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## CHAPTER 2

# The advantages of using sublimation for preserving the antioxidant properties of cranberries

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### Abstract

The benefits of using the sublimation method for preserving the antioxidant properties of cranberries have been studied. Cranberries are known for their antioxidant properties, which help combat infections, reduce the risk of heart disease, and improve arterial pressure. This berry is particularly beneficial in prostate cancer.

Most of the beneficial compounds in cranberries are found in their skin, which may lose its properties during traditional juice extraction. Drying is an alternative method for preserving antioxidants, but traditional methods can lead to a loss of product quality.

Sublimation drying has proven to be the most efficient and innovative method, as it ensures the preservation of cranberry antioxidant properties. After the sublimation cycle, the final moisture content of the material is only 2–5 % of the initial content, guaranteeing the maximum retention of beneficial properties and the production of a high-quality product. This method is promising for maintaining the quality of raw materials during drying and preserving their medicinal properties.

### Keywords

Cranberry, drying technology, sublimation, nutritional value, antioxidant properties, phenolic compounds, polyphenolic compounds, anthocyanins.

### 2.1 The relevance of sublimation drying

In recent times, both in Ukraine and worldwide, the popularity of healthy eating is expanding, which includes consuming fresh or, for example, dried products such as berries and fruits. Providing the population with diverse high-quality and beneficial food products becomes an important task for the food industry. The benefits

of products created by nature form the basis for healthy eating. Consumption of vitamins, micronutrients, and enzymes allows improving the quality of human life.

The drying process is widely used in the food industry to preserve the properties of berries. The use of modern methods contributes to the improvement of drying technologies. Products subjected to drying retain vitamins, nutrients, flavor qualities, color, and aroma, and can easily be reconstituted in various conditions [1].

For effective preservation of the properties of berries during drying, it is necessary to carefully justify the process and drying regime, as it involves complex thermophysical and technological processes. Currently, sublimation drying is considered the most efficient and innovative method for preparing berries and other products for preservation and long-term storage.

The first use of sublimation drying occurred in Paris in 1906 when electrophysiologist Jacques-Arsène d'Arsonval, along with his assistant Frédéric Bordas, first applied this process to preserve the rabies virus. This discovery contributed to the further development of the first vaccine in history against this disease.

Modern equipment for sublimation drying was developed during World War II, when a large number of wounded soldiers were successfully treated thanks to this technology. Additionally, serum was transported from the USA to Europe using a sublimator: previously, it was unsuitable for use in hospitals as a transfusion material because it spoiled during transportation. Initially, sublimation (lyophilization) drying was developed for commercial use to chemically stabilize serum without refrigeration. Subsequently, sublimation began to be used for storing antibiotics of the penicillin series, and this method also made it possible to preserve biological substances [2].

Today, the technological process of drying using sublimation is widely used in processing industries and for treating a wide range of substances. This methodology has become an integral component in industries such as pharmaceuticals, food processing, laboratory activities, and others. Sublimators (lyophilization equipment) are even used for restoring water-damaged documentation, carbohydrate research, and more.

The demand for processing food raw materials with a lyophilizer is due to the ability to evaporate ice without it transitioning into a liquid state. To perform ice sublimation, specific conditions need to be created. The advantage of preserving fruit and berry raw materials through sublimation drying, compared to other methods, is the possibility of further long-term storage of the product at room temperature. The advantage of the method lies in the significant evaporation of moisture during such sublimation processing, resulting in a natural reduction in the weight of the final product. This simplifies the further transportation and handling of the food products. The storage period consequently becomes longer, facilitating the distribution of high-quality products with high nutritional value.

High-quality freezing and sublimation drying today are made possible thanks to PIGO technologies [3]. In the "Yagidnyk" journal, the advantages of freezing and sublimation were discussed as a method for creating the maximum possible added value for products. While freezing allows for the complete preservation of all the nutritional values of food products, the subsequent stage – sublimation – enables the avoidance of all requirements regarding the cold chain and specific temperature conditions during prolonged storage and transportation, as well as modern preservation of the quality of fresh or frozen products. However, the quality of frozen and sublimated fruit and berry products depends on the equipment used by manufacturers. Today, the PIGO company is one of the few companies in the world that offers all three technologies for preserving food raw materials: freezing, drying, and sublimation drying. They refine existing technologies and introduce new solutions to achieve a higher quality end product.

