Food Chemistry **31** (1989) 267–277

Lipid Changes during the Production of Potato Granules

M. Lilja & H. Lingnert

SIK, PO Box 5401, S-402 29 Göteborg, Sweden

(Received 5 February 1988; revised version received and accepted 10 May 1988)

ABSTRACT

Potato granules were produced by an add-back-process. The lipid composition of the potato tubers and the final potato granules were assessed in order to study the influence of the process. The extracted lipids were fractionated into three major classes, neutral lipids, galacto-lipids and phospholipids, on a silicic acid column. The free fatty acids were separated from the neutral lipids by high performance liquid chromatography (HPLC). The fatty acid composition of the three lipid classes as well as the free fatty acid fraction was analysed by gas chromatography. No changes could be observed in the galactolipids and the phospholipids but the free fatty acid content was found to be about ten times higher in potato granules than in the potato tubers.

INTRODUCTION

The lipid content of the potato tuber is very low. The potato variety Bintje, grown in Sweden, contains 5·8–9·0 mg lipids/g of dry weight (Liljenberg *et al.*, 1978). In spite of the low lipid content, lipid oxidation limits the storage time of potato granules. This has been shown in several studies, where different storage conditions have been investigated (Buttery *et al.*, 1961; Quast & Karel, 1972; Sapers *et al.*, 1972, 1973, 1974; Lisberg & Chen, 1973; Sullivan *et al.*, 1974; Konstance *et al.*, 1978; Ooraikul & Moledina, 1981).

Various methods protecting against lipid oxidation during storage have been studied, such as the use of antioxidants, storage in nitrogen

Food Chemistry 0308-8146/89/$03·50

atmosphere, and control of the water content. However, the lipid oxidation probably starts already during the production of potato granules. The lipids may then be exposed to enzymes, such as lipase and lipoxygenase, and conditions such as high temperature and oxygen availability may be highly favourable for autoxidation. Steps to protect the lipids should therefore be taken already in the manufacturing process in order to obtain stable potato granules.

Accordingly, it is of interest to elucidate what lipid changes take place during the production of the potato granules and where in the process they take place. Pun & Hadziyev (1978) studied the production of potato granules using a freeze–thaw process and reported losses of all the lipid classes (neutral lipids, galactolipids and phospholipids) during the process.

Here we report how the composition of lipids and fatty acids in potatoes were affected when producing potato granules by an add-back-process.

MATERIALS

The Swedish variety Bintje was used for this experiment. The tubers were harvested during October 1986 and were stored in darkness at 7°C and 98% relative humidity until used.

The commercial potato granules were produced by AB Felix, Sweden, in their full scale plant in December 1986. The main steps of this production are shown in Fig. 1. It is an add-back process where 85–90% of the produced potato granules are brought back in the mixing step to give a gradual disintegration of the potato cells. All additives (monoglycerides, sodium bisulfite, BHA, citric acid, tetrasodiumpyrophosphate) were added in the mixing step. The granules were packed in aluminium foil bags under nitrogen and stored at −40°C until analysed.

All chemicals used for the extraction, separation and analyses were of analytical grade (Merck, FRG). The *n*-hexane (Fisons plc, Scientific Equipment Division, England) and propan-2-ol (FSA Laboratory Supplies, England) were of HPLC-grade.

The standards linoleic acid, heptadecanoic acid and fatty acid methyl esters were all from Nu Chek Prep. Inc., USA.

METHODS

Production of potato granules without monoglycerides

Monoglycerides are used as an additive in commercial potato granules. This made it impossible to directly compare the tubers and the potato granules

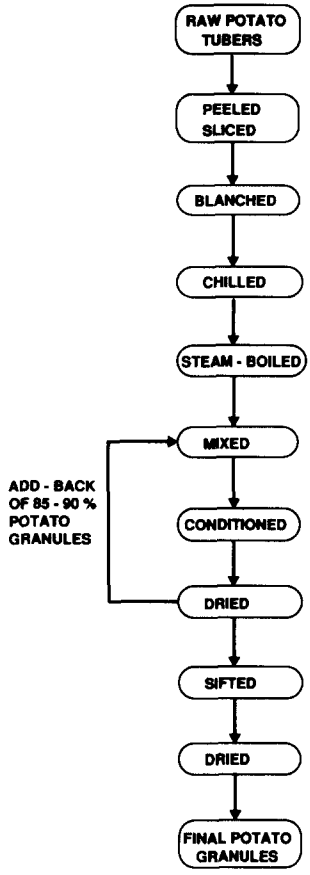

Fig. 1. The steps in the add-back-process of potato granules.

regarding lipid composition. Therefore potato granules were also produced without addition of monoglycerides. The production was carried out in a pilot plant at AB Felix in February 1987. Apart from the monoglycerides, the other additives were used as in the production of commercial potato granules.

