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Flavour degradation in dehydrated convenience foods: changes in carbonyls in quick-cooking rice and Bengalgram *dhal*

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The carbonyl profiles of quick-cooking rice and Bengalgram *(Cicer arietinum) dhal* are reported. Freshly processed rice contained formaldehyde, acetaldehyde, acetone, butanal and hexanal, while freshly processed Bengalgram *dhal* contained 2,4_decadienals, propanal and 2-enals in addition to the above compounds. Incorporation of *vanaspati* (hydrogenated vegetable oil) and refined sunflower oil enhanced the proportion of acetone in quick-cooking rice and *dhal.* On storage, the proportion of hexanal, 2,4-decadienal and 2-heptenal, 2-octenal and 2-nonenal increased, while the proportion of acetone decreased considerably. The concentration of total carbonyls increased considerably on storage. Most of the additional aldehydes were formed from the oxidative degradation of linolenic and linoleic acids which decreased on storage. The rate of autoxidation, as measured by changes in peroxide value, was highest in untreated rice and *dhals* followed by samples containing refined sunflower oil, while the samples containing *vanaspati* autoxidized the slowest. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Flavour deterioration during storage is the most serious limitation to the shelf-life of dehydrated convenience foods, especially cereals and pulses. Although changes in flavour may emanate from a number of factors such as interaction with packaging materials, absorption of malodorous compounds from the storage environment and non-enzymic browning reactions, carbonyls formed from lipid autoxidation during storage of precooked dehydrated cereals and pulses are the major cause of flavour alterations (Vidyasagar *et al.,* 1991). Changes in carbonyl compounds taking place during storage of milk powder (Hall & Andersson, 1985), meat products (Shahidi *et al.,* 1986), bread (Maga, 1974), chapaties (Kannur *et al.,* 1974) and dried vegetables (Lovegren et al., 1979) have been reported, but no information is available on the carbonyl composition of precooked and dehydrated rice and pulses. However, carbonyls have been reported to play a major role in the aroma of raw and cooked rice, including scented varieties (Maga, 1984; Tsugita *et al.,* 1983).

Recently, as a result of consumer demand for instant cooking foods, a number of processes for preparing

quick-cooking rice and pulses have been developed (Patki & Arya, 1994). Most of the quick-cooking cereals and pulses are highly susceptible to flavour deterioration during storage and, in order to provide adequate storage stability, a number of treatments including the use of various oils have been recommended (Patki & Arya, 1994). In order to understand the changes taking place in the carbonyl profile of quick-cooking rice and pulses and the role of some of the treatments, the carbony1 composition of freshly processed and stored quick-cooking rice and pulses has been studied and is reported here.

MATERIALS AND METHODS

Processing of quick-cooking rice

Commercially available milled short-grain rice (10 kg) was soaked in water (30 litres) for 3 h at ambient temperature (20-25°C). Excess water was removed and the soaked rice was cooked in an autoclave at 1.08 kg cm^{-2} steam pressure for 15 min and dried at 80°C in a hot air drier (Model SDA, Type E; Kilburn, Macneil & Mager Ltd., Calcutta) to a moisture level of about 5%.

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Bengalgram *dhal* **flakes**

Dehusked Bengalgram *(Cicer arietinum) dhal* (10 kg) was soaked in water as above and cooked at 1.08 kg cm⁻² pressure for 20 min. Cooked *dhal* was conditioned to a moisture level of 32% by heating at 80°C in a hot air drier and flaked in a roller flaker (Model ER & Turner 460; Ipswich, UK) by maintaining a 0.2 mm gap between rollers according to Patki & Arya (1994). The flakes were dried to 5% moisture at 80°C.

Packaging and storage

Quick-cooking rice and Bengalgram *dhal* flakes were divided into three lots. Samples (100 g) of one lot were packed as such in paper (42 GMS, $g m^{-2}$)-aluminium foil (20 μ m)-polyethylene (37.5 μ m) laminate (PFP) packs (10 cm \times 15 cm). The other two lots were treated with refined sunflower oil (15%, w/w) and *vanaspati* (hydrogenated vegetable oil) (15%, w/w), respectively, and packed in PFP packs. Both treated and untreated samples were stored at 37°C in an incubator. Initially, and after 4 months, six samples from each treatment were removed and analysed in duplicate for peroxide value, fatty acid composition and carbonyl composition.