Therefore, today, more and more producers and processors of berry products are paying attention to the method of storage and processing known as sublimation, which has recently been close to revolutionizing the food industry. This innovative, modern technology allows retaining up to 97 % of nutrients, vitamins, and micronutrients in the raw materials. Sublimated berries, fruits, and vegetables preserve their natural aroma, taste, color, and even their original shape, visually indistinguishable from fresh raw materials.

Such products preserve excellently without any preservatives for at least five years (without access to oxygen and water) while enduring temperature fluctuations (from  $-50\text{ }^{\circ}\text{C}$  to  $+50\text{ }^{\circ}\text{C}$ ), which is a significant advantage compared to other preservation methods. The technological drying process is based on removing moisture from fruit and berry raw materials using heat or cold and heat until they reach a residual moisture level suitable for long-term storage [4].

The complexity of the components of fruit and berry raw materials in their chemical composition leads to quite profound physico-chemical, structural, and biochemical changes during moisture removal at elevated temperatures. This typically results in changes in organoleptic properties and the nutritional value of the product. The nature and extent of these changes depend on the composition and initial properties of the raw material, the methods and drying regimes employed, as well as the amount of moisture removed from the product.

The removal of moisture from the raw material during drying depends on the total moisture content and the type of moisture association with the material. Moisture association with the material is characterized by the amount of free energy of isothermal dehydration, i.e., the force required to remove 1 mole of water at a constant temperature without changing the chemical composition of the raw material.

If there is free moisture in the raw material, then the moisture energy will be zero. With the removal of moisture, the strength of its connection with the berry will increase, and the binding energy will increase. Thus, the lower the moisture content in the berry, the higher the value of the binding energy. If the raw material contains moisture that is subjected to temperature treatment or periodic exposure to moisture and heat, it will change its physical characteristics, affecting the bonds of absorbed liquid [5].

Fruit and berry raw materials are characterized by high moisture content, resulting in a significant amount of water (75–95 %), which creates a favorable environment for the growth of microflora causing spoilage, as well as for various enzymatic reactions and life processes. Therefore, various methods are used to remove moisture from fruit and vegetable products.

Each drying method has its own advantages and disadvantages, and fruit and vegetable products differ in their organoleptic characteristics. For example, products dried by sublimation retain their appearance, volume, color, and taste, and quickly regain their original properties. In turn, fruit and berry raw materials dried with infrared radiation appear better than those dried by convective methods. For solar drying, the raw material is spread out on trays and racks, exposed to direct sunlight in open spaces, or placed in the shade under a shelter with sufficient air circulation. While this drying method does not require significant expenses, it is rather time-consuming (4–20 days), and there is a risk of contamination of the fruit and berry raw materials with sand, dust, and infestation by flies, wasps, etc.

Thanks to modern developments in the technological process of sublimation drying, high-quality flat heaters are used for heating, capable of uniformly heating the product and compensating for heat losses during ice evaporation. Therefore, such equipment configuration for sublimation drying is currently in high demand among professionals [6].

Sublimation drying has also recently been used for the production of spices from various herbs: parsley, dill, basil, marjoram, rosemary, oregano, and other plants for seasoning dishes. Additionally, soluble coffee, various types of tea, and spices are also processed.

In today's world, where diets and weight control have become commonplace, the range of dried products is expanding, for example, through the production of berry snacks. As the number of competitors in the snack market increases, there is an opportunity to expand the range of "healthy" snacks. Consumers focused on a healthy lifestyle carefully scrutinize the product ingredients. They want snacks free from preservatives, flavor enhancers, and harmful additives. Approximately 60 % of consumers are willing to pay extra if it guarantees the quality of the product. Snacks containing

vitamins and micronutrients are popular. This has led to the development of the market for berry pastilles and fruit bars, which are distinguished by an increased amount of beneficial substances.

The technological process of sublimation drying is also known as lyophilization or sublimation. This process is widely used not only in the food industry but also in pharmaceuticals for drying vaccines and food supplements [7].

The technological process of lyophilization consists of the following stages, which must be carried out sequentially: pre-processing of the product – freezing – drying – packaging of the product.

