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The fate of thiamin and riboflavin during the preparation of couscous

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Couscous is an agglomerated and steamed product usually made from durum semolina. The processing of couscous consists of traditional or commercial manufacture followed by preparation in the home prior to consumption. The proximate and particle size analysis of five traditional and four commercial samples is given. Characteristically, the commercial samples were less homogeneous than the traditional ones. The initial thiamin content for both sets of samples was similar (0.26 ± 0.07 mg/100 g and 0.22 ± 0.02 mg/100 g). The riboflavin content of the traditional sun-dried samples tended to be lower than that of the commercial samples (0.037 ± 0.006 g/100 g and 0.066 ± 0.01 μg/100 g).

Average losses during steaming amounted to 15.4 ± 2.7% for thiamin and 36.1 ± 5.7% for riboflavin. It is suggested that eye problems common in supra-Saharan Africa are caused by the sun-drying of couscous which is the cereal staple.

INTRODUCTION

Couscous is an agglomerated and steamed product usually made from durum semolina. Although it has long been a major food staple in much of North Africa, there are very little scientific data on it. Somewhat more information is available on sorghum couscous which is made in sub-Saharan Africa (Galiba *et al.*, 1987, 1988).

Couscous is also prepared from pearl millet (Rooney *et al.*, 1986) and maize (Kodjo, 1981).

A comparison of the characteristics of traditional and commercial wheat couscous has been made by Guezlane *et al.* (1986). These authors found a higher elasticity in the traditionally prepared sample and a lower one in the commercially processed one. The former also showed a lower degradation of carotenoid pigment and a more uniform particle shape. Its acceptability was also superior. However, being sun-dried the risk of aflatoxin production exists (Boutrif & Morse, 1976).

Tan *et al.* (1985), gave an analysis of millet couscous with a value of 0.20 mg/100 g for thiamin and of 0.06 mg/100 g for riboflavin, both at 40% water content. There are apparently no equivalent values for the more common wheat couscous.

In this work the vitamins thiamin and riboflavin were chosen because first they are important in a cereal diet and second, they are very sensitive to processing conditions especially heat and light.

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MATERIALS AND METHODS

All chemicals used were of Analar grade and obtained from BDH, except for the takadiastase used in the thiamin determination, which originated from Fluka Biochemica. Most of the analytical methods were those given by the American Association of Cereal Chemists (AACC, 1983). The reference number is given after each method.

Moisture determination

Moisture was determined by the oven-drying method, using stainless steel dishes at 130°C for 2 h (AACC 44-15A).

Ash determination

This was determined by the AACC method with slight modification (AACC 08-12). The samples were ignited over a bunsen flame until smoke was no longer evolved. They were then heated in a Gallenkamp muffle furnace for 6 h at 600°C. After cooling, 1 ml of distilled water was added to each sample and ashing continued until the ash was white.

Crude protein determination

The Kjeldahl method was employed using copper sulphate as a catalyst and a final boric acid titration (AACC 46-12). The nitrogen factor used was 5.7.

Determination of total fat

This was determined by the method of Pearson (1970). 10 g of the product was boiled for 30 min with 50 ml of 4 M HCl. The sample was then filtered and extracted for 6 h with petroleum spirit (BP 40–60°C).

Sieving analysis

100 g of product was sieved for 5 min in an Endecoth test sieve shaker using circular B.S. sieves ranging from 80 μm to 4 mm mesh size.

Thiamin determination

In the thiochrome method the intense blue fluorescence of thiochrome is detected. This is produced by the oxidation of thiamin in alkaline solution.

Two modifications of the method were made. First, the purification with Decalso was omitted because the blank reading was very low. Second, instead of drying the steamed couscous on the bench, it was freeze-dried. The original method had been designed for cereal grain or bread which have a significantly lower moisture content than couscous, which on bench-drying developed mould. For the thiamin determination, a Perkin–Elmer LS3 fluorescence spectrophotometer at an exciter wavelength of 375 nm and an analyser wavelength of 430 nm was used. The results were returned on a dry basis (AACC 86-80).

Riboflavin determination

Riboflavin fluoresces when exposed to light at a wavelength of 440 nm. The intensity of the fluorescence is proportional to the vitamin concentration of the solution. Riboflavin was measured in terms of the difference between the fluorescence before and after reduction by sodium dithionite. Again, the results were returned on a dry basis (43-039 to 43-042, AOAC, 1984).

