Evaluation of Ketchup Authenticity – Chemical Changes of Markers during Production and Distribution

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Abstract: The set of 12 samples of ketchups with the known NTSS content varying from 4 to 12% was analyzed, the NTSS content was correlated with the content of individual chemical markers (lycopene, β-carotene, pyrrolid-5-one-2-carboxylic acid (PCA, pyroglutamic acid), glucose, fructose, sucrose, citric and malic acid, Na^+, K^+, Ca^{2+}, Mg^{2+}, formol number). The effect of processing and storage conditions to the PCA and lycopene content was followed. NTSS correlates well with K^+, Mg^{2+}, PCA, formol number, malic and citric acid content, no correlation was found for carotenoids content. PCA content, which is formed during the ketchup processing, does not depend on the condition of ketchup processing, because all available precursors are changed already in the beginning stages of tomato processing. Contrary to that the content of carotenoids changes during all ketchup processing and storage and therefore its use as authenticity criteria is limited.

Keywords: food authenticity; chemometry; food falsification; tomato ketchup

INTRODUCTION

Evaluation of food authenticity is often based on the analyses of selected chemical markers, usually the components of raw materials which are used (and declared) for the product production. The results of analyses are compared with tabulated data and the composition of products (the content of raw material, etc.) is estimated. The reliability of the authenticity evaluation depends on various factors especially on the variability of raw materials, in the case of plant products (fruits or vegetables) it is especially variety, agricultural conditions, season, degree of maturity, physiological stage, microbial spoilage, etc. The followed markers, the content of those in raw materials can also undergo to various subsequent change due to the postharvest treatment, storage, production of food products and their storage and distribution. In some cases the databases are obtained by analyses of processed products (cocoa powder, roasted coffee, etc.), when some "standard" conditions of processing and than the "standard" changes are supposed. In majority of other commodities the changes caused during the processing are included during the data interpretation (several various markers are analyzed within wide group of samples for several years, the procedures for interpretation of results are proposed for individual products such as it is e.g. The Code of Practice of AIJN for fruit juices).

Recent Czech Food law defines the qualitative requirements for the fruit and vegetable products, the important and often adulterated parameters are the minimum Soluble Solids content (SS) and minimum content of Natural Tomato Soluble Solids (NTSS), which should be 25 and 30 or 7 and 10 in the categories of ketchup and ketchup Prima, Extra, Special, respectively. During last five years the procedure allowing the estimation of NTSS based on the determination of several chemical markers (lycopene and β-carotene, glutamic acid, pyrrolid-5-one-2-carboxylic acid), different carboxylic acids and ions (citric acid, malic acid, Na, K, Mg, Ca, formol number) was developed. The aim of the presented paper was to evaluate the effect the condition of ketchup processing and storage on the chemical markers, which are used for the NTSS content determination.

EXPERIMENTAL

Model samples of ketchups obtained from main Czech producers with the known NTSS content ranging from 4 to 12% (12 samples of ketchups). Model experiments were done with fresh tomatoes obtained from the local markers. The tomatoes were put into the boiling water, the skin was removed, immediately after peeling the fruits were heated to 90°C, homogenized by kitchen homogenizer and sieved to remove the seeds. In this the way the hot-break process was simulated. The puree was than heated under the different conditions to evaluate the PCA formation and pigments degradation.

PCA. Sample (5 g) and 60 ml water was added to 100ml flask, mixed properly, filled up and filtrated. Five ml of filter liquor added to 25 ml flask, filled up by mobile phase and filtered through 0.45 μm and injected into the HPLC. HPLC condition: column: 250 × 4 mm Ostion LG KS 0800H^+ form, temperature: room temperature, mobile phase: 5 mM H_2SO_4, detection: UV 210 nm, flow: 0.3 ml/min, inject: 20 μl, internal standard.

