

PHYSICAL AND CHEMICAL PARAMETERS OF LATVIAN FRESH CRANBERRIES

Karina Ruse, Tatjana Rakcejeva

*Department of Food Technology, Faculty of Food Technology, Latvia University of Agriculture, Liela iela 2, Jelgava, Latvia,
e-mail: karinaruse@inbox.lv*

Abstract

Cranberries belong to a group of evergreen dwarf shrubs or trailing vines in the genus *Vaccinium* subgenus *Oxycoccus*. Berries contain a diverse array of nutrients with recognized biological activities that promote or contribute to health. The aim of the research was to evaluate physically-chemical parameters of Latvian fresh cranberries. The research was accomplished on fresh Latvian wild and large-berry cranberries harvested in Kurzeme region: wild cranberries and large-berry cranberries variety 'Steven', 'Ben Lear', 'Bergman', 'Pilgrim' and 'Early Black'. The following quality parameters of cranberries were analysed using standard methods: anthocyanins (spectrophotometric), colour (using the colour system CIE L* a* b*), organic acids (high-performance liquid chromatography (HPLC)), polyphenols (HPLC), and pH value (LVS ISO 1132:2001). The research results confirm a close interaction (strong positive correlation ($r=0.919$) between the colour a* component intensity and anthocyanin content. The highest content of benzoic acid was determined in large-berry cranberries of the cultivar 'Early Black' – 13.66 mg 100 g⁻¹, which was by 56% higher than in wild cranberries – 5.98 mg 100 g⁻¹, and by 65% higher than in the cultivar 'Steven' berries – 4.82 mg 100 g⁻¹. The highest content of polyphenol compounds was found in cranberries of the cultivars 'Pilgrim', 'Early Black', and 'Steven'; while the lowest – in cranberries of the cultivar 'Bergman'. The average pH value for all samples was 2.465; it is slightly lower than found in the scientific literature.

Keywords: anthocyanins, organic acids, polyphenols, cranberries.

Introduction

Cranberries are extremely versatile berries. When incorporated into other food products, they provide refreshing flavour as well as a characteristic red colour. Used in combination with other fruits and berries, cranberries can accentuate and enhance the flavours of these fruits and berries. Because of their health gains, cranberries are experiencing an expansion into the food and beverage industry. Available year-round and in a variety of forms, cranberries can be used to improve numerous products and applications in the food and beverage industry (Hui et al., 2006).

Anthocyanins (of the Greek *anthos* = flower and *kianos* = blue) are the most important pigments of the vascular plants; they are harmless and of easy incorporation in aqueous media, which makes them interesting for its use as natural water-soluble colorants (Pazmiño-Durán et al., 2001). Anthocyanins are glycosylated polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium (flavylium) salt which are natural colorants widely distributed in nature (Bordignon-Luiz et al., 2007; Hendry, Houghton 1996). Many researches indicate that anthocyanins are not only nontoxic and nonmutagenic, but they have positive therapeutic properties such as antioxidant, anti-inflammatory, anticarcinogenic, antiviral, and antibacterial properties (Tall et al., 2004).

A limiting factor for the incorporation of anthocyanins in foods is the low stability of these pigments which are influenced by several factors: most important the pH of a system. They are susceptible to light and temperature, different agents can also cause their degradation (oxygen, enzymes etc.) (Jackman, Smith, 1996). The content of anthocyanins in cranberries equals to 20–360 mg·100 g⁻¹ (Wang, Stretch, 2001; Prior et al., 2001).

Colour is an important factor in the consumer's choice

of food products. It is one of the most important characteristics used to define the quality of food and has a decisive influence on the acceptance by the consumer (Hendry et al., 1996). CIELab is a nonlinear transformation of XYZ into coordinates L*, a*, b* and it is used for the colour measurement interpretation (Hoffmann, 2008).