Analysis

For peroxide values, 50 g of powdered samples were treated with 100 ml of chloroform and shaken for 1 h. Aliquots (20 ml) of the chloroform extract were treated with glacial acetic acid (30 ml) and 1 ml of saturated potassium iodide solution. After 15 min the reactants were treated with standard sodium thiosulphate solution and the peroxide value was expressed as mEq O_2 kg⁻¹ fat. For fatty acid composition, aliquots of the chloroform extract were evaporated under vacuum. The residual fat was then saponified by treatment with alcoholic potassium hydroxide and fatty acid esters were prepared using boron trifluoride for transmethylation. They were separated by gas-liquid chromatography (Model Chemito 8510; Bombay, India) on a 10% Diethylene glycol succinate column (8 ft \times 1/8 inch) with nitrogen as carrier gas and flame ionization detection. During analysis, the column temperature was maintained at 190°C while the injector and detector temperatures were maintained at 230°C.

isolation of carbonyls

Samples (100 g) of rice or *dhal* were steam-distilled in an all-glass distillation apparatus and the distillate (750 ml) was collected in 250 ml of 2,4-dinitrophenylhydrazine solution (0.1%) in 2 **N** hydrochloric acid. The reaction mixture was kept overnight at room temperature (15- 34°C) and the precipitated dinitrophenylhydrazones (DNPHS) were filtered. The filtrate was extracted with carbonyl-free chloroform (200 ml). The chloroform extract was washed repeatedly with 0.1 **N** hydrochloric acid, followed by distilled water. The extract was evaporated to dryness and mixed with the precipitated DNPHS.

Separation of DNPHS into classes

DNPHS were dissolved in chloroform and 100 μ l of the solution were applied in the form of a band on MgOcelite (3:1) thin-layer chromatography (TLC) plates which had been previously dried at room temperature and activated at 80°C for 1 h. The plates were developed in a benzene:petroleum ether (60-80°C boiling range) mixture (60:40). In this system, the DNPHS separate into three bands corresponding to saturated aldehydes and ketones, 2-enals and 2,4-dienals. The bands were scraped and extracted with chloroform, and the concentration of carbonyls was calculated by measuring the absorbance at 340 nm using $E_{340}^{1\%} = 22500$.

Separation of DNPHS within a class

Extracts of DNPHS from TLC-separated bands were further resolved by high-performance liquid chromatography (HPLC) (Shimadzu, LC-6A) on RP-18 columns using a gradient elution system and acetonitrile:water mixture as mobile phase. For the first 12 min, the mobile phase consisted of an acetonitrile:water (60:40) mixture. From 12 to 26 min, the proportion of water in the mobile phase was reduced to 20% by following a B curve (concave 2) profile. The proportion of acetonitrile and water in the mobile phase was maintained at 80:20 for 4 min, after which the concentration of water was allowed to increase to 40% in 5 min by linear gradient. The concentration of DNPHS was monitored by ultraviolet detection at 336, 370 and 390 nm for saturated aldehydes and ketones, 2-enals and 2,4-dienals, respectively. In HPLC, the DNPHS separated based on the chain length of the carbonyl in each class. Among the saturated carbonyls, ketones migrated faster than aldehydes having the same number of carbon atoms. The concentrations of the various constituents in the mixture were determined from the peak areas. The authenticity of the various compounds was checked by injecting standard DNPHS. A typical HPLC separation of a mixture of pure DNPHS of 2-alkanones and n-alkanals is shown in Fig. 1.

For determining the extent of recovery in the analytical procedure, standard solutions of hexanal, 2-hexenal and 2,4-decadienal were prepared in carbonyl-free chloroform and known quantities of the carbonyls were added to freshly dried rice samples at the time of steamdistillation. By determining the increase in peak areas of the respective carbonyls over the rice sample and comparing this increase with areas of the peaks obtained by direct injection of the DNPHS of the respective carbonyls, percentage recoveries could be calculated. The overall recoveries of hexanal, 2-hexenal and 2,4-decadienal ranged from 85% to 89% and maximum variation among replicates did not exceed 3% of the mean value.

