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On adulteration of fruit and berry raw materials

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1. SUMMARY

We studied organoleptic, physical, chemical parameters, and nutrient composition of strawberry, raspberry, and melon powders and identified their profile of organic acids and mineral composition produced by a Russian company. It was found that the color and flavor ranges of the studied materials were uncharacteristic of the initial raw materials. The actual protein and lipids levels did not correspond to the ones declared by the manufacturer in the labeling, and were uncharacteristic of the processed raw materials. In all powder samples the sugars were represented by sucrose in 80-97%. This high level of sucrose content indicated the addition of 40.4-52.3% white sugar. The amount and ratio of organic acids did not correspond to the profile of natural raw materials. Thus, the strawberry powder lacked oxalic and tartaric acids, the raspberry raw material lacked malic acid, and the melon material – citric acid. The strawberry powder above the detection limit did not contain such essential macro- and microelements as Ca, Mg, B, Co, the amount of Si, Fe, K was at trace level. The raspberry powder was devoid of detectable amount of Co and K, and B, Ca, Cu, Mg, Mn, Si important for plant life were present in residual amounts. The "obligatory" amount of K, Fe, Ca, Co, Cu, Mg, Mn were absent in the melon powder, which did not correspond to the fundamental laws of the plant physiology. The results obtained allowed to conclude about misinformation and qualitative adulteration of the materials. Currently, there are practically no studies aimed at determining quality and chemical composition of fruit and berry powders in order to identify adulteration, though this type of survey would be great practical interest both for producers and consumers.

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2. Introduction

The modern consumer market of edible raw materials and foods is extremely important strategic part of the modern economy of the Russian Federation. In recent years, the spread of adulterated goods there has reached such a level that it threatens Russia's national security. Adulteration of agricultural raw materials should be regarded as one of the most dangerous types of fraudulent practices, because it creates favorable conditions for unfair competition, leading to stagnation, loss of export potential of domestic food producers and, consequently, to the decrease in the investment appeal of the industry.

Fresh juicy berries and fruits are natural sources of biologically active substances. However, these are seasonal, perishable products. So, to level the seasonal nature of consumption, increase the shelf life of the finished product and reduce the transportation and storage costs, they are often processed and dried **[1, 2]**.

Strawberry (*Fragaria x ananassa, D.*) is known as a berry with high content of organic acids (citric, malic, quinic, salicylic, as well as succinic and traces of shikimic and glycolic upon ripening), vitamins C, PP, E, B_1, B_2, B_6, B_9, K, carotene, pectin and other substances. Strawberry is rich in phenolic compounds which have antioxidant, anti-inflammatory, and anticancer action **[3, 4]**. Ripe raspberry (*Rubus idaeus L.*) contains free organic acids (citric, malic, salicylic), minerals (Co, Cu, K, Na, Fe, Ca, Mg, P) **[1, 5]**, vitamins (B-group, PP, C, provitamin A), tanning substances **[6]**. Raspberry has diuretic, choleretic, anti-anemic effect, helps strengthen the walls of blood vessels and promotes intestinal health **[14]**. Melon fruits (*Cucumis melo*) contain proteins, carbohydrates (sugars, starch, fiber), organic acids, vitamins (B-group, PP, A, C, β-carotene), minerals (K, Na, Fe, Ca, Mn, Mg, Zn). Melon is especially recommended in case of exhaustion, anemia, atherosclerosis, and some other cardiovascular diseases. Melon enhances the effect of antibiotics reducing their toxicity **[7]**.

Rich chemical composition of dried fruit and berry raw materials allows to use them in the production of dairy and baked goods, confectionery, snacks, salads, ketchups, seasonings in order to enrich them with vitamins, minerals, organic acids, fiber, etc. **[8]**. Knowing the chemical composition of fruit and berry raw materials, identifying components forming the organoleptic characteristics not only constitutes a prerequisite for the production of competitive products, but also makes it possible to identify adulteration. The purpose of the research was to assess the quality and to identify the chemical composition of fruit and berry powders. Research objectives were to study organoleptic properties, physical and chemical parameters, as well as nutrient composition of fruit and berry powders comparing them with commonly known data; to identify the profile of organic acids and mineral composition of the plant material under study.

3. Materials and methods

The investigated products were fruit powders of strawberry, raspberry and melon produced by a Russian company. According to the declaration of the manufacturer, the composition of these powders is 100% corresponding natural raw materials containing no preservatives, dyes, or artificial flavorings.

