บทความต้นฉบับ

สารให้กลิ่นที่สำคัญในโปรตีนไฮโดรไลซ์จากพืช : ปริทัศน์

Aroma Impact Compounds of Hydrolyzed Vegetable Protein: A Review

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บทคัดย่อ

ในช่วง 2 ทศวรรษที่ผ่านมานั้นมีการวิเคราะห์องค์ประกอบของสารให้กลิ่นในโปรตีนไฮโดรไลซ์จากพืชอย่างต่อเนื่อง ผลงานวิงานวิจัยที่ได้รับการตีพิมพ์เผยแพร่จำนวนมากรายงานถึงจำนวนของสารระเหยมากมายที่ตรวจพบในโปรตีนไฮโดรไลซ์จากพืช ซึ่งสารระเหยจำนวนมากที่พบนั้นมิได้เป็นสารประกอบสำคัญที่แสดงลักษณะเฉพาะของโปรตีนไฮโดรไลซ์จากพืชเลย ดังนั้นในบทความนี้จะสรุปเฉพาะสารประกอบให้กลิ่นสำคัญที่ตรวจพบเป็นสารระเหยในโปรตีนไฮโดรไลซ์จากพืช รวมไปถึงการเกิดขึ้นและลักษณะกลิ่นของสารประกอบข้างต้นด้วย

คำสำคัญ: โปรตีนไฮโดรไลซ์จากพืช, สารให้กลิ่น

Abstract

The flavor composition of hydrolyzed vegetable protein (HVP) has been extensively investigated during the last two decades. A number of publications reported a various volatile compounds found in HVP. Many of them were not character impact compounds of HVP. Then, this review summaries only the aroma impact compounds that have been identified in the volatiles of HVP. The formation and odor description of those compounds were also provided.

Key words: hydrolyzed vegetable protein (HVP), aroma

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Introduction

Food possesses a set of qualities known as flavor that along with other qualities, such as color, shape, texture, safety, and wholesomeness, determine food quality (*1*). Flavor, as has been noted, is defined as the organoleptic response to the parameters described as taste and flavor volatiles. Taste is largely due to the reaction with receptor sites on the tongue or soft palate, from molecules, which are mainly non-volatile (*2*). Simplify, taste is detected in the mouth. Whereas, volatile flavor, the sensation obtained from interactions with olfactory sites and largely in nasal passages (*2*), are denoted odor if they have been perceived nasally (before eating) and aroma if they have been perceived retronasally via the throat (during eating). Therefore, in the literature the terms flavor, odor or aroma compounds are often synonymously used (*3*).

The complexity and variety of compounds contributed to flavor derived from protein source is considerable. The biggest contribution to flavor is obtained from relatively small fragments of protein. The most common form of fragmentation is hydrolysis (*2*). Amino acids and peptides are produced from this reaction, which may be bitter or sweeter depending on the amino acids and their sequences in the protein (*2*). In addition, amino acids and peptides are chemically reactive and thus are able to involve in many transformations. The transformation, such as reaction with reducing sugar (the Maillard reaction) can form flavoring compounds and pigments (*4*). Then, the hydrolysis and Maillard reactions are most important in flavor formation of heated foods.

Chemical hydrolysis remains one of the most popular forms of protein modification. Peptide bond hydrolysis, both acid and basic, may be used to yield smaller products with more uniform molecular size.

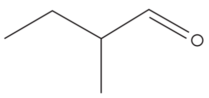
Hydrolysis, using acid as a catalyst such as hydrochloric acid, remains a very well known method of manufacturing hydrolyzed protein. To compare with alkali hydrolysis, Shih (*5*) stated that alkali treatment causes reactions, which are undesirable for food uses. In addition, food protein treated extensively with alkali is not readily digested. The nutritional value is decreased and toxic effects are reported. Whereas, enzymatic hydrolysis is an alternative to the hydrolyzed protein, is produced using protease under more neutral pH and lower temperature. Enzymatic hydrolysis yields products that are lighter in color, contain lower amounts of chlorohydrins and salts, and have a milder pleasant taste (*2*).

