Food Chemistry 38 (1990) 201–210

The Relationship Between Lipid Composition and Oxidative Stability of Potato Granules

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(Received 8 November 1989; accepted 4 December 1989)

ABSTRACT

Lipid oxidation and changes in the lipid composition of potato granules during storage were studied. In particular, the possible rôle of the free fatty acids (FFA) in oxidation and storage stability was examined. Three potato granule materials which differed in FFA content were stored in darkness, in air at 25°C. The lipid oxidation was followed by gas chromatographic headspace analysis of volatile compounds and sensory evaluation was carried out after periods of 12 and 40 weeks of storage. The FFA were analysed by gas chromatography to determine fatty acid composition during storage. All three of the potato granule materials were markedly oxidized. However, the material containing the least original amount of FFA was the most rancid after only 12 weeks storage, according to both the sensory analysis and the content of hexanal. This shows that there was no connection between the original total amount of FFA and the oxidative stability of the potato granules. In the most highly oxidized material the FFA content decreased towards the end of the storage period, but in the other two materials, for which the rate of oxidation was lower, there was a slight increase of the polyunsaturated FFA (C18:2 + C18:3). This indicates that both simultaneous lipolysis and oxidation took place during storage. The fatty acid compositions within the lipid classes; neutral lipids, galactolipids, and phospholipids, were not found to change significantly during storage.

INTRODUCTION

Lipid oxidation limits the storage time of almost all dry food products, even of potato granules in spite of their very low lipid content. Raw potato contains only 5·8–9·0 mg lipids/g of dry matter (Liljenberg *et al.*, 1978) but about 75% of the total fatty acids present are the polyunsaturated linoleic

Food Chemistry 0308-8146/90/$03·50

and linolenic acids (C18:2 and C18:3). The storage stability of potato granules has been investigated many times from different points of view, such as the influence of storage atmosphere (Quast & Karel, 1972; Lisberg & Chen, 1973), water content and original condition of the raw potatoes (Sapers *et al.*, 1973, 1974).

The storage stability of the final product may also be affected by the manufacturing process. The nutrient composition, for example, alters during the production of potato granules. Augustin *et al.* (1979, 1981) reported a loss of 55% of the ascorbic acid and 81% of the thiamine. In earlier studies at our laboratory we have found that, during potato granule production by the add-back process, free fatty acids (FFA) were liberated. The liberation of FFA occurred in the first stages of the process (Lilja & Lingnert, 1989*b*).

Since free fatty acids are known to oxidize more easily than fatty acids bound in glycerides (Popov & Mizev, 1966; Catalano & De Felice, 1970), storage stability may well be influenced by the liberation of FFA during processing. The purpose of the present work was, therefore, to study the relationship between lipid oxidation and other lipid changes during storage of potato granules (in particular changes of the FFA) and, if possible, to elucidate the significance of the liberated FFA in storage stability.

Three commercial potato granule materials with variations in the amount and composition of FFA were stored in darkness at 25°C. The lipid oxidation was followed by both headspace analyses and sensory evaluation, and the amount and composition of FFA were analysed periodically during storage by HPLC and GC.

MATERIALS AND METHODS

Potato granules from the commercial add-back process at AB Felix, Sweden, were withdrawn on three different occasions during a period of 3 months. They were packed in foil bags under nitrogen and were stored at −40°C until the beginning of the storage experiment. Antioxidant, emulsifier and sodium bisulphite were added during the process in order to obtain the final concentration of 20 mg/kg of BHA, 4 g/kg of monoglycerides and 300 mg/kg of sulphite (analysed as SO_2). The water content was about 7%.

All chemicals used for extraction, separation and analyses were of analytical grade (Merck, FRG). The hexane (Fisons plc, Scientific Equipment Division, UK) and propane-2-ol (FSA, Laboratory Supplies, UK) were of HPLC grade. The water used was purified by the Elgastat spectrum reverse osmosis and deionization system (Elga Ltd, UK).

The standards, linoleic acid (C18:2), heptadecanoic acid (C17:0) and fatty acid methyl esters (C6:0—C18:2), were all from Nu Check Prep. Inc., USA.

Storage conditions

The potato granules were packed in 500-ml glass bottles (Sovirel, France) with Teflon-sealed screw caps. An amount of 100 g of potato granules was placed in each bottle. The bottles were stored in darkness at a constant temperature of 25°C. After various storage times, three samples of each material were withdrawn and kept at −40°C until analysis.

