

## 第6章：(2) 熱產生香氣中硫化學的角色

(From "Flavour Development, Analysis and Perception in Food and Beverages, 9- The role of sulfur chemistry in thermal generation of aroma", 2015 Elsevier Ltd. )

## 9.1- Introduction

加工食品的香氣中，**硫**揮發物經常扮演重要的作用，常是低氣味閾值，比起對應的醇類也通常都低好幾次方(表9.1)。例如咖啡的一關鍵香氣化合物，提供烘焙、咖啡般氣味的**2-furanmethanethiol**，閾值0.005–0.12 µg/kg，比對應的2-furanmethanol 低至10,000–100,000倍。

表9.1中的硫醇類(thiols)，其平均氣味閾值低於相關醇類的一百至一億倍。

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Table 9.1 Odour thresholds of thiols and their corresponding alcohols (van Gemert, 2003)

| Thiol                                    | Odour threshold (µg/kg) | Alcohol                                | Odour threshold (µg/kg) |
|--|-------------------------|--|-------------------------|
| Ethanethiol                              | 2                       | Ethanol                                | 3500–190,000,000        |
| 2-Furanmethanethiol (furfural mercaptan) | 0.005–0.12              | 2-Furanmethanol                        | 1900–2000               |
| 3-Mercapto-2-butanone                    | 3                       | 3-Hydroxy-2-butanone                   | 14–10,000               |
| Methanethiol                             | 0.02–4                  | Methanol                               | 14–10,000               |
| 2-Phenylethanethiol                      | 0.05 <sup>a</sup>       | 2-Phenylethanol                        | 0.015–75,000            |
| 3-Methyl-2-buten-1-thiol (prenyl thiol)  | 0.0002–0.005            | 3-Methyl-2-buten-1-ol (prenyl alcohol) | 250–7800                |
| 4-Mercapto-4-methyl-2-pentanone          | 0.0001–0.005            | 4-Hydroxy-4-methyl-2-pentanone         | 44,000–100,000          |
| 1- <i>p</i> -Menthen-8-thiol             | 0.0001 <sup>b</sup>     | α-Terpineol                            | 4.6–15,000              |

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香氣活性硫化合物的舉例與所存在的熱加工食品。肉類(牛、雞、豬)、鮭魚及蘆筍煮熟時，以及焙炒芝麻之烘烤氣味(**roasted smelling**)的**2-acetylthiazole**。

Table 9.2 Aroma-active sulfur compounds in thermally processed foods (examples)

| Compound                        | Odour                | Occurrence (examples)   |
|---------------------------------|----------------------|---|
| 2-Acetylthiazole                | Roasted              | Asparagus <sup>a</sup> , beef <sup>b</sup> , chicken <sup>c</sup> , pork <sup>d</sup> , salmon <sup>e</sup> , sesame <sup>f</sup>   |
| Dimethyl sulfide                | Sulfury, tomato-like | Asparagus <sup>a</sup> , potato <sup>g</sup> , tomato <sup>h</sup>  |
| Dimethyl trisulfide             | Onion-like           | Beef <sup>b</sup> , coffee <sup>i</sup> , cocoa <sup>j</sup> , peanut <sup>k</sup> , pork <sup>d</sup> , potato <sup>g</sup> , sesame <sup>f</sup> , shallots <sup>l</sup>  |
| 2-Furanmethanethiol             | Coffee-like          | Beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , peanut <sup>k</sup> , pork <sup>d</sup> , salmon <sup>e</sup> , sesame <sup>f</sup>  |
| Methanethiol                    | Cabbage-like         | Beef <sup>b</sup> , chicken <sup>c</sup> , peanut <sup>k</sup> , potato <sup>g</sup> , salmon <sup>e</sup>  |
| Methional                       | Potato-like          | Asparagus <sup>a</sup> , beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , pork <sup>d</sup> , hazelnut <sup>m</sup> , peanut <sup>k</sup> , salmon <sup>e</sup> , sesame <sup>f</sup> , tomato <sup>h</sup> , potato <sup>g</sup> |
| 2-Methyl-3-furanthiol           | Meaty                | Beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , pork <sup>d</sup> , sesame <sup>f</sup>  |
| 2-Methyl-3-(methylidithio)furan | Meaty                | Beef <sup>b</sup> , cocoa <sup>j</sup>  |
| Methyl 1-propenyl sulfide       | Garlic-like          | Shallots <sup>l</sup>   |
| 4-Methyl-3-thiazoline           | Earthy, burnt        | Sesame <sup>f</sup>   |
| 3-Mercapto-2-methyl-1-pentanol  | Meaty, onion-like    | Onion <sup>n</sup>  |

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典型的煮熟牛肉般氣味 **2-methyl-3-furanthiol** 對所有煮熟肉的香氣都是關鍵的，也貢獻於咖啡及芝麻香氣。有時，報導的硫氣味物質實際上並不存在於所分析的食品，而是分析過程中生成的人工物質。

Table 9.2 Aroma-active sulfur compounds in thermally processed foods (examples)

| Compound                        | Odour                | Occurrence (examples)   |
|---------------------------------|----------------------|---|
| 2-Acetylthiazole                | Roasted              | Asparagus <sup>a</sup> , beef <sup>b</sup> , chicken <sup>c</sup> , pork <sup>d</sup> , salmon <sup>e</sup> , sesame <sup>f</sup>   |
| Dimethyl sulfide                | Sulfury, tomato-like | Asparagus <sup>a</sup> , potato <sup>g</sup> , tomato <sup>h</sup>  |
| Dimethyl trisulfide             | Onion-like           | Beef <sup>b</sup> , coffee <sup>i</sup> , cocoa <sup>j</sup> , peanut <sup>k</sup> , pork <sup>d</sup> , potato <sup>g</sup> , sesame <sup>f</sup> , shallots <sup>l</sup>  |
| 2-Furanmethanethiol             | Coffee-like          | Beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , peanut <sup>k</sup> , pork <sup>d</sup> , salmon <sup>e</sup> , sesame <sup>f</sup>  |
| Methanethiol                    | Cabbage-like         | Beef <sup>b</sup> , chicken <sup>c</sup> , peanut <sup>k</sup> , potato <sup>g</sup> , salmon <sup>e</sup>  |
| Methional                       | Potato-like          | Asparagus <sup>a</sup> , beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , pork <sup>d</sup> , hazelnut <sup>m</sup> , peanut <sup>k</sup> , salmon <sup>e</sup> , sesame <sup>f</sup> , tomato <sup>h</sup> , potato <sup>g</sup> |
| 2-Methyl-3-furanthiol           | Meaty                | Beef <sup>b</sup> , chicken <sup>c</sup> , coffee <sup>i</sup> , pork <sup>d</sup> , sesame <sup>f</sup>  |
| 2-Methyl-3-(methylidithio)furan | Meaty                | Beef <sup>b</sup> , cocoa <sup>j</sup>  |
| Methyl 1-propenyl sulfide       | Garlic-like          | Shallots <sup>l</sup>   |
| 4-Methyl-3-thiazoline           | Earthy, burnt        | Sesame <sup>f</sup>   |
| 3-Mercapto-2-methyl-1-pentanol  | Meaty, onion-like    | Onion <sup>n</sup>  |

Boiled meats

## 9.2- The Maillard reaction

Maillard reaction plays a central role for sulfur aroma compound formation during cooking, for example, in meat or vegetables like tomato, asparagus and potato.

