

K. Srinivasan, K. Sambaiah & N. Chandrasekhara

Department of Food Chemistry, Central Food Technological Research Institute, Mysore-570 013, India

(Received 7 December 1990; revised version received and accepted 4 February 1991)

Studies were done to monitor loss of active principles of the spices, curcumin, piperine and capsaicin, during domestic cooking, (i.e. boiling of spice mixes with food ingredients). Over 85% loss of curcumin occurred during 15 and 30 min of cooking either in the presence or absence of the souring agent—tamarind. The loss of piperine under similar conditions was 50–60% when black pepper was used as an ingredient of curry powder. The loss of piperine was less when only black pepper was used in the food preparation. Capsaicin losses were of the order of 0–30% during cooking under similar conditions.

INTRODUCTION

Cooking or roasting alters the nature of many food constituents such as starches and proteins by changing their physical, chemical and nutritional properties (Belitz & Grosch, 1987). It also changes the bioavailability of proteins, carbohydrates, lipids and vitamins. No information is available on the extent of destruction of active principles of spices during food processing. Spices are common food adjuncts that impart flavour, aroma or piquancy to foods. The present study was undertaken to evaluate the effect of cooking process variables—temperature, pH and duration—on the stability/extent of destruction of active principles of turmeric (*Curcuma longa*), black pepper (*Piper nigrum*) and red pepper (*Capsicum annum*)—the three most commonly used spices.

MATERIALS AND METHODS

Spices were locally purchased and powdered to pass through a No. 50 mesh sieve. Curry powder was prepared by mixing the dry powdered spices in the following proportions (percent): *Recipe-I*: coriander, 40; turmeric, 20; red pepper, 20; black pepper, 5; cumin, 5; mustard, 5; fenugreek, 2; dry ginger, 1; clove, 1 and cinnamon, 1. *Recipe-II*: 20% turmeric is replaced by additional 20% red pepper in the above spice mix. Curcumin, the yellow spice principle of turmeric, was

Food Chemistry 0308-8146/92/\$05.00 © 1992 Elsevier Science Publishers Ltd, England. Printed in Great Britain obtained from M/s Flavours & Essence Pvt. Ltd, Mysore. Tamarind (*Tamarindus indica*) pulp powder, tur dhal (Red gram; *Cajanus cajan*) and common salt were from a local market. All the chemicals used were of analytical grade and the solvents were distilled before use.

The experimental approach consisted of: (1) addition of the spice powders—turmeric/black pepper/red pepper/spice mix—curry powder to tur dhal slurry and boiling for a given duration for the preparation of a simple South Indian soup: 'Rasam'; (2) Extracting the spice principles—curcumin (turmeric), piperine (black pepper) and capsaicin (red pepper) from the processed food; and (3) Separating the spice principle of interest by thin-layer chromatography and its quantitative determination.

Cooking procedure

A known quantity of tur dhal (split red gram) was cooked in a pressure cooker for 10 min, cooled and mashed. Portions of cooked dhal equivalent to 5 g dry tur dhal were transferred into 250 ml beakers to which were added 0.5 g common salt and one of the spice ingredients: 0.5 g curry powder/0.1 g turmeric powder/ 0.05 g black pepper powder/2 g red pepper powder/ 20 mg curcumin. Tamarind powder (0.5 g) was also added into a parallel set of beakers. The volume of the contents was made up to 100 ml with distilled water in all the beakers. The contents of the beakers were boiled for exactly 15 min/30 min while taking care to maintain the volume around 100 ml by intermittent addition of



water. At the end of this cooking period, they were cooled and the contents were lyophilized. Appropriate controls were also included wherein the samples did not undergo any boiling.

Quantitation of spice principles in the processed food

Spice principles in the lyophilized food materials were extracted with ethyl acetate in a Soxhlet apparatus for 4 h. The extracts were concentrated in a Flash evaporator to a known volume (2 ml) and stored in the dark at -20° C pending further analysis. The individual spice principles were estimated after separation by TLC as described below. Care was taken to minimize the exposure to light during the extraction procedure and TLC separation.