The methodology of such drying, as well as the terms and method of storing food products, depend on their final chemical composition. For example, products containing animal protein should not be subjected to overheating after drying, as it may lead to protein denaturation. Fruit and berry products processed by the sublimation method should be isolated from contact with the surrounding environment, meaning they should be hermetically sealed; otherwise, the fats and vitamin components of the raw material may begin to oxidize. The degree of drying is determined by considering the portion of reducing substances, calculating the exact amount of moisture to be removed. Also, during the preparation of food raw materials for sublimation, a certain bacterial threshold of the products is ensured.

Freezing fruit and berry raw materials can be done either in a specially designed chamber or directly in the lyophilizer by creating a vacuum environment and partial evaporation of moisture. This method is much easier to perform compared to conventional freezing, but it may not be suitable for all food products. During vacuum freezing, the initial indicators of the biochemical composition of the raw materials are lost, so raw meat, fish, as well as juices and purees, are not recommended to be frozen using the vacuum method.

Lyophilization has its technological peculiarities, namely: during pre-freezing, thawing of the raw material before drying must be avoided. During sublimation, products lose between 70 to 90 % of their moisture, and final drying is carried out at positive temperatures. At each stage of drying, the temperature threshold is regulated by technological parameters. The main requirement for maintaining a specific temperature of the product is its biochemical properties and the drying cycle. Different types of raw materials require specific temperature parameters for the sublimation process. More often, the temperature ranges from  $-15$  to  $+35$  °C, but juices from fruit and berry raw materials require temperatures within the range of  $-25$  °C due to their high carbohydrate content, while animal-origin raw materials require temperatures of  $-16$  to  $-20$  °C. During the sublimation stage, approximately 50 % of the moisture evaporates, and about 60 % of the processing cycle time is spent.

At the next stage, the drying of food raw materials is carried out at high temperatures, where the final removal of moisture from the product occurs. To maintain the biochemical composition at a high level and ensure product quality, temperature parameters must precisely meet technological requirements. The duration of processing is significant and depends on the technological process. During the drying stage, the temperature range is between +45 to +85 °C, and the duration can be up to 40 % of the total processing cycle, resulting in a loss of up to 30 % moisture.

One advantage of lyophilization is the preservation of the beneficial properties and taste of the product. The structure of the product becomes porous, which promotes sorption processes: at the beginning of storage, the products actively absorb oxygen, leading to rapid oxidation, and also adsorb moisture, significantly reducing the quality of the raw material. Therefore, to prevent adsorption, it is recommended to compress processed products before packaging, eliminating contact with the surrounding environment. The dried raw material cannot be stored without airtight packaging, so packaging is done immediately after drying. Polymer packaging is most commonly used, incorporating aluminum foil as a component of the packaging. Polymer films also have excellent operational properties, low weight, and high strength.

## 2.2 The chemical composition and biological value of cranberries

Cranberry is a sour berry that is considered one of the healthiest berries due to its unique content of mineral salts and bioactive substances. It is typically added to juices, sauces, and food supplements. Additionally, dried cranberries are an excellent alternative to raisins for baking or garnishing various dishes.

The chemical composition of cranberries includes vitamins: B1, B2, B6, B9, B12, K, C, A, E, PP; minerals: potassium, sodium, calcium, magnesium, phosphorus, iron, iodine, silver, copper, lead, barium, manganese. In addition, flavonoids, glycoside vac-cinine, triterpene acids – oleanolic and ursolic, organic acids – benzoic, citric, quinic, and oxoglutaric have been found in them. Cranberries also contain sugars such as glucose, fructose; polyphenols: quercetin, myricetin; pectin, tannins, nitrogenous and coloring substances, and phytoncides, cyanides. In particular, about 30 types of organic acids have been found in the berry, and the large amount of benzoic acid allows cranberries to be stored throughout the winter without thermal processing and the addition of preservatives. The chemical composition of fresh cranberries (according to the Nutrition resource) [8] is presented in **Table 2.1**.

In summary, fresh cranberries are nutrient-dense fruits rich in vitamins, minerals, and dietary fiber, making them a valuable addition to a balanced diet.