Carotene: 5 g of sample was 3–4 times extracted by mixture petroleum ether-acetone (1:1). Organic phases were filled up to 50 ml flask and filtered through 0.45 μm and injected into the HPLC. HPLC condition: column: PUROSPHER RP18 e, 5 μm, 125 × 4 mm, temperature: room temperature, mobile phase: acetonitrile – chloroform (85:15) + 0.05% solution of BHT, detection: VIS 450 nm, flow: 1 ml/min, inject: 3 μl, internal standard.

RESULTS AND DISCUSSION

The set of 12 samples of ketchups with the known NTSS content varying from 4 to 12% was analyzed, the NTSS content was correlated with the content of individual chemical markers (lycopene, β-carotene, pyrrolid-5-one-2-carboxylic acid, glucose, fructose, sucrose, citric and malic acid, Na^+, K^+, Ca^{2+}, Mg^{2+}, formol number). The correlation coefficients obtained are in the Table 1.

The statistically significant correlation was found for almost all selected markers with exception of carotenoid pigment. The analyzed samples were the three groups of ketchups from the three various producers, produced by slightly different technologies, two of them use the batch production with boiling of ketchups in tank and with the subsequent pasteurization after the filling, another producer uses the hot filling system without pasteurization in package. The raw materials were comparable according to the tomato paste available for the Czech producers, the technology was different especially with respect to heat treatment. From the values of coefficient obtained it can be concluded that the concentration of cations (K^+, Mg^{2+}, Ca^{2+}), malic and citric acids content and formol number are relatively stable parameters. Malic and citric acids content can be affected by the degree of maturity and citric acid is also very often used as the additive to reduce pH value during the tomato paste production. No correlation was found for the carotenoid pigments, which undergo degradation changes (*cis/trans* isomeration, autoxidation, etc.) during the ketchup processing. Concerning the other markers KCl can be included in the recipe to reduce the NaCl content, calcium cations could be present in the water used for the production and higher microbial contamination of tomato paste increases the level of formol number. The content of PCA correlated well with the NTSS content, but on contrary to other markers PCA is formed during the tomato processing from glutamine or glutamic acid:

In spite of the relatively high value of the correlation coefficient the PCA formation can be affected by the production conditions. The PCA content in ketchup depends on the concentration of precursors and also on the temperature history during the processing. Heating enhances the rate of formation [1–3]. The effect of heating on PCA formation in tomato puree is in the Figure 1.

From the kinetic data the *D-t* curve (the dependence of the temperature on the logarithms of the

Table 1. Correlation coefficients R of NTSS and selected chemical markers

Lycopene	β-Carotene	PCA	NH_4^+	K^+
0.21	–0.13	*0.94*	*0.69*	*0.98*
Ca^{2+}	Mg^{2+}	Malic acid	Citric acid	Formol number
0.84	*0.98*	*0.89*	*0.98*	*0.96*

