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The use of peroxide value as a measure of quality for walnut flour stored at five different temperatures using three different types of packaging

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Abstract

Walnut flour, a by-product from the production of cold-pressed walnut oil, can contain up to 20% oil, which contains high levels of polyunsaturated fatty acids and is, therefore, potentially unstable. In this experiment, ground walnut flour was stored in three types of container, polypropylene plastic containers, multi-walled plastic-lined paper bags and manila (brown) paper bags. These containers were stored at mean temperatures of −24.6, 3.3, 10.4, 14.3 and 23.0 °C for 26 weeks. The moisture content and the peroxide value of the oil extracted from the flour were determined every four weeks for 26 weeks. The initial peroxide value of the freshly ground flour was 0.01 ± 0.008 meq O_2/kg oil.

After 26 weeks of storage, all samples had an increased peroxide values when compared to the values for oil extracted from the freshly extracted walnut flour. After 26 weeks storage the mean peroxide levels of all treatments were below 1.0 meq O_2/kg oil, i.e., lower than that found in commercial samples of walnut oil. Overall, it is recommended that walnut flour should be stored below 23 °C with careful consideration given to the moisture content of the storage atmosphere and the type of package used to store the walnut flour.

Keywords: Walnut flour; Storage; Packaging; Moisture content; Peroxide value

1. Introduction

Walnut flour is a new product with potential use in the baking industry as an supplement or even as a replacement for wheat flour in the manufacture of bread, biscuits and cakes. Its other use is to provide a source of natural flavouring in these foods. It is produced from walnut press-cake, a by-product from the cold pressing of walnut kernels. To extract the oil, the walnut kernels are ground, malaxed and then pressed in a hydraulic olive press to squeeze out the oil. The remaining press-cake, which may contain up to 20% residual oil, is then ground to make walnut flour.

Walnut kernels contain between 60% and 75% oil (Garcia, Agar, & Streif, 1994; Savage, 2001). The oil contains high levels of 18:2, 18:3 and 18:1 fatty acids (Garcia et al., 1994; Savage, 2001; Zwartz, Savage, & McNeil, 1999) although the values do vary between cultivars (Greve et al., 1992; Vergano, Botta, & Radicati, 1995; Zwartz et al., 1999). Walnut oil contains approximately 7% saturated, 20% monounsaturated and 73% polyunsaturated fatty acids; these high levels of polyunsaturated fatty acids make walnuts prone to oxidation (Stark, McNeil, & Savage, 2000; Vergano et al., 1995) and may mean that the flour has a limited shelf-life, particularly considering that the large, flour surface area could expose the oil to much air. This could lead to in-

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creased oxidative changes during subsequent storage. While the flour contains less fat than the kernels, its texture suggests that there is still a substantial amount of residual oil in the flour.

A number of storage experiments have been carried out on the storage of in-shell walnuts, walnut kernels and walnut oil. Temperature, light, moisture and exposure to oxygen have been found to be the main contributing factors to oxidation (Jan et al., 1988; Koyuncu & Askin, 1999; Mate, Salveit, & Krochta, 1996; Stark et al., 2000). Savage, McNeil, and Österberg (2001) reported that fresh walnut kernels had peroxide values ranging from 0.15 to 0.29 meq O_2/kg oil and that they could be stored in-shell at room temperature (mean 24 °C) for up to 12 months with only modest rises in peroxide levels. Shelled walnuts can be stored for 10–12 months at 5 °C and 55–65% relative humidity while unshelled walnuts can be stored for up to 18 months under the same conditions (Koyuncu & Askin, 1999). Stark et al. (2000) found that walnut oil stored at room temperature (mean 24 °C) in the dark, in sealed bottles, showed only small rises in peroxide levels after four months storage and remained an acceptable product in terms of its organoleptic properties.

If the press-cake is to be effectively used in the baking industry, it is important to determine how long it can be stored for without any deterioration. This storage trial was set up to determine the storage life of walnut flour with particular reference to the optimum storage temperature and the most effective packaging type. The effectiveness of the storage conditions was assessed by measuring the moisture content and the peroxide value of the extracted oil every four weeks up to a total duration of 26 weeks.

