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Article

Chemical and Sensory Properties of Corn Extrudates Enriched with Tomato Powder and Ascorbic Acid

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Abstract: The chemical and sensory properties of corn extrudates enriched with spray-dried tomato powder (TP) in 4, 6 and 8% ratios were researched. Two extrusion temperature regimes were used: 135/170/170 °C (E1) and 100/150/150 °C (E2). Ascorbic acid (AA) at levels of 0.5 and 1% was also added to the raw mixtures in order to prevent the undesirable oxidation of the constituents, primarily carotenoids. AA was especially efficient in the case of the lutein content and 1% AA, but lutein originating from TP was more sensitive to the extrusion conditions than corn lutein, and zeaxanthin was more sensitive than lutein. Lycopene, α -carotene, 13-*cis*- β carotene and 9-*cis*- β carotene degraded completely in all the samples, at both extrusion regimes. The proposed models for the color of the extrudates showed the significant influence of TP and AA. Extrudates obtained at the E1 temperature regime containing 4% TP and pure corn extrudate with 1% AA were the best-rated samples by the sensory panel.

Keywords: tomato powder; extrusion; carotenoids; ascorbic acid; sensory analysis



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1. Introduction

For over a decade, there has been a growing interest in extruded products with new sensory, physical or chemical properties [1]. There are several reasons for this. First of all, extrusion is a low-cost, energy-efficient process, without process effluents [2]. Moreover, it is a flexible process that enables different applications, like shaping, mixing, encapsulation, flavor generation, conveying [3] and generating products with different textures and shapes, like baby food, pastas, bakery products and snack foods [4]. Although extrusion is a high-temperature/short-time (HTST) process, due to mechanical and heat effects, it changes the food structure and nutritional value of materials, so it is crucial to optimize the process parameters to ensure the maintenance of high nutritional value. Starch gelatinization, the destruction of antinutritional factors, an increase in fiber content and an increase in protein digestibility are considered positive, while the loss of heat-vulnerable ingredients and protein loss due to Maillard browning are negative sides of extrusion cooking [5]. Extruded products are widely consumed in the form of breakfast cereals and snacks, but they are perceived as high-energy junk foods without adequate nutritional properties [6]. Improvement in nutritional value by incorporating different materials like legumes, fruits or vegetables has been widely studied [5]. However, the different possibilities of the extruder conditions, like the screw speed, screw configuration, temperature and moisture, as well as different food matrixes, result in final products with very different textural, sensory and nutritional values [7]. The optimization of the process parameters in order to achieve satisfactory sensory attributes is challenging. Any addition of non-starchy raw material results in texture and expansion alterations compared to usual products, which affects acceptance by consumers [8]. Thus, food industries are still trying to develop novel, value-added products that are not yet in mass production [3].

Tomato is among the most consumed crops worldwide, with a variety of products. Consequently, there is a high amount of waste like peels and seeds, which could be effectively transformed into useful raw material for new products [1]. It is well known that high nutritional value is primarily due to high levels of lycopene with antioxidant, anticarcinogen and immunomodulatory properties. Therefore, the addition of tomato in different forms to extruded products has been previously studied. Some of these studies focused on the physical properties of extruded products [9,10], and some included an analysis of lycopene [1,11,12]. However, it is important to highlight that although lycopene is the predominant carotenoid in tomato, it is not the only one. The authors of [13] showed that lutein, α -carotene and β -carotene originating from tomato also exhibit strong antioxidant activity. An especially important finding was that tomato carotenoids showed the strongest antioxidant potential in a mixture due to the synergistic effect. To the best of our knowledge, there has not been research on the extrusion influence on other tomato carotenoids besides lycopene. The influence of extrusion cooking on carotenoids from other sources like grains, sweet potatoes, pumpkin and carrots has been previously studied [14–18], but their stability depended on the food matrix that they originated from or were combined with. The authors of [19] reviewed current findings on the carotenoid stability during extrusion processing. They concluded that the processing conditions and extruded material are interrelated in a complex manner, so it is crucial to optimize the parameters with improved extruders and process control. There is also an idea to protect carotenoids by encapsulation, which gave good results in the protection of pumpkin peel carotenoids [20], but so far, we have not found research regarding tomato carotenoids.

The aim of this study was to check the stability of the tomato carotenoids lycopene, lutein, α -carotene and β -carotene in combination with corn carotenoids, primarily lutein and zeaxanthin. The objective was to obtain an extruded product with increased nutritional value and satisfactory sensory characteristics by adding tomato powder (TP). Ascorbic acid (AA) was also added to the mixture as a potential protector of the carotenoids, which are strongly vulnerable to oxidation.

2. Materials and Methods

2.1. Sample Preparation

Based on our previous study on the physical characteristics of extruded corn grits enriched with TP [10], corn grits (particle size $> 500 \mu\text{m}$) and spray-dried TP (Cofco Tunhe Co., Ltd., Urumqi—Xinjiang, China) were mixed in 96:4, 94:6 and 92:8 ratios (dry to dry weight), and AA was also added to the mixtures at the 0%, 0.5% and 1% levels (dry basis). The total moisture of the mixtures was set to 15%, and the mixtures were put in plastic bags, sealed and left in the dark for 24 h before the extrusion.

A laboratory single-screw extruder (model Do-Coder, Brabender 19/20 DN, Duisburg, Germany) was used for the experiment. Extrusion experiments were performed at two different temperature regimes: 135/170/170 °C and 100/150/150 °C, with a 4:1 compression ratio screw with a screw speed of 100 rpm and a feed rate of 15 rpm. Obtained extrudates were air-dried at ambient temperature overnight, put in plastic bags, vacuum-sealed and stored in darkness until the analysis.

2.2. Ascorbic Acid Determination

The procedure was previously described in detail in [15]. Triplicate analyses were performed for each sample.

2.3. Carotenoid Determination

Carotenoids were extracted and analyzed according to the method described in [21], with modifications described in [15].

2.4. Fat, Protein, Crude Fiber and Ash Determination

Fat content was determined according to the ISO 6492:2001 method [22]; crude fiber content was determined according to ISO 6865:2000 [23]; ash content was determined according to ISO 5984:2002 [24]; and proteins were determined according to ISO 5983-2:2005 [25]. Each sample was analyzed in 3 replications.