As a result of protein hydrolysis, some reductions in molecular size of protein yield reactive peptides and amino acids. The products of these processes are generally known as protein hydrolysates or hydrolyzed vegetable protein (HVP). The HVP has been used as flavor enhancers such as seasoning sauce, hospital diets for patients and protein liquids/ powders for weight control diets (*6*). The HVP contains the reactants such as amino acids, sugars, and many intermediate and breakdown products, contribute to flavor reactions. For example, reactive amino acids can react with reducing sugar (Maillard reaction) to give Maillard volatile compounds. The flavor is generated from the Maillard reaction and the browning reactions, as same as aroma (*7*). Pathways to flavor in hydrolyzed protein are very similar to those in other heated foods. Moreover, proteins themselves have little flavor. They can influence perceived flavor or can provide the precursors of flavor such as the Strecker degradation of amino acid (*8*). Furthermore, peptides, in terms of contribution to flavor, may range in molecular size and may contribute a variety of flavors both desirable and undesirable off-flavors. However, flavor of protein hydrolysates has to meet the consumer preference. Wheat gluten, corn gluten, defatted soy flour, defatted peanut flour, defatted cotton seed flour and others are sources of proteins for HVP manufacturing. This present paper provides a review on the chacracter impact compounds of hydrolyzed vegetable proteins and their chemical structures as show in figure 1-4.

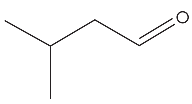
Aldehyde compounds

2- or 3-Methylbutanal has a dark chocolate, malt odor. 2-Methylbutanal was derived from isoleucin (*9*) whereas 3-methylbutanal was the Strecker degradation of leucine (*10*). 3-Methylbutanal is a character impact component of malted barley (*11*). Aaslyng *et al* (*12*) stated that "malt" was an important descriptor and it is likely to be key component in the flavor of both acid-HVP and enzyme-HVP produced from soy. Also, Solina *et al* (*10*) found that 3- and 2-methyl butanal were the highest amount in acid-HVP from soy protein isolate, respectively. Furthermore, Wu and Cadwallader (*13*) confirmed that 3-methylbutanal was a potent odorants a meatlike process flavoring from soybean-based enzyme-HVP which had a high $\log_3$FD factors (Flavor dilution factor).

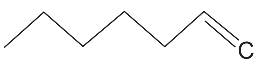
The odor description of hexanal was green/ grassy. Hexanal has been reported as a volatile component of rice bran (*14*). Aaslyng *et al* (*12*) reported that hexanal probably causes an undesirable odor in enzymatic HVP. Beside, Solina *et al* (*10*) stated that hexanal would be derived from the oxidation of linoleic and linolenic acids, two of the major fatty acids found in soy protein isolate. It derived from lipid oxidation and has been correlated with beany taste in enzymatic protein hydrolysates (*15*).



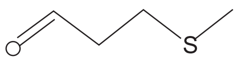
2-Methyl butanal



3-Methyl butanal

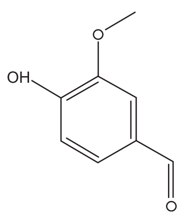


Hexanal



3-Methylthio-propanal or Methional

(*E*)-2-Nonenal



3-Methoxy-4-hydroxybenzaldehyde or Vanillin

Figure 1 Chemical structures of some aldehydes

Several odorous compounds were present in both enzyme and acid HVP produces from soy. 3-Methylthio-propanal or methional is typically described as potato-like. Jarunrattanasri *et al* (*16*) found that methional was the predominat odorant of HVP prepared from partial hydrolysis of rice bran protein concentrate. Methional is the Streker aldehyde of methionine. It has also been found in acid and enzyme HVP heated with a mixture of glucose and xylose (*17*). Moreover, it was also found as a volatile component in soybean-based enzyme-HVP (*13, 18*)

(*E*)-2-Nonenal (cucumber odor) was a predominant odorant in both rice bran protein concentrate and its partial acid HVP (*16*). On the contrary, it was not presented in acid HVP from soy protein isolate (*10*) as well as in acid HVP from soy (*12*). (*E*)-2-nonenal was only presented in enzyme HVP from soy and was probably responsible for the odor of enzyme HVP which may contribute to undesirable odor in enzyme HVP (*12*). Furthermore, (*E*)-2-nonenal is a cardboard-like character impact compound in soybean lecithin and its hydrolysate (*19*).

3-Methoxy-4-hydroxybenzaldehyde or vanillin had a vanilla note. Vanillin belonged to another group of odorants that had intermediate and high potency in rice bran protein concentrate and its partial hydrolysates, respectively (*16*). On the other hand, vanillin was not reported as a predominant odorant produced from rice bran protein concentrate by hydrolysis with concentrated 4 N HCl (*37*). Mega (*20*) found that vanillin was formed from lignin degradation in the presence of air.