**Table 2.1 Chemical composition of fresh cranberries**

<b>Titles</b>	<b>Content per 100 g of raw material</b>	<b>Daily intake requirement</b>
Vitamin C	13.3 mg	22 %
Vitamin E (tocopherol)	1.2 mg	6 %
Vitamin K (phylloquinone)	5.1 mcg	6 %
Vitamin B1 (thiamine)	0.02 mg	10 %
Vitamin B2 (riboflavin)	0.02 mg	10 %
Vitamin B3 (pantothenic acid)	0.30 mg	2.5 %
Vitamin B6 (pyridoxine)	0.1 mg	5 %
Vitamin B9 (folic acid)	1.0 mcg	0.5 %
Vitamin PP (niacin)	0.4 mg	2.5 %
Calcium	14.0 mg	1.4 %
Potassium	105.0 mg	2 %
Magnesium	15.0 mg	5 %
Phosphorus	11.0 mg	1 %
Copper	0.1 mg	3 %
Iron	0.6 mg	7.5 %
Manganese	0.4 mg	18 %
Carbohydrates	12.2 g	4 %
Proteins	0.5 g	0.4 %
Fiber	4.6 g	23 %

Cranberries are included in many dietary supplements, herbal remedies, sauces, and other food products due to their unique content of mineral salts and bioactive substances, making them one of the most beneficial berries.

Cranberries are also a source of antioxidants, specifically polyphenols, including quercetin, myricetin, peonidin, malvidin, and delphinidin. Along with cyanidin and peonidin, these compounds are responsible for the rich red color of cranberries.

Antioxidants are primarily found in the skin of the berry, so there are significantly fewer of them in cranberry juice. This berry has physiological effects on the human body, possessing antioxidant, refreshing, and toning properties. It improves physical and mental performance, stimulates the secretion of gastric and pancreatic juices, exhibits antimicrobial and diuretic effects. The potent antioxidants in the berries fight various infections (bacterial and viral) and lower the level of "bad" cholesterol, while plant compounds have a protective effect.

Cranberries also reduce the risk of heart disease, lower blood pressure, and inhibit the formation of a compound called homocysteine, which is known to damage the lining of blood vessels. Adding cranberries to one's diet can help manage several risk factors for cardiovascular diseases, including systolic blood pressure (the blood pressure level against the walls of the arteries during heart contractions). Cranberries contribute to reducing body mass index (BMI) and improving levels of "good" cholesterol.

Some dietitians classify cranberries as superfoods, which are predominantly plant-based products with high levels of beneficial nutrients. This berry contains powerful antioxidants that fight infections, lower "bad" cholesterol levels, and possess anti-inflammatory properties. Cranberries can be particularly beneficial in prostate cancer due to the presence of ursolic acid, which has antioxidant and anticancer effects. It is believed that this berry is particularly beneficial in prostate cancer due to the presence of ursolic acid, a plant compound with antioxidant, anti-inflammatory, and potential anticancer properties [9, 10].

Cranberries improve the taste of food, promote better digestion, and enhance food absorption. Some dietitians refer to cranberries as stimulators of pancreatic secretion, as they enhance the secretion of the pancreas. In cases of pyelonephritis, cranberries enhance the antibacterial action of other medications, thus contributing to their therapeutic effect.

In medicine, cranberries are recommended for patients recovering from severe illnesses. They have a toning and refreshing effect and enhance the mental and physical abilities of the human body.

The berry possesses bactericidal properties: cranberry juice inhibits the growth and development of *Staphylococcus aureus*, *Escherichia coli*, and *Salmonella bacteria*, reducing the risks of developing ulcerative diseases. Infection caused by the *Helicobacter pylori* bacterium is considered the main cause of stomach inflammation and ulcers. Therefore, the phenolic compounds of cranberries exhibit 9 % inhibition of urease activity, so consuming cranberries may inhibit *Helicobacter pylori* in the gastrointestinal tract.

However, this berry is not beneficial for everyone, as it is not recommended for patients with stomach ulcers. Its consumption in such conditions is only advisable under the recommendation of a doctor depending on the individual's condition [11].

Dried cranberries are recommended for the prevention and treatment of urinary tract infections. Such infections are caused by the bacterium *Escherichia coli*, which attaches to the inner surface of the bladder and urinary tract. Thanks to the presence of type-A proanthocyanidins, which possess anti-adhesive properties, cranberries can prevent the development of the disease.

Consuming dried cranberries strengthens the immune system, prevents the formation of kidney stones, cleanses the lymphatic system from cholesterol, removes heavy metals from the human body, treats and prevents gastritis and ulcers, and also prevents the rapid growth of tumors.