Analysis of volatile products

The analysis of volatiles was performed according to Hall *et al.* (1985). An amount of 20 g of the sample was dispersed in 200 ml of purified water. The slurry was poured into a specially constructed long-necked glass vessel, kept at constant temperature, 25°C, and gently stirred during sampling. A helium volume of 3 litres was purged over the sample (40 ml/min) and the volatile components in the headspace were trapped on a polymer adsorbent, Chromosorb 102 (Johns-Manville, Alltech Associates, USA).

The volatiles were desorbed thermally and separated on a Varian 4600 gas chromatograph. A fused silica capillary column, DB1, 60 m and i.d. 0·32 mm (J. & W. Scientific Inc., USA) was used. The gas chromatograph was temperature programmed, first 30–70°C at a rate of 3°C/min and then 70–200°C at a rate of 20°C/min. The volatiles were detected by a flame ionization detector, 200°C, and identified by using a gas chromatograph/mass spectrometry system (Finnigan 9610-4023) equipped with the same column. Operating conditions were: ionizing voltage, 70 eV, and ion source temperature, 270°C. The mass spectra identification was done using the National Bureau of Standards library of references. A Hewlett Packard lab data system (HP 3357) was used for data collection and evaluation.

Sensory analysis

A panel consisting of five judges undertook a descriptive test of the potato granules. The samples analysed were all the three materials after storage for 12 and for 40 weeks. As a control, one of the materials that had been kept at −40°C for the whole storage period was used. This control material was also used as a known reference sample at each panel session.

Each sample of 70 g was whipped, for 1 min, into 400 ml of boiling water. The potato purée sample was served, in 10-g portions, in stainless steel bowls that were placed on heated plates (55°C) and presented to the judges within

15 min. The seven samples were each judged (in a randomized order) at each session. There were three sessions which were divided into two sittings each, by a 15-min break.

Both odour and flavour were judged for each sample. The odour descriptors used were 'total odour intensity', 'raw potato', 'cardboard' and 'burnt'; and the flavour descriptors were 'total flavour intensity', 'raw potato', 'cardboard', 'burnt' and 'bitter'. The descriptors were selected in introductory experiments using relevant potato granule samples. The intensities of the descriptors were scored on a scale of 0–10 degrees, with 10 indicating a very high intensity.

Lipid analysis

The lipids were extracted, using the Bligh and Dyer (1959) method, and then they were separated on a silicic acid column (Mallincrodt CC4 special) into the three lipid classes, neutral lipids, galactolipids and phospholipids, as described before (Lilja & Lingnert, 1989*a*). The free fatty acids were isolated from the neutral lipids by HPLC, according to Hamilton and Comai (1984), as previously described (Lilja & Lingnert, 1989*b*).

The fatty acids were methanolysed, analysed by gas chromatography and quantified using methods reported previously (Lilja & Lingnert, 1989*a*).

Water content

The water content of the different samples was measured by drying samples of 5 g at 110°C until they reached constant weight (approximately 1 h).

RESULTS AND DISCUSSION

Characterization of materials tested

The potato granule materials (A, B and C) were taken from the ordinary commercial production on three different occasions. The materials are characterized in Table 1, regarding their content of free fatty acids (FFA) and the unsaturation ratio (UR) of these. The final concentrations of added antioxidants (BHA) and sodium bisulphite, as well as the water content of the materials, are also included in the table. The UR was calculated as the ratio of the amount of linoleic acid and linolenic acid (C18:2 + C18:3) to the amount of palmitic acid and stearic acid (C16:0 + C18:0). It can be seen that material A contained the smallest amount of FFA while material C contained the highest amount of FFA, the UR being very similar. Material B

TABLE 1
Characterization of the Potato Granule Materials

Material	*FFA* (*μg/g DM*)[a]	*UR*[b] *of FFA*	*BHA* (*μg/g DM*)[a]	*Sulphite* (*μg/g DM*)[a]	*Water content* (%)
A	150	0·72	29	280	7·3
B	210	0·89	27	450	7·2
C	250	0·72	30	300	6·6

[a] DM = dry matter.

[b] $UR = \frac{(C18:2 + C18:3)}{(C16:0 + C18:0)}$.

was intermediate regarding FFA content but showed the highest UR, which means that these FFA were the most unsaturated. The content of BHA was similar in the three materials but material B contained a higher amount of sulphite than the others. It can also be seen that sample C was slightly drier, 6·6% H_2O, than the other two which had water contents of about 7·2%.