2.5. Color Analysis

The procedure was previously described in detail in [15]. The total color change of each extruded sample in relation to the color of the raw materials (ΔE) was also calculated according to Equation (1):

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (1)$$

where the subscript “0” indicates the initial color values of the raw materials [8].

2.6. Sensory Analysis

The sensory acceptance of a product by customers is crucial for the development of a food product. Therefore, sensory evaluation was carried out in cooperation with a factory that produces extruded snack products. The sensory panel consisted of 10 evaluators employed in the mentioned factory. They are highly experienced evaluators of extruded snacks since they perform sensory evaluations of their own products on a daily basis. The analysis was conducted according to the quantitative response scale method. The uniformity/color, structure/crispness, consistency/chewiness, odor, flavor and overall acceptability were rated. All extrudates obtained at higher extrusion temperatures were evaluated, while only a few samples among the extrudates obtained at lower temperatures were chosen for comparison because of the low grades upon preliminary testing and the instrumental determination of the physical characteristics. The results are presented as mean scores of the sensory attributes.

2.7. Experimental Design and Data Analysis

Color analysis data were analyzed using Design expert 6.0.8. software (Stat-Ease Inc., Minneapolis, MN, USA). The RSM (response surface methodology) was chosen to build up mathematical models, using 3-level factorial design. The TP (variable A) and AA (variable B) levels were set as independent variables, since the chemical compositions of the mixtures were within the focus of this investigation. Mathematical models were built in terms of coded values: variable A: 4%, 6%, 8%/−1, 0, 1, and variable B: 0%, 0.5%, 1%/−1, 0, 1. Statistical significance of the regression coefficients was determined by analysis of variance (ANOVA) at the 95% level. Chemical composition data were analyzed by Statistica 8 software (StatSoft Inc., Tulsa, OK, USA) using post hoc LSD at the 95% level.

3. Results and Discussion

3.1. Extrusion Influence on Ascorbic Acid

Table 1 presents the AA contents in the raw and extruded samples. The corn grits and TP did not contain AA, so the presented values are due to the addition of AA to the extrusion mixtures in 0.5% and 1% ratios. Differences in the results for the same amount of added AA per 100 g can be attributed to the inhomogeneity of the samples since the mixing was performed manually. As previously mentioned, AA was added to the mixtures in order to serve as an antioxidant and to protect the other components sensitive to oxidation, primarily carotenoids. Previous research by the authors of [26–28] showed that AA can survive extreme thermal and mechanical stresses in extruders even at very high temperatures up to 150 °C and screw speeds up to 300 rpm. This can be attributed to the short residence time at high temperatures within the extruder (the HTST process) [26].

Table 1. Ascorbic acid contents in raw and extruded samples ^{A,B,C}.

TP (%)	AA (%)	Ascorbic Acid (mg/100 g) before Extrusion	Ascorbic Acid (mg/100 g) after Extrusion E1	Degradation (%)	Ascorbic Acid (mg/100 g) after Extrusion E2	Degradation (%)
0	0	-	-	-	-	-
0	0.5	402.8 ^{c2} ± 1.69	95.22 ^{a1} ± 1.51	76.36	272.92 ^{b2} ± 1.29	32.25
0	1	789.84 ^{c4} ± 2.52	401.34 ^{a4} ± 1.90	49.19	571.35 ^{b5} ± 4.15	27.66
4	0	-	-	-	-	-
4	0.5	304.15 ^{c1} ± 3.41	96.97 ^{a1} ± 0.47	68.12	244.18 ^{b1} ± 2.66	19.72
4	1	654.86 ^{c3} ± 8.64	354.80 ^{a4} ± 2.16	45.82	516.45 ^{b4} ± 1.30	21.13
6	0	-	-	-	-	-
6	0.5	381.62 ^{c2} ± 5.41	133.10 ^{a2} ± 4.06	65.12	220.35 ^{b1} ± 0.88	42.26
6	1	778.15 ^{c4} ± 1.10	265.14 ^{a3} ± 12.22	65.92	521.30 ^{b4} ± 3.22	33.01
8	0	-	-	-	-	-
8	0.5	306.84 ^{c1} ± 3.03	97.06 ^{a1} ± 2.43	68.37	205.61 ^{b1} ± 0.56	32.99
8	1	607.27 ^{c3} ± 0.98	273.79 ^{a3} ± 12.56	54.91	393.09 ^{b3} ± 0.63	35.27

^A Contents are the mean ± standard deviation of three repetitions. TP—tomato powder level. AA—ascorbic acid level. ^B Means followed by the same letters in the lines are not statistically different at 5% probability. ^C Means followed by the same numbers in the columns are not statistically different at 5% probability. E1—135/170/170 °C extrusion temperatures. E2—100/150/150 °C extrusion temperatures.

Extrusion caused the degradation of AA, and the results were similar to our previous results in [15]. The E1 extrusion conditions caused AA degradation from 45% to 76%, while the E2 extrusion regime resulted in a 21% to 42% loss. A decrease in the AA content was expected as a result of oxidation and the loss of water/solvent at the die [26,27]. However, the results cannot be generalized because the authors of [28] showed that the degradation is also dependent on the matrix of raw materials. In this case, higher extrusion temperatures resulted in higher degradation, but not entirely, so there was still enough AA left to support the hypothesis of carotenoid protection.

3.2. Extrusion Influence on Carotenoids

Table 2 shows the lutein contents in the samples before and after extrusion. The lutein content in the cornmeal was about 3.2 mg/100 g, and it did not change significantly with the addition of 4% and 6% TP but did so only with the addition of 8% TP (4.13–5.96 mg/100 g). Lutein is also one of the carotenoids present in tomatoes [29], and deviations from the expected values in the raw samples with the addition of 4% and 6% TP can be attributed to the inhomogeneity of the samples. The extrusion of corn grits at higher temperatures led to a significant increase in the lutein content compared to the raw samples. In samples containing TP, the proportion of lutein also increased during the E1 extrusion regime, although not to the same extent as in the pure corn samples. Samples with 8% TP after extrusion had lower lutein contents than samples with lower amounts of TP, from which it can be concluded that the lutein originating from TP was less resistant to the extrusion conditions, except in the samples where 1% AA was added and served as the lutein protector, as expected. The increase in the lutein content after extrusion can be attributed to the increased extractability due to the effect of the high pressure and temperature inside the extruder on macromolecules that carotenoids are associated with, like proteins and membrane lipids [30], and to lipoxygenase inactivation. Similar results were obtained in experiments with carrots and pumpkin [15,16].

