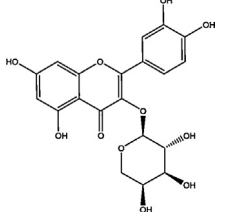
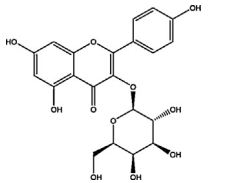
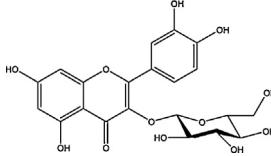
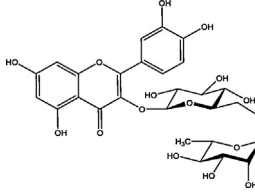
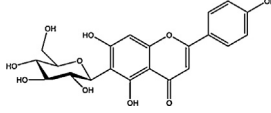
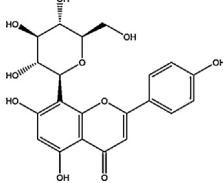
Family	Name	Chemical Structure	Reference
Flavonoids	Quercitrin		[1,36,37]
	Afzelin		
	Astragalin		
	Foeniculic		
	Trifolin		
	isoquercetin		
	Rutin		
	Isovitexin		
	Vitexin		

Table 3 (Continued)

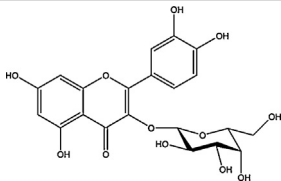
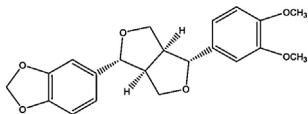
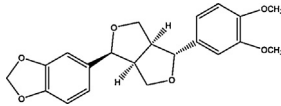
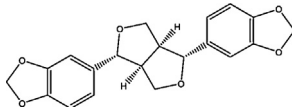
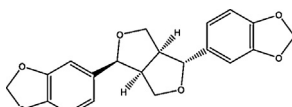
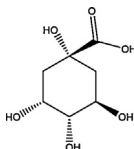
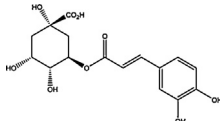
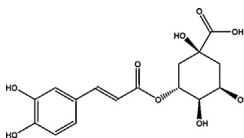
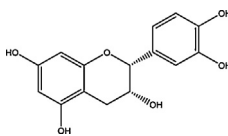
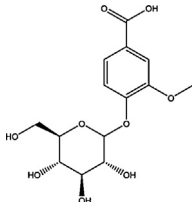
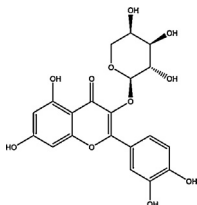
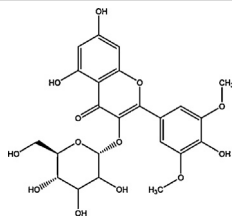
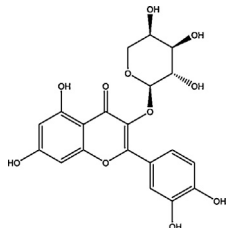
Family	Name	Chemical Structure	Reference
Lignans	Hyperoside		[35]
	Kobusin		
	Fargesin		
	Sesamin		
	Asarinin		
Phenolic acids	Quinic acid (Non-Phenolic acid)		[37]
	Chlorogenic acid		
	3-O-Feruloylquinic acid		
Flavanols	L-Epicatechin		[37]
Polyphenol glycosides	Vanillic acid-4-β-D-glucoside		[37]
	Isorhamnetin-3-O-glucoside		

Table 3 (Continued)

Family	Name	Chemical Structure	Reference
	Syringetin-3-O-glucoside		
	Quercetin-3-O-arabinoside		

vious finding, which showed no sensitization response to repetitive sanshool application [42].

