

# Studies on the Formation of Volatile Compounds in the Model Reaction Systems of HEMF and Meat Flavor Precursors

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## ABSTRACT

There are many cooking methods for Chinese foods. Stewing and roasting are two of the methods frequently used. The sauce usually used is soy sauce. The stewed and roasted meats are flavorful and delicious. They are the favorites of gourmet. The savor and volatile components in soy sauce will react with the savor precursors in meat. The reaction gives the stewed or roasted meat the special flavor. There are many flavor precursors in meats. The most important ones among them are Xylose, Thiamine · HCl, Cysteine · HCl, etc. While HEMF is the main component presented in soy sauce. The purpose of this study is trying to mix HEMF and Xylose, Thiamine · HCl, and Cysteine · HCl under the similar conditions of roasting and stewing meat. Different heating processes were used to investigate the influence of temperature and heating time to the formation meat flavor. The volatile compounds existed in the model systems were studied. The aim is to study whether or not HEMF will react with Xylose, Thiamine · HCl, and Cysteine · HCl to produce any special and important volatile compounds.

Keywords : Model Reaction Systems ; Cysteine · HCl ; Thiamine · HCl ; HEMF

## Table of Contents

目錄封面內頁簽名頁授權書 iii	中文摘要 iv	英文摘要 vii	誌謝 x	目錄 xi	圖目錄 xiv	表目錄 xvii																														
第一章緒論 1	第二章文獻回顧 4	第一節醬油之簡介 4	第二節醬油之種類 9	第三節醬油產業現況及發展趨勢分析 11	第四節肉類香味化學 17	第五節回應曲面實驗設計法 40																														
第三章在模擬滷肉香氣及烤肉香氣的模式反應中HEMF與Cysteine · HCl及HEMF與Thiamine · HCl最適用量比例的決定 摘要 43	第一節前言 44	第二節實驗材料與設備 47	第三節實驗方法 48	第四節結果討論 50	第五節結論 54																															
第四章在模擬滷肉香氣及烤肉香氣的模式反應中HEMF、Thiamine · HCl及Cysteine · HCl最適用量的決定 摘要 55	第一節前言 56	第二節實驗材料與設備 59	第三節實驗方法 60	第四節結果討論 70	第五節結論 72																															
第五章在模擬滷肉香氣及烤肉香氣的模式密閉加熱反應中HEMF Thiamine · HCl、Cysteine · HCl及Xylose最適用量決定 摘要 73	第一節前言 75	第二節實驗材料與設備 77	第三節實驗方法 78	第四節結果討論 86	第五節結論 100																															
第六章以酸鹼區分法分析HEMF與Cysteine · HCl、Thiamine · HCl及Xylose之熱反應液的香氣成分 摘要 112	第一節前言 113	第二節實驗材料與設備 115	第三節實驗方法 117	第四節結果討論 120	第五節結論 121																															
第七章總結論 126	參考文獻 128	圖目錄	圖2.1一般醬油的製造流程圖 5	圖2.2梅納反應的基本反應機制 30	圖2.3梅納反應第一步，醱與胺基酸進行縮合 31	圖2.4Amadori重組反應(路徑一) 32	圖2.5Amadori重組反應(路徑二) 33	圖2.6反應曲面法設計流程圖 42	圖3.1醬油中存在之重要香氣化合物 45	圖3.2HEMF與Thiamine · HCl及HEMF與Cysteine · HCl之最適作用量決定之實驗流程 49	圖4.1HEMF + Thiamine · HCl + Cysteine · HCl之最適作用量決定之實驗流程 63	圖4.2(a)模擬烤肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之回應曲面圖 68	圖4.2(b)模擬烤肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之等高線圖 68	圖4.3(a)模擬滷肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之回應曲面圖 69	圖4.3(b)模擬滷肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之等高線圖 69	圖5.1HEMF + Thiamine · HCl + Cysteine · HCl + Xylose之最適作用量決定之實驗流程 83	圖5.2Likens-Nickerson水蒸氣蒸餾及溶劑萃取裝置 84	圖5.3濃縮塔裝置 85	圖5.4(a)模擬烤肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之回應曲面圖 94	圖5.4(b)模擬烤肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之等高線圖 94	圖5.5(a)模擬烤肉模式反應中Thiamine · HCl與Xylose對應於模式反應液官能品評值之回應曲面 95	圖5.5(b)模擬烤肉模式反應中Thiamine · HCl與Xylose對應於模式反應液官能品評值之等高線圖 95	圖5.6(a)模擬烤肉模式反應中Cysteine · HCl與Xylose對應於模式反應液官能品評值之回應曲面圖 96	圖5.6(b)模擬烤肉模式反應中Cysteine · HCl與Xylose對應於模式反應液官能品評值之等高線圖 96	圖5.7(a)模擬滷肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之回應曲面圖 97	圖5.7(b)模擬滷肉模式反應中Thiamine · HCl與Cysteine · HCl對應於模式反應液官能品評值之等高線圖 97	圖5.8(a)模擬滷肉模式反應中Thiamine · HCl與Xylose對應於模式反應液官能品評值之回應曲面圖 98	圖5.8(b)模擬滷肉模式反應中Thiamine · HCl與Xylose對應於模式反應液官能品評值之等高線圖 98	圖5.9(a)模擬滷肉模式反應中Cysteine · HCl與Xylose對應於模式反應液官能品評值之回應曲面圖 99	圖5.9(b)模擬滷肉模式反應中Cysteine · HCl與Xylose對應於模式反應液官能品評值之等高線圖 99	圖6.1模式反應香氣成分進行酸鹼區分之流程圖 131	表目錄	表2.1胺基酸之呈味性 19	表2.2牛肉之煮肉香氣與烤肉香氣組成分之比較 24	表2.3熱反應香味物質可能進行化學反應 39	表3.1HEMF與Cysteine · HCl進