At the E2 extrusion temperatures, there was also an increase in the lutein content in almost all the samples, although it was lower than at the E1 temperatures, which was expected, since the lower temperatures did not change the structure of the macromolecules as much as the higher temperatures. The authors of [31] showed that extrusion conditions increase the bioaccessibility of lutein and β-carotene, whereby higher temperatures act favorably on the lutein bioaccessibility. This can be attributed to thermal and mechanical

stresses, which soften the cell wall structure and reduce the particle size, creating more surface area for digestive enzymes.

Table 2. Carotenoid contents in samples before and after extrusion ^{A,B}.

<i>BEFORE EXTRUSION</i>							
TP (%)	AA (%)	Lutein mg/100 g	Zeaxanthin mg/100 g	Lycopene mg/100 g	α -Carotene mg $E_{\beta C}/100$ g	9- <i>cis</i> - β -Carotene mg $E_{\beta C}/100$ g	13- <i>cis</i> - β -Carotene mg $E_{\beta C}/100$ g
0	0	3.28 ^b ± 0.25	3.28 ^b ± 0.26	n.d.	n.d.	n.d.	n.d.
0	0.5	3.16 ^b ± 0.25	3.93 ^c ± 0.19	n.d.	n.d.	n.d.	n.d.
0	1	3.26 ^b ± 0.28	4.18 ^{cd} ± 0.21	n.d.	n.d.	n.d.	n.d.
4	0	3.43 ^{bc} ± 0.18	3.82 ^c ± 0.25	11.91 ^a ± 0.21	n.d.	0.24 ^a ± 0.02	n.d.
4	0.5	3.18 ^b ± 0.18	2.94 ^b ± 0.27	26.7 ^b ± 0.16	n.d.	0.52 ^b ± 0.01	n.d.
4	1	3.22 ^b ± 0.23	3.31 ^b ± 0.25	26.98 ^b ± 0.09	n.d.	0.46 ^b ± 0.01	n.d.
6	0	3.08 ^b ± 0.24	4.86 ^{de} ± 0.27	14.23 ^a ± 0.12	n.d.	0.29 ^a ± 0.01	n.d.
6	0.5	4.08 ^c ± 0.24	5.27 ^e ± 0.28	32.78 ^b ± 0.10	n.d.	0.67 ^c ± 0.04	n.d.
6	1	3.20 ^b ± 0.26	5.47 ^f ± 0.22	29.5 ^b ± 0.18	n.d.	0.6 ^c ± 0.01	n.d.
8	0	5.81 ^e ± 0.27	4.44 ^d ± 0.27	54.46 ^d ± 0.10	0.04 ^a ± 0.002	1.18 ^e ± 0.02	0.062 ^a ± 0.003
8	0.5	5.97 ^e ± 0.3	4.75 ^{de} ± 0.23	58.64 ^d ± 0.12	0.03 ^a ± 0.002	1.19 ^e ± 0.002	0.055 ^a ± 0.002
8	1	4.14 ^c ± 0.17	3.98 ^c ± 0.28	40.6 ^c ± 0.15	0.03 ^a ± 0.002	0.85 ^d ± 0.01	0.042 ^a ± 0.002
<i>AFTER EXTRUSION E1</i>							
0	0	8.77 ^g ± 0.24	4.29 ^d ± 0.25	n.d.	n.d.	n.d.	n.d.
0	0.5	8.59 ^g ± 0.19	7.10 ^g ± 0.22	n.d.	n.d.	n.d.	n.d.
0	1	8.45 ^g ± 0.17	4.92 ^e ± 0.16	n.d.	n.d.	n.d.	n.d.
4	0	1.99 ^a ± 0.21	2.38 ^a ± 0.28	n.d.	n.d.	n.d.	n.d.
4	0.5	5.49 ^{de} ± 0.25	5.19 ^e ± 0.14	n.d.	n.d.	n.d.	n.d.
4	1	5.30 ^{de} ± 0.24	4.05 ^c ± 0.27	n.d.	n.d.	n.d.	n.d.
6	0	3.93 ^c ± 0.26	3.59 ^{bc} ± 0.22	n.d.	n.d.	n.d.	n.d.
6	0.5	5.46 ^{de} ± 0.20	4.14 ^{cd} ± 0.23	n.d.	n.d.	n.d.	n.d.
6	1	4.81 ^d ± 0.23	3.02 ^b ± 0.15	n.d.	n.d.	n.d.	n.d.
8	0	4.21 ^c ± 0.21	4.47 ^d ± 0.17	n.d.	n.d.	n.d.	n.d.
8	0.5	3.52 ^{bc} ± 0.28	3.41 ^{bc} ± 0.27	n.d.	n.d.	n.d.	n.d.
8	1	4.70 ^d ± 0.24	3.98 ^c ± 0.24	n.d.	n.d.	n.d.	n.d.
<i>AFTER EXTRUSION E2</i>							
0	0	3.87 ^{bc} ± 0.18	2.82 ^b ± 0.26	n.d.	n.d.	n.d.	n.d.
0	0.5	4.64 ^{cd} ± 0.21	4.95 ^e ± 0.21	n.d.	n.d.	n.d.	n.d.
0	1	4.84 ^d ± 0.29	3.93 ^c ± 0.24	n.d.	n.d.	n.d.	n.d.
4	0	4.43 ^{cd} ± 0.24	3.13 ^b ± 0.20	n.d.	n.d.	n.d.	n.d.
4	0.5	5.32 ^{de} ± 0.27	4.56 ^d ± 0.26	n.d.	n.d.	n.d.	n.d.
4	1	3.64 ^{bc} ± 0.24	3.27 ^b ± 0.22	n.d.	n.d.	n.d.	n.d.
6	0	3.48 ^{bc} ± 0.20	3.00 ^b ± 0.26	n.d.	n.d.	n.d.	n.d.
6	0.5	4.51 ^{cd} ± 0.29	3.66 ^{bc} ± 0.23	n.d.	n.d.	n.d.	n.d.
6	1	3.28 ^b ± 0.27	2.14 ^a ± 0.22	n.d.	n.d.	n.d.	n.d.
8	0	3.89 ^c ± 0.30	4.35 ^d ± 0.23	n.d.	n.d.	n.d.	n.d.
8	0.5	5.09 ^d ± 0.28	4.13 ^{cd} ± 0.21	n.d.	n.d.	n.d.	n.d.
8	1	6.39 ^f ± 0.20	5.56 ^f ± 0.29	n.d.	n.d.	n.d.	n.d.