Extraction of lipids

The tubers were chilled to 0°C before extraction. They were peeled and cut into strips in a Philips food processor (HR 2373/B, 0·6 litres). Approximately 20 g of the strips were immediately refluxed in methanol/water (4:1, v/v) for 5 min as described by Galliard (1972) to inactivate the enzymes. The refluxed mixture was chilled on ice for 10 min and homogenized with an Ultra Turrax for 1 min at fast speed. After homogenization the lipids were extracted using the Bligh & Dyer (1959) method. The weights of the samples were

determined by weighing the tubers before peeling and then weighing peels and waste at once after the samples were taken. The potato granules, 4·0 g, were extracted in the same way except for the heat treatment.

The water content of the potato strips and the potato granules was analysed by weighing the samples before and after drying at 110°C for 1 h.

Fractionating of lipids

The lipids were fractionated into the three major lipid classes; neutral lipids, galactolipids and phospholipids, on a silicic acid column (Mallincrodt CC4 Special) as described by Rouser *et al.* (1967).

The free fatty acids were separated from the neutral lipids by HPLC as described by Chen & Chan (1985). A Shimadzu SCL 6A instrument equipped with a silica acid column (CPtm SPHERESi, 100 × 3·0 mm, 8 μm part., Chrompack, Holland) and an UV-detector (Shimadzu SPD6AV, 205 nm) was used. Hexane/propane-2-ol (6:8, v/v) was used as the mobile phase at a flow rate of 1 ml/min. Linoleic acid was used as a standard for the identification of the retention time of the free fatty acid peak. The free fatty acids from three runs were combined for gas chromatographic analysis of fatty acid composition.

A general scheme of the fractionations is shown in Fig. 2.

Gas chromatographic analysis of fatty acid composition

The fatty acid composition of the three lipid classes and the free fatty acid fraction was analysed by gas chromatography after the fatty acids had been converted into methyl esters. They were methanolysed in 2·5% HCl (g) in methanol (w/w) at 70°C for 1 h, as described by Liljenberg & Kates (1985).

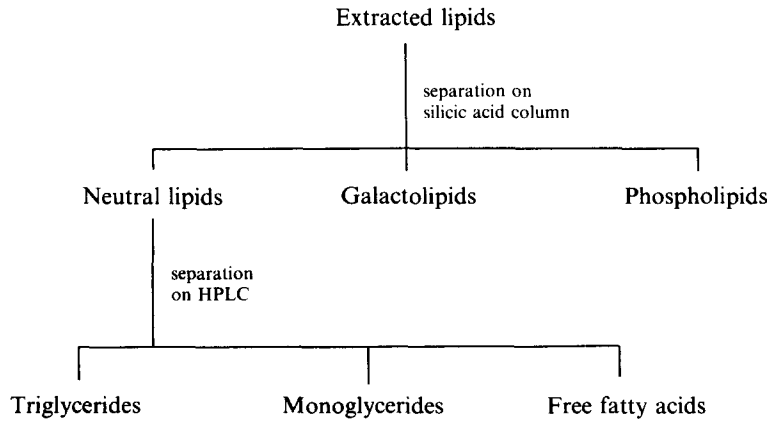

Fig. 2. Lipid separation scheme.

Heptadecanoic acid was used as an internal standard. The methyl esters were analysed by a Hewlett Packard 5890 gas chromatograph using a fused silica capillary column (NB 351, phase thickness 0·20 μm, i.d. 0·32 mm × 25 m, Nordion, Finland). The injection was done in split mode (1:8, 200°C) and with helium as the carrier gas (33 ml/min). The gas chromatograph was temperature programmed, 160–200°C, at a rate of 25°C/min. A flame ionisation detector was used (220°C). The methyl esters were identified by comparing their retention times with known standards and quantified by the use of the internal standard. The identification was verified by using a gas chromatography/mass spectrometry system (Finnigan 9610-4023) with the same column. Operating conditions were: ionising voltage, 70 eV and ion source temperature, 270°C. The mass spectra identification was made using the National Bureau of Standards library of references. The original amounts of lipids in the three lipid classes were calculated on the basis of the fatty acid analyses.