次頁Table 9.3 表列一些重要的硫氣味物質連同食品中最相關的前驅物質。很顯然，半胱氨酸 **cysteine** 是表列中的多種氣味物質之重要前驅物質，事實上，它是梅納反應衍生的硫揮發物的最重要前驅物質，也屬前驅物質的其餘胺基酸為甲硫氨酸 **methionine** 及 **S-methylmethionine** (一種非蛋白質的胺基酸)。

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**Table 9.3** Aroma-active sulfur compounds from Maillard reaction and their precursors in food

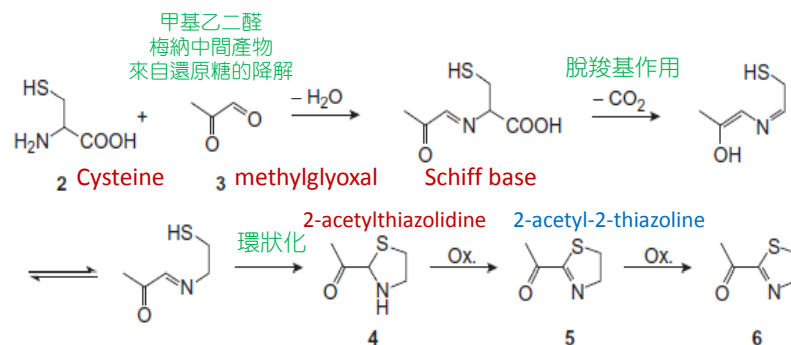
| Compound               | Precursor(s)                |
|------------------------|-----------------------------|
| 2-Acetylthiazole       | Cysteine/monosaccharides    |
| 2-Acetyl-2-thiazoline  | Cysteine/monosaccharides    |
| Dimethyl sulfide       | S-Methylmethionine          |
| 2-Furanmethanethiol    | Cysteine/ribose             |
| Methanethiol           | Methionine/ monosaccharides |
| 3-Mercapto-2-butanone  | Cysteine/monosaccharides    |
| 2-Mercapto-3-pentanone | Cysteine/ribose, thiamine   |
| 3-Mercapto-2-pentanone | Cysteine/ribose             |
| Methional              | Methionine/ monosaccharides |
| 2-Methyl-3-furanthiol  | Thiamine, cysteine/ribose   |

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### 9.2.1- The Maillard reaction of cysteine (模式反應)

Mulders (1973) identified thiazoles, pyrazines and thiophenes in a **ribose/L-cysteine/cystine** browning system. 化合物 5及6 提供 roasted, popcorn-like aroma，肉中都存在。

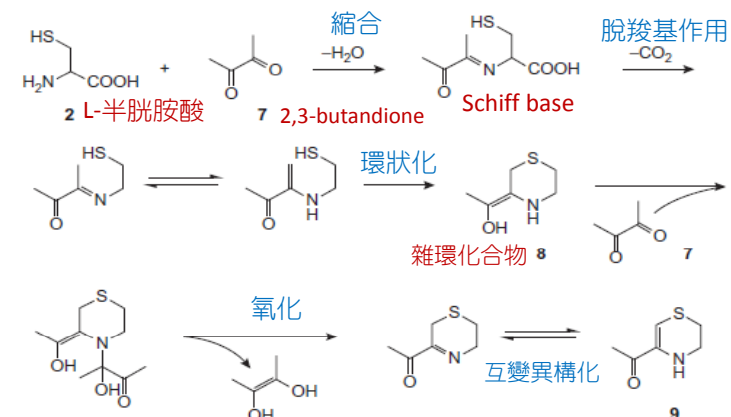


**Figure 9.2** Formation of 2-acetylthiazole (6) from L-cysteine (2) and methylglyoxal (3) (Mulders, 1973).

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L-半胱氨酸和核糖溶液加熱後也鑑定出類似的化合物 5-acetyl-3,6-dihydro-2H-1,4-thiazine，同樣賦予烤、玉米般主調，由L-半胱氨酸和2,3-butanedione反應之形成途徑如圖9.3，只是側反應，主反應的產物 2-methyl-2-acetylthiazolidine。



**Figure 9.3** Formation of 5-acetyl-3,6-dihydro-2H-1,4-thiazine (9) from L-cysteine (2) and 2,3-butanedione (7) (Hofmann and Schieberle, 1995).

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■ L-半胱氨酸和核糖兩者都是生肉的組成分，也是煮肉香氣的重要前驅物質。此導致許多以這兩種前驅物質作模式反應的探討，為了說明煮熟中香氣的形成。

Hofmann and Schieberle (1995) identified the following aroma-relevant sulfur molecules in the volatile fraction of a heated L-cysteine/ribose solution:

2-furanmethanethiol, 3-mercapto-2-pentanone,  
2-methyl-3-furanthiol, 5-acetyl-3,4-dihydro-2H-1,4-thiazine,  
3-mercapto-2-butanone, bis(2-methyl-3-furyl) disulfide,  
2-formylthiophene, 2-acetyl-2-thiazoline,  
1-mercapto-2-propanone,  
2-methyltetrahydrothiophen-3-one and  
3-methyl-3-thiophenethiol.