^A Results were expressed as the mean of three repetitions ± standard deviation. n.d.—not detected. ^B Means followed by the same letters in the columns are not statistically different at 5% probability. TP—tomato powder level. AA—ascorbic acid level. E1—135/170/170 °C extrusion temperatures. E2—100/150/150 °C extrusion temperatures.

The contents of zeaxanthin (Table 2) in the raw samples without TP were from 3.28 to 4.18 mg/100 g, depending on the proportion of AA, while in the samples with TP, they were from 2.93 to 5.46 mg/100 g. Corn extrudates obtained at the E1 temperatures had a higher proportion of zeaxanthin compared to the raw mixtures. Samples with 4% TP and AA had a significant increase in their zeaxanthin contents. In the other samples, there was

a decrease, or a very small increase, compared to the zeaxanthin content before extrusion. Likewise, at lower extrusion temperatures, the zeaxanthin content decreased in the largest number of samples, from which it can be concluded that it is somewhat more sensitive to the conditions prevailing during extrusion than lutein. The authors of [32] also researched the stability of corn lutein and zeaxanthin during extrusion and traditional flaking, and the degradation depended on the formulation of raw materials. The addition of chia and quinoa increased the degradation. Higher level of lipids, especially unsaturated fatty acids, led to the formation of free radicals, which reacted with carotenoid molecules, so β -carotene was completely lost during the processes. The authors of [33] showed that by optimizing the feed moisture between 13.2 and 13.7% and the barrel temperature between 120 and 132 °C, the β -carotene content originating from corn maize can be increased and the lutein and zeaxanthin contents are minimally lost.

The proportion of lycopene in the raw samples increased proportionally to the TP content, ranging from 11 mg/100 g to 58 mg/100 g (Table 2). AA caused an increase in the analyzed lycopene content. After extrusion at both temperature regimes, no lycopene was detected. The authors of [12] showed that lycopene can be retained during extrusion, but in very small amounts. More importantly, they stated that the degree of degradation depends on the source from which the lycopene comes. The use of a physically resistant material such as tomato skin led to a significantly higher preservation of lycopene compared to the use of tomato paste. The same authors attributed the poor retention of lycopene originating from tomato paste to the extreme conditions that were applied during the preparation of the paste itself. It must be kept in mind that the raw material used in this research was spray-dried TP that had already undergone intense oxidation during drying, so the stress caused by extrusion caused the additional degradation of these molecules. Finding suitable, cheap and accessible raw materials is interesting from a nutritional point of view, since it was proved in [1] that extrusion increases the bioaccessibility of lycopene.

α -Carotene and 13-*cis*- β -carotene were detected only in mixtures containing 8% TP (Table 2). During extrusion at both temperature regimes, the complete degradation of these compounds occurred. The high sensitivity of these carotenoids originating from pumpkin during extrusion has been shown [15], but in this research, the ascorbic acid acted favorably on them, which resulted in their preservation.

9-*cis*- β -carotene (Table 2) was not detected in the mixtures containing pure corn grits, and its proportion increased proportionally to the addition of TP: 0.24 mg/100 g in the samples with the addition of 4% TP and 0.29 mg/100 g in those with the addition of 6% TP, while slightly higher values were recorded in the samples with AA (0.52 to 0.67 mg/100 g). AA acted as protection during the extraction and analysis of the samples. No 9-*cis*- β -carotene was detected after extrusion at both temperatures. The authors of [2] investigated the behavior of β -carotene as a model substance during different extrusion conditions, and they showed that 9-*cis*- β -carotene is degraded to a certain extent, but not completely, as this depends on the extrusion temperature, screw speed and dosing location. However, degradation is primarily a consequence of oxidation, and of thermal and mechanical stresses during extrusion. The temperature influence on carotenoids in general has been studied a lot. In the research conducted by the authors of [34], pasteurization did not affect the content of total carotenoids (β -carotene and lycopene) in tomato puree. The authors of [35] found that the degree of loss of the transconfiguration of β -carotene during pasteurization depends primarily on the period of exposure to high temperature, while the rate of the formation of 9-*cis* and 13-*cis* isomers depends on the applied temperature. The authors of [2] stated that the influence of temperature during extrusion on β -carotene needs to be further investigated, since a higher temperature means a lower viscosity of the mass in the extruder (that is, lower mechanical stress). Which of the mentioned parameters dominates and in what way are not yet known.

3.3. Extrusion Influence on Fat, Protein, Crude Fiber and Ash Contents

The addition of 4% and 6% TP to cornmeal caused an increase in the fat content compared to pure corn (Table 3), while the addition of 8% TP resulted in a decrease in the amount of fat compared to pure semolina, which can be attributed to the inhomogeneity of the samples. Extrusion led to a 72 to 94% fat reduction, and higher extrusion temperatures caused greater degradation. The authors of [36] also stated that a higher extrusion temperature causes greater fat oxidation. At higher extrusion temperatures, the samples containing AA had a slightly higher percentage of degradation (although it was statistically insignificant compared to the samples without AA), from which it can be concluded that dehydroascorbic acid, which is formed by the breakdown of AA [37], acted as a pro-oxidant, while at lower extrusion temperatures, this trend was present only at higher proportions of TP. The authors of [38] stated that pro-oxidant properties are possessed by the products of the oxidation by oxygen of dehydroascorbic acid, but those of [39] showed that both ascorbic and dehydroascorbic acid can accelerate the process of oxidation if the LDL is already minimally oxidized. During extrusion, complex compounds are formed between starch and lipids. Furthermore, shear forces disperse fats into small droplets that are spread over the polymers. It is considered that the oxidation of fat during extrusion is not of great importance due to the short processing time; however, there is a risk of rancidity during product storage [7]. Air bubbles trapped in expanded products pose a risk for fat oxidation, and packaging the product in a nitrogen atmosphere does not completely solve this problem during storage.

Table 3. Fat and proteins in raw and extruded samples ^{A,B}.