Fig. 1. RP-HPLC of a mixture of 2,4_dinitrophenylhydrazones of (1) formaldehyde, (2) acetaldehyde, (3) acetone, (4) propanal, (5) 2-butanone, (6) butanal, (7) 2-pentanone, (8) pentanal, (9) 2-hexanone, (10) hexanal, (11) 2-heptanone, (12) heptanal, (I 3) 2-octanone, (14) octanal, (15) 2-nonanone, (16) nonanal, (17) decanal.

Four-month samples were significantly different ($P \le 0.01$) from their corresponding 0-month samples.

RESULTS AND DISCUSSION

Freshly processed quick-cooking rice and *dhals* contained very low concentrations of carbonyls (Table 1). Quick-cooking rice contained mostly saturated aldehydes and ketones; the major carbonyls identified were formaldehyde, acetaldehyde, acetone, butanal and hexanal (Table *2).* Except for formaldehyde, all other carbonyls have been reported earlier in the aroma fraction of cooked rice (Maga, 1984; Buttery *et al.,* 1988; Tsugita

et al., 1983). Formaldehyde has not been reported earlier and is reported here for the first time in quickcooking rice. On the other hand, the carbonyl composition of freshly processed quick-cooking Bengalgram *dhal* was more complex (Table 3). Acetaldehyde, acetone, 2,4-decadienal and hexanal were present in larger proportions, and small amounts of 2-enals were also present. Most of these carbonyls are expected to be formed from oxidative degradation of amino acids and fatty acids during cooking and drying operations.

*Significantly different from untreated samples $(P \le 0.01)$.

Significantly different from *vanaspati*-treated samples ($P \le 0.01$).

Table 3. Concentrations (μ g g⁻¹, mean ± SD) of individual carbonyls in freshly processed quick cooking Bengalgram *dhal* flakes having added *vanaspati* (15%) and refined sunflower oil (15%)

Carbonyls	Bengalgram dhal (without added oil)	Bengalgram $dhal + 15\%$ vanaspati	Bengalgram $dhal + 15\%$ sunflower oil 0.57 ± 0.02 ***	
Formaldehyde	0.17 ± 0.01	0.14 ± 0.01		
Acetaldehyde	1.12 ± 0.02	$0.52 \pm 0.04^*$	2.04 ± 0.04 ***	
Butanal	0.15 ± 0.01	0.12 ± 0.01	0.49 ± 0.02 ***	
Pentanal			0.16 ± 0.01 ****	
Hexanal	0.27 ± 0.01	$0.46 \pm 0.01^*$	1.03 ± 0.01 ***	
Octanal	0.03 ± 0.003		0.21 ± 0.01 ***	
Nonanal	0.25 ± 0.01	$0.15 \pm 0.01^*$	0.42 ± 0.06 *.**	
Decanal	0.24 ± 0.01	$0.001 \pm 0.00^*$	0.24 ± 0.01 ^{**}	
Acetone	22.9 ± 0.20	$25.7 \pm 0.36^*$	67.2 ± 0.82 ***	
Butanone			0.46 ± 0.03 *.**	
Pentanone	0.09 ± 0.01		1.50 ± 0.10 ***	
Octanone	0.11 ± 0.009			
Pentenal	0.07 ± 0.002		0.07 ± 0.003 **	
Heptenal	0.03 ± 0.005		0.08 ± 0.002 ***	
Octenal	0.08 ± 0.003	$0.03 \pm 0.00^*$	0.13 ± 0.01 ****	
Nonenal	0.12 ± 0.009		0.14 ± 0.01 ^{**}	
Decenal	0.02 ± 0.001			
Decadienal	1.65 ± 0.04		2.49 ± 0.09 ****	

*Significantly different from untreated samples ($P \le 0.01$).

**Significantly different from vanaspati-treated samples ($P \le 0.01$).

Incorporation of *vanaspati* and refined sunflower oil considerably altered the total concentration as well as the relative proportion of carbonyls in quick-cooking rice and Bengalgram *dhal* (Tables 2 and 3). Incorporation of additional oil considerably enhanced the proportion of acetone in the carbonyl profile, while addition of refined sunflower oil in rice and *dhal* also increased the proportion of hexanal and 2,4-decadienal (Tables 2 and 3).