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同位素標識核糖、水溶液、pH 5 試驗下，得知核糖的碳骨架完整保留在主要氣味物 2-methyl-3-furanthiol (16)、2-furanmethanethiol (17)及 3-mercapto-2-pentanone。被指出可能是前兩種化合物(來自L-半胱氨酸和核糖)的中間產物 1,4-dideoxypentose (14)形成，假設途徑如圖9.4。然後

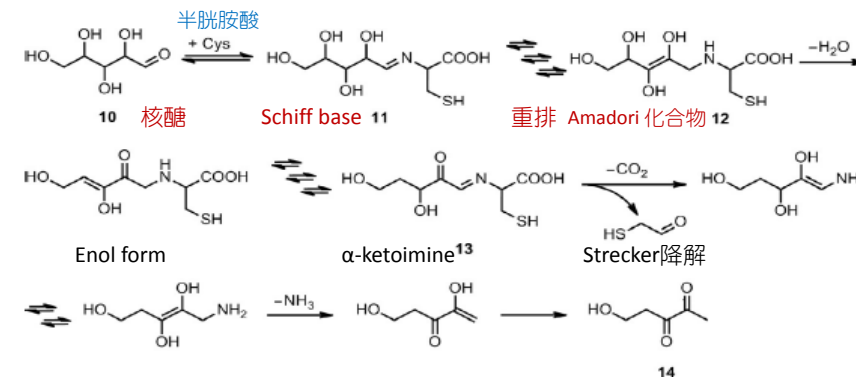


Figure 9.4 Formation of 1,4-dideoxypentose (14) from ribose (10) (Cerny and Davidek, 2003).

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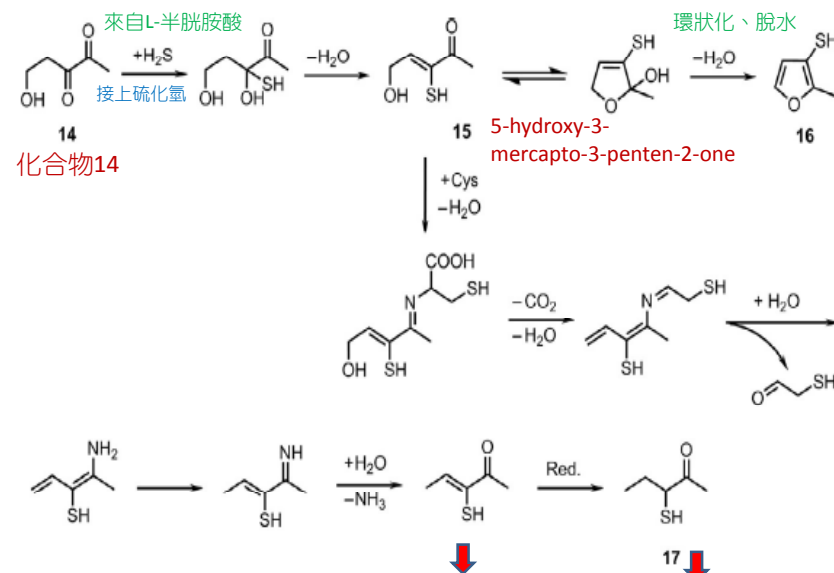


Figure 9.5 Formation of 2-methyl-3-furanthiol (16) and 3-mercapto-2-pentanone (17) from 1,4-dideoxypentose (14) (Cerny and Davidek, 2003).

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α-mercaptoketones (17化合物，3-mercapto-2-pentanone即屬)的另一形成途徑，經梅納反應中間產物的二羰基化合物，接上硫化氫(源自L-半胱氨酸的裂解)、並還原。此外也生成對應的二硫化物。

■ 存在肉中的核糖大多為結合型如 inosine 5'-monophosphate (IMP)，當梅納反應中核糖同L-半胱氨酸被取代為IMP，揮發物中仍是同樣的含硫化合物包括 2-methyl-3-furanthiol、2-furanmethanethiol 及 α-mercaptoketo compounds 等居多，但濃度低很多。ribose 5-phosphate取代核糖則產量更多。

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- ◆影響梅納反應的揮發物組成輪廓之各種因素中，pH值發揮關鍵作用。已熟成肉的pH值通常在5.6附近，當這pH被調整，這將改變煮熟後的風味。

碎肉煮之前先調整至pH 4.0–5.6比更低的pH 產生更多種類的揮發物；

pH 5.6煮熟肉具a natural、boiled meat、fatty aroma，若於pH 4.0則帶更多的腎及肝類似的氣味。

在低pH，2-methyl-3-furanthiol 及2-furanmethanethiol 濃度通常會較高，

L-半胱氨酸和核糖在pH 4.5-6.5的模式系統也顯示，pH 6.5時，含硫氣味物質 2-methyl-3-furanthiol、2-methyl-3-thiophenethiol 以及它們對應的二硫化物濃度都急遽降低。

較高的pH，thiazoles 產生量較多(例如 2-acetylthiazole)。

高pH下硫醇(thiol)的生成減少，一般見解也提及所謂dark-cutting meat 是高pH (動物屠宰前的緊迫，導致減少屠宰後乳酸的形成所引起)而肉香氣低。

實驗也觀察低pH下的硫醇類形成增加，即L-半胱氨酸、核糖及硫胺(thiamine)模式系統由pH 7降至4時，有利於 2-furanmethanethiol、3-mercapto-2-pentanone 及 4,5-dihydro-2-methyl-3-furanthiol 的形成。

另採用同位素標識核糖的試驗也指出，2-furanmethanethiol carbons 全來自核糖，而4,5-dihydro-2-methyl-3-furanthiol 及 3-mercapto-2-pentanone 的碳主要來自硫胺。

### 9.2.2 Interaction of the Maillard reaction and lipid oxidation

梅納反應與脂質氧化兩者都參與含有兩反應的前驅物質胺基酸/還原糖與脂質(譬如不飽和脂肪酸及磷脂質)之大多數加熱食品的香氣產生。兩反應也互相影響，可能抑制或促進作用、或甚至產生了既非脂質氧化也非梅納反應單獨所生成的新化合物。

### 9.2.3 Stability of sulfur compounds

在熱處理後的食物中，硫醇類及其它硫香氣化合物的穩定性對於食物的貯藏壽命，以及對於我們實際消費這些食品時能否依然感知其氣味，可說至關重要。

當溶於有機溶劑，氣味活性硫醇類如3-mercapto-2-butanone、2-methyl-3-furanthiol 及 2-furanmethanethiol 緩慢氧化為對應的二硫化物；舉例 2-methyl-3-furanthiol 溶於乙醚、經6°C一天後減少30%，且bis(2-methyl-3-furyl) disulfide 同時形成。在50°C一天後，Process flavor 的成分 2-methyl-3-furanthiol 減少59%，其次2-furanmethanethiol 下降28%。

☐ 咖啡飲料中的硫醇類(thiols)特別不穩定。這解釋為沖泡咖啡的香氣何在剛沖泡後很快就變化並失去吸引力。

這大部分歸咎於 2-furanmethanethiol (保溫瓶中60分鐘後75%損失)及其它硫醇類的迅速降解(Hofmann and Schieberle, 2002)。在咖啡沖泡時，這聞如咖啡般的2-furanmethanethiol (22) 不可逆地共價鍵結合至 pyrazinium radical cations (32)，結構32類似的化合物類是咖啡黑色素(melanoidins)的部分，乃透過蛋白質結合離胺酸的梅納反應所生成，The binding mechanism is illustrated in 圖9.9.