Ketones compounds

The β-damascenone, which had an applesauce odor, was another odorant found in HVP with very high potency, with the extremely low odor threshold in water (0.00075 ppb or ng/g; *21*). Hence, β-damascenone was an important aroma impact compound in rice bran protein concentrate and especially in its hydrolysates

(*16*). Besides, this compound has been found to predominate in many foods, for example, fresh raspberries (*22*), grape (*23*), apple (*24*) and honey (*25, 26*), and soybean-based enzyme-HVP (*13*). In natural products such as grape, β-damascenone was thought to be formed from the hydrolysis of glycosidic linkage of complex compounds of β-damascenone bound with sugar.

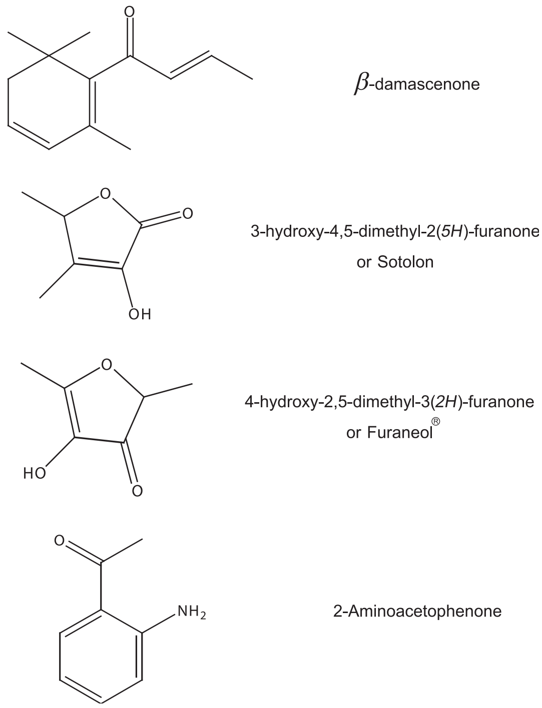


Figure 2 Chemical structures of some ketones

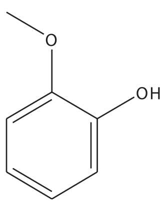
3-hydroxy-4,5-dimethyl-2(*5H*)-furanone or sotolon (curry or seasoning odor) was another odorant found in the acidic fraction in acid HVP from rice bran protein (*16*). Sotolon is a potential flavoring due to its extremely low threshold in water (0.001 ppb; *27*). Also, it was reported as a character-impact compound of fenugreek (*Trigonella foenum-graecum* L.) (*28*). Sotolon was also contributed to the burnt/sweet note of cane sugar (*29*), coffee (*30*), to the spicy/curry note of lovage (*31*). Several hypotheses exist concerning of the formation of sotolon. Sulser *et al* (*32*) described that sotolon was generated from the degradation of threonine. Later, Kobayashi (*27*) reported on the formation of sotolon in sake and wine by an aldol condensation of acetaldehyde and α-ketobutyric acid followed by lactonization. Thermally induced oxidative deamination of 4-hydroxy-isoleucine yields also sotolon (*33*). Hofmann and Schieberle (*34*) detected sotolon after heating of an aqueous solution containing hydroxyacetaldehyde and 2,3-butanedione at pH 5. And in the model study of the formation of sotolon during storage of citrus juice.

4-hydroxy-2,5-dimethyl-3(*2H*)-furanone or Furaneol® had a strawberry-like note at low concentration and exhibited a burnt sugar-like note at higher concentrations. In general, Furaneol® occurs naturally in various fruits, such pineapple (*35*), strawberry (*36*), among others. Furaneol® has been found in HVP from soy (*13*), and rice bran protein (*16, 37*). Furaneol® occurs naturally in four forms: (I) 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone glucoside, (II) 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone 6'-O-malonyl-β-D-glucopyranoside, (III) 4-methoxy-2,5-dimethyl-3(*2H*)-furanone (mesifuran) as well as free (IV) 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone (*38*). It was believed that the naturally occurring furanones in fruit and microorganism were enzymatically formed. However, a number of publication were studied of chemical formation of Furaneol®(*39*, *40*, *41*, *42*).