Dried cranberries are obtained by dehydration, which involves removing moisture from fresh cranberries (*Vaccinium Oxycoccus*) with the addition of sugar to neutralize acidity. Some manufacturers, in the production of dried cranberries, coat them with a small amount of vegetable oil to prevent them from sticking together. For example, in the United States, they are called "craisins", akin to our raisins. They contain such microelements as phosphorus and magnesium, manganese, potassium, iron, and zinc, as well as calcium and copper. The vitamin complex includes vitamins B6, B12, E, C (20 % of the daily norm), K, and A.

Flavonoids in dried cranberries reduce the amount of cholesterol that deposits on the walls of arteries, thereby protecting the body from atherosclerosis, while antioxidants repair cells in the cardiovascular system damaged by free radicals.

Dried cranberries are extremely beneficial for the health of the human digestive system. In folk medicine, they are featured in many recipes as an effective remedy for stomach and duodenal ulcers. They are also considered as a remedy for cancer due to their anti-tumor properties. "Dehydrated" northern berries are characterized by a high content of vitamin C and antioxidants, which are capable of inhibiting the development of malignant cells, for example, in breast cancer. Moreover, regular consumption of dried cranberries reduces the risk of osteoporosis and joint diseases.

Thanks to the unique chemical composition, dried cranberries prevent bacteria from sticking to tooth enamel, thus blocking the formation of dental plaque and preventing tooth decay. This also leads to improved oral health. According to the Center for Oral Biology proanthocyanidins benefit oral health by preventing bacteria from adhering to the surface of teeth.

### **2.3 Technological process of sublimation in the production of dried berries**

Dehydration or sublimation drying is used to preserve the antioxidant properties of fruit and berry products, as well as any ingredients. Both methods allow preserving the freshness and nutritional value of the product for a long time. Thus, fruits, berries, and vegetables can be consumed not only during their typical ripening seasons but also throughout the entire year.

Technological lines enable the organization of continuous flow production of goods, including sequential preparation of raw materials and materials, technological

operations, and packaging of finished products. In the technological line, all production operations are performed in a specific sequence, taking into account the main technical and economic indicators.

The dehydrator, as one of the components of the technological line, is unique equipment designed for drying berries, fruits, vegetables, and so on. With the help of the dehydrator, moisture is removed from the raw materials, and then they are placed in a freezer to preserve them for a long period. The dehydration process is extremely simple and does not require any excessive effort; processing occurs automatically. The product, after thawing, retains its unique taste and aromatic properties almost unchanged, and any changes in appearance occur due to dehydration, which is the basis of the dehydrator's operation.

The dehydration and drying processes occur as follows: the food dehydrator removes water from the product by air circulation at low temperatures.

To ensure that plant raw materials remain preserved for as long as possible, it is necessary to remove moisture, as such products deteriorate very quickly. The processes of decay occur as a result of bacterial action, which initiates chemical processes in the structure of biomaterials. The main factors under which bacteria degrade the quality of raw materials are temperature – as bacteria become active only at certain temperatures, and moisture or water. Thus, by altering both factors, their shelf life can be extended. Dehydration removes a high percentage of moisture contained in the raw material, but to extend the shelf life of the product, it is necessary to subject it to drying, that is, to carry out the process of complete dehydration of the raw material.

Sublimation drying can occur under vacuum or at normal atmospheric pressure. The process at low temperature and atmospheric pressure takes a considerable amount of time, so equipment capable of creating a vacuum is used to expedite it. Decreasing the pressure enhances more efficient evaporation by increasing the mass transfer coefficient. Since vacuum drying takes place in a sealed chamber, convective heat transfer is insufficient. To ensure intensive evaporation in a vacuum environment, heat is generated to evaporate moisture, which is then transferred to the products through heat conduction from heated metal surfaces (via contact with electric heaters) or through radiation from heated screens (using infrared radiation) [1].

The sublimation process consists of three sequential stages: product preparation, freezing, sublimation, and the final drying stage.

Initially, the product is frozen to temperatures lower than its solidification point. This creates ice crystals in the berries, which disappear during the sublimation stage. During the sublimation stage, the main drying process occurs – slow, uniform heating to the temperature at which water transitions from a solid to a gaseous state.

The freezing stage affects the quality of the final product; if it is conducted very rapidly and deeply, the ice crystals will be small and will evaporate very quickly. Drying requires the application of heat at a temperature not exceeding 40 °C.

