

Article

Soluble Carbohydrates in Several Transylvanian Potato Cultivars

Edward Muntean ^{1,*}  and Nina Băraşcu ^{2,*}
¹ Department of Food Science, Faculty of Food Science and Technology, University of Agricultural Sciences and Veterinary Medicine Cluj Napoca, 3-5 Calea Mănăştur, 400372 Cluj Napoca, Romania

² National Institute for Research and Development for Potato and Sugar Beet Braşov, 2 Fundăturii Str., 500470 Braşov, Romania

* Correspondence: emuntean@usamvcluj.ro (E.M.); nina.barascu@gmail.com (N.B.)

Abstract: This paper is the first to report the soluble carbohydrate content at harvest for eight Transylvanian potato cultivars: Christian, Cumidava, Kronstadt, Riviera, Roclas, Rustic, Tampa and Zamolxis. The aim of this study is to explore the soluble carbohydrate composition of the above-mentioned cultivars, since such quantitative information is important for breeding programs, consumers and processing units. High performance liquid chromatography was used for analysis, separations being achieved using a Prominence Shimadzu system with a refractive index detector, under isocratic conditions with a mobile phase consisting of acetonitrile: water (80:20%) delivered at 1 mL/min; baseline separations of the target analytes were accomplished with an EC 250/4 Nucleodur 100–5 NH₂ RP column in less than 10 min. The carbohydrate concentrations were found to range from 24.03 mg/100 g (Zamolxis) to 76.58 mg/100 g (Riviera) for fructose, while the corresponding range was from 52.78 mg/100 g (Zamolxis) to 232.97 mg/100 g (Riviera) for glucose and from 238.41 mg/100 g (Zamolxis) to 378.45 (Cumidava) for sucrose. Chromatographic data were then subjected to chemometric analysis; the association of these complementary techniques allowed a fast selection of cultivars with low-reducing carbohydrate content for food processing purposes—the cultivars Zamolxis, Kronstadt, Christian and Roclas were outlined exhibiting both the lowest reducing carbohydrate content and the lowest sucrose content.

Keywords: potatoes; fructose; glucose; sucrose; carbohydrates; HPLC; acrylamide precursors



Citation: Muntean, E.; Băraşcu, N. Soluble Carbohydrates in Several Transylvanian Potato Cultivars. *Plants* **2023**, *12*, 70. <https://doi.org/10.3390/plants12010070>

Academic Editors: Itziar A. Montalbán, Paloma Moncaleán and Jorge Canhoto

Received: 21 October 2022
Revised: 9 December 2022
Accepted: 20 December 2022
Published: 23 December 2022



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Potato (*Solanum tuberosum* L.) is the most important vegetable in the human diet; it has a high yielding, a high nutritive value, while giving elevated returns to farmers [1]. Potato is a nutritious, tasty and inexpensive vegetable, a staple food of many people, covering a large share in the economic balance of numerous countries. Potato tubers supply high amounts of carbohydrates and also a significant content of proteins, minerals, carotenoids and vitamin C [2–5]; they have a wide variety of table, processed, livestock feed and industrial uses, and in the meantime, are much appreciated for their health-related benefits [6,7]. As there is a continuous increase in the demand of processed food, the potato processing industry is a fast growing sector.

The content of soluble carbohydrates from potato is an important factor for both consumers' acceptability and processing plants, strongly influencing their taste, nutritive value and behavior during the heat treatment; the monosaccharides fructose and glucose (reducing carbohydrates) and the non-reducing disaccharide sucrose are the major soluble carbohydrates found in potato tubers [8–13]. The overall soluble carbohydrate content (SCC) of potato tubers is low, at around 0.5–1% of the fresh weight, depending on the factors such as genotype, maturity, physiological state, temperature during growth, mineral nutrition, irrigation, storage duration and storage conditions [10,14–16]. During low temperature storage, the SCC increases significantly in most genotypes [17–19]; this

process, also known as “cold induced sweetening”, depends on factors such as the storage temperature, dormancy break, sprouting after dormancy break and tuber senescence [17].

The reducing carbohydrate content is one of the most important parameters that influences the processing quality of potatoes; a higher value for this renders potato tubers unsuitable for use as raw material for processing, especially for dehydrated and fried products. Potato tubers that contain high concentrations of reducing carbohydrates lead to unacceptable brown colored chips and fries as a result of the Maillard reaction between these compounds and amino acids [20,21]; besides, the Maillard reaction is also related to the formation of the hazardous acrylamide in the case of high-temperature processed potato products [22–25]. Acrylamide is a reported carcinogen [26], food processing units preferring potato cultivars with lower SCC for limiting its formation [23,27–29]. The SCC of potato tubers is important not only for the above-mentioned issues but also for their acceptance by consumers; the higher this content is, the sweeter their taste is. Previous research on SCC from potato tubers revealed that sucrose is the major carbohydrate component of these and the most important involved in their sweetness [8,9,13,15,25,30–32].

Among the reported analytical methods utilized for SCC's determination, the chromatographic methods are the most common techniques [33,34]. The gas chromatographic methods were the first ones able to provide a good resolution for these compounds, but they required a laborious and time-consuming derivatization step [35,36]. High performance liquid chromatography (HPLC) is more convenient regarding sample preparation, currently being the most used method [8,13,37]. HPLC with refractive index detection (RID) was used for the determination of soluble carbohydrates in food products, because of its numerous advantages (e.g., reliability, simplicity, price) [10,32,38,39]. Some major drawbacks of RID such as the lack of sensitivity and the incompatibility with gradients can be compensated using other types of detection, such as evaporative light scattering detection [40–42], electrochemical detection [43,44] or mass spectrometry [29,45,46], but prices and systems' complexity are higher. Using HPLC, non-derivatized carbohydrates are usually separated on silica-based amino columns [47]; ion chromatography can provide an alternative to such separations [29,48–50], while capillary electrophoresis offers a different approach [51,52]. In most cases, the soluble carbohydrate extraction was accomplished using ethanolic solutions, heating and mixing providing a higher efficiency for the extraction procedure. Unfortunately, the liquid–solid extraction process is not selective, leading to an extract which contains, besides the desired analytes, many other compounds; some of them can affect the chromatographic separations, leading even to an early degradation of HPLC columns' performances, hence a sample preparation stage is a must in analysis (Carrez method, dialysis, solid phase extraction-SPE, etc.). SPE is a rapid and reproducible sample preparation technique that allows a selective removal of co-extracted substances [53]. A faster alternative to traditional methods, mainly used in food quality testing, is near infrared spectroscopy, which is able to predict the carbohydrate content in potatoes in minutes, with minimal or no sample preparation [54–59].