Organic acids are primary metabolites, which can be found in great amounts in all plants, especially in berries. Organic acids are naturally found in fruits and berries. Many berries contain a variety of free acids which are colourless compounds soluble in water, ethanol; but insoluble in the nonpolar solvents benzene or petroleum ether. These acids are weakly acidic and can accumulate in the cellular vacuoles of plants. Some of the acids are components of the citric acid cycle, while others are intermediates in the pathway leading from carbohydrates to either aromatic compounds or isoprenoid derivatives (Arslan, Özcan, 2011; Dashek, Micales, 1997). Organic acids are biologically important because they form part of different biochemical metabolic routes such as the Krebs cycle (Arslan, Özcan, 2011; Silva et al., 1991). The concentration of organic acids is an important factor influencing the organoleptic properties of berries (Koyuncu, Dilmaçunal, 2010; Lee, 1993).

Phenolic compounds are secondary metabolites that are derivatives of the pentose phosphate and phenylpropanoid pathway in plants. These compounds one of the most widely occurring groups of phytochemicals are of considerable physiological and morphological importance in plants (Pupponen-Pimia, 2001). Many small fruit phenolic compounds are good sources of natural antioxidants and have inhibitory effects on mutagenesis and carcinogenesis. During the past decades, extensive analytical research has been carried out on the separation and determination of

phenolic constituents in various fresh fruit products and environmental samples. The unique antibacterial activities of cranberry implicate that cranberry may possess a very different flavonoid and phenolic composition from other kinds of fruits. An efficient separation and quantitation method is essential for understanding the components of flavonoid and phenolic antioxidants in cranberry and their health benefits. Phenolic compounds are not temperature resistant; therefore treatment at elevated temperatures will negatively influence polyphenol compound activity (Chen et al., 2001).

Therefore the aim of the current research was to evaluate physically-chemical parameters of Latvian fresh cranberries.

Materials and Methods

The research was accomplished on fresh Latvian wild and large-berry cranberries harvested in Kurzeme region in 2010: wild cranberries and large-berry cranberries variety 'Steven', 'Ben Lear', 'Bergman', 'Pilgrim' and 'Early Black'.

During the experiments, the following quality parameters of cranberries were controlled using standard methods:

- anthocyanins were determined by means of "Spectrophotometer Anthocyanins Determination Method" using a 6705 UV/VIS Spectrophotometer JENWAY (Bordignon-Luiz et al., 2007);
- a colour parameters of fresh cranberries were determined by direct reading with a COLOR TEC PMC. The colour parameters such as luminance (L^*) ranging from 0 (black) to 100 (white) on a vertical axis, red saturation index (a^*), and yellow saturation index (b^*), were evaluated (McGuire, 1992);
- pH of berries was measured using potentiometric method LVS ISO 1132:2001 using Jenway 3510 pH metre. Prior to the determination of pH, cranberries were chopped by the blender; organic acids were extracted with water using the method of Hernandez et al. (2009);
- phenolic compounds were determined using a high-performance liquid chromatography (HPLC) with UV detection (at 280 nm) (Berregi et al., 2003).

Microsoft Excel software was used for the research purpose to calculate mean arithmetical values and standard deviations of the mathematical data used in the research. SPSS 20.0 software was used to determine the significance of research results, which were analysed using the following test methods: Sheffe test, two-factor ANOVA, and three-factor ANOVA analyses to explore the impact of factors and their interaction, and the significance effect (p-value).

Results and Discussion

Anthocyanins

The anthocyanins give to cranberries bright red colour and work like antioxidant. The changes of temperature during berries growing are closely related with low

content of anthocyanins in the cranberries. For example, the high temperature inhibits the formation of anthocyanins in the berries (Prior et al., 2001). During present research it was detected that the highest anthocyanin content was in large-berry cranberries variety 'Pilgrim' and 'Early Black', respectively $898 \pm 12 \text{ mg } 100 \text{ g}^{-1}$ and $839 \pm 8 \text{ mg } 100 \text{ g}^{-1}$ in dry matter what was by 66% and 63% higher comparing to anthocyanin content in wild cranberries. The lowest anthocyanin content was detected in wild cranberries, as $306 \pm 4 \text{ mg } 100 \text{ g}^{-1}$ (Figure 1), and in large-berry cranberries variety 'Ben Lear' – $492 \pm 4 \text{ mg } 100 \text{ g}^{-1}$. Obtained results suggest that in the large-berry cranberries varieties 'Pilgrim' and 'Early Black' is the lowest red pigment intensity – they are not so red.