TP (%)	AA (%)	Fat (%)			Proteins (%)		
		Before Extrusion	After Extrusion E1	After Extrusion E2	Before Extrusion	After Extrusion E1	After Extrusion E2
0	0	0.315 ^b ± 0.007	0.078 ^a ± 0.001	0.083 ^a ± 0.001	7.59 ^x ± 0.03	8.50 ^z ± 0.01	8.28 ^y ± 0.02
0	0.5	0.315 ^b ± 0.007	0.064 ^a ± 0.001	0.055 ^a ± 0.000	7.55 ^x ± 0.03	8.50 ^z ± 0.08	8.23 ^y ± 0.01
0	1	0.315 ^c ± 0.007	0.057 ^a ± 0.004	0.093 ^b ± 0.010	7.41 ^x ± 0.05	8.48 ^z ± 0.09	8.21 ^y ± 0.01
4	0	0.335 ^b ± 0.007	0.081 ^a ± 0.014	0.082 ^a ± 0.021	8.22 ^x ± 0.02	8.52 ^y ± 0.03	8.53 ^y ± 0.01
4	0.5	0.340 ^b ± 0.014	0.080 ^a ± 0.040	0.093 ^a ± 0.011	8.12 ^x ± 0.04	8.48 ^y ± 0.01	8.53 ^y ± 0.02
4	1	0.320 ^c ± 0.000	0.073 ^a ± 0.001	0.088 ^b ± 0.007	7.98 ^x ± 0.08	8.41 ^y ± 0.01	8.41 ^y ± 0.13
6	0	0.335 ^b ± 0.021	0.067 ^a ± 0.010	0.088 ^a ± 0.004	8.34 ^x ± 0.02	8.66 ^y ± 0.01	8.70 ^y ± 0.05
6	0.5	0.320 ^c ± 0.014	0.053 ^a ± 0.030	0.075 ^b ± 0.008	8.27 ^x ± 0.03	8.61 ^y ± 0.01	8.65 ^y ± 0.01
6	1	0.300 ^c ± 0.000	0.027 ^a ± 0.004	0.078 ^b ± 0.007	8.21 ^x ± 0.05	8.58 ^y ± 0.05	8.60 ^y ± 0.01
8	0	0.250 ^c ± 0.014	0.016 ^a ± 0.000	0.075 ^b ± 0.000	8.44 ^x ± 0.04	8.84 ^y ± 0.01	9.05 ^z ± 0.04
8	0.5	0.255 ^b ± 0.021	0.017 ^a ± 0.018	0.052 ^a ± 0.006	8.32 ^x ± 0.03	8.79 ^y ± 0.03	8.96 ^z ± 0.01
8	1	0.260 ^b ± 0.014	0.015 ^a ± 0.001	0.041 ^a ± 0.016	8.26 ^x ± 0.01	8.66 ^y ± 0.12	8.81 ^z ± 0.06

^A Results were expressed as the mean of three repetitions ± standard deviation. ^B Means followed by the same letters in the lines are not statistically different at 5% probability. TP—tomato powder level. AA—ascorbic acid level. E1—135/170/170 °C extrusion temperatures. E2—100/150/150 °C extrusion temperatures.

The protein content in the corn grits used in this research was 7.59%, and in the TP, it was 15.25%. Consequently, the addition of TP to the corn grits led to an increase in the amount of protein in the raw mixtures, compared to pure corn (Table 3). The extrusion process resulted in an increase in the proportion of protein in all the samples. A slightly higher increase occurred during extrusion at the E2 temperatures, although the difference in the proportions between the extrudates is not statistically significant. This is the consequence of protein denaturation (i.e., the transformation of secondary, tertiary and quaternary structures and the inactivation of enzyme inhibitors present in raw food). Therefore, otherwise hard-to-digest protein molecules are available to digestive enzymes [40].

A preliminary analysis of the raw materials used in this research showed that the proportion of fiber in the TP (6.14%) was significantly higher than that in the corn grits (0.54%). So, the fiber content in the raw mixtures increased proportionally to the proportion of TP (Table 4). At the E1 extrusion temperatures, there were no significant changes in the proportion of fibers (except for two samples, where the changes were very small—0.03 and 0.06%). The authors of [41] also showed that there was no change in the total amount of fiber during extrusion, but the amount of insoluble fiber decreased, and the amount of soluble fiber increased. In contrast, some studies resulted in an increase in the amount of insoluble fibers [42,43]. At the E2 extrusion temperatures in part of the samples, there was a decrease in the proportion of fibers, but although it was a statistically significant change, the biggest decrease was only by 0.08% compared to the raw mixtures. The authors of [44] also noticed a slight decrease in the total fiber content, but it was statistically insignificant. The decrease can be explained by the loss of soluble fiber, primarily pectic substances [45].

Table 4. Crude fiber and ash contents in raw and extruded samples ^{A,B}.

TP (%)	AA (%)	Crude Fiber (%)			Ash (%)
		Before Extrusion	After Extrusion E1	After Extrusion E2	Before Extrusion
0	0	0.54 ^b ± 0.01	0.53 ^b ± 0.01	0.49 ^a ± 0.01	0.30 ± 0.00
0	0.5	0.51 ^b ± 0.01	0.52 ^b ± 0.01	0.47 ^a ± 0.01	0.30 ± 0.01
0	1	0.50 ^b ± 0.01	0.50 ^b ± 0.01	0.45 ^a ± 0.01	0.29 ± 0.01
4	0	0.80 ^a ± 0.01	0.79 ^a ± 0.02	0.78 ^a ± 0.01	0.59 ± 0.01
4	0.5	0.74 ^a ± 0.01	0.73 ^a ± 0.01	0.72 ^a ± 0.01	0.76 ± 0.01
4	1	0.71 ^b ± 0.01	0.70 ^b ± 0.01	0.68 ^a ± 0.01	0.68 ± 0.01
6	0	0.84 ^a ± 0.01	0.81 ^a ± 0.02	0.81 ^a ± 0.01	0.80 ± 0.02
6	0.5	0.82 ^b ± 0.01	0.79 ^a ± 0.01	0.80 ^{ab} ± 0.02	0.76 ± 0.01
6	1	0.76 ^a ± 0.01	0.76 ^a ± 0.01	0.73 ^a ± 0.03	0.72 ± 0.01
8	0	0.92 ^a ± 0.02	0.91 ^a ± 0.02	0.90 ^a ± 0.01	0.70 ± 0.02
8	0.5	0.88 ^b ± 0.02	0.87 ^b ± 0.02	0.80 ^a ± 0.02	0.72 ± 0.01
8	1	0.84 ^b ± 0.02	0.78 ^a ± 0.02	0.76 ^a ± 0.01	0.93 ± 0.01

^A Results were expressed as the mean of three repetitions ± standard deviation. ^B Means followed by the same letters in the lines are not statistically different at 5% probability. TP—tomato powder level. AA—ascorbic acid level. E1—135/170/170 °C extrusion temperatures. E2—100/150/150 °C extrusion temperatures.