The purpose of this study is to explore the soluble carbohydrate composition of several Transylvanian potato cultivars, on which, up to the present, there are no data; such quantitative information is important for breeding programs [60], consumers and processing units. The study is relevant because besides dry matter, the SCC is an important quality parameter for assessing the potential of potato tubers to produce acceptable processed products with appropriate color and taste; the sucrose concentration of tubers is also an indicator of their maturity; hence, it can also be considered as a decision tool for harvesting [61]. An optimized HPLC–RID method was used in this study, after an SPE stage, which is necessary since certain matrix compounds can interfere with the chromatographic separation while negatively affecting the analytical column. For a fast highlight of the cultivars with low reducing carbohydrate content which can be considered for food processing purposes, chromatographic data were subjected to chemometric analysis.

2. Results

The SCC of potato tubers is a result of a complex equilibrium between starch degradation, starch biosynthesis and respiration. Chromatographic analysis revealed different soluble carbohydrate fingerprints for the studied genotypes, a representative one being presented in Figure 1.

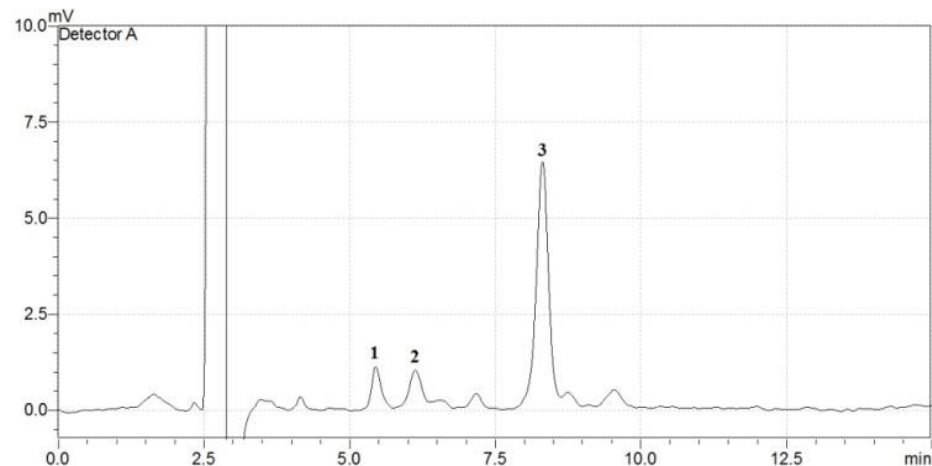


Figure 1. Representative chromatographic fingerprint of soluble carbohydrates having sucrose as major component (Zamolxis cultivar). Peak D's: 1—fructose, 2—glucose, 3—sucrose.

Table 1 summarizes the obtained data for the studied potato cultivars; it highlights that the major soluble carbohydrate is sucrose, followed by glucose and fructose; for sucrose, the concentration range was from 238.41 mg/100 g (Zamolxis) to 378.45 (Cumidava), for glucose, the corresponding range was from 52.78 mg/100 g (Zamolxis) to 232.97 mg/100 g (Riviera), while for fructose, the concentrations ranged from 24.03 mg/100 g (Zamolxis) to 76.58 mg/100 g (Riviera). The dry matter ranged from 18.74% (Riviera) to 24.11% (Rustic). The lowest concentrations of reducing carbohydrates were recorded for Zamolxis, Kronstadt, Christian and Roclas cultivars (76.81 to 99.01 mg/100 g).

Table 1. SCC in potato cultivars at harvest (mean values of three replicates \pm standard deviation; means followed by different superscript letters within the same column indicate significant differences, established using one-way ANOVA with post-hoc Tukey's HSD test ($p < 0.05$)).

Cultivar	Fructose [mg/100 g]		Glucose [mg/100 g]		Sucrose [mg/100 g]		Dry Matter (DM) [%]		Reducing Carbohydrates [mg/100 g]
Christian	35.12	$\pm 1.73^c$	60.58	$\pm 2.96^c$	260.12	$\pm 13.04^b$	20.20	$\pm 1.20^a$	95.70 ^d
Cumidava	38.91	$\pm 1.68^c$	154.51	$\pm 7.61^b$	378.45	$\pm 18.91^a$	24.05	$\pm 1.43^a$	193.42 ^c
Kronstadt	25.60	$\pm 1.21^c$	63.83	$\pm 2.87^c$	249.83	$\pm 12.47^b$	21.40	$\pm 1.29^a$	89.43 ^d
Riviera	76.58	$\pm 3.75^a$	232.97	$\pm 11.45^a$	283.71	$\pm 14.11^b$	18.74	$\pm 1.05^b$	309.55 ^a
Roclas	25.43	$\pm 1.25^c$	73.58	$\pm 3.57^c$	255.61	$\pm 10.15^b$	22.94	$\pm 1.34^a$	99.01 ^d
Rustic	54.28	$\pm 2.61^b$	196.52	$\pm 9.71^a$	325.11	$\pm 15.96^{a,b}$	24.11	$\pm 1.25^a$	250.8 ^b
Tampa	34.81	$\pm 1.69^c$	167.92	$\pm 8.29^b$	350.29	$\pm 17.33^a$	22.56	$\pm 1.33^a$	202.73 ^c
Zamolxis	24.03	$\pm 1.21^c$	52.78	$\pm 2.54^c$	238.41	$\pm 11.83^b$	23.39	$\pm 1.35^a$	76.81 ^d
Min	24.03		52.78		238.41		18.74		76.81
Max	76.58		232.97		378.45		24.11		309.55

For the fructose content, the obtained results showed no significant differences for the cultivars Christian, Cumidava, Kronstadt, Roclas, Tampa and Zamolxis; however, there was a significant differences ($p < 0.05$) between these and the cultivars Rustic and Riviera. For the glucose content, there were no significant differences for the cultivars Christian, Kronstadt, Roclas and Zamolxis, as well as for the cultivars Cumidava and Tampa/Rustic and Riviera. For sucrose, there were no significant differences for the cultivars Christian, Kronstadt, Riviera, Rustic, Roclas and Zamolxis, as well as for cultivars Cumidava, Rustic and Tampa.

Statistical analysis of dry matter contents highlighted only a significant difference, for the cultivar Riviera; for the other cultivars, there were no significant differences ($p < 0.05$). For the most relevant parameter—the reducing carbohydrates—there were no significant differences between cultivars Christian, Kronstadt, Roclas and Zamolxis, as well as for cultivars Cumidava and Tampa; however, there was a significant difference ($p < 0.05$) between these and the cultivars Rustic and Riviera.