Storage of quick-cooking rice and Bengalgram *dhal* led to an increase in the concentration of most of the carbonyls except acetone, which decreased considerably (Tables 4 and 5). Relatively, increases were most prominent in hexanal, decadienal, octenal and heptenal concentrations. After 4 months of storage, the concentration of hexanal in Bengalgram *dhal* increased about 28 times while that of decadienal increased about 53 times. The concentrations of 2-heptenal, 2-octenal and 2-nonenal also increased several-fold. The odour

threshold of most of the carbonyls ranges from 0.07 to 15 ppb (Buttery *et al.,* 1988), thus all fhese compounds are expected to influence the flavour of stored quickcooking rice and Bengalgram *dhal.*

Incorporation of additional oil with processed rice and *dhal* is expected to influence the concentration of carbonyls and other volatile compounds in two ways. Firstly, the added oil will dissolve the naturally occurring lipids and therefore the rate of autoxidation in the stored product will be governed by the stability of the added oil. Also, the carbonyls formed will be determined by the fatty acid composition of the added oil. Secondly, the added oil will act as a solvent for the volatile carbonyls, which will help in their retention in the product. Lower concentrations of hexanal and 2,4 decadienal in the sample having added *vanaspati* rather than in those having added sunflower oil, as well as those without added fat, support the above reasoning since both hexanal and 2,4-decadienal are formed

		$Rice + 15\%$ sunflower oil		
0.07 ± 0.002	$0.04 \pm 0.001^*$	0.17 ± 0.003 ****		
0.12 ± 0.001	0.13 ± 0.01	0.26 ± 0.01 ****		
0.09 ± 0.003	0.08 ± 0.006	0.18 ± 0.03 ****		
0.10 ± 0.01	0.12 ± 0.01	0.19 ± 0.03 ***		
9.46 ± 0.48	$3.74 \pm 0.08^*$	6.79 ± 0.13 ***		
0.04 ± 0.005	0.14 ± 0.005 [*]	0.19 ± 0.01 ***		
0.13 ± 0.02	$0.23 \pm 0.03^*$	0.34 ± 0.03 ****		
0.02 ± 0.00	0.14 ± 0.007 [*]	0.31 ± 0.002 ***		
5.06 ± 0.08	$4.70 \pm 0.06^*$	$4.70 \pm 0.07^*$		
0.02 ± 0.00	0.02 ± 0.001	0.01 ± 0.00 ^{**}		
	0.12 ± 0.003 [*]	$0.13 \pm 0.004^*$		
	0.16 ± 0.004 [*]	0.32 ± 0.003 ****		
0.06 ± 0.003	$0.24 \pm 0.01^*$	0.52 ± 0.01 ***		
0.08 ± 0.008	$0.35 \pm 0.02^*$	0.83 ± 0.01 ***		
0.03 ± 0.002	0.25 ± 0.02 [*]	0.42 ± 0.04 ***		
0.07 ± 0.004	$0.36 \pm 0.07^*$	0.48 ± 0.01 [*]		
6.30 ± 0.08	$5.48 \pm 0.02^*$	27.4 ± 0.62 ***		
	Rice (without added oil)	$Rice + 15%$ vanaspati		

Table 4. Concentrations (μ g g⁻¹, mean \pm SD) of individual carbonyls in quick-cooking rice having added *vanaspati* (15%) and refined **sunflower oil (15%) and stored in paper-aluminium foil-polyethylene laminate (PFP) packs at 37°C for 4 months**

Significantly different from untreated samples ($P \le 0.01$).

 \cdot Significantly different from *vanaspati*-treated samples ($P \le 0.01$).

 γ Significantly different from untreated control samples ($P \leq 0.01$).

**Significantly different from *vanaspati*-treated samples ($P \le 0.01$).

Values after 30, 60 and 120 days were significantly different $(P \le 0.01)$ from initial value, and treated samples were different $(P \le 0.01)$ from their corresponding untreated samples after 30, 60 and 120 days of storage.