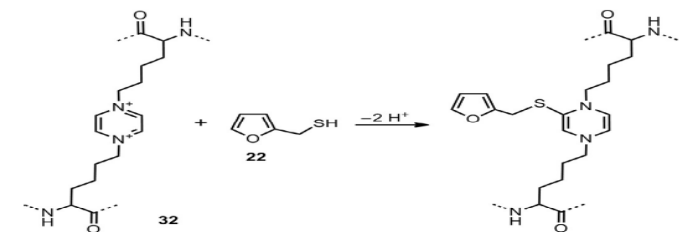


Figure 9.9 Irreversible binding of 2-furanmethanethiol (22) to pyrazinium Maillard intermediates (32) from coffee melanoidins (Hofmann and Schieberle, 2002).



如同thiols，在食品中disulfides的穩定性較低。當水中加熱，可能因水解而形成對應的硫醇類。

食品中，二硫化物可另外和食品蛋白質交互作用，當二硫化物在溶液中和egg albumin一起加熱，轉變成對應的 thiols 2-methyl-3-furanthiol、2-furanmethanethiol，由和蛋白質結合的L-半胱氨酸的氧化還原反應所引發(圖9.10)，作者提出蛋白質的 thiol基和二硫化物的互換；舉例bis(2-methyl-3-furyl) disulfide (33) 釋出2-methyl-3-furanthiol (16)。

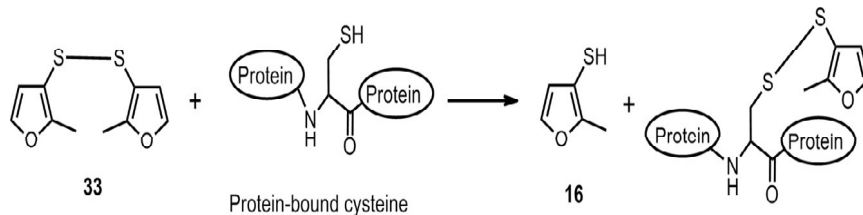


圖9.10 Formation of 3-methyl-3-furanthiol (16) from its disulfide (33) and egg albumin

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## 9.2.4 Cysteine S-conjugates from the Maillard reaction

半胱氨酸S-共軛物(cysteine S-conjugates)於各種水果與蔬菜都存在，也知攝食時會釋出對應的硫醇類(thiols)，釋出為酵素性，由口腔微生物引發。最近從L-cysteine/xylose熱反應溶液的非揮發區分中發現2-methyl-3-furanthiol (38)及2-furanmethanethiol (37)的半胱氨酸S-共軛物，當嚐了水溶液，兩共軛物因口腔微生物而酵素性斷裂，釋出對應的硫醇類氣味物質，引起肉及烤氣味印象。假設的反應途徑如圖9.11。核糖的梅納中間產物 furanmethanol (35)受半胱氨酸的親核性攻擊而產生S-(2-furfuryl)-L-cysteine (37)；攻擊(35)的3-位置則產生中間產物36，並透過重排而生成S-(2-methyl-3-furyl)-L-cysteine (36)。

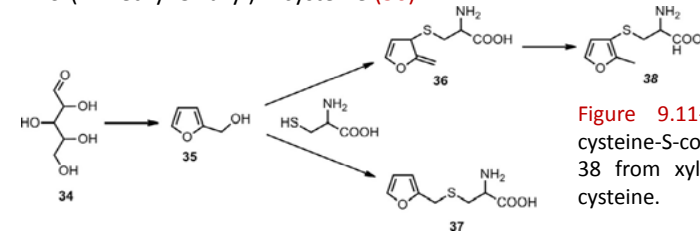


Figure 9.11- Formation of cysteine-S-conjugates 37 and 38 from xylose (34) and L-cysteine.

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## 9.3 The Strecker degradation

The Strecker degradation in food is often associated with the Maillard reaction because the latter provides dicarbonyl compounds (e.g. deoxyosones, 2,3-butanedione, 2,3-pentanedione) for the reaction with amino acids. L-Cysteine and methionine are the two only sulfur-containing protein-derived amino acids. The Strecker degradation with methionine (39) is illustrated in 圖9.12 (a,b).

Buhr et al. (2010) 發現乾式加熱(譬如麥芽、可可的烘烤)的食品接觸水後(猶如咀嚼過程)會釋出醛類，例如麥芽溶劑萃取及分析之前先浸水，甲硫醇methional 濃度增加100倍。

後來，鑑定3-oxazolines (構造48)是口中各相應醛的有效前驅物質，它們在乾燥條件的 Strecker降解期間，透過其enol Strecker中間產物的閉環而形成。圖9.12 (c)

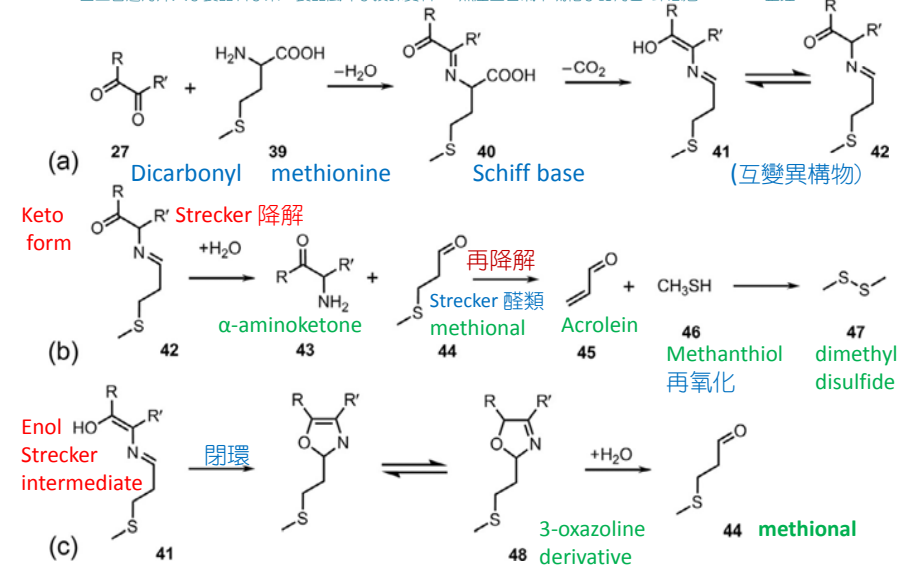
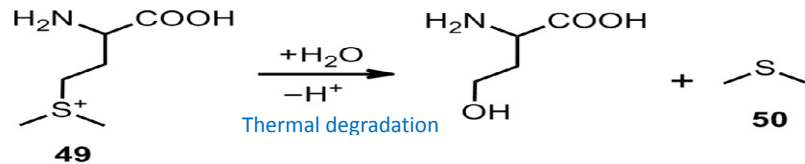