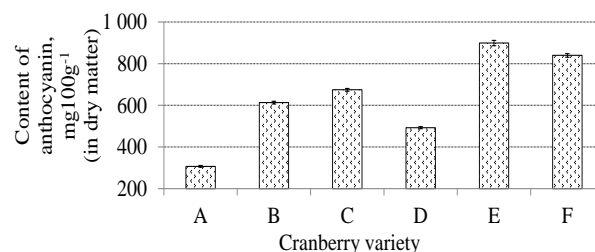


Figure 1. Content of anthocyanins

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

In scientific literature is mentioned, that the anthocyanin content in Latvian large cranberries is in the range from 186 mg% to 604 mg% (Ripa, 1992). Different results were obtained by Wang, Stretch (2001) and Prior et al., (2001), where anthocyanin content in cranberries is in the range from 360 mg 100 g⁻¹. Such differences could be explained with the berry cultivar and the characteristics of growing conditions.

Intensity of colour compounds

The L^* colour compound value indicates colour saturation level in the product. The research data show, that the colour of wild cranberries (23.39 ± 1.22) is darker then colour of large-berry cranberries (Figure 2). If compare the large-berry cranberries 'Steven' and wild cranberries, the 'Steven' berries are brighter – L^* colour compound value is 17.00 ± 0.69 .

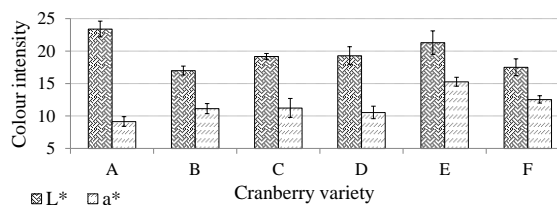


Figure 2. Intensity of L^* and a^* colour

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

The a^* colour compound value mainly indicate the red colour of product. As results of the current research demonstrate, cranberry of variety 'Pilgrim' are redder

(a^* colour compound value is 15.28 ± 0.74) (Figure 3). The 'Pilgrim' berries red colour is on average by 40% higher comparing to wild cranberries – the red colour value was 9.15 ± 0.69 . Red colour intensity changes are closely related with the anthocyanins content in the berries. It is the reason, why large cranberries have more pronounced colours (Figure 1), what mainly could be explained with higher content of anthocyanins in berries.

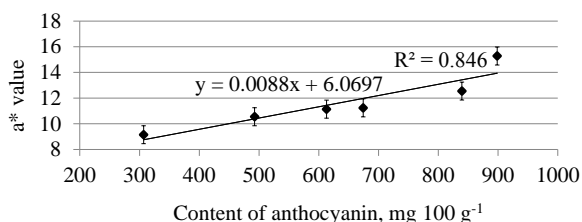


Figure 3. The a^* colour intensity and anthocyanin content correlation analysis of fresh cranberries

The research results confirm a good correlation ($r=0.919$) (Figure 3) between the colour a^* component intensity and anthocyanin content in analysed cranberries.

pH

Significant difference in pH value was detected between cranberries varieties 'Steven' and 'Pilgrim' ($p=0.020$; $\alpha=0.050$), and between 'Steven' and 'Early Black' ($p=0.020$; $\alpha=0.050$) (Figure 4). The average pH value for all berries samples was 2.465; it is slightly lower than found in the scientific literature – the pH value of cranberry juice is 3.000 (Ripa, 1992).

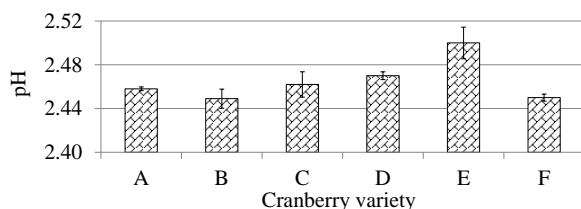


Figure 4. pH value

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

Possible presence and abundance of organic acids, mainly citric, malic, quinic, and benzoic acids, are responsible for cranberries characteristically low pH (Figure 4). These acids also aid in the stabilization and protection of anthocyanins, and help protect the much desired red color of cranberries. In theory, the pH should also affect the cranberry phenolic ability to inhibit lipid peroxidation and their free radical-scavenging capacity (Cailleta et al., 2011).