Minerals are generally stable during food processing, and there is little chance of their changing during extrusion. Therefore, the ash content (Table 4) was analyzed in the raw mixtures only. The addition of TP to the corn grits resulted in an increase in the ash content proportional to the TP ratio. Extrusion can affect the absorption of minerals from food into the body. Phytates form insoluble complexes with minerals and thus reduce their absorption into the body, but they are hydrolyzed by extrusion [46]. Mineral absorption also depends on fiber. Cellulose, lignin and some hemicelluloses affect the mobility of the gastrointestinal tract and reduce the absorption of minerals. During extrusion, some parts of the fibers are reorganized, and thus their ability to bind minerals changes [47].

3.4. Color of the Extrudates

The mathematical models for the L* values:

$$L^* E1 = 69.38 - 2.93 \cdot A - 1.02 \cdot B + 0.070 \cdot A^2 - 0.5 \cdot B^2 + 1.07 \cdot AB/R^2 = 0.9861 \quad (2)$$

$$L^* E2 = 68.11 - 2.70 \cdot A - 1.63 \cdot B + 0.35 \cdot A^2 - 0.12 \cdot B^2 + 0.32 \cdot AB/R^2 = 0.9692 \quad (3)$$

The extrusion process led to a statistically significant change in the L* value in relation to the raw mixtures, and between extrudates obtained at different temperatures. Extrusion at both temperatures led to an increase in the L* value compared to the raw mixtures, with a higher temperature meaning a greater change. Such an influence of temperature

was also shown in [8,12] and can be explained by the fact that the extrudate samples became lighter due to the incorporation of air into the structure. The addition of AA at both temperatures caused a smaller change in the L^* value compared to the mixtures. The influence of the TP and AA addition on the L^* color value of extrudates obtained at the E1 and E2 extrusion temperatures is presented in Figure 1 and described by models (2) and (3). Based on the analysis of variance (Table 5), both quadratic mathematical models have an excellent correlation with the experimental data. The addition of TP and AA had a significant negative linear influence on the L^* at both extrusion temperatures, while at the E1 temperature regime, their interaction also had a significant influence (Table 6). Thus, the addition of TP and AA led to lower L^* values (darker samples compared to pure corn extrudates), but in fact, the addition of AA decreased the total change compared to the initial sample. This can be connected with the fact that these samples had a lower expansion, which means less incorporated air in the structure.

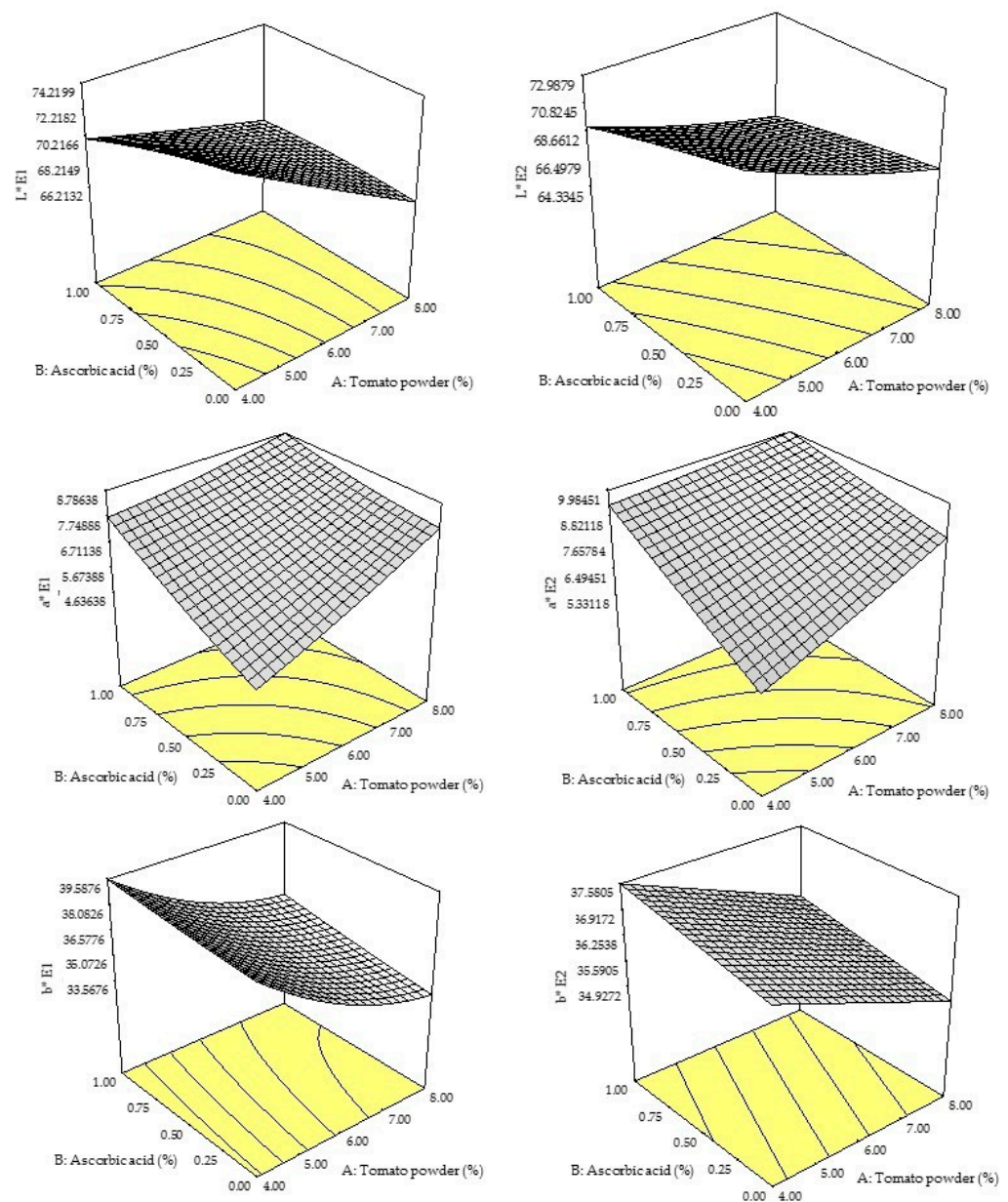


Figure 1. Response surface plots for color values as a function of tomato powder level and ascorbic acid level.