Organoleptic characteristics of the fruit powders were studied according to GOST 8756.1-2017. Moisture content was determined according to GOST 33977-2016, fat and protein content – according to MU 4237-86 guidelines, non-volatile acids – according to M 04-47-2012, sugars – according to M 04-69-2011, metal and foreign impurities, contamination with grain pests – according to GOST 15113.2-77, food fibers – using the generally accepted method **[9]**, minerals – according to MUK 4.1.1482-03 and MUK 4.1.1483-03 guidelines. All measurements were carried out in three replications.

4. Results and discussion

Sensory evaluation of the quality of the studied materials showed the following: in appearance, the samples of processed strawberries, raspberries, and melons were finely ground homogeneous loose odorless powders, which is uncharacteristic of each type of the original natural raw material. The colour was identified as intense, uniform throughout the mass of the powders, uncharacteristic of dried products, with the following tones: pink with a gray hue for the strawberry powder, light burgundy for the raspberry powder, and light yellow for the melon powder. A sweet taste was noted in the strawberry and melon, and a sour taste in the raspberry material.

According to the results of physical and chemical study of plant materials, no deviations were found from the normal values. Thus, the moisture content of the powders under study was within the range of 4.2-5.1% (in various literature data, the range is 4-12% **[1]**, no infestation with grain pests or presence of metallic and foreign impurities were found.

Fruits and berries have rich chemical composition, which makes them unique elements of a healthy diet **[5]**. In this regard, we investigated the main nutrients contained in the studied samples of fruit and berry powders.

To begin with, we compared the obtained test results with the information on the product packaging. We

found that the actual levels of protein and lipids content did not correspond to the ones stated in the labeling, which indicates misinformation of the consumers. Thus, the amount of proteins and fats in the strawberry powder was 26 and 3.5 times lower, in the raspberry powder – 8 and 60 times higher, respectively, in the melon powder, contrary, it was slightly higher, as for protein in particular – by 55% (***Table 1***) than the labelling of the products.

Taking into account the fact that drying significantly increases the concentration of dry substances and, consequently, biologically active components **[1, 2]**, it was determined that not all samples of the plant powders contained protein and fat even within the generally known range for fresh raw materials. For example, the amount of protein and lipids in the strawberry powder should be 7.0 g/100 g and 1.0 g/100 g, respectively **[1]**. The obtained results were far below.

Table 1. Nutrient Composition of Fruit and Berry Powders

Indicator	Results					
	Strawberry		Raspberry		Melon	
	Actual content	Range for fresh berries in literature	Actual content	Range for fresh berries in literature	Actual content	Range for fresh fruits in literature
Mass fraction of protein, %	0.20±0.01	5.2* g 0.8 g/100 g[a]	0.50±0.03	4.0* g 0.72-1.67[c]	0.31±0.02	0.2* g 0.174-0.674[e] 6.4**[d]
Mass fraction of fat, %	0.37±0.02	1.3* g 0.1 g/100 g[a]	0.05±0.01	3,0* g 0.65[c]	0.11±0.01	0.0* g 0.09-0.26[e] 3.5**[d]
Mass fraction of sucrose, %	52.31±2.24	0.14[b] 2.88-10.82 g/kg[g]	40.42±2.64	0.15[b] 0.80-1.86[i]	41.13±3.22	4-8[d]
Mass fraction of glucose, %	1.24±0.09	2.34[b] 5.02-15.92 g/kg[g]	2.00±0.11	1.84-3.20[b, f]	5.72±0.26	1.1-2.8[d]
Mass fraction of fructose, %	0.34±0.02	2.59[b] 27.66-45.16 g/kg[g]	1.85±0.10	2.10-3.85[b, f]	4.70±0.29	0.75-2.02[d]
Dietary fiber content, g/100 g	3.91±0.20	1.5-2.1%[b, h]	2.72±0.14	3.0-3.9[b, c]	1.40±0.07	23.90**[d]
soluble	1.30±0.10	0.96%[h]	0.91±0.05	0.5-1.8[c, h]	0.40±0.02	no data
insoluble	2.61±0.20	0.85%[h]	1.81±0.11	1.9-3.1[c, h]	1.00±0.05	no data

Note: *content indicated on the packaging of fruit and berry powders, **in terms of dry matter.