Principal component analysis (PCA) of the obtained data was accomplished using four variables (the contents of fructose, glucose and sucrose, as well as the dry matter), leading to the model from Figure 2a, which explains 93.19% of data variability, revealing two data clusters—one including the cultivars Cumidava, Tampa and Rustic, while the other one includes the cultivars Christian, Kronstadt, Roclas and Zamolxis. The first cluster contains medium-late cultivars, suitable for autumn-winter consumption, their tubers being characterized by the highest concentrations of sucrose and glucose and the highest loadings on the second principal component (PC2). The second cluster includes cultivars with lower concentrations of fructose and glucose, with low loadings on both PC1 and PC2. The Riviera cultivar has a distinct position in this context, being the only genotype which exhibited the highest amounts of fructose and glucose, containing in the meantime an important amount of saccharose.

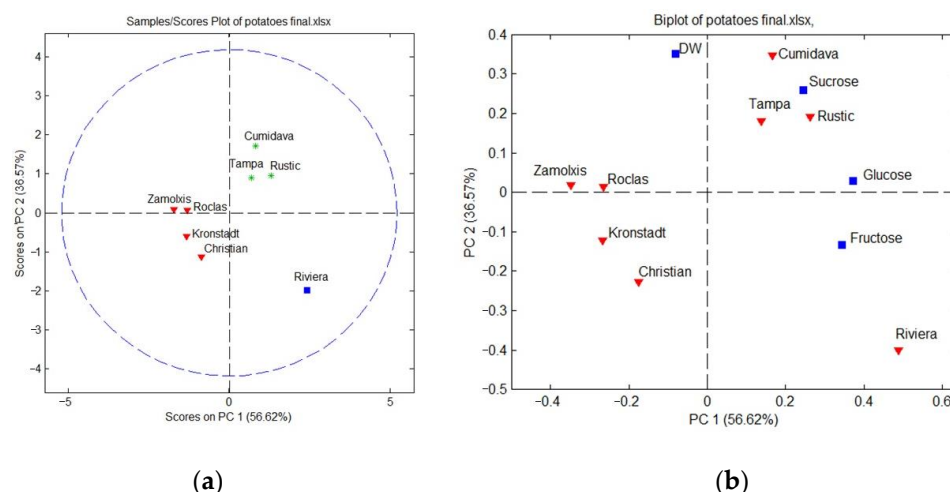


Figure 2. PCA scores (a) and biplot (b) for potato samples.

The biplot from Figure 2b reveals a positive correlation between the content of reducing carbohydrates; the correlation analysis (Table 2) for the obtained data also shows a strong and significant correlation between the concentrations of fructose and that of glucose, with a high Pearson's coefficient (0.8748), which is in agreement with the former reported results [8,12]; sucrose was also significantly correlated with the reducing carbohydrate content but with lower coefficients, showing a moderate relationship with the reducing carbohydrate content for the studied genotypes at harvest. Cluster analysis was accomplished by Ward's method, using Mahalanobis distance, leading to the dendrogram from Figure 3, validating the results obtained by PCA.

Table 2. Correlation matrix for the studied variables.

	Fructose	Glucose	Sucrose	DM
Fructose	1			
Glucose	0.8748	1		
Sucrose	0.2933	0.6527	1	
DM	−0.4622	−0.1181	0.4013	1

Note: DM—dry matter.

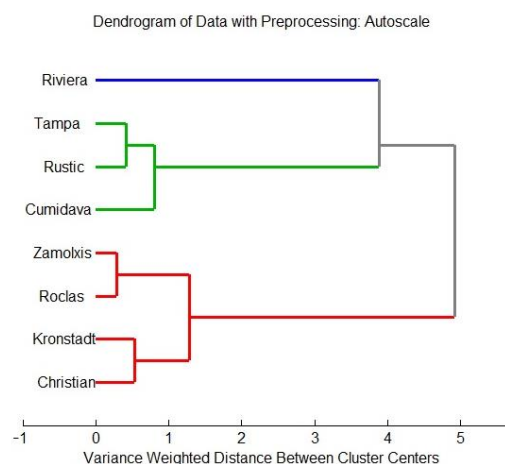


Figure 3. Dendrogram for cluster analysis (Ward's method, using Mahalanobis distance).

3. Discussion

As highlighted in the introductory section, it is generally recognized that the higher the levels of reducing carbohydrates, the lower the suitability of potato tubers for processing is; besides, by the reaction of reducing carbohydrates with free amino groups during frying and baking (Maillard reaction), the formation of a color can make crisps and chips unacceptable for consumers and even hazardous due to the formation of acrylamide. Because an important desirable characteristic of potato genotypes designed for chipping is a low SCC, many researches have been devoted to the investigation of this issue. In similar studies with the reported one various concentrations of soluble carbohydrates were published, but relatively close with ours; comparing our results with most of the available results in the literature, the variability of the SCC in Transylvanian potato genotypes is lower. Hence, three American cultivars were stated with 80–800 mg/100 g fresh weight (FW) fructose, 160–890 mg/100 g FW glucose and 70–260 mg /100 g FW sucrose [13]; four potato cultivars from Cyprus were found to contain 0–27 mg/100 g FW fructose, 0–153 mg/100 g FW glucose and 750–1370 mg /100 g FW sucrose [12]. In a study on nine Italian potato genotypes and 22 American ones, fructose ranged from 0 to 60 mg/100 g FW, glucose from 20 to 620 mg/100 g FW and sucrose from 40 to 1390 mg/100 g FW [25].

Since several authors reported values relative to the dry weight (DW), Table 3 provides another instance of data from Table 2 in which the results were expressed in g/100 g DW. Four potato genotypes from Virginia were found to contain 0.04–0.07 g/100 g DW fructose, 0.06–0.35 g/100 g DW glucose and 0.34–0.66 g/100 g DW sucrose [11]. In studies performed on Colombian genotypes, the authors found a high variability of concentrations, with the following ranges: 0.1–1.48 g/100 g DW fructose, 0.25–4.53 g/100 g DW glucose and 0.93–1.1 g /100 g DW sucrose [9], then 0.03–2.72 g/100 g DW fructose, 0.05–2.80 g/100 g DW glucose and 0.64–2.95 g /100 g DW sucrose [8].