Laboratory preparation of couscous

This was based on the traditional method. 100 g of dried couscous was washed three times with tap water using 200 ml of water for each washing. The wet couscous was then left for 15 min to hydrate. It was then placed into the upper section of the couscousiére (Fig. 1), the lower one containing 1.5 litres of boiling water. The junction between the two sections was sealed with a damp cloth to force the steam through the couscous in the upper section. Steaming was continued for 10 min. The couscous was then placed into a dish, weighed and 10% water added to the steamed weight. It was then stirred for 1 min. After 5 min rest it was again steamed for 10 min. 10% water was again added as before and the couscous steamed for the third and last time for another 10 min.

In a duplicate experiment 20 g was removed for the vitamin determination after each steaming, frozen to

Fig. 1. A couscoussiére.

−20°C and freeze-dried in a SB freeze-drier (Model No. 4, Folkestone, Kent) for 24 h at 45 torr. The final moisture content of these samples was between 2 and 3%.

RESULTS AND DISCUSSION

Nine samples of couscous were obtained, of which five were traditionally manufactured in Algeria (Table 1, Nos 1–5). The Fine (No. 1, Seffa) is normally only used for a sweet dish and the coarse (No. 5) is eaten on special occasions only. It was the only one to contain spices. The type usually eaten is the medium couscous (Nos 2 and 3), although the coarse (No. 4, Berkoukes) is sometimes preferred. Samples Nos. 6–9 were of commercial manufacture. The first two of these (Nos 6 and 7) were made in France. Sig (No. 8) was of Algerian manufacture.

According to the packet label only medium size durum semolina was used for samples 6, 7 and 8, whereas traditional couscous is made from two grades of semolina, usually medium and fine.

Table 2 shows the proximate analysis of couscous. The moisture content was satisfactory and would indicate a reasonable shelf-life. Samples 1–5 had been sun-dried, while the commercial samples 6–9 would have been subjected to industrial dehydration.

Protein and fat contents are consistent with the use of hard wheat, either vulgare or durum. Table 3 gives size distribution of the samples. That this varies for the traditional samples is perhaps not surprising, however, the great difference in particle range for the commercial samples was unexpected. There is at present no size standardisation of these.

The photomicrographs (Fig. 2 and Fig. 3) are of particular interest. The commercial sample was much less homogeneous than the traditional one, probably due to

Table 1. Ingredients used in couscous preparation

Sample No.	Type	Semolina			Flour	Added salt
		Fine	Medium	Coarse		
	Traditional					
1	Fine (Seffa)	+	+	–	+	+
2	Medium	+	+	–	–	+
3	Medium	+	+	–	+	+
4	Coarse (berkoukes)	+	–	+	+	+
5	Coarse + Spices	+	–	+	–	+
	Commercial					
6	Sipa	–	+	–	–	–
7	Ferrero	–	+	–	–	–
8	Sig	–	+	–	–	–
9	Local	–	+	–	–	–

+ = present, – = absent.

Table 2. Proximate analysis of couscous samples

Sample	Moisture	Protein $n = 5.7$	Fat	Ash	Total carbohydrate (by difference)
Traditional					
1 Fine	12.1	12.2	1.13	1.30	73.3
2 Medium	9.8	14.3	1.27	1.24	73.4
3 Medium	11.2	14.3	1.21	1.20	72.1
4 Coarse	10.5	13.1	1.23	1.31	73.9
5 Coarse + Spices	9.4	14.1	1.32	1.49	73.6
Commercial					
6 Sipa	12.0	13.6	1.10	1.14	72.2
7 Ferrero	11.7	12.9	0.93	1.21	73.3
8 Sig	11.8	13.6	1.06	1.27	72.3
9 Leeds sample	11.2	12.9	0.90	1.03	74.0

Samples: g/100 g, dry basis, $n = 3$.

Table 3. Particle size of couscous (mm)

Sample No.	< 0.7	0.7–1.0	1.1–1.4	1.5–2.5	2.6–2.8	> 2.9
1	0	3.3	25.9	62.5	8.3	0
2	0	0.1	4.6	67.5	27.8	0
3	0	0.1	2.1	64.3	33.5	0
4	0	0	0.4	60.8	31.7	7.1
5	0	0	0	74.8	25.2	0
6	0.5	7.3	38.3	53.9	0	0
7	0	0.6	30.2	69.2	0	0
8	30.2	44.5	21.4	3.9	0	0
9	4.0	7.8	46.0	42.2	0	0

Overtails per 100 g, $n = 2$.

much less working. This difference had already been observed by Guezlane *et al.* (1986) and was typical. There appeared to be little difficulty in distinguishing the two types under the microscope. Whether particle distribution and structure has an effect on eating characteristics is at present unknown.