2. Materials and methods

2.1. Samples and storage conditions

Fresh walnuts, consisting of a range of different cultivars, were harvested from local orchards in July, 2001, and stored in their shells in open mesh bags (onion storage bags) at 15 °C. In October 2001, the nuts were processed by A Cracker of a Nut, West Melton, Canterbury, NZ. The nuts were cracked using a ring shell cracker (Meyer Machine Company, San Antonio, TX, USA) and the kernels ground and malaxed at 35 °C for 15 min in an olive malaxer (Enoagricola Rossi, Calzalaro, Italy) and pressed in a hydraulic olive press (Enoagricola Rossi, Calzalaro, Italy) using no additional heat treatment to extract the oil. The resulting dry press-cake was ground in a hammer mill to produce walnut flour.

A representative sub-sample of walnut flour from this single pressing of commercial walnut oil sourced from a range of cultivars, was divided into the following portions: 500 g into round, 1 l polypropylene plastic containers with polyethylene sealing lids (Vertex Pacific, Hamilton, NZ), 1.5 kg into white multi-wall paper bags with a 11 μm high density polyethylene lining (Carter Holt Paper Bag Division, Penrose, Auckland, NZ) and 1.5 kg into greaseproof paper lined manila (brown) paper bags (Unibag, Sydenham, Christchurch, NZ). The white and brown paper bag openings were folded and taped securely, after expelling as much air as possible. Three of each type of container were then stored at five different temperatures, −20.6, 3.3, 10.4, 14.3 and 23 °C. The temperature and relative humidity were monitored using a Tinytalk™ temperature data logger and a Tinytag™ relative humidity data logger (Gemini Data Loggers, West Sussex, UK). Triplicate sub-samples from each of the storage containers, at each temperature, were taken at time zero and every four weeks for 26 weeks. These sub-samples were stored in sealed plastic bags at −20 °C until analysis commenced.

2.2. Chemical analysis

Dry matter, protein, fibre and total oil contents of fresh walnuts and walnut flour were determined using standard AOAC methods.

2.3. Oil extraction and peroxide analysis

A modified method of Hara and Radin (1978) was used to extract the lipid from the walnut flour for peroxide determination. Approximately 8 g of flour were weighed into a 50 ml Kimax™ tube (Kimble, Vineland, NJ, USA) and 20 ml of hexane/isopropanol (3:2 v/v) (BDH, AR) were added. The tubes were then rotated in a Hybaid oven (MII, Hybaid, Ltd., Ashford, UK) for 10 min at room temperature (20 °C), then left to settle at 4 °C in the dark, then decanted into a 50 ml centrifuge tube. Ten ml of 6.7% w/v sodium sulphate (BDH, Poole, UK) were then added to the centrifuge tube and the tube was inverted several times. The extract was centrifuged at 3000 rpm for 10 min at 4 °C. The supernatant was then transferred into a 100 ml round-bottom flask and placed on a Büchi Rotovapor-R (Postfach, Switzerland) set at 40 °C and evaporated to dryness. The peroxide value of this sample of oil was then determined using the IDF standard method 74A (IDF, 1991).

2.4. Statistical analysis

Statistical analysis was conducted using GenStat, 7th Edition (Rothamsted Experimental Station). The analysis of the difference between means was done by analysis of variance (ANOVA); the level of significance was determined by a given p value, and the location of

differences between means was determined by the calculation of the least significant difference (lsd).

3. Results

3.1. Proximate composition

After cold-pressing, walnut flour contained a high amount of residual oil, 20.3 ± 1.1 g/100 g wet matter (WM) and 10.5 ± 0.9 g moisture/100 g WN (Table 1). The fat content of the walnut flour could be considered to form a significant part of its composition; whole grain wheat flour has 1.87% fat (USDA, 2004) hence the decision to evaluate the use to measuring the peroxide value of the oil in the flour to determine the quality of this wheat flour product over time.

3.2. Moisture content

Table 2 shows the mean temperature and relative humidity of each of the five storage conditions over the 26 weeks of the experiment. Using these measurements, it is possible to calculate the amount of water in the atmosphere of each storage incubator, expressed on the same basis (g water/kg dry air).