Sichuan pepper imparts a unique flavor and its numbing and tingling sensation can cause sensory changes in perceiving other flavors. Bader et al. have successfully correlated the numbing and tingling sensation with taste compound extracted from Sichuan pepper and determined their perceiving thresholds. In which, hydroxy- α -sanshool, Hydroxy- γ -sanshool, bungeanool, isobungeanool, hydroxy- ϵ -sanshool and hydroxy- ζ -sanshool are responsible for the tingling and paresthetic sensation and hydroxy- β -sanshool and hydroxy- γ -isosanshool impart a numbing and anesthetic sensation [34]. Compare to the molecules that impart a tingling sensation, molecules that impart a numbing sensation doesn't possess a cis-double bond, which in accordance with previous finding of structure activity relationship [40]. This research also found that hydroxyl- α -sanshool will increase salvation in human subjects. Since taste compounds need to first dissolve in saliva to reach taste receptors. And the protein components in saliva are subject to change after elicitation of those tingling and numbing components. The change may further impact the perception of other tastes. We have reason to believe there are scientific reasons to support an early assumption that the numbing and tingling sensation will change human perception of basic tastes.

5. Application

5.1. Culinary

Sichuan pepper is a widely used spice in Asian cuisine. It is one of the five spices characterized in Five-Spice powder, which are commonly made with star anise, Sichuan pepper, cassia, clove and fennel. Ginger, galangal and black cardamom can be added optionally. The five-spice powder has wide usage in Chinese kitchen including marinating meat, adding flavor to flour batter of fried vegetables and meat.

Nowadays, as exotic and adventurous food trends emerging among consumers especially the millennial generation, we see more Sichuan pepper flavored package food products on market, for example, instant Ramen noodles, Tseng noodles Samyang Mala Spicy Chicken Ramen, crispy fried chicken, and beef jerky. Also chefs are infusing a splash of Sichuan peppercorn in fine dishes creation, not only to spice savory entrée but also in flavoring desserts like ice cream and tarte tartin.

5.2. Flavor modulation

Chemesthetic compounds in Sichuan pepper including sanshools and hydroxyl sanshools were proposed to be included in the liquid cooling sensate formulation together with selected cooling agents and an isothiocyanate compound which gives warming, tingling sensation to provide an increased sensation of pungency [44]. This formulation is expected to be used in flavors and fragrances to offer an adventurous and interesting sensorial experience. Sanshools were also used as flavor improving substance in fruit juice containing food product together with selected cooling agents and refreshing agents to increase flavor acceptability under normal or warm extended storage condition [45].

5.3. Antibacterial

Sichuan pepper and its character component, sanshool amide, were proved to be able to inhibit the formation of heterocyclic amines (HAs) in beef grilling process. The study focused on four HAs, PhIP, IQx, MeIQx and 4,8-DiMeIQx, which are regulated as possible human carcinogens by the International Agency for Research on Cancer (IARC). The inhibition effect of both ground Sichuan pepper powder and hydroxyl- β -sanshool solution were evaluated at 3 dilution levels, and results showed that both Sichuan pepper and hydroxyl- β -sanshool can effectively reduce the levels of HAs up to 80% [23]. Essential oils derived from hydro-distillation of *Z. bungeanum* fruit can inhibit growth of common foodborne pathogen including bacteria strains from both gram positive and gram negative families [9]. Oh et al. studied the inhibitory effect of oil obtained from *Z. shinifolium* seeds by press or hydro distillation on foodborne viral surrogates and showed that oil obtained from pressing of *Z. shinifolium* has antiviral effect but not the oil obtained from hydro distillation [11]. Neither study specifies what the active component in the oil that gives the antibacterial or antiviral effect is. Extract of *Z. piperitum* was reported to possess broad-spectrum anticoronavirus function against two HRVs and four enteroviruses [46].