For the fructose content, the obtained results showed no significant differences for the cultivars Christian, Cumidava, Kronstadt, Roclas, Tampa and Zamolxis; however, there is significant difference ($p < 0.05$) between these and the cultivars Rustic and Riviera. For the glucose content, there are no significant differences for the cultivars Christian, Kronstadt, Riviera, Roclas and Zamolxis, as well as for the cultivars Cumidava, Rustic and Tampa. For sucrose, there are no significant differences for the cultivars Christian, Kronstadt, and Rustic, as well as for cultivars Cumidava, Riviera, Rustic and Tampa, respectively for the cultivars Kronstadt and Rustic. For the reducing carbohydrates and for the total SCC, there are no significant differences between cultivars Christian, Kronstadt, Roclas and Zamolxis, as well as for cultivars Cumidava, Rustic and Tampa; however, there is significant difference ($p < 0.05$) between these cultivars and Riviera.

Table 3. Mean values of SCC in potato cultivars at harvest expressed in g/100 g DW (means followed by different superscript letters within the same column indicate significant differences, established using one-way ANOVA with post-hoc Tukey's HSD test ($p < 0.05$)).

Cultivar	Fructose	Glucose	Sucrose	Reducing Carbohydrates	Total SCC
Christian	0.17 ^c	0.30 ^b	1.29 ^b	0.47 ^c	1.76 ^c
Cumidava	0.16 ^c	0.64 ^a	1.57 ^a	0.80 ^b	2.38 ^b
Kronstadt	0.12 ^c	0.30 ^b	1.17 ^{b,c}	0.42 ^c	1.59 ^c
Riviera	0.41 ^a	1.24 ^b	1.51 ^a	1.65 ^a	3.17 ^a
Roclas	0.11 ^c	0.32 ^b	1.12 ^c	0.43 ^c	1.55 ^c
Rustic	0.23 ^b	0.82 ^a	1.35 ^{a,b}	1.04 ^b	2.39 ^b
Tampa	0.15 ^c	0.74 ^a	1.55 ^a	0.90 ^b	2.45 ^b
Zamolxis	0.10 ^c	0.23 ^b	1.02 ^c	0.33 ^c	1.35 ^c
Min	0.10	0.23	1.02	0.33	1.35
Max	0.41	1.24	1.57	1.65	3.17

In all published cases, sucrose was the major carbohydrate, while fructose and glucose concentrations were smaller than those of sucrose; this is also the case in our study, with glucose/fructose ratios higher than one, possibly due to the relatively high activity of fructokinase diminishing the content of fructose in tubers [62]. A higher content of glucose than that of fructose is also common in other types of potato at harvest [63,64]. The cultivar with the highest overall SCC (593.26 mg/100 g) and also with the highest reducing carbohydrate content (309.55 mg/100 g) is Riviera, while at the other extreme of the dataset, the Zamolxis cultivar had the lowest overall SCC (315.22 mg/100 g) and the lowest reducing carbohydrate content (76.81 mg/100 g). The recommended values for the reducing carbohydrate content considered to be appropriate for acceptable flavor, browning and acrylamide content in roasted and baked potato products are in the range 0.1–0.5 g/kg DW [65], but in some cases, can be lower than 0.035 g/100 g DW [28].

4. Materials and Methods

4.1. Plant Material

Eight potato varieties (Christian, Cumidava, Kronstadt, Riviera, Roclas, Rustic, Tampa and Zamolxis) were cultivated on the experimental fields of the National Institute of Research and Development for Potato and Sugar Beet Brasov, Romania, under the same growing conditions, on a chernozemic soil with the following characteristics: clay—30%, pH—6, humus—4.5%, mobile phosphorus—50 ppm, mobile potassium—over 100, with the degree of base saturation—85%. The experimental field was located at 45°40′26″ N 25°32′11″ E, in a temperate climate area, with the average temperatures and the amount of rainfall during the vegetation period presented in Figure 4. For basic fertilization, 500 kg/ha complex N:P:K—15:15:15 were applied. The revitalization work was carried out mechanically on 4 May 2020, followed by a pre-emergent herbicide treatment with Surdone (1.2 kg/ha. The emergence of potatoes was delayed due to the low amount of precipitation in April. The climatic conditions imposed the application between 4 June and 20 August of nine treatments for the control of potato blight (*Phitophthora infestans*): 1—Ridomil 2.5 kg/ha; 2—Consento 2.0 L/ha; 3—Lieto 450 g/ha; 4—Ridomil 2.5 kg/ha; 5—Cariol Star 0.6 L/ha; 6—Cymco 2.5 kg/ha; 7—Infinito 1.4 L/ha + Lebosol P 5 L/ha; 8—Lieto 450 g/ha; 9—Shirlan 0.4 L/ha. To control aphids and *Leptinotarsa decemlineata*, two treatments were applied, one with Biscaya 0.2 L/ha, the other with Proteus 110OD 0.4 L/ha.

All cultivars were sown on 19 April 2020, then the tubers were harvested on 2 October for the Riviera cultivar, on 12 October for the Christian, Kronstad, Roclas, Zamolxis cultivars and on 26 October for the Cumidava, Rustic and Tampa cultivars, at the maturity stage (Figure 5). The studied potato varieties fall into the following maturity groups: Riviera is a very early variety, Roclas, Christian, Zamolxis, Kronstad are medium early varieties while Cumidava, Tampa and Rustic are medium late varieties. We must mention here that

the climatic conditions in the Brasov area do not always ensure the thermohydric needs of the early and semi-early varieties to show their characteristic earliness. Cumidava, Tâmpa and Rustic varieties are suitable for autumn-winter consumption, while the varieties Roclas, Christian, Kronstad are suitable for early and summer–autumn consumption and Zamolxis variety for summer–autumn consumption [66]. The varieties Tâmpa, Roclas, Zamolxis and Kronstad are the most appropriate for processing [67,68]. Most of these potato varieties were patented by the above-mentioned institute [69], being also recorded in the Official Catalogue of Romanian Potato varieties [70].

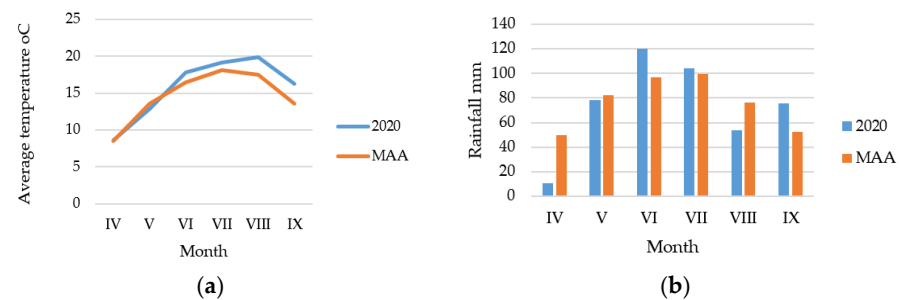


Figure 4. Average temperatures (a) and the amount of rainfall (b) during the vegetation period (MAA: multi-annual average).