行模式反應之溫度時間組合 51 表3.2 HEMF與Thiamine · HCl進行模式反應之溫度時間組合 51 表3.3 HEMF與 Cysteine · HCl反應液進行九分制喜好性官能品評試驗結果 52 表3.4 HEMF 與 Thiamine · HCl 反應液進行九分制喜好性官能品評之結果 53 表4.1 HEMF與Thiamine · HCl及Cysteine · HCl反應液中心混成實驗設計之組合 61 表4.2 HEMF與Thiamine · HCl及Cysteine · HCl反應液中心混成實驗設計變數 62 表4.3 模擬烤肉實驗設計表及反應液官能品評分數 64 表4.4 模擬滷肉實驗設計表及反應液官能品評分數 65 表4.5 模擬烤肉中心混成實驗之迴歸分析表 66 表4.6 模擬滷肉中心混成實驗之迴歸分析表 67 表5.1 於模擬烤肉條件下之中心混成實驗設計變數 81 表5.2 於模擬滷肉條件下之中心混成實驗設計變數 81 表5.3 中心混成實驗設計之組合 82 表5.4 模擬烤肉之實驗設計表及反應液官能品評數 90 表5.5 模擬滷肉實驗設計表及反應液官能品評分數 91 表5.6 於仿烤肉模式反應之中心混成實驗之迴歸分析表 92 表5.7 於仿滷肉模式反應之中心混成實驗之迴歸分析表 93 表5.8 由加熱HEMF及其它香味前驅物質於模擬烤肉香氣之反應液中所鑑定到的揮發性香氣成分 102 表5.9 由加熱HEMF及肉類香氣前驅物質於模擬滷肉香氣之反應液中所鑑定到的揮發性香氣成分 104 表6.1 HEMF及其它香味前驅物質在模擬烤肉香氣之最適條件下反應之反應液，利用酸鹼區分法新鑑定到的揮發性香氣成分 122 表6.2 HEMF及其它香味前驅物質在模擬滷肉香氣最適條件下反應之反應液，利用酸鹼區分法新鑑定到的揮發性香氣成分 124