5.4. Antioxidants

Polysaccharides extracted from *Z. bungeanum* pericarps were proved to possess excellent antioxidant properties [22]. The polysaccharide used in this study was crude without purification and separation and the mechanism of its antioxidant property remains unknown. Study conducted by Hisatomi et al isolated and

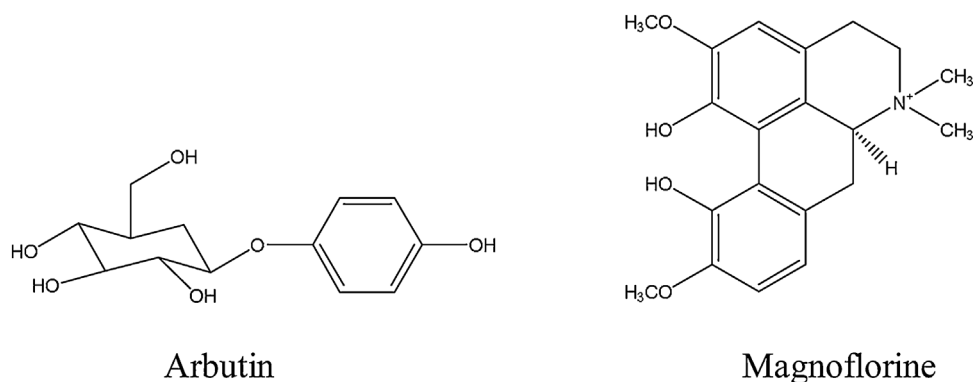


Fig. 1. Chemical structure of arbutin and magnoflorine.

identified tocopherol isomer α , β , γ , δ , arbutin and magnoflorine (Fig. 1) from *Z. piperitum* pericarps and seeds. The ethyl acetate extract of pericarp and methanol extract of seed showed strong antioxidation property with ferric thiocyanate and thiobarbituric acid methods [16].

Extract of *Z. bungeanum* leaf was tested to be an effective antioxidant, protecting lipid from oxidation in salted fish processing [21]. The study showed chlorogenic acid, hyperoside and quercitrin to be the major polyphenols in the extract that offer antioxidant property. *Z. bungeanum* leaf extract was also showed to be able to increase the activity of naturally possessed antioxidant enzyme in fish during salting process.

6. Future perspectives

This review provides a general picture of compositional makeup, sensory mechanism and application of Sichuan pepper, which will support a better understanding and future research on Sichuan pepper.

As mentioned above, researches have been done on component analysis, sensory mechanism and potential applications. The volatiles components are responsible for the citrus, woody, spicy aroma of Sichuan pepper, which leads to its successful application in fine fragrances creation. The alkylamides are responsible for the distinguished numbing, tingling sensation of Sichuan pepper, and make it an irreplaceable spice in Asian cuisine. Also, Sichuan pepper is rich in polyphenols, which makes the extract a good source of antioxidants.

There are a few issues raised from literature review that need further investigation: firstly, few study focused on component analysis of multiple *Zanthoxylum* genus using the same analytical approach, which are expected to provide insights on differentiating *zanthoxylum* genus based on their volatile and nonvolatile components. Secondly, component analysis of Sichuan pepper after roasting or handling with other heating processing techniques has not been studied. Thus the components change and the changing mechanism remains unknown. Thirdly, studies are needed to understand how the numbing and tingling sensation will change human perception of basic tastes. In addition, no sensory lexicon has been developed on Sichuan pepper. It is of interest to establish a standardized vocabulary and connect it with individual component.