Figure 5. Potato cultivars used in this study.

4.2. Chemicals and Standards

HPLC grade acetonitrile and analytical grade ethanol, as well as carbohydrate standards (D-glucose, fructose and sucrose) were from Merck (Darmstadt, Germany). Ultrapure water with a specific resistance of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ was utilized for preparation of mobile phases as well as for samples' dilution, being obtained from a Direct Q 3UV Smart system (Millipore, Darmstadt, Germany). The mobile phase was filtered through a $0.45 \mu\text{m}$ membrane (Millipore Corp., Bedford, MA, USA) and then degassed using an Elmasonic S30 H ultrasonic bath (Elma Hans Schmidbauer GmbH & Co., Singen, Germany).

4.3. Sampling and Extraction

The potato tubers were manually harvested. Five mature and healthy potato tubers without mechanical damages were selected from each cultivar and stored in the dark, at 18°C , for one week. Prior to analysis, they were washed with tap water and dried with paper towels, then peeled manually and diced. After homogenization, representative samples of around 10 g were selected; these were weighed and subjected to extraction and dry matter determination. Three sample replicates were provided for each cultivar and for each type of determination. Carbohydrate extraction was accomplished in a blender, adding 100 mL of 80% ethanol to each sample and homogenizing it for 2 min; the resulting suspension was transferred in a 250 mL flask which was placed in an ultrasonic bath (Elmasonic S30 H, Elma Hans Schmidbauer GmbH & Co., Germany), where it was kept at 60°C for one hour. After cooling, 80% ethanol was added to bring the total volume to 250 mL, the system being therefore mixed for a proper homogenization. After sedimentation, 5 mL of the supernatant was collected and subjected to solid phase extraction.

4.4. Solid Phase Extraction (SPE)

SPE was used for removing the unwanted co-extracted compounds as well as for protecting the analytical column, using Sep-Pak C_{18} cartridges (Waters Associates Inc., Milford, MA, USA). The cartridges were first preconditioned by flushing with 4 mL methanol, then with 4 mL ultrapure water at a flow rate of 1 mL/min [47,53]; 5 mL extracts were passed through the activated cartridges, discarding the first milliliter, then the eluates were collected in 2 mL vials, being subjected to HPLC.

4.5. HPLC Analysis

Analyses were performed on a Shimadzu Prominence HPLC system, consisting of one LC-20AP solvent delivery module, a DGU 20As online degasser, an automatic sample injector SIL-10AF, a RID-10A differential refractive index detector, a CTO-20A column oven and a CBM-20A system controller. Isocratic separations were conducted at 35°C using an EC 250/4 Nucleodur 100–5 NH_2 RP column ($250 \times 4.6 \text{ mm}$, Macherey-Nagel)—a multimode column protected by a pre-column ($30 \text{ mm} \times 4.6 \text{ mm}$), with a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$ acetonitrile in water (80:20 $v/v\%$) as the mobile phase—an optimized Macherey-Nagel procedure [71]; the injection volume was $10 \mu\text{L}$. Under these conditions, baseline separations of the target carbohydrates were accomplished in less than 10 min. The compounds' identification was based both on comparison of the retention times with those of standards and on co-elution after spiking with authentic standards. Quantification was performed by the external standard method. Calibration curves were established using a mixture of fructose, glucose and sucrose standards, at five concentrations (Table 4). Recoveries were calculated by analyzing spiked samples, revealing percentages in the range of 95.27% for fructose and 98.83% for sucrose.

Table 4. Calibration details.

Carbohydrate	Calibration Range [mg/L]	Equation	R ²
Fructose	22.04–551.03	$C = 0.012827 \times A + 0.693289$	0.99756
Glucose	16.97–424.31	$C = 0.014052 \times A + 2.871871$	0.99893
Sucrose	16.22–911.52	$C = 0.024985 \times A + 2.252326$	0.99581

Note: C—concentration; A—peak area.

4.6. The Dry Matter Content

The dry matter content was determined using an AL01-05-100 forced air drying oven (Advantage Lab GmbH, Darmstadt, Germany), by heating samples of around 200 g at 105 °C for eight hours; weighing was accomplished using a Kern ABJ 220 N analytical balance (Kern & Sohn GmbH, Balingen, Germany).

4.7. Data Analysis

HPLC instrument control, data acquisition and chromatographic data analysis were accomplished using LCSolution (Shimadzu Corporation, Japan); statistical analysis was performed in Excel (Microsoft) and in SPSS version 17 (SPSS Inc., Chicago, IL, USA), where the means were processed using analysis of variance and Tukey's honestly significant difference test, at $p \leq 0.05$. The results were reported as means \pm standard error; differences among means are presented using different letters (results with the same letter were not significantly different, at $p < 0.05$). Principal component analysis and cluster analysis were performed using MatLab (Mathworks Inc., Natick, MA, USA) after mean center preprocessing.

5. Conclusions

The obtained results may enable consumers and processors to select the most appropriate potato cultivars with low levels of acrylamide precursors for baking or frying, and also for best chipping performances. The association of HPLC and multivariate analysis allows a fast selection of cultivars with low-reducing carbohydrate content, such as Zamolxis, Kronstadt, Christian and Roclas, these also exhibiting the lowest sucrose content (these cultivars will generate the smallest amounts of acrylamide during frying and baking, as well as a desirable color); more than that, this association revealed clusters with biological relevance, providing valuable data for breeding programs.

The analytical approach used here, involving HPLC analysis of carbohydrates employing SPE, provides a rapid and reliable means to determine the SCC in potato tubers with rapid, specific, reliable and sensitive measurements. SPE affords a convenient removal of the matrix interferences, while maintaining the chromatographic column's integrity and assuring reproducible and good quality separations; it uses small sample and solvent volumes, is fast, simple and relatively cheap, leading to an eluent which can be injected into the HPLC system.

The results of this work contribute relevant knowledge to the SCC of several Transylvanian potato cultivars, enabling a better understanding of the biochemical processes of carbohydrate formation in potato tubers, as well as to use them accordingly as suitable raw materials for processing.