RESULTS AND DISCUSSION

Lipid analyses were made on fresh tubers, potato granules with no added monoglycerides and commercial potato granules.

Contents of neutral lipids, galactolipids and phospholipids

Figure 3 shows the amounts of the three main lipid classes in the tubers, in the commercial potato granules and in the potato granules with no added monoglycerides. No lipid losses during the process could be found. The amounts of galactolipids and phospholipids were quite similar in the three materials while there was 3–4 times as much neutral lipids in the commercial potato granules compared with tubers and pilot plant produced potato granules. This discrepancy was due to the added monoglycerides. The results shown in Fig. 3 are means based on at least five analyses of potato granules and at least ten analyses of tubers. The largest standard deviation was found within the potato samples, due to the variation between individual tubers.

Pun & Hadziyev (1978) reported that the total lipid content was reduced by 14·7% during the freeze–thaw-process. The neutral lipids and the phospholipids were the most affected. However, similar changes could not be observed in this study.

Fatty acid composition of the three lipid classes

The fatty acid composition of the three lipid classes is shown in Table 1. As a comparison the fatty acid composition of the monoglycerides used in the

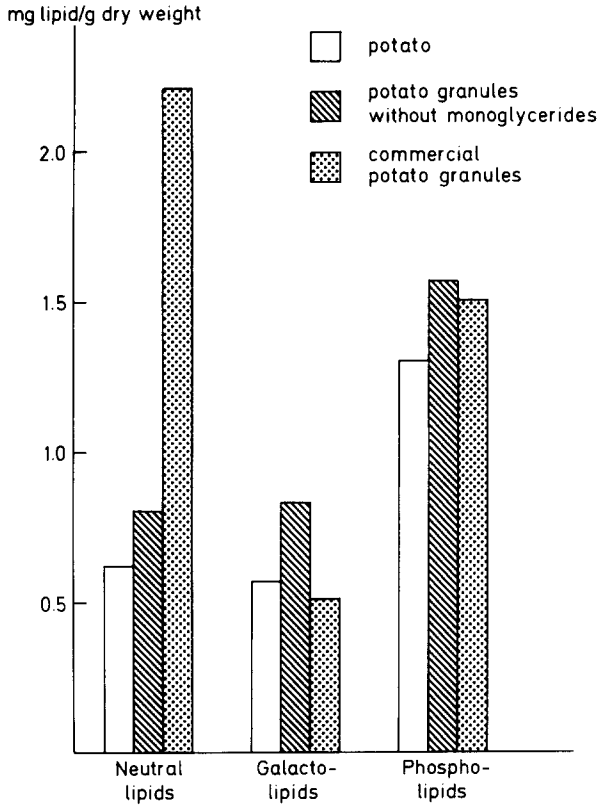

Fig. 3. Amounts of the three major lipid classes in the potato tubers and the potato granules.

commercial process is included in the Table. The galactolipids and the phospholipids were quite unaffected by the manufacturing process. If lipids were oxidised during the process, the amounts of the polyunsaturated fatty acids, linoleic and linolenic acid (C18:2 and C18:3) would be expected to decrease. However, no such change could be observed in the galactolipids or in the phospholipids.

The neutral lipids of the commercial potato granules and the raw potatoes are difficult to compare since the addition of monoglycerides in the commercial process resulted in high amounts of saturated fatty acids, mainly palmitic acid (C16:0) and stearic acid (C18:0). The fatty acid composition of the neutral lipids is also shown in Fig. 4 presenting the amounts as μg per g of dry weight of tubers and potato granules.

From Fig. 4 it can be concluded that linoleic acid (C18:2) and linolenic acid (C18:3) in the neutral lipids, as well, were unaffected by either the commercial process or the pilot plant process.

Palmitic acid (C16:0) and stearic acid (C18:0) were the dominating fatty

TABLE 1

The Fatty Acid Composition (%) of the Lipid Classes in Raw Potato, Potato Granules (with no added monoglycerides) and Commercial Potato Granules. (The fatty acid composition of the monoglycerides used in the commercial process is shown as well. The standard deviations are shown in parentheses. The values correspond to at least ten potato samples, and at least five samples of potato granules.)