References

- [1] V. Bhatt, S. Sharma, N. Kumar, U. Sharma, B. Singh, Simultaneous quantification and identification of flavonoids, lignans, coumarin and amides in leaves of *Zanthoxylum armatum* using UPLC-DAD-ESI-QTOF-MS/MS, *J. Pharm. Biomed. Anal.* 132 (2017) 46–55.
- [2] G. Epple, B.P. Bryant, I. Mezine, S. Lewis, *Zanthoxylum piperitum*, an Asian spice, inhibits food intake in rats, *J. Chem. Ecol.* 27 (2001) 1627–1640.
- [3] L. Xiang, Y. Liu, C. Xie, X. Li, Y. Yu, M. Ye, S. Chen, The chemical and genetic characteristics of Sichuan pepper (*Zanthoxylum bungeanum* and *Z. armatum*) cultivars and their suitable habitat, *Front. Plant Sci.* 7 (2016) 467.
- [4] P. Ravindran, G. Pillai, K. Nirmal Babu, M. Divakaran, S. Malhotra, Minor and under-utilized spices and herbs, in: S. Ochatt, S.M. Jain (Eds.), *Breeding of Neglected and Under-Utilized Crops, Spices, and Herbs*, Science Publishers, 2007, p. 76.
- [5] L. Jiang, K. Kubota, Formation by mechanical stimulus of the flavor compounds in young leaves of Japanese pepper (*Xanthoxylum piperitum* DC), *J. Agric. Food Chem.* 49 (2001) 1353–1357.
- [6] Z.L. Cardeal, M.D. Gomes da Silva, P.J. Marriott, Comprehensive two-dimensional gas chromatography/mass spectrometric analysis of pepper volatiles, *Rapid Commun. Mass Spectrom.* 20 (2006) 2823–2836.
- [7] X. Yang, Aroma constituents and alkylamides of red and green Huajiao (*Zanthoxylum bungeanum* and *Zanthoxylum schinifolium*), *J. Agric. Food Chem.* 56 (2008) 1689–1696.
- [8] O.K. Yoon, D.-S. Lee, Mulberry paper bag μ -solid phase extraction for the analysis of five spice flavors by gas chromatography-mass spectrometry, *Bull. Korean Chem. Soc.* 30 (2009) 35–42.
- [9] R.X. Zhu, K. Zhong, W.C. Zeng, X.Y. He, X.Q. Gu, Z.F. Zhao, H. Gao, Essential oil composition and antibacterial activity of *Zanthoxylum bungeanum*, *Afr. J. Microbiol. Res.* 5 (2011) 4631–4637.
- [10] W.R. Diao, Q.P. Hu, S.S. Feng, W.Q. Li, J.G. Xu, Chemical composition and antibacterial activity of the essential oil from green huajiao (*Zanthoxylum schinifolium*) against selected foodborne pathogens, *J. Agric. Food Chem.* 61 (2013) 6044–6049.
- [11] M. Oh, M.S. Chung, Effects of oils and essential oils from seeds of *Zanthoxylum schinifolium* against foodborne viral surrogates, *Evid. Based Complement. Altern. Med.* 2014 (2014) 135797.
- [12] G. Wu, H. Wu, Analgesia synergism of essential oil from pericarp of *Zanthoxylum schinifolium* and *Verapamil*, *Evid. Based Complement. Altern. Med.* 2014 (2014) 505876.
- [13] P.N. Ravindran, M. Divakaran, G.S. Pillai, Other herbs and spices: achiote to Sichuan pepper, in: *Handbook of Herbs and Spices*, 2012, pp. 534–556.
- [14] H. McGee, *On Food and Cooking*, Scribner, 2004.
- [15] K.C. Albin, C.T. Simons, Psychophysical evaluation of a sanshool derivative (alkylamide) and the elucidation of mechanisms subserving tingle, *PLoS One* 5 (3) (2010) e9520.
- [16] E. Hisatomi, M. Matsui, A. Kobayashi, K. Kubota, Antioxidative activity in the pericarp and seed of Japanese pepper (*Xanthoxylum piperitum* DC), *J. Agric. Food Chem.* 48 (2000) 4924–4928.
- [17] C. Artaria, G. Maramaldi, A. Bonfigli, L. Rigano, G. Appendino, Lifting properties of the alkamide fraction from the fruit husks of *Zanthoxylum bungeanum*, *Int. J. Cosmet. Sci.* 33 (2011) 328–333.
- [18] Y. Lan, H. Li, Y.Y. Chen, Y.W. Zhang, N. Liu, Q. Zhang, Q. Wu, Essential oil from *Zanthoxylum bungeanum* Maxim. and its main components used as transdermal penetration enhancers: a comparative study, *J. Zhejiang Univ. Sci. B* 15 (2014) 940–952.
- [19] Y. Lan, Q. Wu, Y.Q. Mao, Q. Wang, J. An, Y.Y. Chen, W.P. Wang, B.C. Zhao, N. Liu, Y.W. Zhang, Cytotoxicity and enhancement activity of essential oil from *Zanthoxylum bungeanum* Maxim. as a natural transdermal penetration enhancer, *J. Zhejiang Univ. Sci. B* 15 (2014) 153–164.
- [20] X. Tang, X. Zhou, J. Wu, J. Li, Bai, A novel function of sanshools: the alleviation of injury from metolachlor in rice seedlings, *Pestic. Biochem. Physiol.* 110 (2014) 44–49.
- [21] J. Li, F. Wang, S. Li, Z. Peng, Effects of pepper (*Zanthoxylum bungeanum* Maxim.) leaf extract on the antioxidant enzyme activities of salted silver carp (*Hypophthalmichthys molitrix*) during processing, *J. Funct. Foods* 18 (2015) 1179–1190.
- [22] P. Li, L. Zhou, Y. Mou, Z. Mao, Extraction optimization of polysaccharide from *Zanthoxylum bungeanum* using RSM and its antioxidant activity, *Int. J. Biol. Macromol.* 72 (2015) 19–27.