Values in *italic* are significant at $P < 0.05$, $n = 12$

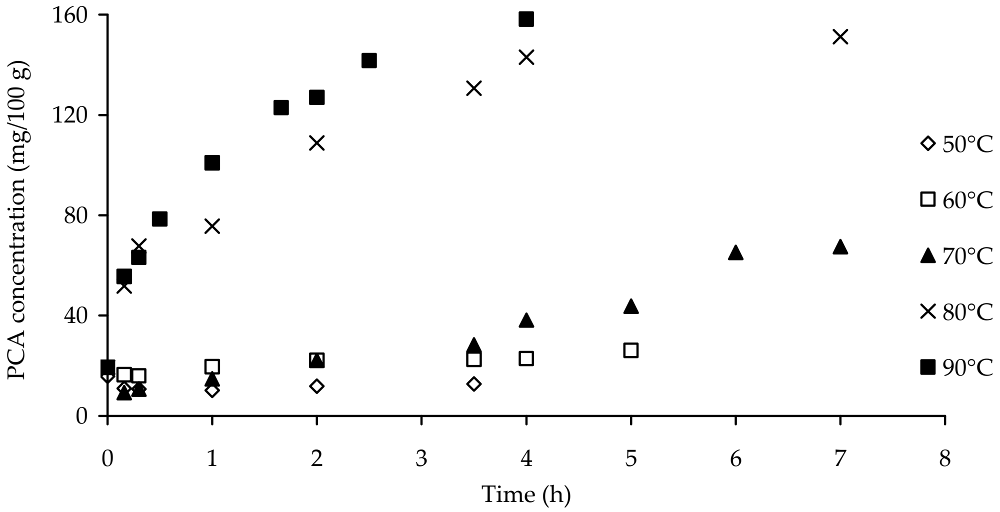

Figure 1. Production of PCA in tomato puree during heating at various temperatures

time needed to increase the PCA concentration in one order). The parameters of *D-t* curve of the PCA formation are: z = 12–18.6°C, D_{100} = 8–16 min. Fresh tomatoes do not contain almost any PCA (content in fresh fruit and vegetable is very low or zero [3]); final concentration of PCA in ketchup is about 160 mg/kg depending to the content of precursors. The increase of the PCA content during the production is about 1 or 2 orders. From this data it is obvious, that to produce 80–100% of PCA in ketchup, the C_{100} (cooking value of the process) should be about 8–16 min. The cooking values of the individual operations of the tomato processing are in the Table 2. It is obvious, that the

Table 2. Temperatures and times by tomatoes processing

Operation	Temperature	Time	Cooking value C_{100} (min)
Raw material storage	15°C	to 1440 min	0.04
	0–5°C	to 10 days (14 400 min)	0.11
Hot-brake	90°C	1 min	0.29
	82–94°C	0.25 min	0.12
	65–90°C	min (10)	2.89
Cold brake	20–30°C	Hours (5)	0.05
Concentration (evaporation)	82–84°C	5–10 min	1.37
	45°C	5–10 min	0.01
Sterilization	sterilizer of slurry 90°C	5–10 min	2.89
	sterilization in package 90°C	5–10 min	2.89
Tomato paste storage	up to 30°C	max. 1 year	88.94
Ketchup production	mixing 50°C vacuum boiling at 65°C heating at 90°C cooling and filling (chemically preserved filled in plastic package) hot filling or pasteurization in package	5–30 min	2–9

C value to reach maximum PCA concentration in ketchup is low enough to be got during the tomato paste production and therefore PCA can be reliable chemical marker for the determination of NTSS.

In order to explain the low levels of correlation coefficients for carotenoid pigments and NTSS content in ketchups the course of pigment degradation during heating of tomato puree was followed. Tomato pulp sample was heated at 90°C under atmospheric pressure and daylight. The pulp samples were drawn after heating intervals of 0, 0.5, 1, 2, 4 h. The fresh prepared tomato pulp contained about 33.27 mg/100 g in dry matter and after 4 hours at 90°C the lycopene content was about 19.96/100 g dry matter. The main causes of tomato lycopene degradation during the processing are isomerization and oxidation. Thermal processing generally causes some loss of lycopene in tomato-based foods. Heat induces isomerization of the all-*trans* to *cis* forms. The *cis*-isomers increase with temperature and processing time. In processed tomato products, oxidation is a complex process and depends on many factors, such as processing condition, moisture, temperature and the presence of pro- or antioxidants and lipids [4]. The carotenoid content in ketchup is more affected by the conditions of processing and distribution than the others markers, therefore the pigments are not very reliable authenticity criteria.

CONCLUSION

The NTSS content in ketchup and other tomato products can be estimated according to the content of K^+, Mg^{2+}, PCA, formol number, malic and citric acid content. PCA content, which is formed during the ketchup processing, does not depend on the condition of ketchup processing, because all available precursors are changed already in the beginning stages of tomato processing. Contrary to that the content of carotenoids changes during all ketchup processing and storage and therefore its use as authenticity criteria is limited.

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