The moisture contents of each of the samples of walnut flour stored in the three different types of packaging at the five different storage temperatures are shown in Fig. 1. Overall, the plastic container with a sealing lid was most effective at controlling the moisture content of the walnut flour while the brown paper bags allowed the greatest change in moisture content of the stored walnut flour. The hottest storage condition (23.0 °C) led to the highest moisture content in the incubator air (Table 2) and, in all of the treatments, the moisture content of the walnut flour rose when it was stored at 23.0 °C, particularly toward the end of the storage time. The driest atmosphere (0.3 g water/kg dry air) was maintained by the lowest temperature (−24.6 °C) and the moisture content of the walnut flour remained constant over the 26 weeks of storage for all three of the storage treatments at this temperature. The 3.3 °C storage temperature had the driest, non-frozen, atmosphere (2.1 g water/kg dry air) and this led to a slow reduction in the moisture content of the walnut flour stored in the brown paper bags. At 10.4 °C, the storage atmosphere contained 14% more moisture than at 14.3 °C and this difference was enough to give an overall increase in the moisture content of the walnut flour stored in brown paper bags at 10.4 °C over the 26 weeks.

Table 2
Mean psychometric data of the storage conditions over 26 weeks

Mean storage temperature (°C)	Mean relative humidity (%)	Moisture content of the storage environment (g water/kg dry air)
−24.6	70.0	0.3
3.3	43.8	2.1
10.4	86.5	6.7
14.3	58.4	5.9
23.0	67.4	11.7

3.3. Peroxide value

The initial peroxide value of freshly pressed flour was very low, 0.01 ± 0.008 meq O_2/kg oil. Overall, the peroxide value rose very slowly over the 26 weeks of storage (Table 3). The lowest mean peroxide level was achieved by storage in the plastic containers (mean value at week 26 over all the temperatures was 0.42 ± 0.08 meq O_2/kg oil), while storage in the plastic-lined white paper bags gave a mean value at week 26, over all the temperatures, of 0.49 ± 0.11 meq O_2/kg oil. The mean peroxide value of all the meals stored for 26 weeks in the unlined brown paper bags was 0.73 ± 0.10 meq O_2/kg oil.

4. Discussion

The initial peroxide value of the fresh flour was very low (0.01 ± 0.008 meq O_2/kg oil), especially when compared to fresh walnut oil which Sheen (1999) reported to be (0.04–0.35 meq O_2/kg oil), depending on the cultivar analysed. Savage et al. (2001) reported that fresh walnut kernels had peroxide values ranging from 0.15 to 0.29 meq O_2/kg oil. The peroxide values of some commercially available imported and locally produced walnut oils analysed at the same time are shown in Table 4. Two samples of walnut oil freshly imported from France gave similar values. The ''Kernels'' oil was prepared from selected cultivars and the ''Wild'' oil was pressed from a range of unselected cultivars and was known to be from old stock. Even with this high peroxide value (6.29 meq O_2/kg oil) the ''Wild'' oil had an excellent taste and aroma. The peroxide levels in the walnut flour are lower than all samples of cold-pressed walnut oil, except for the

Table 1
Mean composition of walnut flour compared to the original kernels (g/100 g WM)

	Moisture	Ash	Crude protein	Crude fibre	Total oil
Walnut flour	10.5 ± 0.9	4.7 ± 0.1	39.1 ± 1.3	18.5 ± 1.7	20.3 ± 1.1
Walnut kernels	5.1 ± 0.7	1.9 ± 0.9	15.2 ± 0.5	3.1 ± 1.3	68.6 ± 0.9