[a] Karkh *et al.*, 2014, / [b] Akimov *et al.*, 2020, / [c] Akimov *et al.*, 2021, / [d] Sannikova, 2009, / [e] Erenova, 2010, / [f] Dulov, 2021, / [g]Pochitskaya *et al*., 2019, / [h]Baygarin *et al.*, 2015, / [i] Medvedkov *et al.*, 2015.

The most important indicator of the quality of fruits and berries is their sugar content, which depends on both the characteristics of a certain variety and weather conditions in the period of crop formation **[5, 7]**. It is known that for fresh raspberries, the content of sugars is 4-10 %, for dried berries - 34.5-42.2% **[5]**. Fresh strawberries contain 7.3-11.7% of sugars, which, as in raspberries, are represented mainly by fructose, glucose, and sucrose; their amount varies from 5.9 to 8.9 % **[3, 4]**. In the fruits of cultivated melon, the level of sugars is 7.0-21.0% **[7, 10]**.

It was found that the ratio of mono- and disaccharides in the studied raw materials did not correspond to the data obtained by a number of scientists in practical studies **[5, 6, 10, 11, 12, 13]**. As for sugar content in strawberries, fructose should prevail significantly, in melon – sucrose, whereas in raspberries fructose and glucose content should be equivalent. It was revealed that in all samples of plant materials sugars were 80-97% represented by sucrose, and its high level indicated 40.4-52.3% addition of white sugar. In addition, the quantitative levels of monosaccharides in the strawberry powder did not even fall within the lower limits of their content established for fresh berries.

Plant material is distinguished first of all by the presence of dietary fiber, regular consumption of which contributes to the prevention of overweight and obesity, gastrointestinal, cancer, and cardiovascular diseases.

It was determined that by the content of dietary fiber, the studied samples of vegetable material were closer to the levels of characteristic of fresh juicy berries and fruits, since it is known, for example, that the amount of dietary fiber in dried chopped strawberries is not less than 8.0 g/100 g **[5]**. In our case the dietary fiber content of our samples were only 3.91±0.20 g/100 g.

It is well known that berry and fruit raw materials are characterized by a specific profile of organic acids and macronutrients, and the analysis of their content allows to determine adulteration or to prove its natural character **[8]**. So, these characteristics were studied in more detail. According to a number of authors, citric acid predominates in raspberry, while the content of malic acid is significantly lower. Salicylic acid in raspberries, which has bactericidal, antipyretic, and analgesic action, is of particular importance **[5, 6]**. Strawberries contain malic, benzoic, citric, tartaric, oxalic, succinic, and salicylic acids with the predominance of citric and malic ones **[11]**. Organic acids in cultivated varieties of melon are represented by malic and succinic acids, whereas citric and glucuronic acids appear during storage **[10]**. According to the test results, the amount and ratio of organic acids in the studied fruit powders did not correspond to the profile of natural raw materials (***Table 2***). Thus, oxalic and tartaric acids were absent in the strawberry powder, malic acid – in the raspberry raw material, and citric acid – in the melon material (their concentration stayed below the limit of detection).

Table 2. Profile of Organic Acids and Mineral Elements of Fruit and Berry Powders