The principle of operation of a sublimation-vacuum dryer lies in the fact that at low atmospheric pressure (the "triple point" threshold, calculated for water at a pressure of 0.01 °C 611, 657 Pa), water exists only in solid and gaseous states. Therefore, under these conditions, vapor can directly convert to ice without passing through the liquid phase.

During the technological process of sublimation, it is important to adhere to the sequence of stages, which include:

1. Preparation of the substance or product for drying, which may involve concentrating the products, modifying their composition, reducing vapor pressure, or increasing the surface area of the product. Pieces of the product may be individually frozen to transfer the solvent to a free state before the drying stage.

2. Freezing, which can be done, for example, in laboratory conditions using a special rotating flask in a "shell freezer". This process increases the surface area of the product to accelerate drying. In industrial settings, freezing occurs in lyophilization equipment, where the material is cooled below its triple point to ensure optimal sublimation. The triple point refers to the freezing period when the liquid in the raw material can simultaneously exist in three phases: liquid, solid, and gaseous. This feature guarantees sublimation rather than melting, and the large crystals formed during freezing are better suited for sublimation. To obtain such crystals, either freezing must be carried out for a long time or the temperature must be cyclically raised and lowered. However, this type of freezing is not suitable for berry production because they freeze slowly, affecting their texture and reducing nutritional value. Therefore, fruit and berry raw materials need to be rapidly frozen to prevent crystal formation altogether. The freezing stage is one of the most critical phases of the entire sublimation process. If not properly executed, the raw material becomes unsuitable for further processing.

3. The primary stage of drying involves reducing pressure while delivering heat to the product to sublimate ice. During this phase, approximately 95 % of the liquid is removed from the product. It is not advisable to accelerate this process because excessive heat can severely disrupt the structure and damage the raw material. The pressure in the chamber can be controlled using a partially formed vacuum aimed at accelerating drying. The condenser cold chamber and condenser plates contribute to the secondary freezing of the liquid. The condenser does not affect the freezing of the product; instead, it prevents vapor from entering the vacuum pump and operates at a temperature of less than -50 °C.

4. The secondary drying stage involves the removal of unfrozen liquid molecules, while the remaining ice has already sublimated. Lyophilization is regulated here by the isotherms of material adsorption. The drying temperature environment is higher than in the first stage and may even be above 0 °C. The pressure is lowered to stimulate desorption.

After the sublimation process is complete, the vacuum environment created in the working chamber is replaced by inert gases, and the dried product is sealed. The final water content in the product after sublimation can be a maximum of 4 %.

Adhering to the conditions is the key to quality sublimation drying. Therefore, the majority of moisture in the product should be present in the frozen state, and the total volume of ice should not be less than 70 % of the product's weight. It is essential to control the sublimation of ice by monitoring the pressure difference between the vapor emissions above the product's surface and the vapor in the chamber. Maintaining the pressure level is crucial because precise indicators ensure the transition of ice into a vapor state bypassing the liquid phase. Condensation of vapor emissions should be carried out using special evaporative devices.

During the drying process, the berries reach a certain temperature and release heat during the evaporation of ice. To compensate for heat losses and maintain a specific temperature regime, continuous heat supply is necessary. The vapor generation boundary gradually shifts from the surface layers of the raw material to its center, complicating effective heat transfer. Therefore, sorted berries should be stored at room temperature before loading into the sublimator. After the equipment is turned on, the vacuum pump reduces the pressure in the chamber to 10–30 Pa.

Thanks to the vacuum environment and partial evaporation of moisture, the raw material begins to freeze. A larger percentage of the raw material's moisture transforms into crystalline ice. Then the technological process of sublimation occurs. Due to the operation of the vacuum pump, the moisture that has turned into vapor is transferred to the desublimator, and the air from it enters the atmosphere. The final stage of the sublimation drying process is the activation of heaters, which provide heat, thereby removing the remaining moisture from the product. The equipment also includes a defroster section for thawing the ice.

So, let's outline the main steps of sublimation:

*Step 1. Preparation.* Cleaning the berries, the possibility of disinfection, and then loading the tray with prepared berries into the drying chamber.

*Step 2. Freezing.* A vacuum is created in the chamber, and cranberries are cooled to their solidification temperature. The better the freezing (considering the speed and depth of freezing), the finer the ice crystals will come out in the berries, and the faster they will then turn into vapor.