Organic acids

Cranberries are rich in bioactive components, such as, phenols and organic acids, which can provide berry antimicrobial activity (Puupponen-Pimia et al., 2001; Rauha et al., 2000).

Organic acids were determined in cranberries as follow: tartaric acid, quinic acid, malic acid, succinic acid, benzoic acid (Fig. 5).

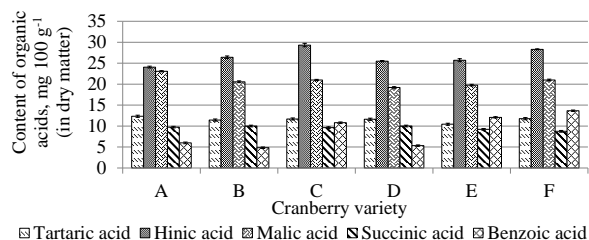


Figure 5. Content of organic acids

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

It should be noted that the benzoic acid content is one of the most important parameters for berry bactericidal properties. The highest content of benzoic acid was determined in large-berry cranberries of the variety 'Early Black' – $13.66 \text{ mg } 100 \text{ g}^{-1}$, which was by 56% higher than in wild cranberries – $5.98 \text{ mg } 100 \text{ g}^{-1}$, and by 56% higher than in the variety 'Steven' berries – $4.82 \text{ mg } 100 \text{ g}^{-1}$ (Figure 5). The mathematical data processing outlines that the benzoic acid content is significantly different in all cranberry varieties ($p=0.0001$; $\alpha=0.0500$), except wild cranberries and cranberries of the variety 'Ben Lear' ($p=0.0430$; $\alpha=0.0500$). There are no significant differences between the large-berry variety 'Steven' and 'Ben Lear' ($p=0.0500$; $\alpha=0.0500$) cranberries.

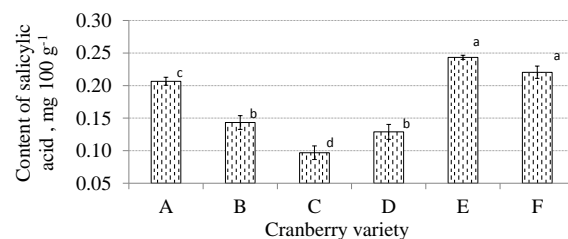


Figure 6. Content of salicylic acid

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

The highest salicylic acid content was found in cranberry variety 'Pilgrim' – $0.2434 \pm 0.0032 \text{ mg } 100 \text{ g}^{-1}$ it was by 15% higher comparing to salicylic acid content in wild cranberries – $0.2066 \pm 0.0062 \text{ mg } 100 \text{ g}^{-1}$ and by 60% higher comparing to salicylic acid content in 'Bergman' cranberries – $0.0968 \pm 0.0105 \text{ mg } 100 \text{ g}^{-1}$ in dry matter (Figure 6). In the present research it was proved, that in cranberries is highest hinic acid content ($24.0000\text{--}29.0000 \text{ mg } 100 \text{ g}^{-1}$) (Figure 5), however lowest (Figure 6) – salicylic acid content ($0.0968\text{--}0.2434 \text{ mg } 100 \text{ g}^{-1}$). Such difference mainly could be explained with individuality of the variety (Celik et al., 2008).

Polyphenols

The most important polyphenol function is protection of plant decay modes (Dixon, Paiva, 1995; Bennet, Wallsgrave, 1994). There are caused by phenol

changes, like excessive exposure to UV light, mechanical damage or microbial infection. The environmental factors have the significant effect on the content of phenolic compounds in berries. Within present research it was established that in cranberry more popular polyphenols are rutin, catechin, caffeic acid and chlorogenic acid (Figure 7).