Changes during storage

Samples were withdrawn after 2, 4, 8, 12, 20 and 40 weeks of storage. The lipid oxidation was followed by headspace analyses and sensory evaluation.

Development of volatiles

Of the volatiles formed, hexanal was used as an indicator of lipid oxidation. The formation of hexanal in the potato granules is shown in Fig. 1. As can be seen, the materials were markedly oxidized during the storage period, materal A being oxidized more rapidly than the other two. Materials B and C contained less hexanal throughout the whole storage period.

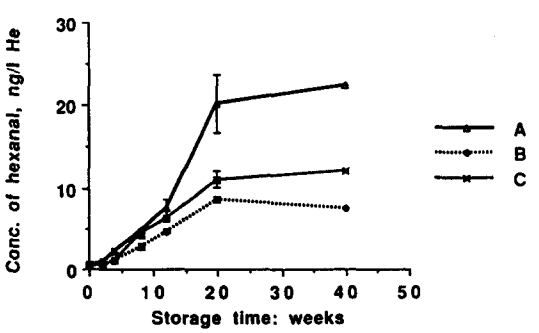

Fig. 1. The development of hexanal in the potato granules (materials A, B and C) during storage in darkness at 25°C.

Sensory changes

Since the sensory analysis was limited to only five judges and three repetitions, the evaluation of the results must be made with some caution. During the storage period the odour intensity was significantly changed from the control material only in the descriptors 'total odour intensity' and 'cardboard'. For both these odours the intensity was increased during storage. The flavour intensity, however, was significantly changed for all descriptors after both 12 and 40 weeks of storage. In addition it has previously been reported that flavour evaluation is more sensitive than odour evaluation (Hall & Lingnert, 1984).

The flavour intensity of 'raw potato' decreased during storage while the intensities of all the other descriptors increased. The intensities of the flavours 'raw potato' and 'cardboard' are shown in Fig. 2. The 'raw potato' intensity decreased during storage to almost the same extent in the three different materials. 'Cardboard' or 'paper' are flavour descriptors that have often been found to be associated with lipid oxidation in dry foods (Hall & Lingnert, 1984). As is seen in Fig. 2(b), there was a faster evolution of the flavour 'cardboard' in material A, although the intensity was never

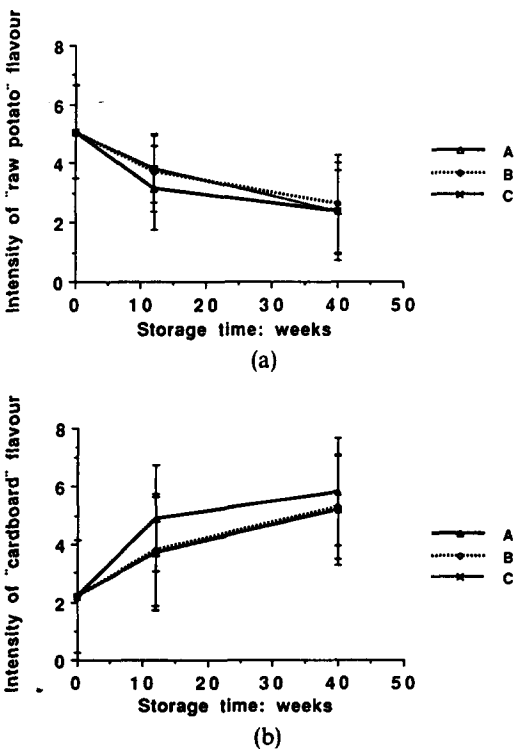

Fig. 2. Flavour changes during storage of potato granules (materials A, B and C). (a) The descriptor 'raw potato'; (b) the descriptor 'cardboard'.

significantly different from that of materials B and C. This is, however, well in accordance with the development of hexanal shown in Fig. 1. Material C was judged to have a slightly more burnt flavour after storage than the other two materials. The could be due to the lower water content of this material.

Obviously, the potato granule materials oxidized during the storage and they were perceived as rancid. Based on hexanal formation as well as sensory evaluation, material A was found to oxidize somewhat more rapidly than the other two materials. However, this could not be explained by differences in the initial FFA content, the degree of unsaturation of the FFA, water content, etc. (see Table 1).