圖9.12- Strecker reaction of methionine: (a) Formation of the decarboxylated Schiff base intermediate 42; (b) Formation of methional (44) under aqueous conditions and subsequent decomposition to methanthiol (46) and dimethyl disulfide (47); (c) Formation of 3-oxazoline derivative 48 under dry conditions and release of methional (44) in the presence of water.

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圖9.13- Formation of **dimethyl sulfide** (50) from S-methylmethionine (49)

甲硫氨酸的S-甲基化形式之S-methylmethionine (49) 是存在各種蔬菜還有麥芽的一種非蛋白質的胺基酸，其含量：番茄 2.8 mg/kg、麥芽 6 mg/kg、高麗菜 81 mg/kg、芹菜 176 mg/kg、蘆筍 53–252 mg/kg 等。它的加熱降解(Figure 9.13)產生dimethyl sulfide (50)。帶有sulfurous odour 強力貢獻於前列食物的香氣，在麥芽中過量會造成不良主調。

## 9.4 Thiamine degradation

呋喃衍生物2-methyl-3-furanthiol (16)與其二硫化物(disulfides)，是煮牛肉及其他肉類的香氣影響化何物，賦予肉氣味(meaty odour)主調。

- 前節曾強調L-半胱氨酸和核糖的梅納反應為產生這氣味物質的有效率機制，但比較探討生肉中也近似低濃度的前驅物質，點出**硫胺(thiamine) (51)**的關係更大。L-cysteine (0.65 mM) 及ribose (1.34 mM) 溶液加熱至沸騰，只產生0.2 µg/L的2-methyl-3-furanthiol，但當核糖以很低濃度(0.06 mM)的硫胺取代，產量則增1500倍至300 µg/L。因此，在肉香氣中(16)的最重要前驅物質似是硫胺，結合L-半胱氨酸，當作硫化氫的來源。

圖9.14：酸性條件下，如同肉中，硫胺的thiazole ring水解，中間產物52移除甲酸、分裂為一級裂解產物53與5-hydroxy-3-mercapto-2-pentanone (54)。Van der Linder等(1978)推測產物54是4,5-dihydro-2-methyl-3-furanthiol (55)及2-methyl-3-furanthiol (16)的主要中間產物，產物54的閉環、再脫水導致55生成，再氧化產生2-methyl-3-furanthiol (16)。

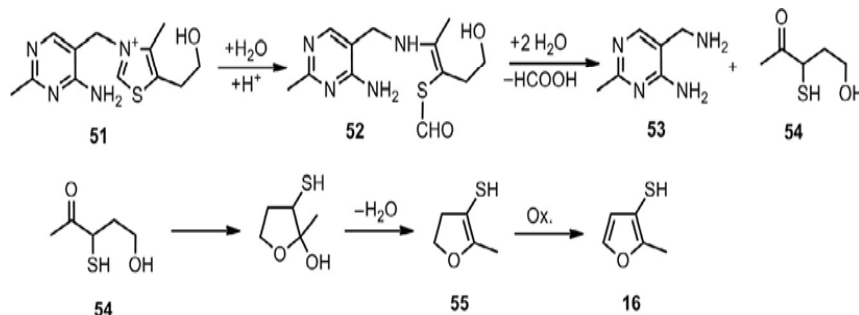


Figure 9.14 Formation of 2-methyl-3-furanthiol (16) from thiamine (51) via 5-hydroxy-3-mercapto-2-pentanone (54) (Van der Linde et al., 1978).

圖9.15：鹼性條件下，OH<sup>-</sup>離子攻擊硫胺中連結兩雜環的碳原子，一級裂解產物的嘧啶(pyrimidine)衍生物56及5-(2-hydroxyethyl)-4-methylthiazole (sulfurol) (57)形成。

在pH 8，硫胺降解仍依照圖9.14的機制而產生2-methyl-3-furanthiol (16)及4,5-dihydro-2-methyl-3-furanthiol (55)，但噻唑衍生物(thiazole derivates)如源自sulfurol的4-methyl-5-vinylthiazole (58)、4,5-dimethylthiazole (59)及4-methylthiazole (60)變成更重要。

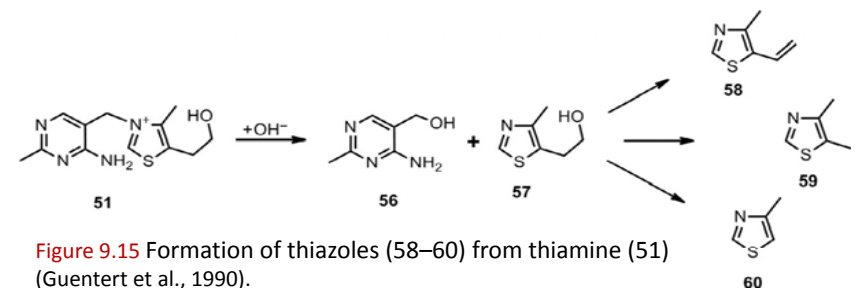
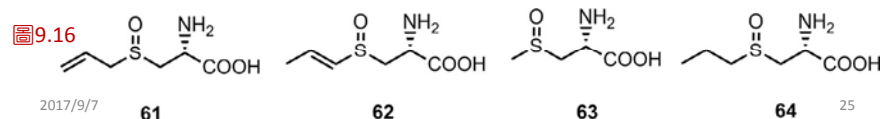


Figure 9.15 Formation of thiazoles (58–60) from thiamine (51) (Guentert et al., 1990).