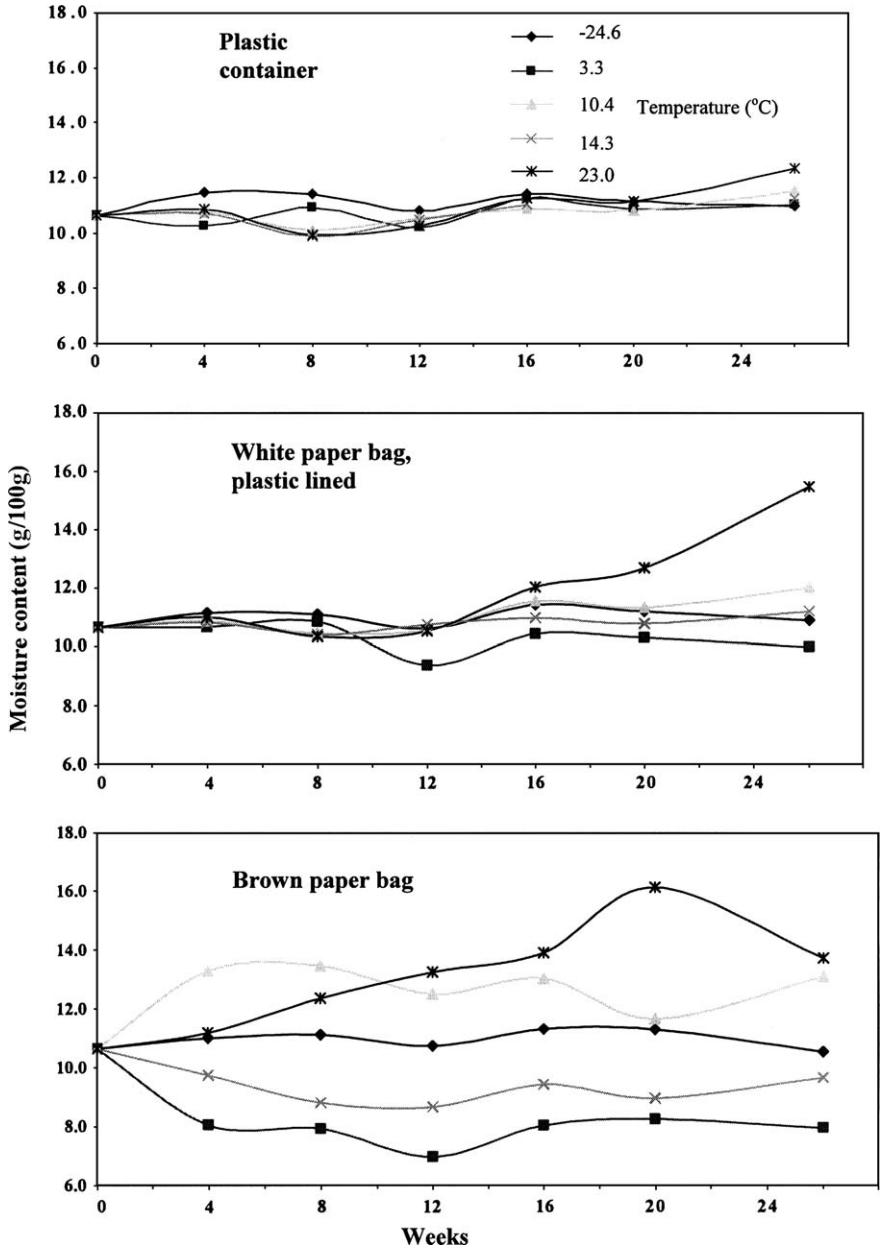

Fig. 1. Moisture content of walnut flour stored at five different temperatures and in three different type of packaging.

one sample of flour stored at 23.0 °C for 12 weeks in paper bags (1.21 meq O_2/kg oil).

Data from this experiment suggest that the residual oil contained in ground walnut flour is more stable than walnut oil stored in sealed bottles. The data also show that, provided the walnut flour is kept sealed and stored below 23 °C, it can be easily stored for up to six months, even though the flour contains 20.3% total oil. As the flour had been ground to a fine powder with a large surface area, it might have been expected that the oil would oxidize rapidly, particularly as it contained high levels of polyunsaturated fatty acids. It is possible that the oil in the walnut flour remained stable because the flour contained high levels of vitamin E, a natural antioxidant. Savage, McNeil, and Dutta (1998) reported that the mean total tocopherol content of walnuts grown in New Zealand was relatively high (360 μg total tocopherol/g oil).