## REFERENCES

- 參考文獻 1.朱紹洪(1980)天然食用香料。朱紹洪編譯，食品工業發展研究所食品工業叢書 92-94、120-122。 2.仇志強、吳淳美(1982)滷肉的揮發性成份。食品工業發展研究所研究報告第285號。 3.何其黨(1991)食品加工過程所生成的香味，香料資訊。 4.李敏雄、郭錦富(1987)醬油香味成份之研究。中國農業化學會誌25(1):83-93。 5.林麗雲，(1998)蔴油製造的研究，國立台灣大學農業化學研究所博士論文。 6.苑永弘(1999)大蒜中之含硫胺基酸在肉類香味研發上之應用研究。大葉大學食品工程研究所碩士論文。 7.張玉琴(2000)以豬肉酵素水解液製備豬肉香料。大葉大學食品工程研究所碩士論文。 8.許人平(1992)含硫化合物在肉類反應香料中所扮演的角色。食品工業月刊24(8):40-48。 9.郭錦富，(1991)，原料比例對醬油品質之影響，國立台灣大學農業化學研究所博士論文。 10.陳秀蓮、馮筱慧、葉錦桐、蘇女淳、程竹青(1993)中式調理食品用肉類調味料之研究與發展(四)-以梅納反應製造肉類及仿肉類調味料。食品工業發展研究所研究報告920號。 11.陳怡宏，(1985)，中國式滷肉香味之研究，國立台灣大學農業化學研究所碩士論文。 12.程竹青(1987)肉類香氣。食品香料化學與加工。115-131。 13.程竹青、鄭靜桂(1988a)以化學合成法及香料合成法製造中式食品香料(一)。食品工業發展研究所研究報告505號。 14.程竹青、鄭靜桂(1988b)以化學合成法及香料合成法製造中式食品香料(二)。食品工業發展研究所研究報告505號。 15.程安環(2000)肉燥紅蔥調味油製備之研究。大葉大學食品工程研究所碩士論文。 16.彭秋妹、王家仁(1991)食品官能檢查手冊。食品工業發展研究所。新竹，p.10-33。 17.劉黛蒂(1993)糖和胺基酸在肉類香氣化合物合成上的應用。食品工業月刊25(1):29-37。 18.闕文仁、鄧世正編著(1977)「實用醬油釀造學」，台灣，台北。 19.Burton, H.S. and McWeeny, D.J. (1963) Non-enzymatic browning reactions consideration of sugar stability. *Nature*. 197, 266-8. 20.Boudreau, J.C.; Oravec, J., Hoang, N.K. and White, T.D. (1979) Flavor and the taste of foods. in *Food Taste Chemistry*, ACS. Sympo. Ser. 115, Boudreau, J.C., Ed., ACS, Washington, D.C., 1. 21.Brinkman, H. W., Copier, H.; de Leuw, J. J. M, and Tjan, S. B. (1972) Components contributing to beef flavor. *J. Agric. Food Chem.*, 20: 177. 22.Batzer, O. F.; Santoro, A. T., Tan, M. C.; Landmann, W. A. and Schweigert, B. S. (1960) Precursors of beef flavor *J. Agric. Food Chem.*, 8:498. 23.Chang, S. S. and Peterson, R.J. (1977) Symposium: the basis of quality in muscle foods: recent developments in the flavor of meat. *J. Food Sci.*, 42:298. 24.Chang, S. S., Hirai, C., Reddy, B. R., Herz, K. O., Kato, A., and Simpa, G. (1968) Isolation and identification of 2,4,5-trimethyl-3-oxazoline and 3,5-dimethyl-1,2,4-trithiolane in the volatile flavor compounds in boiled beef. *Chem. Ind.* 1639. 25.Davies, R., Falkiner, E.A., Wilkson, J.F., and Peer, J.L. (1951). Ester formation by yeasts, 1. Ethyl acetate formation by *Hansenula* species. *Biochem. J.* 49:58. 26.Dwivedi, B.K. (1975) Meat flavor. *CRC Crit. Revs. Food Technol.*, 487. 27.Fukuzaki, K. (1972) Naturally fermented shoyu. *Shokuno, Kagaku.*, 7:47-59. 