## 9.5 Allium species 蔥屬種類

蔥屬種類如**洋蔥及大蒜鱗莖**的香氣是含硫氣味物所支配，其主要前驅物質為 *S*-alk(en)yl-L-cysteine sulfoxides [*S*-烷(烯)基-L-半胱氨酸亞砜類；下圖9.16)。 *S*-Allyl-L-cysteine sulfoxide [*S*-烯丙基-L-半胱氨酸亞砜；61)是**大蒜**的主要成分(達2.4 g/kg)，**洋蔥**以 *S*-1-propenyl-L-cysteine sulfoxide (*S*-丙烯-L-半胱氨酸亞砜；62) (2 g/kg) 最多，*S*-methyl-L-cysteine sulfoxide (*S*-甲基-L-半胱氨酸亞砜；63)及*S*-propyl-L-cysteine (*S*-丙基-L-半胱氨酸；64) 在兩者都存在。*S*-Methyl-L-cysteine sulfoxide 也存在於十字花科甘藍、花椰菜及青花菜等。除了L-cysteine sulfoxide derivatives，*S*-alkyl-L-cysteines (*S*-烷基-L-半胱氨酸類)及*S*-alkenyl-L-cysteines (*S*-烯基-L-半胱氨酸類)也存在洋蔥及大蒜，例如大蒜的 *S*-allyl-L-cysteine。



洋蔥或大蒜鱗莖搗碎或切片，酵素 alliinase (蒜甘酶)一旦接觸 *S*-alk(en)yl-L-cysteine sulfoxides，迅速生成 sulfenic acids (次磺酸類)及隨後的alkylthiosulfonates (烷基硫代磺酸鹽)，硫揮發物的**非加熱型香氣**即開始產生。

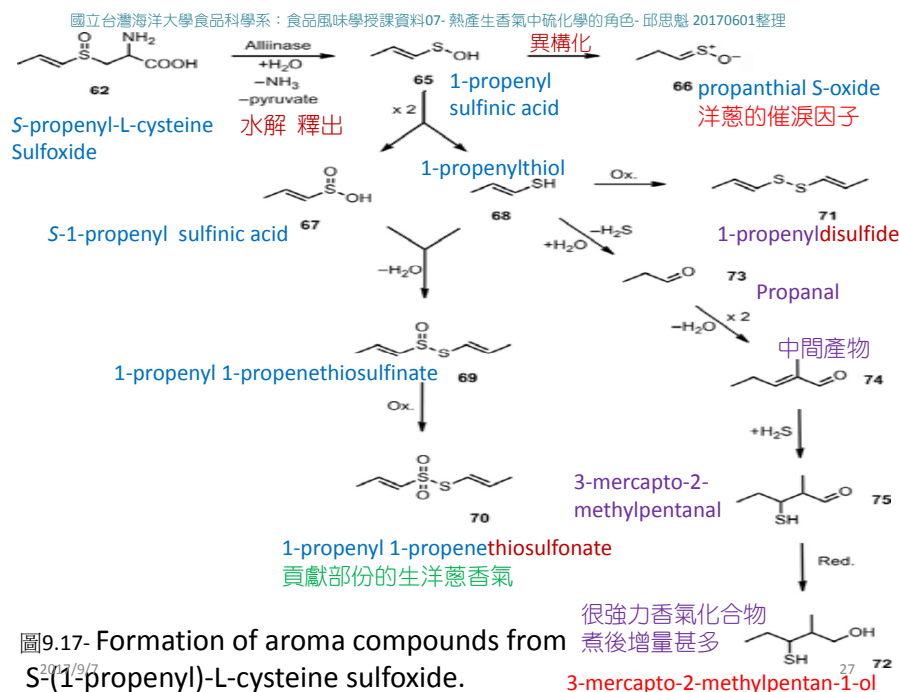
以*S*-propenyl-L-cysteine sulfoxide 為例的級聯反應(圖9.17)。

Thiosulfonates (硫代亞磺酸鹽類)及thiosulfonates (硫代磺酸鹽類)很不穩定，**蒸煮時**會變化、連同其它化學反應的發生而產生複雜的揮發物混合物，煮洋蔥時，透過硫醇(thiol)如 1-propenylthiol (68) 的氧化而形成 **propyl 及 1-propenyldisulfide (71)**，對香氣是重要的。而在大蒜，則以 allyl disulfide (丙烯基二硫化物) 居多。

**3-mercapto-2-methylpentan-1-ol (72)**, was recently identified as a very potent aroma compound in onion.

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前提及 *S*-alk(en)yl-L-cysteine derivatives 同 L-cysteine sulfoxides 存在於蒜屬品種。大蒜中*S*-allyl-L-cysteine可能貢獻煮熟中的香氣生成，*S*-allyl-L-cysteine和葡萄糖的加熱反應產生 a garlic-like and green aroma，和 diallyl sulfide 及 diallyl disulfide 為主要揮發物。*S*-allyl-L-cysteine 若被 *S*-propyl-L-cysteine 取代，主要形成 dipropyl disulfide。

- 以AEDA探討**油炸火蔥 (紅蔥頭; fried shallots; *A. ascalonicum*)** 相關的硫氣味物質：methyl propenyl sulfide、methyl propenyl disulfide、methyl propenyl trisulfide、dimethyl trisulfide、propenyl propyl disulfide 及 methyl propyl trisulfide 等為 aroma-relevant，若也加入蒜頭油炸，透過 allylthiosulfonate (**allicin 蒜素**) 的降解而額外生成2-vinyl-(4H)-1,3-dithiine (green, pungent, garlic-like) 及 diallyl trisulfide (leek-like, garlic-like)。蒜素本身提供 lingering、sulfury、onion-like aftertaste等。

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有可能 *S*-alkyl-L-cysteines 及 sulfoxides 的Strecker降解，在煮蔥的與其它蔬菜時的香氣形成扮演作用，*S*-methyl-L-cysteine (75) 和 glyoxal (76) 的反應產生 Strecker 醛之 2-methylthioacetaldehyde (77)，帶有 a burnt、roasted、pungent smell之氣味物質(圖9.18)。結構77 也存在於煮過的青花菜(0.5 mg/kg)，同樣地，*S*-allyl-L-cysteine的Strecker降解產生2-allylthioacetaldehyde，煮過大蒜中約 1 mg/kg。

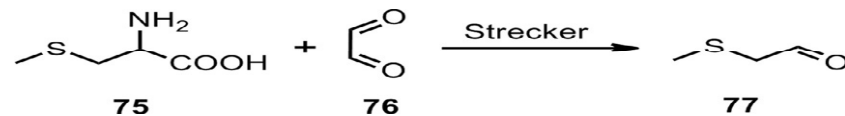


圖9.18- Formation of 2-methylthioacetaldehyde from *S*-methylcysteine.