Data from this experiment clearly show that storage either in a sealed plastic container, or plastic-lined white paper bag, is the best method for long-term storage of walnut flour. However, Jan et al. (1988) showed that shelled nuts were stored best in sealed cans, followed by laminated foil (PVDC-Polyethylene) pouches. They showed that polyethylene packaging was not effective for maintaining the organoleptic quality of the shelled walnuts and that storage at temperatures below room temperature was more effective for maintaining the

Table 3
Mean peroxide values (meq O_2/kg oil) of walnut flour stored for up to 26 weeks in three different types of container at five different temperatures

Mean temperature (°C)	Storage time (weeks)					
	4	8	12	16	20	26
Plastic container						
−24.6	0.01	0.01	0.00	1.18	0.50	0.65
3.3	0.00	0.04	0.00	0.02	0.39	0.57
10.4	0.00	0.02	0.01	0.32	0.22	0.38
14.3	0.01	0.05	0.00	0.36	0.30	0.24
23.0	0.01	0.29	0.62	0.30	0.41	0.28
White paper bag						
−24.6	0.00	0.01	0.00	0.52	0.61	0.74
3.3	0.00	0.06	0.00	0.34	0.31	0.70
10.4	0.01	0.03	0.02	0.25	0.34	0.55
14.3	0.03	0.06	0.02	0.18	0.27	0.30
23.0	0.07	0.38	0.62	0.63	0.27	0.18
Brown paper bag						
−24.6	0.01	0.02	0.00	0.22	0.59	0.87
3.3	0.01	0.03	0.02	0.12	0.54	0.66
10.4	0.02	0.09	0.14	0.66	0.41	0.39
14.3	0.04	0.03	0.00	0.35	0.24	0.74
23.0	0.02	0.28	1.21	0.35	0.35	0.98

Source of variation	d.f	*F*	Probability	L.s.d. (5%)
Package type	2	6.02	**	0.05
Temperature	4	13.35	***	0.06
Storage time (week)	5	55.64	***	0.07
Package type × temperature	8	2.51	*	0.11
Package type × storage time	10	2.29	*	0.11
Storage time × temperature	20	11.96	***	0.15
Package type × temperature × Storage time	40	2.89	***	0.26

Table 4
Peroxide value of several commercially available oils in NZ

Commercial walnut oil	Peroxide value (meq O_2/kg oil)
Clovis France (Charbonneaux Brabant, Reims, France)	1.21
Gastronomiquement Votre (Soripa, Gretz-Armainvilliers, France)	1.02
Kernelz (A Cracker of a Nut, Canterbury, NZ)	0.97
Wild (A Cracker of a Nut, Canterbury, NZ)	6.29

quality of the shelled walnuts. Jan et al. (1988) went on to show that nuts packed under nitrogen kept their organoleptic quality better than nuts packed in air, especially when stored at 5 °C.

The long-term storage of flours is not a recommended commercial practice and very few long-term storage experiments have been carried out on any flours. However, Manan, Kalra, Kulkarni, Joshi, and Berry (1991) carried out a storage trial on mixtures of Bengal gram flour (*Cicer arietinum*) and *Colocasia esculenta* (taro) mash to make a snack product. The mixed product was stored for 40 days at 30–35 °C, either in polypropylene pouches or in sealed tins. The moisture content rose by 2.8% and the peroxide levels rose from 0 to 1.07 meq O_2/kg oil during storage. At these temperatures, the shelf-life of this product was reported to be 30 days when stored in the plastic pouches; the product was reported to store better in sealed tins. The storage characteristics of this mixed snack product show similar trends in the peroxide value and moisture content of the walnut flour.

5. Conclusions

Walnut flour can be stored for up to 26 weeks in plastic containers or plastic-lined paper bags without any major changes of the moisture content or peroxide levels. Storage in brown paper bags at 23.3 °C leads to a steady increase in moisture content over 26 weeks. Storage of walnut flour for up to 26 weeks in a sealing plastic container and plastic-lined paper bags gave lower peroxide levels in the oil than did storage in brown paper bags. Overall, it is recommended that walnut flour should be stored below 23 °C with careful consideration given to the moisture content of the storage atmosphere and the type of package.

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