Changes in the FFA

Figure 3(a) shows the changes in total amounts of FFA in the three potato granule materials during the storage period. No obvious changes during the storage period can be observed, although there is a weak trend of decreasing FFA content in material A. This might be connected with the higher degree of oxidation in material A as compared to the two other materials, as manifested in the hexanal development.

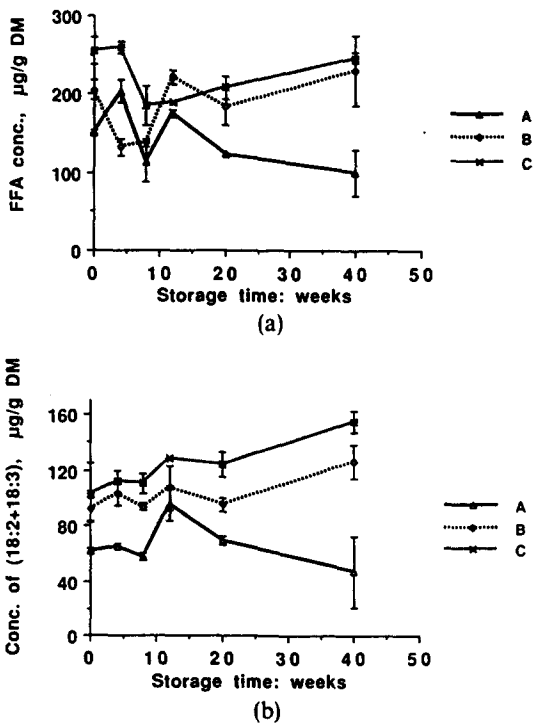

Fig. 3. The changes of FFA in the potato granules (materials A, B and C) during storage in darkness at 25°C. (a) The changes in total FFA; (b) the changes in polyunsaturated fatty acids (C18:2 + C18:3).

The content of polyunsaturated fatty acids (C18:2 + C18:3) in the FFA during storage is shown in Fig. 3(b). The amounts of polyunsaturated free fatty acids seem to increase slightly in materials B and C during storage, while a decrease can be noticed in material A; this parallels the result for total FFA. It is possible that lipolysis and oxidation of the liberated FFA proceed simultaneously during storage, resulting in a net increase of FFA when the rate of oxidation is slow and a net decrease when the rate of oxidation is high (as may be the case in material A). However, from the present results it is not possible to determine the exact rôle of the free fatty acids in the overall oxidation of potato granules during storage.

Changes in fatty acid composition in various lipid classes

Buttery *et al.* (1961) analysed the changes in the total fatty acid composition of potato granules during storage at 24°C, both in air and in oxygen. In their study the per cent amount of both linoleic acid and linolenic acid decreased from 74·1 to 55·3% during a storage period of 20 weeks in air. In the present work, no similar decrease could be established. One explanation of the difference in the results could be that the potato granules in the work by Buttery *et al.* were produced without antioxidants, which made the lipid oxidation much faster than in this study, where the potato granules did contain antioxidants.

We also analysed the fatty acid composition of the various lipid classes; neutral lipids, galactolipids and phospholipids, before storage and after 40 weeks of storage. However, even within each lipid class, no consistent changes during storage could be established. Neither was there any significant decrease in the amounts of lipids during storage. This is no surprise, since oxidation of a very small part of the lipids is enough to give an objectionable, rancid flavour, since the threshold values of many of the volatiles formed are very low. However, in an accelerated storage test at 60°C, both the amounts of phospholipids and their UR were observed to decrease in the materials A and C.

CONCLUSIONS

Three potato granules with variation in free fatty acid (FFA) content were stored in darkness at 25°C. The total amount of FFA decreased in the material that oxidized fastest but slowly increased when the lipid oxidation was slower. The polyunsaturated fatty acids (C18:2 + C18:3) followed the same pattern.

After a storage time of only 12 weeks, the potato granules containing the smallest original amount of FFA had oxidized the most, according both to

measurements of the volatile product hexanal and to sensory evaluation of the stored materials. The material containing the most unsaturated FFA was least oxidized during the storage. Consequently, the original amount of FFA did not, alone, predict the storage stability, nor did a higher degree of unsaturation of these FFA give a faster lipid oxidation.

No significant changes, during storage, could be established in the fatty acid composition within the isolated lipid classes.

ACKNOWLEDGEMENTS

This project was supported by grants from AB Felix, Sweden, and the National Swedish Board for Technical Development. The authors also wish to thank Catherine Lundborg and the members of the panel for their help with the sensory analysis.

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