

# Biodegradation Mechanism of Capsaicinoids

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Red pepper, *Capsicum annuum* L., is a popular spice in Korea. Capsaicin is the main pungent principle in it. Medicinally pungency and stimulatory effects of capsaicin and its analogs (capsaicinoids) have been utilized as counter-irritant and rubefacient externally and internally as gastric stimulant.

Assay of capsaicinoids was carried out after separation with argentized TLC. Although the contents of pungent principles and their mutual ratio (capsaicin:dihydrocapsaicin) varies from sample to sample, it was found that the Korean red pepper has less than 0.1% of capsaicinoids of dry weight of the red pepper. It was also found to contain more of saturated capsaicin homolog than capsaicin (olefinic) itself.

Though capsaicinoids exhibit bacteriostatic action, their toxic action on molds is much weaker than on certain bacteria. In this aspect one might assume that capsaicin will be oxidized and thereby lose its pungent character after fermentation. When capsaicin and dihydrocapsaicin were exposed to *Aspergillus niger*, they were transformed to more polar phenolic compounds. In order to characterize the main transformed compounds they were fermented for 48 hours.

Utilizing silicic acid column chromatography, oily products were isolated. The presence of vanillylamide moiety was confirmed by comparison of its UV absorption pattern with that of authentic capsaicin. NMR, IR and GC-Mass analysis data were obtained after derivatization

of the oily products to their acetate form. It was concluded that the transformed primary metabolites of capsaicin and dihydrocapsaicin are: trans-8-hydroxymethyl-N-vanillyl-6-nonamide and 8-hydroxymethyl-N-vanillylnonanamide. Furthermore, to clarify the degradation mechanism of capsaicinoids' side chain, capsaicin was exposed to *A. niger* and fermented for a long period of time, and much polar transformed products were accumulated. The accumulated products were isolated after chromatography, and NMR and GC-Mass spectroscopic analysis were carried out after methylation. With the data obtained from NMR and Mass spectroscopic analysis it was concluded that they are 2-methyl-N-vanillylcarbamoyl-3(E)-octanoic acid and N-vanillylcarbamoylbutyric acid. Under the same line of experiment nonoylvanillylamide which possesses same order of pungency as that of capsaicin, was also fermented with *A. niger*. Two products were isolated from the fermented broth. One of them was characterized as  $\gamma$ -hydroxyl compound: 9-hydroxy-nonoylvanillylamide while the other was characterized as N-vanillylcarbamoylbutyric acid. With these data a degradation pathway of capsaicinoids' side chain is now proposed as following: Metabolic fate of capsaicin and its analogs in animal liver has not been reported yet. However, we have got some evidences to support the fact that capsaicin may undergo metabolic changes in liver by mixed function oxidase. Capsaicin and other capsaicinoids were incubated with

liver homogenates or microsomes of rats. The homogenates were supplemented with NADP and glucose-6-phosphate while liver microsomes were supplemented with NADPH. The metabolit

es were isolated after chromatography and spectral analysis was carried out. The proposed structure of capsaicinoids metabolites is N-(4, 5-dihydroxy-3-methoxybenzyl)-acylamide.