Table 5. Analysis of variance for fitted models of product.

Response	Source	df	Sum of Squares	Mean Squares	F-Value	p-Value
L* E1	Regression	5	62.62	12.52	99.04 185.42	<0.0001 <0.0001
	Lack of fit	3	0.88	0.29		
	Pure error	4	6.320×10^{-3}	1.580×10^{-3}		
	Residual	7	0.89	0.13		
	Total	12	63.51			
L* E2	Regression	5	60.30	12.06	76.50 100.27	<0.0001 0.0003
	Lack of fit	3	1.09	0.36		
	Pure error	4	0.014	3.620×10^{-3}		
	Residual	7	1.10	0.16		
	Total	12	61.40			
a* E1	Regression	5	14.21	2.84	18.87 31.00	0.0006 0.0031
	Lack of fit	3	1.01	0.34		
	Pure error	4	0.043	0.011		
	Residual	7	1.05	0.15		
	Total	12	15.26			
a* E2	Regression	5	18.39	3.68	18.84 111.70	0.0006 0.0003
	Lack of fit	3	1.35	0.45		
	Pure error	4	0.016	4.030×10^{-3}		
	Residual	7	1.37	0.20		
	Total	12	19.75			
b* E1	Regression	5	40.88	8.18	30.05 162.28	0.0001 0.0001
	Lack of fit	3	1.89	0.63		
	Pure error	4	0.016	3.880×10^{-3}		
	Residual	7	1.90	0.27		
	Total	12	42.79			
b* E2	Regression	5	6.32	3.16	4.88 3859.97	0.0333 <0.0001
	Lack of fit	3	6.48	0.65		
	Pure error	4	1.120×10^{-3}	2.800×10^{-4}		
	Residual	7	6.49	1.08		
	Total	12	12.81			
ΔE E1	Regression	5	19.77	3.95	7.93 1614.87	0.0084 <0.0001
	Lack of fit	3	3.49	1.16		
	Pure error	4	2.880×10^{-3}	7.200×10^{-4}		
	Residual	7	3.49	0.50		
	Total	12	23.26			
ΔE E2	Regression	5	12.77	2.55	2.35 3896.11	0.1477 <0.0001
	Lack of fit	3	7.60	2.53		
	Pure error	4	2.600×10^{-3}	6.500×10^{-4}		
	Residual	7	7.60	1.09		
	Total	12	20.37			

The mathematical models for the a* values:

$$a^* E1 = 6.99 + 1.06 \cdot A + 1.02 \cdot B + 0.12 \cdot A^2 + 0.13 \cdot B^2 - 0.53 \cdot AB/R^2 = 0.9309 \quad (4)$$

$$a^* E2 = 8.24 + 0.95 \cdot A + 1.37 \cdot B + 0.046 \cdot A^2 + 6.034 \times 10^{-3} \cdot B^2 - 0.63 \cdot AB/R^2 = 0.9308 \quad (5)$$

The a* value increased proportionally to the proportion of TP, which is in line with expectations, since TP is intensely red-colored. The E1 extrusion temperatures caused a decrease in the a* values in the corn extrudates with the addition of AA, while the E2 temperatures resulted in an increase. Such a decrease in the a* value by increasing the extrusion

temperature was shown by the authors of [8,12], which suggest the greater degradation of pigments at higher temperatures, while the authors of [48] showed the opposite effect. According to models (4) and (5) and the analysis of variance (Tables 5 and 6), the addition of TP and AA at both extrusion temperatures had a significant positive linear influence on the a^* value (Figure 1). The interaction of these two variables also had a significant impact. The increase in the a^* value as a result of the AA addition implies that AA, as an antioxidant, reduces the degradation of pigments, as previously described in the case of lutein.

The mathematical models for the b^* values:

$$b^* E1 = 35.75 - 2.45 \cdot A + 0.56 \cdot B + 0.94 \cdot A^2 + 0.058 \cdot B^2 + 0.17 \cdot AB/R^2 = 0.9555 \quad (6)$$

$$b^* E2 = 36.25 - 0.96 \cdot A + 0.37 \cdot B/R^2 = 0.4937 \quad (7)$$

At the E1 extrusion temperatures, the TP addition had a significant negative linear and positive quadratic effect on the b^* value (model (6), Tables 5 and 6, Figure 1). The addition of AA had a significant linear positive impact on the b^* , which proves yellow-pigment protection (Table 5). At the E2 extrusion temperatures, the proposed linear mathematical model shows statistical significance (Table 5) but a poor correlation with the experimental data ($R^2 = 0.4937$). The addition of TP had a significant influence on the b^* value (Table 6).

The mathematical models for the total color change (ΔE):

$$\Delta E E1 = 5.30 - 0.42 \cdot A - 0.87 \cdot B - 1.52 \cdot A^2 + 1.36 \cdot B^2 + 1.21 \cdot AB/R^2 = 0.8499 \quad (8)$$

$$\Delta E E2 = 4.77 - 0.78 \cdot A - 0.52 \cdot B - 0.27 \cdot A^2 + 1.56 \cdot B^2 + 0.31 \cdot AB/R^2 = 0.6288 \quad (9)$$

The values for the ΔE mostly ranged between 3 and 6, which is considered to be the average visibility of the color change. At both extrusion temperatures, the addition of AA resulted in less color change compared to the raw mixtures.

Considering that the addition of AA and TP had a significant influence on the L^* , a^* and b^* parameters at the E1 temperatures, TP had a significant negative quadratic influence on the ΔE , and AA had a significant negative linear and positive quadratic influence (Table 6). Proposed model (9) for the E2 extrusion temperatures was not significant (Table 5) and the correlation (0.6288) to the experimental data was not very good, but among all the proposed models, this one had the best fitting. AA had a significant positive quadratic influence on the total color change.

Table 6. Degrees of significance (p -values) of the polynomial regression model coefficients corresponding to each response *.