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## 9.6 Roasted sesame seeds

焙炒芝麻散發a pleasant roasted, burnt, sulfury aroma。AEDA 及定量試驗指出這大受含硫分子2-furanmethanethiol (22)、2-phenylethanethiol (78) 與受 2-acetyl-1-pyrroline 及 4-hydroxy-2,5-dimethyl-3(2H)-furanone 的影響。明顯地，2-furanmethanethiol 來自結構未知的水不溶前驅物質、非從梅納反應系統的L-半胱氨酸/核糖。

後來的研究顯示圖9.18中的化合物，在AEDA具高FD係數 ( $\geq 32$ )或高OAV值。

已知剛炒芝麻的氣味雖很令人喜歡，卻不穩定。硫的肉般氣味物質 2-methyl-1-propene-1-thiol (79)、2-methyl-1(E)-butene-1-thiol (80)、2-methyl-1(Z)-butene-1-thiol (81)、3-methyl-1(E)-butene-1-thiol (82) 及 3-methyl-1(Z)-butene-1-thiol (83)在炒過芝麻中的含量為 20–800  $\mu\text{g/kg}$ ，其OAVs 為 27–2400，但有相當的揮發性。由於其ene-thiol 結構，他們能和水而水解成對應的醛類及硫化氫，類似於1-propenylthiol (68)降解為propanal (73) (Figure 9.17)，1-alkenethiols 的前驅物與形成機制仍都未知。

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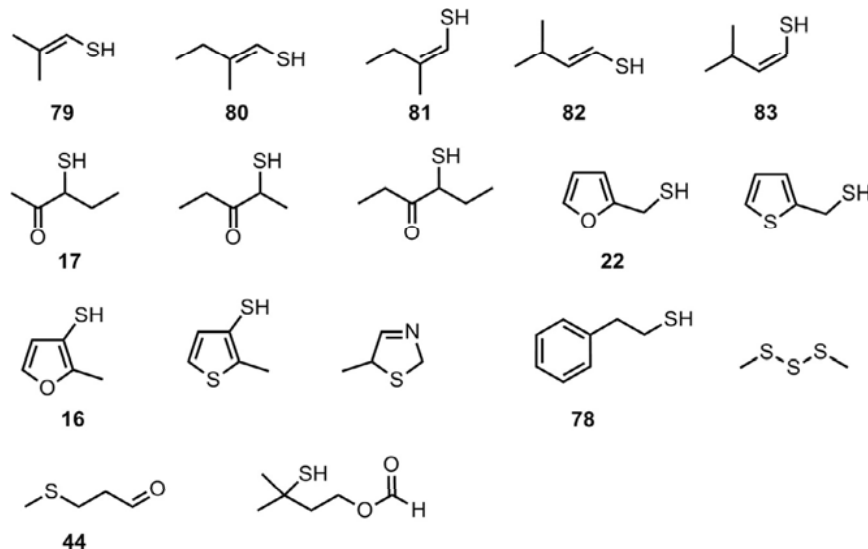
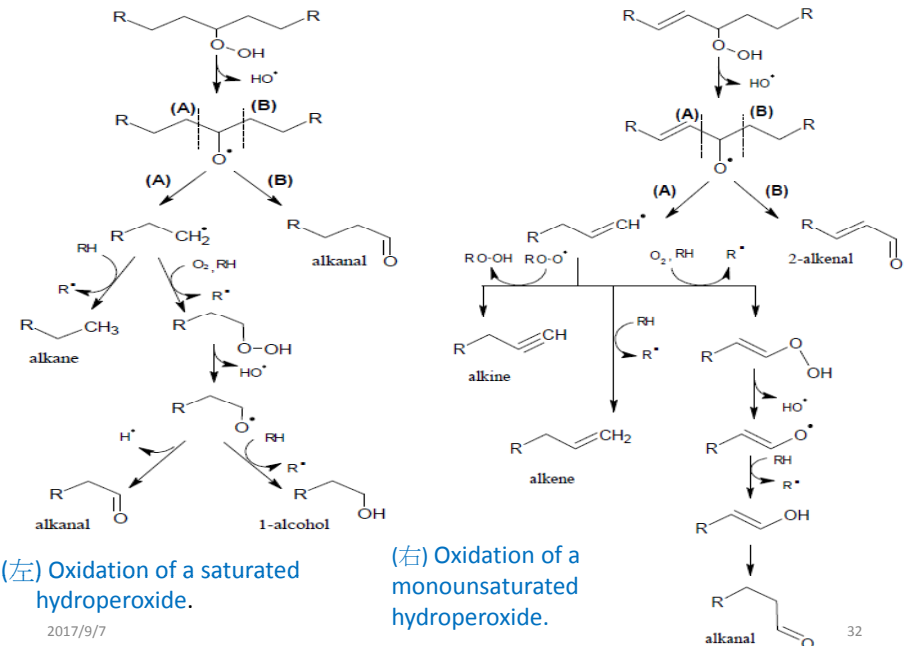


Figure 9.19 Aroma-active thiols in roasted sesame seeds (Tamura et al., 2010, 2011).

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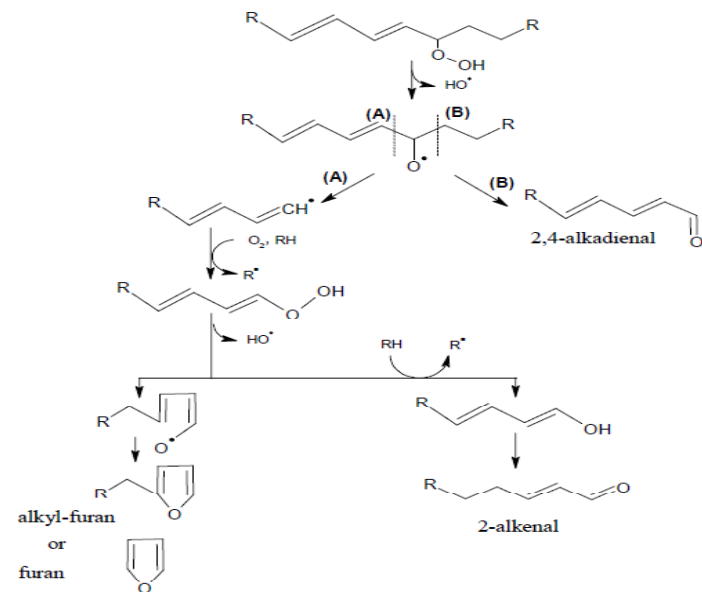
(左) Oxidation of a saturated hydroperoxide.

(右) Oxidation of a monounsaturated hydroperoxide.

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Oxidation of a polyunsaturated hydroperoxide.