28. Fukushima, D. (1985) Fermented vegetable protein and related foods of Japan and Chian. *Food Reviews International* 1:149-209. 29. Guntert, M., Bertram, J., Hopp, R., Silberzahn, W., Sommer, H. and Werkhoff, P. (1992) Thermal generation of flavor compounds from thiamine and various amino acids. in: *Recent developments in flavor and fragrance chemistry*. p.215-239. 30. Hamada, S., Ogawa, J., Kadosawa, T., and Aso, K. (1965). On the sugar compounds in soy sauce. *J. Ferment. Technol.* 34:407. 31. Hashida, W. (1974) Flavor potentiation in meat analoge. *Food Trade Rev.*, 21. 32.Heath, H. (1970) Flavors: a brief consideration of chemistry and technology. *Flavor Ind.* 586. 33. Hofmann, T. and Schieberle, P. (1998) Quantitative model studies on the effectiveness of different precursor systems in the formation of the intense food odorants 2-furfurylthiol and 2-methyl-3-furanthiol. *J. Agric. Food Chem.* 46(1):235-241. 34.Hornstein, I. and Crowe, P. F. (1960) Flavor studies on beef and pork. *J. Agric. Food Chem.*, 8: 494. 35.Hornstein, I., Crowe, P. F, and Sulzbacher, W. L. (1960) Constituents of meat flavor: beef. *J. Agric. Food Chem.*, 8: 65. 36.Horstein, I. and Crowe, P. E. (1963) Food flavors and odors. Meat flavor: lamb. *J. Agric. Food Chem.* 11: 147. 37.Hirai, C., Herz, K. O., Pokorny, J., and Chang, S. S. (1973) Isolation and identification of volatile flavor compounds in boiled beef. *J. Food Sci.* 33: 377. 38. Ishigami, Y., Ishidawa, H., and Moriguchi, S. (1965). "Studies on the organic acids in soy sauce. Changes in the amounts of organic acids during mash process" *J. Ferment. Technol.* 43:110. 39. Joachim R. and Werner B. (1994) Sulfur-containing furans in commercial meat flavorings. *J. Agric. Food Chem.* 42(10):2254-2259. 40. Kanbe, C., and Uchida, K. (1983) Conversion of L-malate to L-lactate by *Pediococcus halophilus*. 57:1211. 41. Kirimura, A (1967) Flavor potentiators, in *Symp. foods: the chemistry and physiology of flavors*. Schultz, H.W., Day, E.A, and Libbey, L.M, Eds, AVI Westport, Conn., 515. 42. Kirimura, J., Shimizu, A., Kimizuka, A., Ninomiya, T., and Katsuya, N (1969) The contribution of peptides and amino acids to the taste of foodstuffs. *J. Agric. Food Chem.*, 17:689. 43. Labuza, T.P. (1980). Effect of water activity on the reaction kinetics of food