Source	$L^* E1$	$L^* E2$	$a^* E1$	$a^* E2$	$b^* E1$	$b^* E2$	$\Delta E E1$	$\Delta E E2$
A	<0.0001	<0.0001	0.0003	0.0012	<0.0001	0.0154	0.1937	0.1081
B	0.0002	<0.0001	0.0004	0.0001	0.0328	0.2888	0.0196	0.2597
A^2	0.7543	0.1824	0.6256	0.8674	0.0203	-	0.0090	0.3763
B^2	0.2803	0.6410	0.5837	0.9825	0.8592	-	0.0151	0.0415
AB	0.0005	0.1566	0.0282	0.0242	0.5353	-	0.0110	0.5706

* Significant at $p < 0.05$.

3.5. Sensory Analysis

The evaluation was carried out in such a way that all the extrudates obtained at higher extrusion temperatures were evaluated, while only a few samples were chosen for comparison among the extrudates obtained at lower temperatures because they practically had unacceptable sensory properties due to high hardness. The results are presented in Table 7.

Table 7. Sensory analysis of selected products.

TP (%)	AA (%)		Uniformity/Color	Structure/Crispness	Consistency/Chewiness	Odor	Flavor	Overall Acceptability
0	0	E1	2.51 ^{bc}	3.14 ^a	2.74 ^{abc}	2.57 ^{bc}	2.97 ^{abcde}	3.49 ^{abc}
0	0.5	E1	3.31 ^{efg}	3.86 ^{abcd}	2.97 ^{abc}	2.57 ^{bc}	3.20 ^{cde}	3.98 ^{bcd}
0	1	E1	3.43 ^{fg}	4.29 ^d	3.31 ^c	2.49 ^{abc}	3.31 ^{de}	4.21 ^d
0	0.5	E2	3.66 ^g	3.14 ^a	2.60 ^{ab}	2.80 ^c	3.43 ^e	3.77 ^{bcd}
4	0	E1	3.31 ^{efg}	4.00 ^{bcd}	3.31 ^c	2.31 ^{ab}	3.09 ^{bcde}	4.08 ^{cd}
4	0.5	E1	3.10 ^{def}	3.75 ^{abcd}	2.90 ^{abc}	2.25 ^{ab}	2.83 ^{abcde}	3.71 ^{bcd}
4	1	E1	2.50 ^{bc}	3.50 ^{abc}	2.90 ^{abc}	2.25 ^{ab}	2.50 ^{ab}	3.41 ^{ab}
6	0	E1	3.10 ^{def}	4.13 ^{cd}	3.10 ^{bc}	2.33 ^{ab}	2.70 ^{abcd}	3.84 ^{bcd}
6	0.5	E1	2.80 ^{cd}	4.13 ^{cd}	3.30 ^c	2.25 ^{ab}	2.80 ^{abcde}	3.82 ^{bcd}
6	1	E1	2.70 ^{bcd}	3.75 ^{abcd}	2.90 ^{abc}	2.10 ^a	2.60 ^{abc}	3.51 ^{abc}
8	0	E1	2.30 ^{ab}	3.88 ^{abcd}	3.00 ^{abc}	2.25 ^{ab}	2.50 ^{ab}	3.48 ^{abc}
8	0.5	E1	2.90 ^{cde}	3.75 ^{abcd}	3.00 ^{abc}	2.33 ^{ab}	2.50 ^{ab}	3.62 ^{abcd}
8	1	E1	2.60 ^{bc}	3.88 ^{abcd}	3.10 ^{bc}	2.18 ^{ab}	2.40 ^{ab}	3.51 ^{abc}
4	0	E2	2.50 ^{bc}	4.00 ^{cd}	3.10 ^{bc}	2.33 ^{ab}	3.00 ^{bcde}	3.73 ^{bcd}
6	0.5	E2	2.00 ^a	3.25 ^{ab}	2.50 ^a	2.18 ^{ab}	2.30 ^a	3.06 ^a

TP—tomato powder level. AA—ascorbic acid level. E1—135/170/170 °C extrusion temperatures. E2—100/150/150 °C extrusion temperatures. Means followed by the same letters in the columns are not statistically different at 5% probability. The results are presented as mean scores of sensory attributes.

The sample containing 6% TP and 0.5% AA produced at the E2 extrusion temperatures achieved two out of the maximum four points for uniformity/color. The best grades were given to the sample without TP but containing 0.5% AA (3.66) and to the sample with 4% TP (3.31). In general, samples that received higher scores for structure also received higher scores for consistency: corn extrudates containing 1% AA, and samples containing 4% TP without AA obtained at the E1 extrusion temperatures. The lowest score for smell, statistically significantly different from the others, was given to the sample containing 6% TP and 1% AA, produced at the E1 extrusion temperatures, while the best score was given to the sample of pure semolina (2.49 out of a maximum of 3). Likewise, the best marks for taste were given to the pure corn extrudates and the samples containing 4%TP (3 or more out of 4), while the marks fell proportionally to the increase in the proportion of TP. With regard to the mentioned properties, the best overall quality rating (above 4 out of the maximum rating of 5) was given to the extrudates of corn with 1% AA and 4% TP, both produced at the E1 extrusion temperatures, which is to be expected since they received the best or very high ratings for each of the assessed properties. Likewise, the lowest overall quality score was given to the sample containing 6% TP and 0.5% AA extruded at the lower E2 temperatures.

4. Conclusions

The starting assumption of producing an extruded product with increased nutritional value compared to pure corn extrudates, and, at the same time, satisfactory sensory characteristics by adding TP, was confirmed by using the E1 extrusion temperatures. Extrudates obtained at the E2 temperatures did not have acceptable sensory results. The E1 extrusion temperatures led to increased protein contents, no change in the fiber contents and decreased fat contents. AA was added to the extrusion mixtures in order to protect valuable components susceptible to oxidation, primarily carotenoids. We showed that AA survived the extrusion conditions at both extrusion regimes, so it could serve as an antioxidant. Unfortunately, the tomato carotenes did not have stability for the extrusion conditions, even in the presence of AA. The lutein and zeaxanthin contents, in contrast, increased during extrusion, especially at the E1 temperatures and with the AA addition. Both AA and TP influenced the final color of the extrudates. Additional research is necessary to find suitable sources of the main tomato carotenes, primarily lycopene, with better stability in extrusion conditions.

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