*Step 3. Sublimation.* The frozen berries are slowly heated to the point where ice transitions into vapor, which is directly the process of drying the raw material. After removing the water, the dried berries should be placed in a sealed package for at least twenty hours.

The use of freeze-drying is a modern method of producing berry snacks. Plant-based and berry snacks, such as cranberry pastille, can be utilized in special diets for individuals following a vegetarian or healthy eating regimen, or those with dietary restrictions or allergies. Today, employing such a production method for cranberry pastille allows for significant expansion of the market for antioxidant-rich products and meets consumer demand.

## **2.4 Assessment of the nutritional value and antioxidant properties of cranberries**

Berries naturally have capillaries and a porous structure. The membrane of the capillaries is elastic and swells during moisture absorption. During moisture removal, the berry undergoes shrinkage and may become brittle.

Fresh cranberries have a high-water content and a low percentage of dry matter. Most of the beneficial compounds in cranberries are found in the berry's skin and may be lost during juice extraction. Since it's impossible to eat fresh berries year-round, dried berries can serve as an alternative source of beneficial compounds and valuable antioxidants.

The assessment of the nutritional value and antioxidant properties of cranberries was conducted using standard methodologies [12].

The organoleptic evaluation of fresh and dried berries was conducted using expert tasting methods, with pre-prepared evaluation forms using a 5-point scoring system. The obtained results were averaged and presented in a radar chart. Calculations of the results and the significance of the research factors were performed using the statistical computer program Excel with the QIMacros<sup>®</sup> add-on.

Quantitative determination of anthocyanins and flavonoids content was carried out using spectrophotometric methods.

The energy value was determined using energy coefficients: 1 g of fats – 9.0 kcal (37.7 kJ); 1 g of carbohydrates – 3.75 kcal (15.7 kJ); 1 g of starch – 4.1 kcal (17.2 kJ); 1 g of organic acids – 2.5–3.6 kcal (10.5–15.1 kJ); 1 g of proteins – 4.0 kcal (16.7 kJ). The actual caloric content of the raw material was calculated taking into account the digestibility coefficients: proteins – 84.5 %, fats – 94 %, carbohydrates – 95.6 %.

To determine the energy value in the International System of Units (SI), i.e., in kilojoules, the conversion coefficient was used: 1 kcal=4.186 kJ. The energy value of the product was calculated per 100 grams of edible portion.

To assess the quality of the raw material, a sensory evaluation of cranberries was conducted based on organoleptic indicators. In order to determine changes in quality indicators, experimental batches of dried (sublimated) berries of two varieties, "Black Veil" and "Washington", were prepared. The tasting was conducted for fresh and dried cranberries, and the results of the organoleptic evaluation of the product quality are presented in **Table 2.2**.

The cranberries subjected to sublimation drying were in a stage of technical ripeness, which was determined by their size, external appearance, color, characteristic taste and aroma, and consistency. Only high-quality raw material is suitable for drying, while wilted, overripe, unripe, cracked, or berries affected by diseases or pests are not suitable for drying.

Based on results of cranberry tasting evaluation, the flavor profile of "Black Veil" fresh cranberries received high ratings across all parameters, with a score of 5.0 for taste, aroma, and external appearance, and 4.5 for color and consistency. The flavor profile is described as "Sweet and sour".

"Washington" fresh cranberries also received high ratings, with a score of 4.5 for taste and color, and 5.0 for aroma, consistency, and external appearance. The flavor profile is described as "Sweet-sour".

In comparison, the dried "Black Veil" cranberries received slightly lower ratings across all parameters, with a score of 3.8 for taste and aroma, 4.0 for color and consistency, and 3.8 for external appearance. The flavor profile is described as "Sweet".

Similarly (**Fig. 2.1**), the dried "Washington" cranberries also received slightly lower ratings compared to the fresh ones, with a score of 4.0 for taste, 4.1 for aroma, 3.8 for color, 4.0 for consistency, and 3.5 for external appearance. The flavor profile is described as "Sweet".