Curcumin

(Ravindranath et al., 1981) Aliquots of the ethyl acetate extracts (quadruplicate) of the lyophilized food material and reference curcumin (6 μ g) were spotted on silica gel-G coated plates (20×20 cm). The plates were developed with the upper phase of the solvent system: benzene-ethanol-water-acetic acid (100:27.5:7.5:0.5 v/v) in a chamber pre-equilibrated with the above solvent system for 2 h. The yellow curcumin bands were scraped off and quantitatively transferred to centrifuge tubes. Curcumin in the scrapings was extracted with 4 ml acetone, centrifuged at 2000 rpm for 5 min and 2 ml of the clear supernatant was used for the rubrocurcumin reaction. Two millilitres of acetonic extract was transferred to another test tube into which were successively added, 1 ml 7.5 mg% boric acid (in acetone) and 1 ml 5 mg% oxalic acid (in acetone). The contents of the tube were evaporated to dryness over a hot water bath. The residue was redissolved in 2 ml ethanol and the absorption of the purple colour was measured at 550 nm.

Piperine

(Ganesh Bhat & Chandrasekhara, 1985) Aliquots of ethyl acetate extracts of the cooked food material were spotted on silica gel-G coated plates (20×20 cm) along with reference piperine ($4 \mu g$). Plates were developed with petroleum ether ($60-80^{\circ}C$)-acetone (65:35v/v) in a chamber pre-equilibrated with the same solvent system for $1\frac{1}{2}$ h. In order to locate the piperine bands, the developed plates were scanned in an automatic Camag TLC Scanner (Model 2), mounted on a Fluorimeter (Model III, Turner Assoc.) attached to a W-W Recorder (Model 1100, Scientific Instruments Inc.). The individual lanes were scanned using a primary filter No. 110-811 and a neutral density filter No. 110-813 (10%) as a secondary filter, and Lamp No. 110-850 (Emission 310-390 nm). The piperine bands thus located were scraped off and eluted with 2 ml chloroform. After centrifugation, the piperine extracts were quantitated by absorption measurement at 345 nm.

Capsaicin

(Srinivasan et al., 1981) Aliquots of ethyl acetate extracts (quadruplicate) were spotted on silica gel-G coated plates (20×20 cm) along with reference capsaicin (40 μ g). Plates were developed with petroleum ether (60-80°C)-acetone (65:35 v/v) in a chamber preequilibrated with the same solvent system for $1\frac{1}{2}$ h. The developed plates were air-dried and then sprayed uniformly with fresh Gibb's reagent (0.1% 2,6-dichloroquinone-4-chlorimide in methanol). The plates, when dry, were exposed to ammonia vapours in a closed chamber for exactly 1 min. The blue-coloured zones of capsaicin thus visualized were scraped off and quantitatively transferred to centrifuge tubes containing 2 ml water. The tubes were vortexed for 10 min to extract the colour and centrifuged at 2000 rpm for 2 min. Absorption of the clear blue supernatants was read at 610 nm.

RESULTS AND DISCUSSION

Spices are common additives or adjuncts to the diet and are consumed in a variety of combinations depending on taste preferences. The present investigation was undertaken to determine the extent to which the active principles of spices survive the domestic cooking treatments and finally remain in the food. The most common domestic method of cooking is boiling the food ingredients in water. Hence in the present study, the various spice ingredients were boiled in water along with other food ingredients for different intervals of time. pH variation was brought about by the presence or absence of tamarind which is the most commonly used souring agent in Indian homes. In the absence of tamarind, the pH of the food preparation was 6.1 while the inclusion of tamarind, at the 0.5% level, brought down the pH to 5.1.

As shown in Table 1, cooking for 15 min or 30 min reduced the content of curcumin by 86-91% when curry powder or turmeric powder were used in the food preparation. This substantial loss of curcumin occurred at either pH. In contrast, when pure curcumin was used in place of turmeric powder or curry powder, its loss was 20-28\% at pH 6.1 and 41-45\% at pH 5.1.