	Storage period (months)	Fatty acids $(\%)^a$					
		$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Rice (without added oil)	0 4	1.2 ± 0.03 0.8 ± 0.02	36.3 ± 0.10 36.7 ± 0.12	5.3 ± 0.15 3.8 ± 0.06	46.0 ± 0.26 48.9 ± 0.09	9.7 ± 0.26 4.6 ± 0.06	
$Rice + 15%$ vanaspati	0 4	0.3 ± 0.002 0.1 ± 0.003	16.7 ± 0.09 12.0 ± 0.20	10.6 ± 0.06 12.3 ± 0.19	63.1 ± 0.15 65.0 ± 0.52	7.0 ± 0.20 7.0 ± 0.20	
$Rice + 15\%$ sunflower oil	$\bf{0}$ 4	0.1 ± 0.002 0.2 ± 0.001	7.8 ± 0.01 7.4 ± 0.20	4.7 ± 0.07 6.0 ± 0.05	35.6 ± 0.03 47.0 ± 0.17	50.8 ± 0.21 37.4 ± 0.63	
Bengalgram dhal (without added oil)	0 4	0.2 ± 0.001 0.2 ± 0.001	11.1 ± 0.12 11.1 ± 0.22	1.6 ± 0.04 1.1 ± 0.02	23.4 ± 0.18 25.0 ± 0.13	60.7 ± 0.15 60.5 ± 0.04	2.8 ± 0.04 1.8 ± 0.05
Bengalgram $dhal + 15%$ vanaspati	$\mathbf 0$ 4	0.3 ± 0.004 0.1 ± 0.002	15.1 ± 0.32 12.1 ± 0.30	7.6 ± 0.12 8.5 ± 0.19	50.2 ± 0.08 51.9 ± 0.39	25.4 ± 0.06 25.9 ± 0.01	1.1 ± 0.03 0.9 ± 0.02
Bengalgram $dhal + 15%$ sunflower oil	0 4	0.1 ± 0.001 0.1 ± 0.002	7.8 ± 0.09 7.7 ± 0.11	3.1 ± 0.05 2.7 ± 0.07	33.5 ± 0.26 44.4 ± 0.34	54.4 ± 0.16 43.9 ± 0.17	1.0 ± 0.03 0.4 ± 0.01

Table *7.* **Fatty acid composition (%) of quick-cooking rice and Bengalgram** *dhal* **flakes having added** *vanaspati* **(15%) and sunflower oil (15%) and stored in paper-aluminium foil-polyethylene laminate (PFP) packs at 37°C for 4 months**

"Mean of three values, Maximum variation among replicates did not exceed 3% of the mean.

through autoxidation of linoleic acid. *Vanaspati* is low in linoleic acid, and samples of processed rice and *dhal* containing *vanaspati* are therefore relatively more stable and undergo autoxidation at a slower rate. Peroxide values of rice and *dhal* samples containing *vanaspati* were the lowest. The samples containing *vanaspati* were therefore expected to have lower concentrations of hexanal and 2,4-decadienal, which was in fact observed in the present study. Both quick-cooking rice and Bengalgram *dhal* containing *vanaspati* autoxidized at a much slower rate (Table 6), and losses in linoleic acid were also not appreciable (Table 7). On the other hand, the rates of autoxidation in quick-cooking rice and *dhal* were highest in samples without any added fat, followed by samples having added sunflower oil (Table 6). This is mainly due to larger surface area per unit weight of lipids available for reaction with oxygen in quick-cooking rice and *dhal* containing no added oil. Rice and *dhal* contain about 2-5% lipids and, during, cooking and drying operations, these lipids become evenly dispersed over a large surface area because of the porous nature of quick-cooking cereals and pulses. Accordingly, exposed surface area per unit weight of lipid in untreated samples is much higher than in those with added vegetable oils. Therefore, the rate of autoxidation in untreated quick-cooking rice and pulses was expected to be higher, as was observed.

Higher concentrations of total carbonyls and 2,4 decadienal in stored samples having added sunflower oil despite a lower level of autoxidation are due to the better entrapment of volatile carbonyls in the added sunflower oil as compared to untreated samples. Higher concentrations of total carbonyls in freshly processed Bengalgram *dhal* than in rice may also be due to higher retention of carbonyls in *dhal* due to its higher lipid level. It is also interesting to observe that propanal, which is formed from the autoxidation of linolenic acid, is present in stored Bengalgram *dhal* but absent in stored rice.

The results of the present study suggest that carbonyls play an important role in the flavour of both freshly prepared and stored quick-cooking rice and Bengalgram *dhal.* In freshly prepared quick-cooked rice, only saturated carbonyls were present, while in Bengalgram *dhal* both saturated and unsaturated carbonyls were detected. The nature and concentration of carbonyls were influenced by the nature of fat/oil added during processing. On storage, the proportion of unsaturated carbonyls, 2-enals and 2,4-dienals increased considerably. Added fats/oils also influenced the nature and concentration of carbonyls formed during storage.

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