Author Contributions: Conceptualization, E.M.; methodology, E.M.; field experiments, N.B.; sampling and sample preparation, N.B. and E.M.; formal analysis, E.M.; investigation, E.M. and N.B.; resources, E.M. and N.B.; data curation, E.M. and N.B.; writing—original draft preparation, E.M.; writing—review and editing, E.M. and N.B.; visualization, E.M. and N.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Upadhyaya, C.P.; Bagri, D.S. Biotechnological Approaches for Nutritional Improvement in Potato (*Solanum tuberosum* L.). In *Genome Engineering for Crop Improvement*; Upadhyaya, S.K., Ed.; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2021; pp. 253–280. [CrossRef]
- Ezekiel, R.; Singh, N.; Sharma, S.; Kaur, A. Beneficial Phytochemicals in Potato—A Review. *Food Res. Int.* **2013**, *50*, 487–496. [CrossRef]
- Leonel, M.; Do Carmo, E.L.; Fernandes, A.M.; Soratto, R.P.; Ebúrneo, J.A.M.; Garcia, É.L.; Dos Santos, T.P.R. Chemical Composition of Potato Tubers: The Effect of Cultivars and Growth Conditions. *J. Food Sci. Technol.* **2017**, *54*, 2372–2378. [CrossRef] [PubMed]
- Love, S.L.; Pavek, J.J. Positioning the Potato as a Primary Food Source of Vitamin C. *Am. J. Potato Res.* **2008**, *85*, 277–285. [CrossRef]
- USDA. FoodData Central. 2022. Available online: <https://fdc.nal.usda.gov/> (accessed on 24 September 2022).
- Camire, M.E.; Kubow, S.; Donnelly, D.J. Potatoes and Human Health. *Crit. Rev. Food Sci. Nutr.* **2009**, *49*, 823–840. [CrossRef] [PubMed]
- Visvanathan, R.; Jayathilake, C.; Chaminda Jayawardana, B.; Liyanage, R. Health-Beneficial Properties of Potato and Compounds of Interest. *J. Sci. Food Agric.* **2016**, *96*, 4850–4860. [CrossRef] [PubMed]
- Duarte-Delgado, D.; Núñez-López, C.E.; Narváez-Cuenca, C.E.; Restrepo-Sánchez, L.P.; Melo, S.E.; Sarmiento, F.; Kushalappa, A.C.; Mosquera-Vásquez, T. Natural Variation of Sucrose, Glucose and Fructose Contents in Colombian Genotypes of *Solanum tuberosum* Group Phureja at Harvest. *J. Sci. Food Agric.* **2016**, *96*, 4288–4294. [CrossRef]
- Duarte-Delgado, D.; Narváez-Cuenca, C.E.; Restrepo-Sánchez, L.P.; Kushalappa, A.; Mosquera-Vásquez, T. Development and Validation of a Liquid Chromatographic Method to Quantify Sucrose, Glucose, and Fructose in Tubers of *Solanum tuberosum* Group Phureja. *J. Chromatog. B* **2015**, *975*, 18–23. [CrossRef]
- Elmore, J.S.; Mottram, D.S.; Muttucumaru, N.; Dodson, A.T.; Parry, M.A.J.; Halford, N.G. Changes in Free Amino Acids and Sugars in Potatoes Due to Sulfate Fertilization and the Effect on Acrylamide Formation. *J. Agric. Food Chem.* **2007**, *55*, 5363–5366. [CrossRef]
- Okeyo, J.A.; Kushad, M.M. Composition of Four Potato Cultivars in Relation to Cold Storage and Reconditioning. *HortTechnology* **1995**, *5*, 250–253. [CrossRef]
- Kyriacou, M.C.; Ioannides, I.M.; Gerasopoulos, D.; Siomos, A.S. Storage Profiles and Processing Potential of Four Potato (*Solanum tuberosum* L.) Cultivars Under Three Storage Temperature Regimes. *J. Food Agric. Environ.* **2009**, *7*, 31–37.
- Wilson, A.M.; Work, T.M.; Bushway, A.A.; Bushway, R.J. HPLC Determination of Fructose, Glucose, and Sucrose in Potatoes. *J. Food Sci.* **1981**, *46*, 300–301. [CrossRef]
- Kumar, D.; Singh, B.P.; Kumar, P. An Overview of the Factors Affecting Sugar Content of Potatoes. *Ann. Appl. Biol.* **2004**, *145*, 247–256. [CrossRef]
- Matsuura-Endo, C.; Kobayashi, A.; Noda, T.; Takigawa, S.; Yamauchi, H.; Mori, M. Changes in Sugar Content and Activity of Vacuolar Acid Invertase During Low-Temperature Storage of Potato Tubers from Six Japanese Cultivars. *J. Plant Res.* **2004**, *117*, 131–137. [CrossRef] [PubMed]
- Salem, E.; Hassan, A.A.; Awad, M.F.; Mansour, E.; Desoky, E.S.M. Impact of Exogenously Sprayed Antioxidants on Physio-Biochemical, Agronomic, and Quality Parameters of Potato in Salt-Affected Soil. *Plants* **2022**, *11*, 210. [CrossRef]
- Brown, J.; Mackay, G.R.; Bain, H.; Griffith, D.W.; Allison, M.J. The Processing Potential of Tubers of the Cultivated Potato, *Solanum tuberosum* L., after Storage at Low Temperatures. 2. Sugar concentration. *Potato Res.* **1990**, *33*, 219–227. [CrossRef]
- Pereira, A.D.S.; Tai, G.C.C.; Yada, R.Y.; Coffin, R.H.; Souza-Machado, V. Potential for Improvement by Selection for Reducing Sugar Content after Cold Storage for Three Potato Populations. *Theor. Appl. Genet.* **1994**, *88*, 678–684. [CrossRef]
- Zhang, H.; Hou, J.; Liu, J.; Zhang, J.; Song, B.; Xie, C. The Roles of Starch Metabolic Pathways in the Cold-Induced Sweetening Process in Potatoes. *Starch* **2017**, *69*, 1600194. [CrossRef]
- Mackay, G.R.; Brown, J.; Torrance, C.J.W. The Processing Potential of Tubers of the Cultivated Potato, *Solanum tuberosum* L., After Storage at Low Temperature. 1. Fry Colour. *Potato Res.* **1990**, *33*, 211–218. [CrossRef]
- Xiong, X.; Tai, G.C.C.; Seabrook, J.E.A. Effectiveness of Selection for Quality Traits During the Early Stage in the Potato Breeding Population. *Plant Breed.* **2002**, *121*, 441–444. [CrossRef]
- Martinez, E.; Rodriguez, J.A.; Mondragon, A.C.; Lorenzo, J.M.; Santos, E.M. Influence of Potato Crisps Processing Parameters on Acrylamide Formation and Bioaccessibility. *Molecules* **2019**, *24*, 3827. [CrossRef]
- Morales, F.; Capuano, E.; Fogliano, V. Mitigation Strategies to Reduce Acrylamide Formation in Fried Potato Products. *Ann. N. Y. Acad. Sci.* **2008**, *1126*, 89–100. [CrossRef] [PubMed]
- Vinci, R.M.; Mestdag, F.; De Meulenaer, B. Acrylamide Formation in Fried Potato Products—Present and Future, a Critical Review on Mitigation Strategies. *Food Chem.* **2012**, *133*, 1138–1154. [CrossRef]
- Vivanti, V.; Finotti, E.; Friedman, M. Level of Acrylamide Precursors Asparagine, Fructose, Glucose and Sucrose in Potatoes Sold at Retail in Italy and in the United States. *J. Food Sci.* **2006**, *71*, C81–C85. [CrossRef]
- Friedman, M. Acrylamide: Inhibition of Formation in Processed Food and Mitigation of Toxicity in Cells, Animals and Humans. *Food Funct.* **2015**, *6*, 1752–1772. [CrossRef]
- Lim, P.; Jinap, S.; Sanny, M.; Tan, C.; Khatib, A. The Influence of Deep Frying Using Various Vegetable Oils on Acrylamide Formation in Sweet Potato (*Ipomoea batatas* L., Lam) Chips. *J. Food Sci.* **2014**, *79*, T115–T121. [CrossRef]