Table 4 shows the effect of steaming on thiamin and riboflavin concentrations following the traditional method of preparation. The couscousière was open when used so that light had access to the material being steamed. The original concentration of thiamin is rather variable in the traditional samples but very uniform in the commercial ones produced in France (Nos 6, 7 and 9). The commercial one made in Algeria has a low thiamin content.

The riboflavin concentration tends to be lower in the traditional sun-dried samples than in the commercial ones. This is not surprising since the deleterious effect of light on riboflavin is well documented (Cheldelin & Lane, 1943; Singh *et al.*, 1975; Kearsley & Rodriguez, 1981; Woodcock *et al.*, 1982). Sample No. 5 (coarse with spices) has a significantly higher level of riboflavin, probably because of the added spices, or their protective effect.

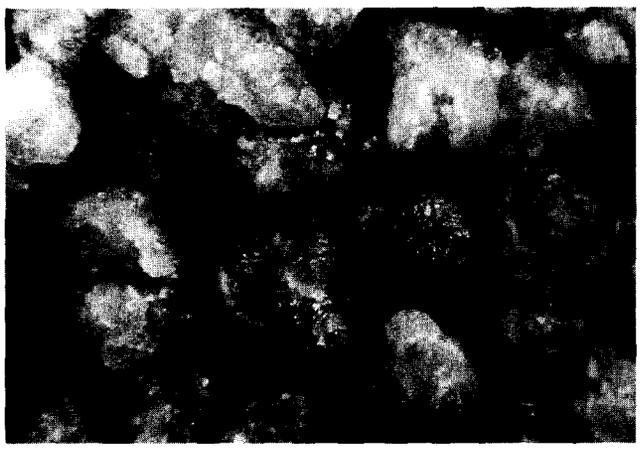

Fig. 2. Traditional couscous.

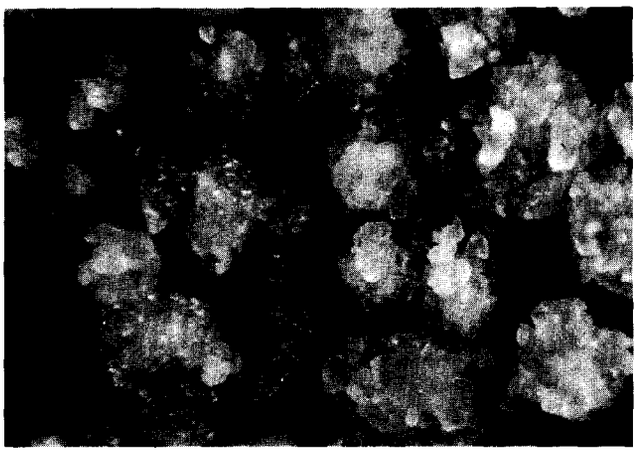

Fig. 3. Couscous: a commercial sample.

Table 4. Effect of steaming on thiamin (B_1) and riboflavin (B_2) concentration during couscous preparation

Samples	Zero time		10 min		20 min		30 min		% Loss	
	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2
Traditional										
1 Fine	0.203	0.028	0.189	0.024	0.176	0.021	0.166	0.019	18.2	32.1
2 Medium	0.366	0.039	0.349	0.034	0.334	0.029	0.317	0.026	13.4	33.3
3 Medium	0.275	0.037	0.257	0.031	0.242	0.026	0.228	0.022	17.1	40.5
4 Coarse	0.209	0.043	0.195	0.036	0.185	0.029	0.175	0.025	16.3	41.9
5 Coarse + Spices	0.227	0.074	0.216	0.067	0.207	0.060	0.198	0.055	12.8	25.7
Commercial										
6 Sipa	0.227	0.058	0.209	0.048	0.195	0.039	0.182	0.033	19.8	43.1
7 Ferrero	0.225	0.060	0.215	0.053	0.204	0.046	0.197	0.041	12.4	31.7
8 Sig	0.192	0.091	0.182	0.077	0.173	0.065	0.162	0.057	15.6	37.4
9 Leeds sample	0.229	0.054	0.219	0.046	0.209	0.039	0.200	0.033	12.7	38.9
Mean ± SD	0.239	0.054	0.226	0.046	0.214	0.039	0.203	0.034	15.0	36.1
	±	±	±	±	±	±	±	±	±	±
	0.053	0.02	0.051	0.02	0.050	0.01	0.047	0.01	2.7	5.7

$n = 3$, mg/100 g, dry weight.

