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Formation of Alkylpyridines ("off-flavor" components) from the Thermal Interactions of Amino Acids and Lipid Degradation Products in Model Systems

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Ammonia released from each five amino acids (glycine, L-aspartic acid, L-asparagine, L-glutamic acid, L-glutamine) under oil conditions and its effects on the formation of alkylpyridines were studied. Only asparagine and glutamine among the five amino acids used generated ammonia readily by deamidation of amide side chains at 180°C under oil conditions, even though both of them produced less ammonia than under aqueous conditions. However, the difference in the relative amount of ammonia released between asparagine and glutamine was larger under oil conditions and much more free ammonia was liberated from glutamine than asparagine. These different patterns of deamidation may be due to the different deamidation mechanism under both conditions. From the thermal interactions of the five amino acids with 2,4-decadienal, it was found that free ammonia could be more effective in forming alkylpyridines such as 2-pentylpyridine under both aqueous and oil conditions. Labeling study using unlabeled and labeled asparagine-amide-¹⁵N and glutamine-amide-¹⁵N was performed to investigate the relative contribution of amide nitrogen to the formation of alkylpyridines. It indicated that most nitrogens in pyridine rings come from free ammonia. However, α -amino groups bound in amino acids might be also involved in the formation of alkylpyridines in aqueous systems if free ammonia was not available. To examine the relative reactivities of alkadienals for the formation of alkylpyridines, a mixture of (t,t)-2,4-heptadienal, (t,t)-2,4-nonadienal, and (t,t)-2,4-decadienal was heated with glutamine or glutamic acid under aqueous and oil conditions. In the case of glutamine which released free ammonia relatively readily under both conditions, the total amount of alkylpyridines was larger in oil-containing systems whereas some alkylpyridines such as 3-ethylpyridines, 4-ethylpyridines, 3-butylpyridines, 3-pentylpyridines, and 4-pentylpyridine could be identified only in the aqueous systems. However, glutamic acid made only small amount of 2-alkylpyridines among alkylpyridines in both systems compared to glutamine. In addition, the difference in the amount of total alkylpyridines formed from glutamic acid was not large under the aqueous and oil conditions.