28. McCann, L.C.; Bethke, P.C.; Simon, P.W. Extensive Variation in Fried Chip Color and Tuber Composition in Cold-Stored Tubers of Wild Potato (*Solanum*) Germplasm. *J. Agric. Food Chem.* **2010**, *58*, 2368–2376. [\[CrossRef\]](#)
29. Zhu, F.; Cai, Y.-Z.; Ke, J.; Corke, H. Compositions of Phenolic Compounds, Amino Acids and Reducing Sugars in Commercial Potato Varieties and Their Effects on Acrylamide Formation. *J. Sci. Food Agric.* **2010**, *90*, 2254–2262. [\[CrossRef\]](#)
30. Amjad, A.; Javed, M.S.; Hameed, A.; Hussain, M.; Ismail, A. Changes in Sugar Contents and Invertase Activity During Low Temperature Storage of Various Chipping Potato Cultivars. *Food Sci. Technol.* **2019**, *40*, 340–345. [\[CrossRef\]](#)
31. Georgelis, N.; Fencil, K.; Richael, C.M. Validation of a Rapid and Sensitive HPLC/MS Method for Measuring Sucrose, Fructose and Glucose in Plant Tissues. *Food Chem.* **2018**, *262*, 191–198. [\[CrossRef\]](#)
32. Weiß, K.; Alt, M. Determination of Single Sugars, Including Inulin, in Plants and Feed Materials by High-Performance Liquid Chromatography and Refraction Index Detection. *Fermentation* **2017**, *3*, 36. [\[CrossRef\]](#)
33. Herrero, M.; Cifuentes, A.; Ibáñez, E.; del Castillo, M.D. Advanced Analysis of Carbohydrates in Foods. In *Methods of Analysis of Food Components and Additives*; Otles, S., Ed.; CRC Press: Boca Raton, FL, USA, 2011; Volume 2, pp. 135–159. [\[CrossRef\]](#)
34. Molnár-Perl, I. Role of Chromatography in the Analysis of Sugars, Carboxylic Acids and Amino Acids in food. *J. Chromatogr. A* **2000**, *891*, 1–32. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Davies, H.V. Rapid Determination of Glucose, Fructose and Sucrose in Potato Tubers by Capillary Gas Chromatography. *Potato Res.* **1988**, *31*, 569–572. [\[CrossRef\]](#)
36. Varns, J.L.; Shaw, R. An Internal Standard for Rapid Analysis of Potato Sugars by Gas Chromatography. *Potato Res.* **1973**, *16*, 183–187. [\[CrossRef\]](#)
37. Karkacier, M.; Erbas, M.; Uslu, M.K.; Aksu, M. Comparison of Different Extraction and Detection Methods for Sugars Using Amino-Bonded Phase HPLC. *J. Chromatogr. Sci.* **2003**, *41*, 331–333. [\[CrossRef\]](#)
38. Hernández, J.L.; González-Castro, M.J.; Alba, I.N.; de la Cruz Garcia, C. High-Performance Liquid Chromatographic Determination of Mono- and Oligosaccharides in Vegetables with Evaporative Light-Scattering Detection and Refractive Index detection. *J. Chromatogr. Sci.* **1998**, *36*, 293–298. [\[CrossRef\]](#)
39. Jalaludin, I.; Kim, J. Comparison of Ultraviolet and Refractive Index Detections in the HPLC Analysis of Sugars. *Food Chem.* **2021**, *365*, 130514. [\[CrossRef\]](#)
40. Condezo-Hoyos, L.; Pérez-López, E.; Rupérez, P. Improved Evaporative Light Scattering Detection for Carbohydrate Analysis. *Food Chem.* **2015**, *180*, 265–271. [\[CrossRef\]](#)
41. Dvořáčková, E.; Šnobllová, M.; Hrdlička, P. Carbohydrate Analysis: From Sample Preparation to HPLC on Different Stationary Phases Coupled with Evaporative Light-Scattering Detection. *J. Sep. Sci.* **2014**, *37*, 323–337. [\[CrossRef\]](#)
42. Young, C.S. Evaporative Light Scattering Detection Methodology for Carbohydrate Analysis by HPLC. *Cereal Foods World* **2002**, *47*, 14–16. [\[CrossRef\]](#)
43. Corradini, C.; Lantano, C.; Cavazza, A. Innovative Analytical Tools to Characterize Prebiotic Carbohydrates of Functional Food Interest. *Anal. Bioanal. Chem.* **2013**, *405*, 4591–4605. [\[CrossRef\]](#)
44. Mechelke, M.; Herlet, J.; Benz, J.P.; Schwarz, W.H.; Zverlov, V.V.; Liebl, W.; Kornberger, P. HPAEC-PAD for Oligosaccharide Analysis—Novel Insights Into Analyte Sensitivity and Response Stability. *Anal. Bioanal. Chem.* **2017**, *409*, 7169–7181. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Barzen-Hanson, K.A.; Wilkes, R.A.; Aristilde, L. Quantitation of Carbohydrate Monomers and Dimers by Liquid Chromatography Coupled with High-Resolution Mass Spectrometry. *Carbohydr. Res.* **2018**, *468*, 30–35. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Salman, M.; Abdel-Hameed, E.S.S.; Bazaid, S.A.; Al-Shamrani, M.G.; Mohamed, F.A. Liquid Chromatography-Mass Spectrometry (LC-MS) Method for the Determination of Sugars in Fresh Pomegranate Fruit Juices. *Der Pharma Chem.* **2014**, *6*, 320–333.
47. Martínez Montero, C.; Doderio, R.; Guillén Sánchez, D.A.; Barroso, C.G. Analysis of Low Molecular Weight Carbohydrates in Food and Beverages: A Review. *Chromatographia* **2004**, *59*, 15–30. [\[CrossRef\]](#)
48. Guignard, C.; Jouve, L.; Bogéat-Triboulot, M.B.; Dreyer, E.; Hausman, J.F.; Hoffmann, L. Analysis of Carbohydrates in Plants by High-Performance Anion-Exchange Chromatography Coupled with Electrospray Mass Spectrometry. *J. Chromatogr. A* **2005**, *1085*, 137–142. [\[CrossRef\]](#)
49. Lamb, J.D.; Myers, G.S.; Edge, N. Ion Chromatographic Analysis of Glucose, Fructose and Sucrose Concentrations in Raw and Processed Vegetables. *J. Chromatogr. Sci.* **1993**, *31*, 353–357. [\[CrossRef\]](#)
50. Suksom, W.; Wannachai, W.; Boonchiangma, S.; Chanthai, S.; Srijaranai, S. Ion Chromatographic Analysis of Monosaccharides and Disaccharides in Raw Sugar. *Chromatographia* **2015**, *78*, 873–879. [\[CrossRef\]](#)
51. Mantovani, V.; Galeotti, F.; Maccari, F.; Volpi, N. Recent Advances in Capillary Electrophoresis Separation of Monosaccharides, Oligosaccharides and Polysaccharides. *Electrophoresis* **2018**, *39*, 179–189. [\[CrossRef\]](#)
52. Zhou, D.D.; Zhang, Q.; Li, S.P.; Yang, F.Q. Capillary Electrophoresis in Phytochemical Analysis (2014–2017). *Sep. Sci. Plus* **2018**, *1*, 676–701. [\[CrossRef\]](#)
53. Xu, W.; Liang, L.; Zhu, M. Determination of Sugars in Molasses by HPLC Following Solid-Phase Extraction. *Int. J. Food Prop.* **2015**, *18*, 547–557. [\[CrossRef\]](#)
54. Ayvaz, H.; Santos, A.M.; Moyseenko, J.; Kleinhenz, M.; Rodriguez-Saona, L.E. Application of a Portable Infrared Instrument for Simultaneous Analysis of Sugars, Asparagine and Glutamine Levels in Raw Potato Tubers. *Plant Foods Hum. Nutr.* **2015**, *70*, 215–220. [\[CrossRef\]](#) [\[PubMed\]](#)