Changes in piperine and capsaicin levels of food as a result of heat processing are shown in Tables 2 and 3, respectively. The loss of piperine during cooking was in the range 53–62% when curry powder was used as the spice ingredient and here pH did not make any difference to the extent of piperine loss. With black

Table 1. Changes in curcumin levels during domestic cooking

| Spice ingredient added to Tur dhal mash (Total volume: 100 ml) | | Boiling conditions | | | | |
|---|----------------------|----------------------------|--------|--------------------------------|--------|--|
| | Control- uncooked | Without tamarind pH 6·1 | | With tamarind (0.5%) pH 5.1 | | |
| | | 15 min | 30 min | 15 min | 30 min | |
| Curry powder-l | 9.63 | 1.33 | 1.24 | 1.10 | 0.90 | |
| | ±0·87 | ±0.07 | ±0·15 | ±0.09 | ±0.08 | |
| (% Loss) | | (86-2) | (87.2) | (88.6) | (90.7) | |
| Turmeric powder | 46.2 | 6.17 | 5.91 | 4 90 | 4.76 | |
| | ±2.32 | ±0.52 | ±0·42 | ±0·47 | ±0.23 | |
| (% Loss) | | (86.6) | (87·2) | (89.4) | (89·7) | |
| Curcumin | 19·5 | 15.5 | 14.0 | 11.4 | 10.7 | |
| | ±1.31 | ±1.70 | ±1-13 | ±0.48 | ±0.51 | |
| (% Loss) | | (20.4) | (27.9) | (41.3) | (45.1) | |

Values (mg curcumin/g spice or spice mix used in food preparation) are mean ±SEM of six samples.

Values in parentheses indicate percent loss over control (uncooked) values.

pepper as the spice ingredient, piperine loss was lower at pH 6·1 (13–17%) when compared to 49–54% loss at pH 5·1 (Table 2). Capsaicin losses were less than those of curcumin or piperine under similar conditions of pH and duration of cooking. At the normal pH of 6·1, capsaicin loss was negligible during 15 min cooking while at pH 5·1, the loss was around 19% (Table 3). Slightly higher losses (19–33%) of capsaicin were recorded when the duration of cooking was increased to 30 min at either pH. Curry powder-II, which is devoid of turmeric, was used here to evaluate changes in piperine and capsaicin during cooking because curcumin—the constituent of turmeric—would interfere with TLC separation of piperine and capsaicin and their quantitation.

Thus, it is evident from these observations that substantial losses of curcumin and piperine, the active principles of turmeric and black pepper, would occur during cooking of foods. Generally, there is not much difference between pH 5·1 and 6·1, or the durations 15 min and 30 min, as regards losses of curcumin or piperine. In contrast, the losses of capsaicin, the active principle of red pepper, are much less under similar condi-

Table 2. Changes in piperine levels during domestic cooking

| Spice ingredient added to Tur dhal mash (Total volume: 100 ml) | Control- uncooked | Boiling conditions | | | | |
|---|----------------------|----------------------------|--------|--------------------------------|--------|--|
| | | Without tamarind pH 6·1 | | With tamarind (0.5%) pH 5.1 | | |
| | | 15 min | 30 min | 15 min | 30 min | |
| Curry powder-II | 1.74 | 0.75 | 0.69 | 0.81 | 0.66 | |
| | ±0.04 | ±0.05 | ±0.03 | ±0.05 | ±0.05 | |
| (% Loss) | | (56-9) | (60-3) | (53-4) | (62.1) | |
| Black pepper | 36.3 | 31.5 | 30-1 | 18-3 | 16.7 | |
| powder | ±1.18 | ±1.20 | ±1.97 | ±0.84 | ±1.26 | |
| (% Loss) | | (13.2) | (17.1) | (49.6) | (54-0) | |

Values (mg piperine/g spice ingredient used in food preparation) are mean ±SEM of six samples.

Values in parentheses indicate percent loss over control (uncooked) values.