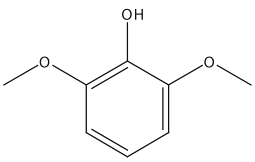
2-Aminoacetophenone had a grape, sweet, corn tortilla and foxy aroma note. This compound was hypothesized to be important in the aroma of muscadine grape juice (*43*) and has been identified as causing an undesirable flavor in fermented tuna sauce (*44*) and milk product (*45*, *46*). 2-Aminoacetophenone may be a characteristic aroma component of rice bran protein concentrate, since not only did it have highest $\log_3$FD factor but its odor is very similar to that of rice bran protein concentrate (*16*). According to Buttery and Ling (*47*), the 2-aminoacetophenone was probable formed by a breakdown of amino acid tryptophan during the lime treatment of corn. In the presence of air, tryptophan can be oxidized to kynurenine, which was converted to 2-aminoacetophenone (*48*) under the alkaline conditions used during the preparation of masa. Hoenicke *et al* (*49*) stated that tryptophan and its metabolites, particularly indole-3-acetic acid, were considered to be potential precursors of 2-aminoacetophenone. Later (*50*), they found that the formation of 2-aminoacetophenone was triggered by an oxidative degradation of indole-3-acetic acid after sulfuration with potassium bisulfite via the intermediates 3-(2-formylaminophenyl)-3-oxopropionic acid and 2-formamidoacetophenone.

Alcohols and Phenols

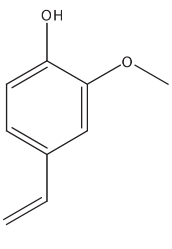
The 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) imparted strong smoky note. Many researchers reported that most of phenols are major contributors to wood smoke aroma. Particularly, guaiacol, which had a low odor threshold value (2.5 ppb in water; *51*), has been found both in acid and enzyme-hydrolyzed soy protein (*12*), soybean-based enzymatically hydrolysates (*13*), partial hydrolysis of rice bran protein (*16*), acid hydrolyzed HVP from rice bran (*37*) and extruded enzyme hydrolyzed soybean protein (*52*). The presence of guaiacol and syringol were considered an undesirable effect on overall aroma of HVP from rice bran protein since they imparted atypical smoky notes (*16*). Mega (*20*) pointed out that phenol and its derivative are most directly related to lignin degradation. Initial degradation by fission occurs with the heterocyclic furan, pyran rings and ether linkage of lignin. This eventually results in the production of guaiacol, which in turn can further degrade to form phenol and cresol. Mega (*20*) also proposed the schematic of lignin degradation to its derivatives such as 2-methoxy-4-vinylphenol (*p*-vinylguaiacol), vanillin and guaiacol. *p*-Vinylguaiacol contributed a spicy, clovelike note.



2-methoxyphenol
or Guaiacol



2,6-dimethoxyphenol
or Syringol

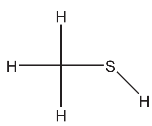


2-methoxy-4-vinylphenol
or *p*-Vinylguaiacol

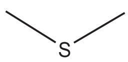
Figure 3 Chemical structures of some alcohols and phenols

Sulfur containing compounds

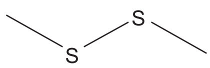
In addition to sulfur containing compounds such as 3-methylthio-propanal (potato like odor), methanethiol (sulfurous, rotten odor), dimethyl sulfide (sulfurous, fresh corn odor), dimethyl disulfide (sulfurous), dimethyl trisulfide (sulfurous, cabbage, garlic odor) and dimethyl tetrasulfide (cooked cabbage) were found in HVP. These compounds were considered to be either thermally generated aroma active compounds from sulfur-containing amino acids or Maillard reaction products (*53*). In previous studies, Martin and Ames (*54*) explained that three sulfides (dimethyl sulfide, dimethyl disulfide and dimethyl trisulfide) were identified in the glucose/methionine model system. Dimethyl disulfide was produced in the highest amounts. Especially, in methionine alone and methionine/glucose model systems were found that dimethyl disulfide were the predominant compounds generated in these systems. Yu and Ho (*55*) also found that methionine sulfoxide or methionine was heated with glucose at 180°C for 1h. And they postulated that methional sulfoxide was primary formed from methionine sulfoxide during reaction and that it degraded mainly to methanethiol (which subsequently oxidized to dimethyl disulfide), with only small proportion being transformed to methional. It should be explained why dimethyl disulfide was found only in methionine/fructose Maillard model system.



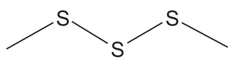
Methanethiol



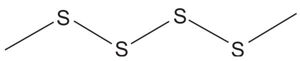
Dimethyl sulfide



Dimethyl disulfide



Dimethyl trisulfide



Dimethyl tetrasulfide

Figure 4 Chemical structures of some sulfur containing compounds

Conclusion

The present article provides a summary of the most important aroma impact compounds in hydrolyzed vegetable protein. The predominant odorants in HVP were varies depended on protein sources and hydrolysis conditions. Some of them were detected in a high concentration. Whereas the rest found in low concentration but they were predominant odorant due to their very low odor threshold values.

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