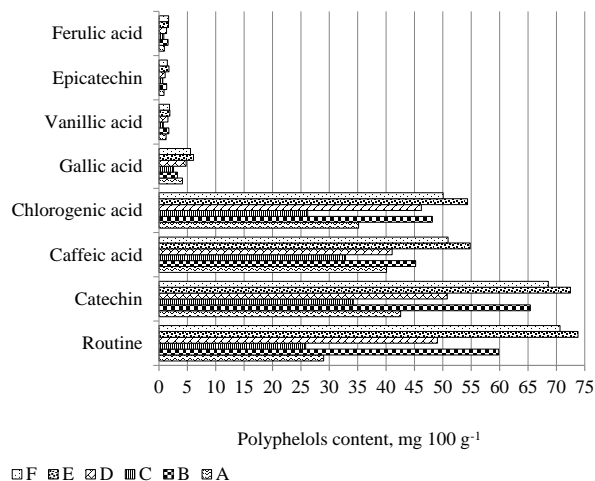


Figure 7. Content of polyphenols in fresh cranberries (in dry matter)

A – wild, B – 'Steven', C – 'Bergman', D – 'Ben Lear', E – 'Pilgrim', F – 'Early Black'

The highest content of analysed compounds was found in cranberries of the variety 'Pilgrim', 'Early Black', and 'Steven'; while the lowest – in cranberries of the variety 'Bergman' (Figure 7). There is a significant difference ($p=0.0001$, $\alpha=0.0500$) in the content of polyphenol in cranberries.

Conclusions

The highest anthocyanin content was found in cranberry varieties 'Pilgrim' and 'Early Black', the lowest in wild cranberries.

The colour of wild cranberries is darker than the colour of large-berry cranberries.

The highest content of benzoic acid was determined in large-berry cranberries of the variety 'Early Black', which was by 56% higher than in wild cranberries – 5.98 mg 100 g⁻¹, and by 56% higher than in the variety 'Steven' berries – 4.82 mg 100 g⁻¹ in dry matter.

The highest salicylic acid content was found in cranberry variety 'Pilgrim' berries; it was by 15% higher comparing to salicylic acid content in wild cranberries and by 60% higher comparing to salicylic acid content in 'Bergman' cranberries.

The highest content of polyphenol compounds was found in cranberries of the variety 'Pilgrim', 'Early Black', and 'Steven'; while the lowest – in cranberries of the variety 'Bergman'.

Acknowledgment

The research and publication has been prepared within the framework of the ESF Project "Formation of the Research Group in Food Science", Contract No. 2009/0232/1DP/1.1.1.2.0/09/APIA/VIAA/122.

The research and publication has been prepared within the framework of the ESF Project "Support for LLU doctoral studies implementation", Contract No. 2009/0180/1DP/1.1.2.1.2/09/IPIA/VIAA/017.

The authors would like to express acknowledgements to Fredijs Dimins from Latvia University of Agriculture, Department of Chemistry, for technical advice in organic acids and polyphenol determination.

References

- Arslan D., Özcan M.M. (2011) Influence of growing area and harvest date on the organic acid composition of olive fruits from Gemlik variety. *Journal of Scientia Horticulturae*, Vol. 130, p. 633–641.
- Bennet R.C., Wallsgrave R.M. (1994) Secondary metabolites in plant defence mechanisms. *Tansley Review*, No. 72. *New Phytol*, Vol. 127, p. 617–633.
- Berregi I., Santos J. I., Gloria del Campo, Miranda J.I. (2003) Quantitative Determination of (-)- Epicatechin in Cider Apple Juice by HNMR. *Talanta*, Vol. 61, Iss. 2, p. 139–145.
- Bordignon-Luiz M.T., Gauche C., Gris E.F., Falcao L.D. (2007) Colour stability of anthocyanins from Isabel Grapes (*Vitis labrusca L.*) in model systems. *LWT-Food Science and Technology*, Vol. 40, Iss. 4, p. 594–599.
- Cailleta S., Côté J., Doyonb G., Sylvainc J.-F., Lacroixa M. (2011) Antioxidant and antiradical properties of cranberry juice and extracts. *Food Research International*, Vol. 44, Iss. 5, p. 1408–1413.
- Celik H., Ozgen M., Serce S., Kaya C. (2008) Phytochemical accumulation and antioxidant capacity at four maturity stages of cranberry fruit. *Journal of Scientia Horticulturae*, Vol. 117, p. 345–348.
- Chen H., Zuo Y., Deng Y. (2001) Separation and determination of flavonoids and other phenolic compounds in cranberry Juice by high-performance liquid chromatography. *Journal of Chromatography A*, Vol. 913, Iss. 1–2, p. 387–395.
- Dashek W.V., Micales A.M. (1997) Methods in plant biochemistry and molecular biology. **In:** *Isolation, Separation, and Characterization of organic Acids*. Dashek W.V. (Ed.), CRC Press, Boca Ration, FL, USA, p. 107–113.
- Dixon R.A., Paiva N.L. (1995) Stress-induced phenylpropanoid metabolism. *Journal of Plant Cell*, Vol. 7, p. 1085–1097.
- Hendry G.A., Houghton J.D. (1996) *Natural Food Colorants*. Glasgow: Backie Academic and Professional. p. 348.
- Hernandez Y., Lobo M.G., Gonzalez M. (2009) Factors affecting sample extraction in the liquid chromatographic determination of organic acids in papaya and pineapple. *Food Chemistry*, Vol. 114, Iss. 2, p. 734–741.
- Hoffmann G. (2008) *CIELab Color Space*. p. 2–3.
- Hui H.Y., Barta J., Pilar Cano M., Gusek T., Sidhu J.S., Sinha N. (2006) *Handbook of Fruits and Fruit Processing*. USA: Blackwell Publishing. 697 p.
- Jackman R.L., Smith J.L. (1996) *Natural Food Colourants*. Glasgow: London, p. 244–309.