Fatty acid	*Neutral lipids*				*Galactolipids*			*Phospholipids*		
	Raw potato	*Potato granules without mono-glycerides*	*Commercial potato granules*	*Mono-glycerides*	*Raw potato*	*Potato granules without mono-glycerides*	*Commercial potato granules*	*Raw potato*	*Potato granules without mono-glycerides*	*Commercial potato granules*
C8:0	—	—	—	0·02 (0·01)						
C10:0	—	—	0·11 (0·04)	0·07 (0·003)						
C12:0	0·03 (0·04)	0·10 (0·02)	0·41 (0·06)	0·03 (0·05)						
C14:0	0·39 (0·12)	1·09 (0·05)	2·29 (0·26)	3·46 (0·22)	0·08 (0·05)	0·14 (0·07)	0·13 (0·03)	0·17 (0·02)	0·14 (0·01)	0·21 (0·03)
C16:0	15·22 (1·84)	18·47 (1·02)	21·00 (1·73)	30·06 (1·22)	12·06 (1·59)	13·36 (2·09)	11·74 (0·40)	20·48 (0·98)	20·19 (0·24)	19·46 (0·29)
C16:1	0·03 (0·05)	0·10 (0·14)	0·20 (0·08)	0·01 (0·007)	0·13 (0·17)	0·06 (0·06)	0·09 (0·08)	0·11 (0·09)	0·14 (0·06)	0·15 (0·12)
C18:0	4·93 (0·54)	20·20 (0·50)	34·94 (1·30)	66·24 (1·45)	7·38 (0·75)	7·70 (0·68)	8·15 (0·37)	5·92 (0·31)	5·98 (0·11)	6·46 (0·14)
C18:1	5·13 (3·48)	1·80 (1·22)	18·57 (4·30)	0·007 (0·006)	0·42 (0·24)	0·34 (0·04)	0·63 (0·22)	0·29 (0·08)	0·44 (0·10)	1·56 (0·32)
C18:2	38·96 (4·36)	31·24 (0·80)	12·74 (1·61)	0·11 (0·10)	51·13 (3·88)	49·12 (1·65)	52·07 (0·47)	50·27 (2·54)	49·56 (0·16)	48·99 (0·41)
C18:3	35·34 (3·22)	27·11 (1·22)	9·95 (1·88)	—	28·94 (3·42)	29·35 (1·29)	27·29 (1·19)	22·86 (2·79)	23·70 (0·36)	23·31 (0·17)

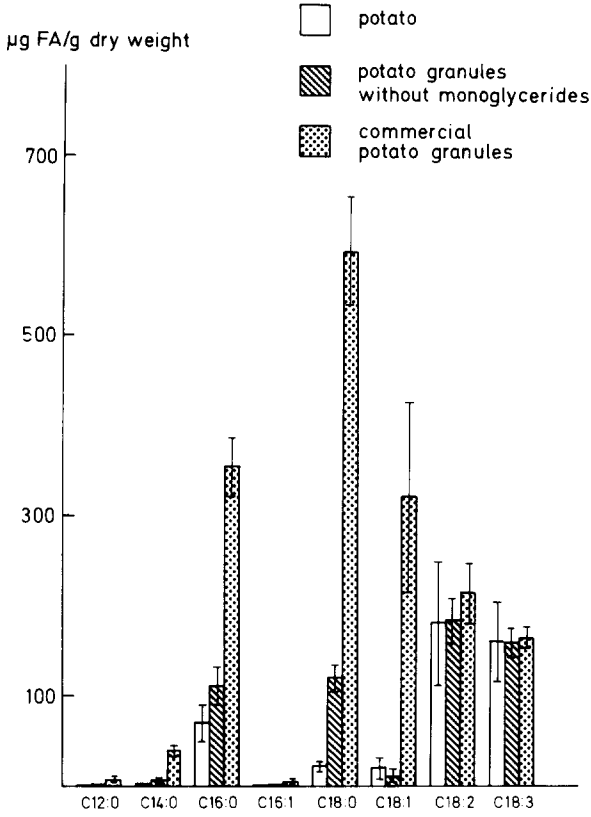

Fig. 4. The fatty acid composition of the neutral lipids in the potato tubers and in the potato granules.

acids in the neutral lipids of the commercial potato granules as a result of the added monoglycerides. However, Fig. 4 shows that even the pilot plant-processed potato granules contained higher amounts of palmitic and stearic acid than the raw potatoes did. The relation between the extra C16:0 and C18:0 is very similar to the relation between these fatty acids in the added monoglycerides, indicating that the monoglycerides contaminate these potato granules as well. The explanation may be that we had to use commercial potato granules with added monoglycerides to start the pilot plant. (Previously produced granules are always needed when an add-back-process is started.) Some of the original material may remain in the process equipment for a considerable time. Our samples were taken after the process had been going on for about 40 h. According to the results shown in Fig. 4 the pilot plant-processed potato granules still contained approximately 10% of the original commercial granules. This is also in accordance with the higher bar for neutral lipids in Fig. 3. However, another explanation for this could be that the lipids were more easily extracted from the potato granules than from the tubers.