55. Chen, J.Y.; Zhang, H.; Miao, Y.; Asakura, M. Nondestructive Determination of Sugar Content in Potato Tubers Using Visible and Near Infrared Spectroscopy. *Jpn. J. Food Eng.* **2010**, *11*, 59–64. [\[CrossRef\]](#)
56. Fernández-Ahumada, E.; Garrido-Varo, A.; Guerrero-Ginel, J.E.; Wubbels, A.; Van der Sluis, C.; Van der Meer, J.M. Understanding Factors Affecting Near Infrared Analysis of Potato Constituents. *J. Near Infrared Spectrosc.* **2006**, *14*, 27–35. [\[CrossRef\]](#)
57. Haase, N.U. Rapid Estimation of Potato Tuber Quality by Near-Infrared Spectroscopy. *Starch* **2006**, *58*, 268–273. [\[CrossRef\]](#)
58. Haase, N.U. Prediction of Potato Processing Quality by Near Infrared Reflectance Spectroscopy of Ground Raw Tubers. *J. Near Infrared Spectrosc.* **2011**, *19*, 37–45. [\[CrossRef\]](#)
59. Lebot, V. Near Infrared Spectroscopy for Quality Evaluation of Root Crops: Practical Constraints, Preliminary Studies and Future Prospects. *J. Root Crops* **2012**, *38*, 3–14.
60. Dale, M.F.B.; Bradshaw, J.E. Progress in Improving Processing Attributes in Potato. *Trends Plant Sci.* **2003**, *8*, 310–312. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Heltoft, P.; Wold, A.B.; Molteberg, E.L. Maturity Indicators for Prediction of Potato (*Solanum tuberosum* L.) Quality During Storage. *Postharvest Biol. Technol.* **2017**, *129*, 97–106. [\[CrossRef\]](#)
62. Sowokinos, J.R. Biochemical and Molecular Control of Cold-induced Sweetening in Potatoes. *Am. J. Potato Res.* **2001**, *78*, 221–236. [\[CrossRef\]](#)
63. Murniece, I.; Karklina, D.; Galoburda, R.; Sabovics, M. Reducing Sugar Content and Colour Intensity of Fried Latvian Potato Varieties. *LLU Raksti* **2010**, *24*, 20–30.
64. Rodríguez Galdón, B.; Ríos Mesa, D.; Rodríguez Rodríguez, E.M.; Díaz Romero, C. Influence of the Cultivar on the Organic Acid and Sugar Composition of Potatoes. *J. Sci. Food Agric.* **2010**, *90*, 2301–2309. [\[CrossRef\]](#)
65. Biedermann-Brem, S.; Noti, A.; Grob, K.; Imhof, D.; Bazzocco, D.; Pfefferle, A. How Much Reducing Sugar May Potatoes Contain to Avoid Excessive Acrylamide Formation During Roasting and Baking? *Eur. Food Res. Technol.* **2003**, *217*, 369–373. [\[CrossRef\]](#)
66. Bozeşan, I.; Draica, C. Tâmpa: A New Potato Variety for Autumn-Winter Consumption. *Sci. Pap. Ann. ICPC Braşov* **2001**, *XXVIII*, 9–18.
67. Chiru, S. The “Roclas” Potato Variety. *Sci. Pap. Ann. ICPC Braşov* **1995**, *XXII*, 33–38.
68. Chiru, S. The “Rustic” Potato Variety. *Sci. Pap. Ann. ICPC Braşov* **1995**, *XXII*, 38–43.
69. INCDCSZ Patents—Patents from the National Institute of Research and Development for Potato and Sugar Beet Brasov, Romania. Available online: <https://potato.ro/brevete-si-certificari/> (accessed on 25 May 2022).
70. INCDCSZ Catalogue—Official Catalogue of Romanian Potato Varieties from the National Institute of Research and Development for Potato and Sugar Beet Brasov, Romania. Available online: http://www.potato.ro/_publicatii_files/soiuri/soiuri/Soiuri%20romanesti%20Eng.pdf (accessed on 25 May 2022).
71. MN App.No. 122160—Macherey Nagel Application Database. Available online: <https://chromaappdb.mn-net.com> (accessed on 15 September 2022).

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.