Indicator	Results					
	Strawberry		Raspberry		Melon	
	Actual content	Range for fresh berries in literature	Actual content	Range for fresh berries in literature	Actual content	Range for fresh fruits in literature
Content of organic acids, mg/dm³, of which:						
Oxalic acid	not measured	0.10-0.41 g/kg[h]	not measured	no data	not measured	no data
Tartaric acid	not measured	0.02-0.05 g/kg[h]	not measured	no data	not measured	no data
Malic acid	2342.0±12.4	1.18-6.21 g/kg[c,h]	not measured	7.4-63.0 mg/100 g[c,d]	629.6±34.4	29.0-34.8 mg/100 g[e]
Citric acid	3236.0±19.5	3.32-6.64 g/kg[c,h]	29540.0±187.2	466-1750 mg/100 g[c,d]	not measured	1.8-4.7 mg/100 g[e]
Succinic acid	1587.0±10.2	no data	2437.0±14.6	no data	430.4±32.5	0.6-6.2 mg/100 g[e]
Content of mineral elements, mg/dm³, of which:						
B	not measured	185 μg%[g]	0.41±0.02	170-230 μg%[g]	not measured	no data
Ca	not measured	40 mg/100 g[g]	12.21±1.07	262.0-490.0[d]	not measured	160.0** mg%[i]
Co	not measured	4.0 μg%[g]	not measured	1.60-2.36 μg%[g]	not measured	no data
Cu	not measured	no data	0.16±0.01	0.16-1.00[4] 85-280 μg%[g]	not measured	1.96-4.94[e]
Fe	0.70±0.04	11.0[a, b]	5.64±0.34	2.9-13.4[d] 0.74-1.62 mg%[g]	not measured	3.53-11.9[e] 10.0** mg%[i]
K	72.20±4.23	1520[a], 1618[b]	not measured	1340.0-3880.0[d]	not measured	1130.0-1173.8[h] 1180[e]
Mg	not measured	172[a], 190[b]	30.17±1.67	105.0-677.0[d]	not measured	104.3-108.4[f] 130.0** mg%[i]
Mn	0.42±0.02	no data	3.99±0.22	220-650 μg%[g]	not measured	no data
Mo	0.096±0.006		0.088±0.006	12-18 μg%[g]	0.092±0.004	no data
Na	42.80±2.75		417.00±25.46	10.0-41.1[d]	43.84±2.57	320.0[e, f]
P	19.81±1.12		161.06±11.78	no data	14.23±1.12	120.0** mg%[i]
Pb	not measured	no data	0.15±0.01	not more than 0.4*	not measured	no data
Si	3.21±0.23	99.0 mg%[g]	10.43±0.92	31.0-46.0 mg%[g]	3.86±0.19	no data
Zn	0.76±0.04	no data	2.21±0.18	2.9-5.3[d]	0.53±0.03	1.11-3.86[e]

Notes: *according to TR CU 021/2011, ** in terms of dry matter.

[a] Stepanov *et al.,* 2013, / [b] Karkh *et al.,* 2014, / [c] Akimov *et al.,* 2020, / [d] Akimov *et al.,* 2021, / [e] Sannikova, 2009, / [f] Erenova, 2010, / [g] Dulov, 2021, / [h] Pochitskaya *et al.*, 2019 / [i] Medvedkov *et al.,* 2015

Strawberries and raspberries are known to be rich in macro- and micronutrients. Thus, 100 g of strawberries cover 330% of the daily demand in Si, 264% in B, 40% in Co; 100 g of raspberries – 120% of the daily demand in Si, 250% in B **[11]**. Si is involved in the metabolism of most mineral elements and vitamins. It's lack leads to the decrease of digestibility of Ca, Fe, Co, Mn and metabolic disturbance. B plays an important role in the prevention and treatment of bone disease.

Co is a coenzyme of many enzymes, it activates the metabolism of fats and synthesis of folic acid **[11]**. The berries also contain Fe, Zn, Mn, Cu, Mo etc. It was determined that the strawberry powder under study did not contain in detectable amount of intrinsic essential macro- and microelements, namely Ca, Mg, B, Co, the amount of Si, Fe, K was at the trace level, indicating that the material was not natural. The raspberry powder turned out to be devoid of Co, K, whereas the amount of B, Ca, Cu, Mg, Mn, Si, important for the plant life, was residual. The mineral composition of melon fruit includes K, Ca, Mg, P, Na, Fe. K is of extreme importance in the mineral nutrition of melon. The higher level of potassium nutrition increases productivity, disease resistance, accumulation of ascorbic acid and sugars **[15]**. The content of Fe, which plays a leading role in the formation of red blood cells – carriers of oxygen – is 17 times higher in melon than in milk **[16]**. When testing the mineral profile of the melon powder, it was found that it lacked the plant physiologically "obligatory" amount of K, Fe, Ca, Co, Cu, Mg, Mn, which does not correspond to the fundamental laws of physiology of the plant itself. The results allowed us to conclude about the qualitative adulteration of this plant material.

5. Conclusions

The results of physical and chemical tests of the studied raw materials showed deviations from the norms. Studying the levels of proteins and fats of products of strawberry, raspberry, and melon powders confirmed the fact of adulteration. The data obtained during organoleptic evaluation of quality and identification of profile of sugars, organic acids, and mineral elements allowed us to conclude that the powders under study were not natural fruit and berry raw materials.

6. Conflicts of interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the content of this paper.

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