In addition Table 1 and Fig. 4 show a high amount of oleic acid (C18:1) in the commercial potato granules. As seen in Table 1, there was a poor reproducibility in the analysis of this fatty acid. The mass spectrometry showed that this peak contained more than oleic acid. The presence of at least one aldehyde (6,12-octadecadienal) was indicated in the same peak.

The fatty acid composition of potato lipids may vary between different varieties of potato and even between individual potato tubers. On the whole our results show very similar fatty acid patterns to previous reports by Pun & Hadziyev (1978) and Galliard (1973) except for the amount of linolenic acid (C18:3) which was higher in our study.

The content and composition of free fatty acids

In Fig. 5 is shown the composition of the free fatty acids in the raw potatoes and the potato granules. The free fatty acid contents were 10·17, 104·4 and 100·1 (μg fatty acids/g dry matter) in potato tubers, commercial potato granules and pilot plant produced potato granules, respectively. It is obvious that free fatty acids were released during the process, in the commercial granules as well as in the pilot plant-produced granules. The potato granules

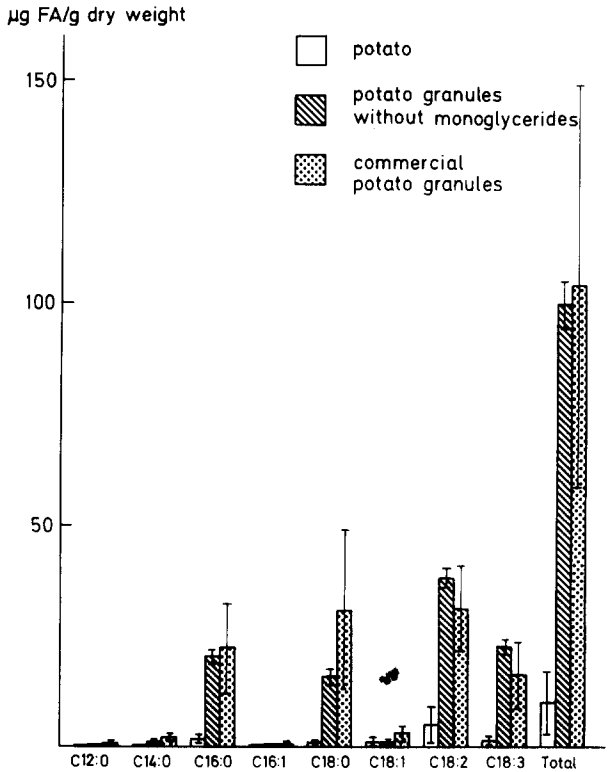

Fig. 5. Amounts and composition of the free fatty acids in the potato tubers and in the potato granules.

contained approximately ten times more free fatty acids than the potato tubers. Palmitic, stearic, linoleic and linolenic acid were the main free fatty acids released. These were also the main acids of the intact lipids. Hence, no specificity in the formation of free fatty acids could be noticed. These results are different from those of Pun & Hadziyev (1978) who reported the amount of free fatty acids to slightly decrease during the freeze–thaw-process (from 150 μg/g dry matter to 115 μg/g dry matter). However, in that study the original amounts of free fatty acids in the potato tubers were obviously considerably higher.

One probable reason for the liberation of free fatty acids might be that the potato tuber contains high activity of lipolytic acylhydrolase (Galliard & Matthew, 1973). This may cause lipid hydrolysis especially during the first part of the process before this enzyme is inactivated.

The free fatty acid content may be of importance for the further stability of the potato granules during storage. Free fatty acids in general are likely to be more easily oxidised than the fatty acids bound to the glycerol backbone of the triglycerides, galactolipids and phospholipids, since they are more mobile and more hydrophilic, which increases the possibilities of contact with oxygen and water-soluble pro-oxidants. In pure oil systems free fatty acids also have been reported to increase the oxidation (Popov & Mizev, 1966; Catalano & De Felice, 1970).

Therefore, it is likely that the storage stability of potato granules can be improved by minimising the lipid hydrolysis during the process. Studies on the rôle of free fatty acids during storage are in progress.

CONCLUSIONS

The add-back-process did not cause changes in the amounts and composition of fatty acids in the galactolipids or the phospholipids. Neutral lipids were difficult to compare due to the addition of monoglycerides.