The concentration of both vitamins decreased with increasing steaming time. After 30 min of processing, thiamin losses varied from 12.4 to 19.8%; those for riboflavin from 25.7 to 43.1%. The sensitivity of thiamin to heat depends strongly on the pH (Jansen, 1972; Fellciotti & Esselen, 1957). Dwivedi & Arnold (1972) used s^{35} labelled thiamin in studying the mechanism of the thermal breakdown of thiamin in model systems. They reported that heating thiamine solutions at pH 6 resulted in cleavage of the vitamin at the methylene bridge between the thiazole and pyrimidine constituents. The sensitivity to heat of thiamin in cereal products is well documented (Rice & Beuk, 1944; Farrer, 1955; Chaudhri, 1972; Beetner *et al.*, 1974; Uzogara *et al.*, 1991).

The rates of destruction of the vitamins during 30 min of steaming are given in Figs 4 and 5. These were determined graphically as semilogs of the percentages

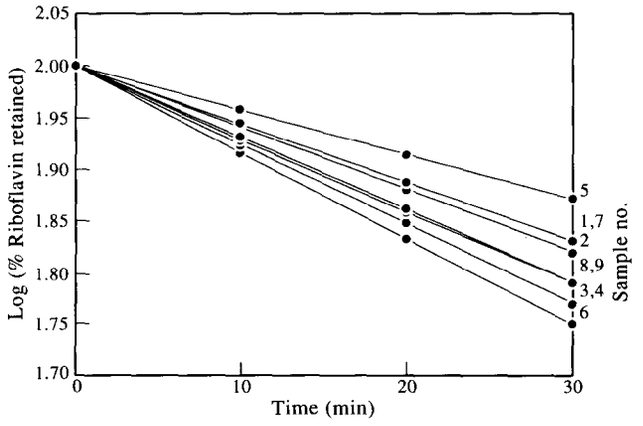

Fig. 4. Rate of destruction for riboflavin during steaming.

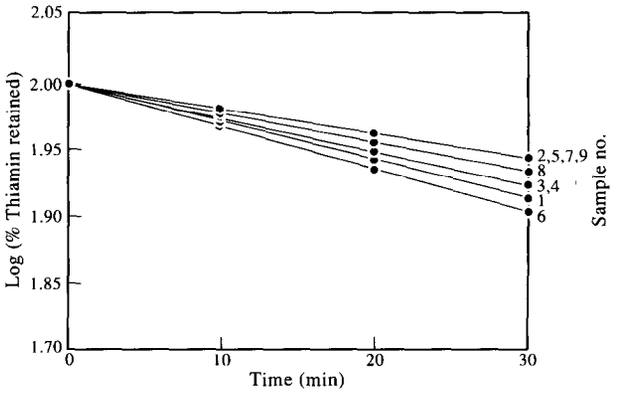

Fig. 5. Rate of destruction for thiamin during steaming.

Table 5. Kinetic parameters for thiamin (B_1) and riboflavin (B_2) during steaming

Samples	K (min)		$*t_{1/2}$ (min)		$**D$ (min)	
	B_1	B_2	B_1	B_2	B_1	B_2
Traditional						
1 Fine	0.0069	0.0131	100	53	333	177
2 Medium	0.0046	0.0138	150	50	500	167
3 Medium	0.0062	0.0176	113	39	377	131
4 Coarse	0.0061	0.0176	113	39	377	131
5 Coarse	0.0046	0.0099	150	70	500	232
Commercial						
6 Sipa	0.0076	0.0192	91	36	303	120
7 Ferrero	0.0026	0.0130	150	53	500	177
8 Sig	0.0054	0.0153	128	45	426	150
9 Leeds sample	0.0046	0.0161	150	43	500	143
Mean ± SD	0.0056 ± 0.0011	0.0150 ± 0.0030	127 ± 24	48 ± 10	424 ± 75	159 ± 34

$*t_{1/2}$ calculated from the equation $t_{1/2} = 0.693/K$.$**D$ calculated from the equation $t_{90} = 2.302/K$.

retained versus steaming time. 100% retention is the vitamin content immediately before processing. These results show that the destruction of both vitamins increases with increasing steaming time and follows a first order reaction. From the resulting straight lines obtained, the first order rate constant, K, has been calculated (Table 5). For thiamin a half time of 127 ± 24 min was found. This is not very significant, but in practice the product is often left to cook for much longer. For riboflavin a half time of 48 ± 10 min was found. This is very striking and shows the deleterious effect of light and heat on riboflavin.

In many of the poorer countries, a cereal diet is the main source of the B vitamins. Since riboflavin is largely destroyed during sun-drying one would expect a wide-ranging deficiency of the vitamin where sun-dried couscous is a staple. The deficiency symptoms of riboflavin include intolerance to light, blurring of vision and corneal changes and this fact might explain the relatively high levels of eye problems in North African countries. The addition of synthetic riboflavin to some staple food is therefore indicated.

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