- [23] M. Zeng, J. Wang, M. Zhang, J. Chen, Z. He, F. Qin, Z. Xu, D. Cao, J. Chen, Inhibitory effects of Sichuan pepper (*Zanthoxylum bungeanum*) and sanshoamide extract on heterocyclic amine formation in grilled ground beef patties, *Food Chem.* 239 (2018) 111–118.
- [24] O.K. Yoon, D.-S. Lee, Mulberry paper bag μ -solid phase extraction for the analysis of five spice flavors by gas chromatography-mass spectrometry, *Bull. Korean Chem. Soc.* 30 (1) (2009) 35–42.
- [25] S. Wei, H. Zhang, Y. Wang, L. Wang, X. Li, Y. Wang, H. Zhang, X. Xu, Y. Shi, Ultrasonic nebulization extraction-heating gas flow transfer-headspace single drop microextraction of essential oil from pericarp of *Zanthoxylum bungeanum* Maxim, *J. Chromatogr. A* 1218 (29) (2011) 4599–4605.
- [26] Q. Ye, Rapid analysis of the essential oil components of dried *Zanthoxylum bungeanum* Maxim by Fe₂O₃-magnetic-microsphere-assisted microwave distillation and simultaneous headspace single-drop microextraction followed by GC-MS, *J. Sep. Sci.* 36 (12) (2013) 2028–2034.
- [27] L. Jiang, K. Kubota, Differences in the volatile components and their odor characteristics of green and ripe fruits and dried pericarp of Japanese pepper (*Xanthoxylum piperitum* DC.), *J. Agric. Food Chem.* 52 (2004) 4197–4203.
- [28] L. Jiang, K. Kubota, Formation by mechanical stimulus of the flavor compounds in young leaves of Japanese pepper (*Xanthoxylum piperitum* DC.), *J. Agric. Food Chem.* 49 (2001) 1353–1357.
- [29] H.J. Behrendt, T. Germann, C. Gillen, X. Hatt, R. Jostock, Characterization of the mouse cold-menthol receptor TRPM8 and vanilloid receptor type-1 VR1 using a fluorometric imaging plate reader (FLIPR) assay, *Br. J. Pharmacol.* 141 (2004) 737–745.
- [30] Z.F. Zhao, R.X. Zhu, K. Zhong, Q. He, A.M. Luo, H. Gao, Characterization and comparison of the pungent components in commercial *Zanthoxylum bungeanum* oil and *Zanthoxylum schinifolium* oil, *J. Food Sci.* 78 (10) (2013) C1516–C1522.
- [31] K. Mizutani, Y. Fukunaga, O. Tanaka, N. Takasugi, Y.-I. Saruwatari, T. Fuwa, T. Yamauchi, J. Wang, M.-R. Jia, F.-Y. Li, Y.-K. Ling, Amides from Huajiao, pericarps of *Zanthoxylum bungeanum* MAXIM, *Chem. Pharm. Bull.* 36 (1988) 2362–2365.
- [32] K.H. Jang, Y.H. Chang, D.-D. Kim, K.-B. Oh, U. Oh, J. Shin, New polyunsaturated fatty acid amides isolated from the seeds of *Zanthoxylum piperitum*, *Arch. Pharm. Res.* 31 (2008) 569–572.
- [33] S. Huang, L. Zhao, X.L. Zhou, M. Ying, C.J. Wang, J. Weng, New alkylamides from pericarps of *Zanthoxylum bungeanum*, *Chin. Chem. Lett.* 23 (2012) 1247–1250.