Free fatty acids were released during the process. The contents of free fatty acids were about ten times higher in the potato granules than in the potato tubers.

ACKNOWLEDGEMENTS

The project was supported by AB Felix and by the National Swedish Board for Technical Development.

REFERENCES

Bligh, E. G. & Dyer, W. J. (1959). A rapid method of total lipid extraction and purification. *Can. J. Biochem. Phys.*, **37**(8), 911–17.

Buttery, R. G., Hendel, C. E. & Boggs, M. M. (1961). Off-flavours in potato products. Autoxidation of potato granules. *J. Agric. Food. Chem.*, **9**(3), 245–52.

Catalano, M. & De Felice, M. (1970). Autoxidation of fats. I. Influence of free fatty acids. *Riv. Ital. Sostanze Grasse*, **47**(10), 484–92. (*Chem. Abs.* (1971), **74**, 375, 98425t.).

Chen, S. F. & Chan, P. H. (1985). One-step separation of free fatty acids and phospholipids in brain tissue extracts by high-performance liquid chromatography. *J. Chrom.*, **344**, 297–303.

Galliard, T. (1972). Fatty acid composition of immature potato tubers. *Phytochem.*, **11**, 1899–1903.

Galliard, T. (1973). Lipids of potato tubers. I. Lipid and fatty acid composition of tubers from different varieties of potato. *J. Sci. Food Agric.*, **24**, 617–22.

Galliard, T. & Matthew, J. A. (1973). Lipids of potato tubers. II. Lipid degrading enzymes in different varieties of potato tuber. *J. Sci. Food Agric.*, **24**, 623–27.

Konstance, R. P., Sullivan, J. F., Talley, F. B., Calhoun, M. J. & Craig, J. C., Jr (1978). Flavour and storage stability of explosion-puffed potatoes: Autoxidation. *J. Food Sci.*, **43**, 411–14.

Liljenberg, C. & Kates, M. (1985). Changes in lipid composition of oat root membranes as a function of water-deficit stress. *Can. J. Biochem. Cell. Biol.*, **63**, 77–84.

Liljenberg, C., Sandelius, A.-S., & Selstam, E. (1978). Effect of storage in darkness and in light on the content of membrane lipids of potato tubers. *Physiol. Plant.*, **43**, 154–9.

Lisberg, G. & Chen, T.-S. (1973). Storage stability of dehydrated potato granules packaged in cans and cartons. *J. Food Sci.*, **38**, 363–4.

Ooraikul, B. & Moledina, K. H. (1981). Physicochemical changes in potato granules during storage. *J. Food Sci.*, **46**, 110–16.

Popov, A. D. & Mizev, I. D. (1966). Pro-oxidative action of free fatty acids in the autoxidation of fats. *Rev. Fr. Corps Gras*, **13**(10), 621–6. (*Chem. Abs.* (1967), **66**, 1200, 12134x.)

Pun, W. H. & Hadziyev, D. (1978). Lipids in raw and granulated potatoes. *J. Inst. Can. Sci. Technol. Aliment.*, **11**(3), 134–41.

Quast, D. G. & Karel, M. (1972). Effects of environmental factors on the oxidation of potato chips. *J. Food Sci.*, **37**, 584–8.

Rouser, G., Kritchevsky, G., Simon, G. & Nelson, G. J. (1967). Quantitative analysis of brain and spinach leaf lipids employing silicic acid column chromatography and acetone for elution of glycolipids. *Lipids*, **2**(1), 37–40.

Sapers, G. M., Panasiuk, O., Talley, F. B. & Osman, S. F. (1972). Flavour quality and stability of potato flakes. Volatile components associated with storage changes. *J. Food Sci.*, **37**, 579–83.

Sapers, G. M., Panasiuk, O. & Talley, F. B. (1973). Flavour quality and stability of potato flakes. Effects of raw material and processing. *J. Food Sci.*, **38**, 586–9.

Sapers, G. M., Panasiuk, O. & Talley, F. B. (1974). Flavour quality and stability of potato flakes: Effects of drying conditions, moisture content and packaging. *J. Food Sci.*, **39**, 555–8.

Sullivan, J. F., Konstance, R. P., Calhoun, M. J., Talley, F. B., Cording, J., Jr & Panasiuk, O. (1974). Flavour and storage stability of explosion-puffed potatoes: Non-enzymatic browning. *J. Food Sci.*, **39**, 58–60.