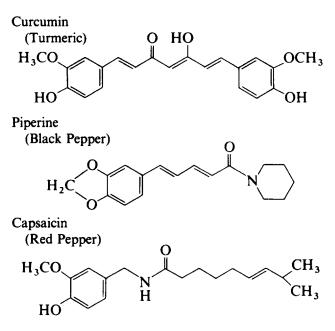
Table 3. Changes in capsaicin levels during domestic cooking

| Spice ingredient added to Tur dhal mash (Total volume: 100 ml) | Control- uncooked | Boiling conditions | | | | |
|---|----------------------|----------------------------|-----------------|--------------------------------|-----------------|--|
| | | Without tamarind pH 6·1 | | With tamarind (0.5%) pH 5.1 | | |
| | | 15 min | 30 min | 15 min | 30 min | |
| Curry powder-II | 0·714 ±0·046 | 0·734 ±0·032 | 0-477 ±0-025 | 0·577 ±0·062 | 0.508 ±0.047 | |
| (% Loss) | | (0) | (33-2) | (19.2) | (28.8) | |
| Red pepper | 1.72 | 1.66 | 1.39 | 1.39 | 1.18 | |
| powder | ±0.21 | ±0·18 | ±0.09 | ±0·10 | ±0.07 | |
| (% Loss) | | (3.5) | (19·2) | (19·2) | (31-3) | |

Values (mg capsaicin/g spice ingredient used in food preparation) are mean ±SEM of six samples.

Values in parentheses indicate percent loss over control (uncooked) values.

tions. Also, the pH difference, as well as the duration of boiling, makes a difference to the extent of capsaicin loss. It may be noted here that the chemical structures of the three spice principles evaluated here have a common basic skeleton but different side chains.



It has been reported that curcumin in aqueous media is highly stable at pH below 7.0 at ambient temperature (Tonnesen & Karlsen, 1985b). However, at pH more than 7.0, curcumin is extremely unstable even at ambient temperature (Tonnesen & Karlsen, 1985b). Alkaline degradation of curcumin has been reported to give ferulic acid and feruloyl methane (Tonnesen & Karlsen, 1985a), and that the feruloyl methane part of curcumin rapidly forms condensation products which are yellow to brownish yellow in colour. There is no information about the stability of curcumin in aqueous solutions at higher temperatures. The loss of curcumin which we have observed in the present study, is contrary to the general belief that curcumin may be stable in aqueous solutions at pH either neutral or acidic. The rubrocurcumin reaction employed here for the quantitation of curcumin is highly specific and hence the loss of curcumin that was observed cannot be attributed to interferences or inadequacies of the quantitation procedure. It is also interesting to note that capsaicin is somewhat resistant to heat under the experimental conditions although it is quite similar in its structure to curcumin.

REFERENCES

Belitz, H. D. & Grosch, W. (1987). Food Chemistry, Springer Verlag, Berlin.

Ganesh Bhat, B. & Chandrasekhara, N. (1985).

Determination of piperine in biological tissues by thin layer chromatography and ultraviolet absorption densitometry. J. Chromatogr., 338, 259-63.

- Ravindranath, V., Satyanarayana, M. N. & Rao, M. V. L. (1981). Rubrocurcumin reaction and its use in microdetermination of certain organic acids. *Indian J. Chem.*, 20, 907-9.
- Srinivasan, M. R., Satyanarayana, M. N. & Rao, M. V. L. (1981). A thin layer chromatographic method for the estimation of capsaicin and related compounds. *Res. & Ind.*, 26, 180-3.
- Tonnesen, H. H. & Karlsen, J. (1985a). Studies on curcumin and curcuminoids-V: Alkaline degradation of curcumin. Z. Lebensm. Unters. Forsch., 180, 132–4.
- Tonnesen, H. H. & Karlsen, J. (1985b). Studies on curcumin and curcuminoids-VI: Kinetics of curcumin degradation in aqueous solution. Z. Lebensm. Unters. Forsch., 180, 402–4.