deterioration. *Food Technol.* 34(2):36-44. Leahy, M.M. (1985) The effects of pH, types of sugar and amino acid and water activity on the kinetics of the formation of alkyl pyrazines. Ph.D. Thesis, Feb., University of Minnesota, Department of Food Science and Nutrition, St. Paul, Minnesota.

45. Linkeback, D.R. (1982) *Food Carbohydrates*. The AV Publishing company, Inc. p113-133. 46. Liebich, H. M. Douglas, D. R. Zlatkis, A. Muggler-Chavan, F. and Donzel, A. (1972) Volatile components in roast beef. *J. Agric. Food Chem.* 20: 96. 47. MacLeod, G. (1986) The scientific and technological basis of meat flavors. In *Developments in Food Flavours*, ed. Brich, G. G. ; Lindley, M.G, Elsevier, London. p191-223. 48. MacLeod, G. and Seyyedain-A. M. (1981) Natural and simulated meat flavors (with particularly reference to beef). *CRC Crit. Rev. Food Sci. Nutr.* 14:309-437. 49. Mabrouk, A.F. (1976) Nonvolatile nitrogen and sulfur compounds in red meats and their relation to flavor and taste. *ACS Symp. Ser.* 26, Charalambous, G. and Katz, I., Eds., ACS, Washington, D.C., 146. 50. Macleod G. and Coppock, B. M., (1977) A comparison of the chemical composition of boiled and roasted aromas of heated beef. *J. Agric. Food Chem.*, 25:113. 51. Macleod, G. and Seyyedain, A. M. (1981) Natural and simulated meat flavors. *CRC Crit. Revs. Food Sci. and Nutr.* 14-309. 52. Min, D.B.S., Ina, K., Peterson, R. J. and Chang, S.S. (1977) The alkylbenzene in roast beef. *J. Food Sci.* 42:503. 53. Nunomura, N., Sasaki, M. and Yososka, T. (1984). Soy sauce flavor components ; Neutral fraction. *Agr. Biol. Chem.* 48:1762. 54. Peter W., Jurgen B., Roland E., Mattias G., Manfred K., and Walter K.S. (1990) Isolation and characterization of volatile sulfur-containing meat flavor components in model systems. *J. Agric. Food Chem.* 38(3):777-791. 55. Pittet, A. O. and Hruza, D.E., (1974) Comparative study of flavor properties of thiazole derivatives. *J. Agric. Food Chem.* 22:264. 56. Sanderson, A., Pearson, A.M., and Schweigert, B.S. (1966) Effect of cooking procedure on flavor component of beef: carbonyl compounds. *J. Agric. Food Chem.*, 14:245. 57. Self, R., Casey, J. C. and Swain, T. (1963) The low boiling volatiles of cooked foods. *Chem. Ind.*, 863. 58. Tressl, R., Bahri, and D Holzer, M., (1977) Formation of flavor components in asparagus. .formation of flavor components in cooked asparagus. *J Agric. Food Chem.* ,25:459. 59. Wasserman, A.E. (1979) Symposium on flavor chemical basis for meat flavor: a review. *J. Food. Sci.* , 44:6. 60. Watanabe, K. and Sato, Y. (1971) Gas chromatographic and mass spectral analyses of heated flavor compound of beef fats. *Agric. Biol. Chem.* 20: 96-101. Watanabe, K. and Sato, Y. (1972) Shallow fried beef: additional flavor components. *J. Agric. Food Chem.* 20: 174. 62. Tonsbeek, C. H. T., Plancken, A. J. and , von der Weerdhof, T. (1968) Components contributing to beef flavor: isolation of 4-hydroxy-5-methyl-3(2H) furanone and its 2,5-dimethyl homoloh from beef broth. *J. Agric. Food Chem.*, 16: 1016. 63. Tonsbeek, C. H. T., Copier, H., and Plancken, A. J. (1971) Components contributing to beef flavor. Isolation of 2-acetyl-2-thiazoline from beef broth. *J. Agric. Food Chem.* 19: 1014. 64. Yueh, M. H. and Strong, F. M. (1960) Some volatile constituents of cooked beef. *J. Agric. Food Chem.*, 8: 491. 65. Yu, T. H. and Wu, C. M. (1988) Effect of heating on garlic essential oils. *Food Sci.* 15(4): 385-393. 66. Yu, T.H., Wu, C.M. , and Ho, C.T. (1994) Meat-like flavor generated from thermal interactions of glucose and alliin or deoxyalliin. *J. Agric. Food Chem.* 42(4):1005-1009.