- [34] M. Bader, T.D. Stark, C. Dawid, S. Löscher, T. Hofman, All-trans-configuration in *Zanthoxylum alkylamides* swaps the tingling with a numbing sensation and diminishes salivation, *J. Agric. Food Chem.* 62 (2014) 2479–2488.
- [35] V. Kumar, S. Kumar, B. Singh, N. Kumar, Quantitative and structural analysis of amides and lignans in *Zanthoxylum armatum* by UPLC-DAD-ESI-QTOF-MS/MS, *J. Pharm. Biomed. Anal.* 94 (2014) 23–29.
- [36] K. Zhong, X.-J. Li, A.-N. Gou, Y.-N. Huang, Q. Bu, H. Gao, Antioxidant and cytoprotective activities of flavonoid glycosides-rich extract from the leaves of *Zanthoxylum bungeanum*, *J. Food Nutr. Res.* 2 (7) (2014) 349–356.
- [37] L.C. Yang, R. Li, J. Tan, Z.T. Jiang, Polyphenolics composition of the leaves of *Zanthoxylum bungeanum* Maxim. grown in Hebei, China, and their radical scavenging activities, *J. Agric. Food Chem.* 61 (2013) 1772–1778.
- [38] E. Sugai, Y. Morimitsu, Y. Iwasaki, A. Morita, T. Watanabe, K. Kubota, Pungent qualities of sanshool-related compounds evaluated by a sensory test and activation of rat TRPV1, *Biosci. Biotechnol. Biochem.* 69 (10) (2005) 1951–1957.
- [39] E. Sugai, Y. Morimitsu, K. Kubota, Quantitative analysis of sanshool compounds in Japanese pepper (*Xanthoxylum piperitum* DC.) and their pungent characteristics, *Biosci. Biotechnol. Biochem.* 69 (10) (2005) 1958–1962.
- [40] C.C. Galopin, S.M. Furrer, A. Goetze, Pungent and tingling compounds in Asian cuisine, in: C.-T. Ho, T. Hofmann, W. Pickenhagen (Eds.), *Challenges in Taste Chemistry and Biology*, vol. 867, Amer. Chem. Soc. Symp. Ser., 2004, pp. 139–152.
- [41] J.Y. Koo, Y. Jang, H. Cho, C.-H. Lee, K.H. Jang, Y.H. Chang, J. Shin, U. Oh, Hydroxy-alpha-sanshool activates TRPV1 and TRPA1 in sensory neurons, *Eur. J. Neurosci.* 26 (2007) 1139–1147.
- [42] D.M. Bautista, Y.M. Sigal, A.D. Milstein, J.L. Garrison, J.A. Zorn, P.R. Tsuruda, R.A. Nicoll, D. Julius, Pungent agents from Szechuan peppers excite sensory neurons by inhibiting two-pore potassium channels, *Nat. Neurosci.* 11 (2008) 772–779.
- [43] C. Menozzi-Smarrito, C.E. Riera, C. Munari, J. Le Coutre, F. Robert, Synthesis and evaluation of new alkylamides derived from alpha-hydroxysanshool, the pungent molecule in szechuan pepper, *J. Agric. Food Chem.* 57 (2009) 1982–1989.
- [44] A.K. Moza, S.E. Rohde, J.C. Leffingwell, D. Leffingwell, Use of a liquid cooling sensate to provide a pungent, warming or tingling sensate composition, United States US 2008/0038386 A1 (2008).
- [45] T. Shimizu, Y. Shigeta, S. Kunieda, Food products containing a fruit component, United States US 2007/0092623 A1 (2007).
- [46] H.J. Choi, Evaluation of antiviral activity of *Zanthoxylum* species against picornaviruses, *Osong Publ. Health Res. Perspect.* 7 (6) (2016) 400–403.