15. Koyuncu M.A., Dilmaçunal T. (2010) Determination of vitamin C and organic acid changes in strawberry by HPLC during cold storage. *Journal Notulae Botanicae Horti Agrobotanici Cluj-Napoca*, Vol. 38 Iss. 3, p. 95–98.
16. Lee H.S. (1993) HPLC method for separation and determination of non-volatile organic acids in orange juice. *Journal of Agriculture and Food Chemistry*, Vol. 41, p. 1991–1993.
17. McGuire R.G. (1992) Reporting of objective color measurements. *Journal of Horticultural Science*, Vol. 27, p. 1254–1255.
18. Pazmiño-Durán A.E., Giusti M.M., Wrolstad R.E., Glória B.A. (2001) Anthocyanins from oxalis triangularis as potential food colorants. *Journal of Food Chemistry*, Vol. 75, Iss. 2, p.211–216.
19. Prior R.L., Lazarus S.A., Cao G., Muccitelli H., Hammerstone J.F. (2001) Identification of procyanidins and anthocyanins in blueberries and cranberries (*Vaccinium Spp.*) using high-performance liquid chromatography/mass spectrometry. *Journal of Agricultural and Food Chemistry*, Vol. 49, p. 1270–1276.
20. Puupponen-Pimia R., Nohynek L., Meier C., Kahkonen M., Hoinonen M., Hopia A., Oksman-Caldentey K.M. (2001) Antimicrobial properties of phenolic compounds from Finnish berries. *Journal of Applied Microbiology*, Vol. 90, p. 494–507.
21. Rauha J.P., Remes S., Heinonen M., Hopia A., Kahkonen M., Kujala T., Pihlaja K., Vuorela H., Vuorela P. (2000) Antimicrobial effects of Finish plant extracts containing flavonoids and other phenolic compounds. *International Journal of Food Microbiology*, Vol. 56, p. 3–12.
22. Ripa A. (1992) *Cranberries, bog bilberry, cowberry in the garden*. Riga: Avots. 104 p. (in Latvian)
23. Silva G.H., Chase R.W., Hammercshmidt R., Cash J.N. (1991) After-cooking darkening of Spartan Pearl potatoes as influenced by location, phenolic acids, and citric acid. *Journal of Agricultural and Food Chemistry*, Vol. 39, p. 871–873.
24. Tall J.M., Seeram N.P., Zhao C., Nair M.G., Meyer R.A., Raja S.N. (2004) Tart cherry anthocyanins suppress inflammation-induced pain behaviour in rat. *Journal of Behaviour Brain Research*, Vol. 153, Iss. 1, p. 181–188.
25. Wang S.J., Stretch A.W. (2001) Antioxidant capacity in cranberry is influenced by cultivar and storage temperature. *Journal of Agricultural and Food Chemistry*, Vol. 49, p. 969–974.