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Table 1. Volatile compounds produced by heating tristearin to 192°C.

| Homologous series | Number of carbons | Major compounds |
|-------------------|-------------------|-----------------|
| Aldehydes         | 3–17              | hexanal         |
|                   |                   | heptanal        |
|                   |                   | octanal         |
| Methyl ketones    | 3–17              | 2-heptanone     |
|                   |                   | 2-nonanone      |
|                   |                   | 2-decanone      |
| Acids             | 2–12              | hexanoic acid   |
|                   |                   | pentanoic acid  |
|                   |                   | butanoic acid   |
|                   |                   | heptadecane     |
| Hydrocarbons      | 4–17              | nonane          |
|                   |                   | decane          |
|                   |                   | γ-butyrolactone |
| γ-Lactones        | 4–14              | γ-pentalactone  |
|                   |                   | γ-heptalactone  |
|                   |                   | octanol         |
| Alcohols          | 4–14              | nonanol         |
|                   |                   | decanol         |

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Table 2. Fatty acids composition (%) triacylglycerol (neutral lipids) and phospholipids (polar lipids) of the *longissimus muscle* in pigs, sheep and cattle.

|                   | Neutral lipids |       |        | Polar lipids |       |        |
|-------------------|----------------|-------|--------|--------------|-------|--------|
| Fatty acid        | Pigs           | Sheep | Cattle | Pigs         | Sheep | Cattle |
| 14:00             | 1.6            | 3.0   | 2.7    | 0.3          | 0.4   | 0.2    |
| 16:00             | 23.8           | 25.6  | 27.4   | 16.6         | 15.0  | 14.6   |
| 16:1 <i>n</i> - 7 | 2.6            | 2.2   | 3.5    | 0.8          | 1.5   | 0.8    |
| 18:00             | 15.6           | 13.6  | 15.5   | 12.1         | 10.4  | 11.0   |
| 18:1 <i>n</i> - 9 | 36.2           | 43.8  | 35.2   | 9.4          | 22.1  | 15.8   |
| 18:2 <i>n</i> - 6 | 12.0           | 1.5   | 2.3    | 31.4         | 12.4  | 22.0   |
| 18:3 <i>n</i> - 3 | 1.0            | 1.2   | 0.3    | 0.6          | 4.6   | 0.7    |
| 20:4 <i>n</i> - 6 | 0.2            | nd    | nd     | 10.5         | 5.9   | 10.0   |
| 20:5 <i>n</i> - 3 | nd             | nd    | nd     | 1.0          | 4.1   | 0.8    |

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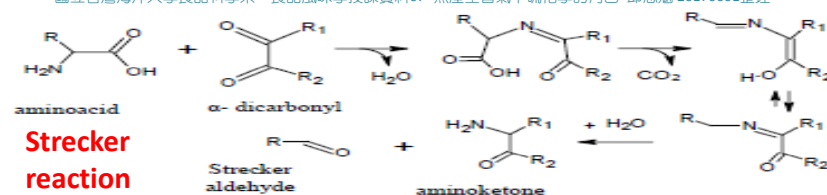


Table- Strecker aldehydes detected by GC-O in cooked beef extractions, amino acid precursor, and odour threshold.

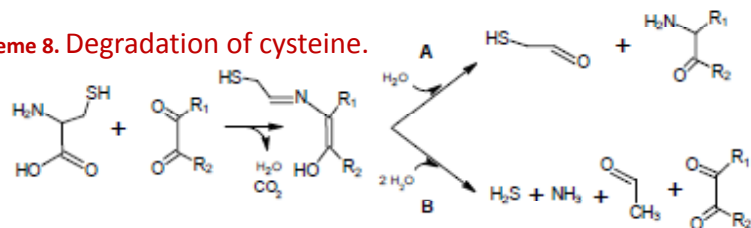
| Strecker aldehyde                      | Structure                 | Amino acid precursor | Odour threshold |
|--|---------------------------|----------------------|-----------------|
| ethanal<br>= acetaldehyde              | <chem>CC=O</chem>         | α-alanine/cysteine   | 25              |
| propanal                               | <chem>CCC=O</chem>        | α-aminobutyric       | -               |
| 2-methylpropanal                       | <chem>CC(C)C=O</chem>     | valine               | 2               |
| 3-methylbutanal                        | <chem>CC(C)CC=O</chem>    | leucine              | 3               |
| 2-methylbutanal                        | <chem>CCC(C)C=O</chem>    | isoleucine           | 4               |
| methional                              | <chem>CCSCC=O</chem>      | methionine           | 0.2             |
| 2-phenyletanal<br>= phenylacetaldehyde | <chem>c1ccccc1CC=O</chem> | phenylalanine        | 4               |

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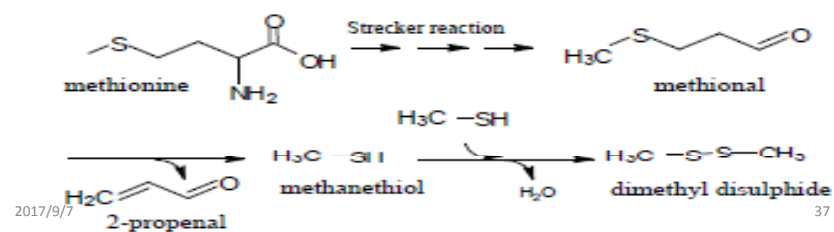
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**Cysteine degradation** 特別地重要，乃產生了涉及肉風味中高活性化合物的形成之中間產物。

**Scheme 8. Degradation of cysteine.**



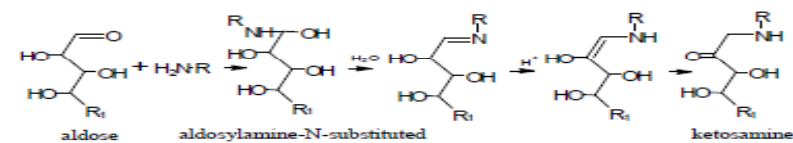
**Scheme 9. Degradation of methionine to methional, methyl mercaptan (or methanethiol) and dimethyl disulphide.**



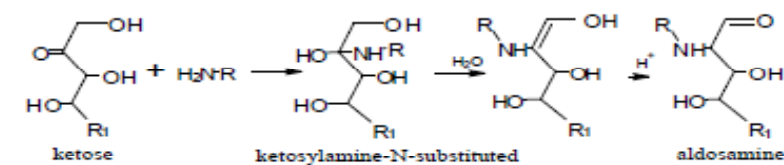
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**Scheme 10. Amadori rearrangement.**



**Scheme 11. Heyns rearrangement.**



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