**Table 2.2** Results of cranberry tasting evaluation

Variety	Evaluation on a 5-point scale					Flavor profile
	Taste	Aroma	Color	Consistency	External Appearance	
Black Veil	5.0	5.0	4.5	4.8	5.0	Sweet and sour
Washington	4.5	5.0	4.8	4.5	5.0	Sweet-sour
Dried Black Veil	3.8	4.0	4.0	4.1	3.8	Sweet
Dried Washington	4.0	4.1	3.8	4.0	3.5	Sweet

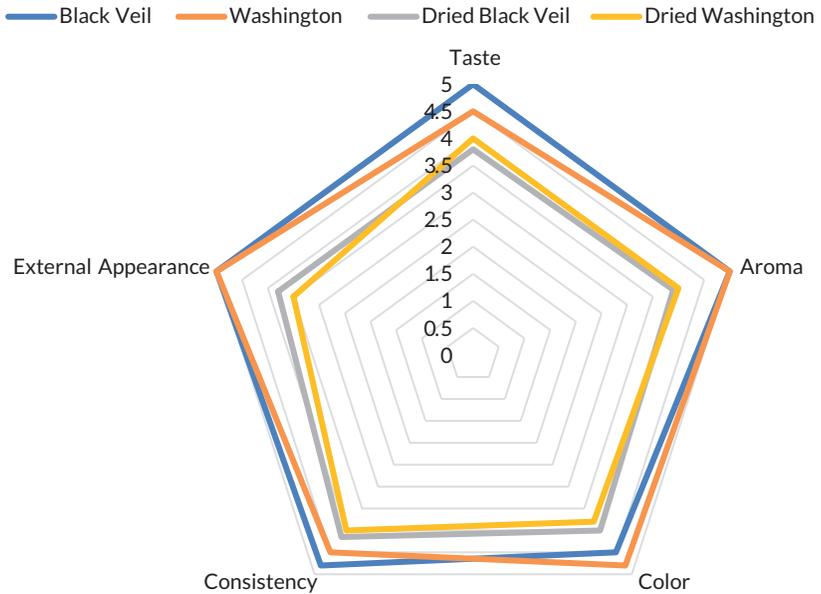


Fig. 2.1 Results of organoleptic evaluation of fresh and dried cranberries

Dried cranberries stand out with an attractive appearance, non-sticky berries, a sweet taste, and rich aroma. It was not possible to determine a preference for a particular variety because both varieties have excellent taste and an elastic, unbroken structure after the sublimation drying process, indicating the preservation of quality indicators and the ability for transportation and storage of the final product.

During the study of the antioxidant properties of cranberries, the presence and content of biologically active compounds in the berry were identified and determined (Table 2.3).

Dried cranberries contain a higher concentration of procyanidins compared to fresh ones (0.36 % vs. 0.14 %). This suggests that the drying process may result in the concentration of procyanidins in cranberries. Both fresh and dried cranberries contain phenolic compounds, with dried cranberries having a slightly higher content (1.32 % vs. 1.16 %). Similar to phenolic compounds, dried cranberries have a higher concentration of polyphenolic compounds compared to fresh ones (0.92 % vs. 0.48 %). Overall, the drying process affects the concentration of various antioxidant compounds in cranberries, with some compounds being concentrated while others are reduced.

**Table 2.3** Content of biologically active compounds in cranberries

Quantitative contents	Based on absolutely dry raw material ( $m=5$ ), %	
	Fresh Cranberries	Sublimated (dried) Cranberries
Anthocyanins	0.23±0.01	0.16±0.01
Procyanidins	0.14±0.01	0.36±0.01
Phenolic compounds	1.16±0.01	1.32±0.01
Polyphenolic compounds	0.48±0.01	0.92±0.01

The biochemical composition of dried cranberry products contains a significant amount of compounds with biological activity. Phenolic compounds such as anthocyanins, leucoanthocyanins, and catechins contribute to increased enzyme activity and improved elasticity of blood vessels. Pectins found in cranberries form strong compounds with heavy and radioactive metals, aiding in their removal from the body.

Based on the results of conducted research, it can be concluded that freeze-dried cranberries retain biologically active compounds at a high level. Therefore, cranberries are a very beneficial fruit, possessing anti-inflammatory, antibacterial, hypotensive, immunomodulatory, antioxidant, antiviral, and cytotoxic properties.

Berry snacks in the form of pastilles are becoming increasingly popular due to their high content of vitamins, minerals, and antioxidants, as well as their low saturated fat and cholesterol compared to traditional meat or dairy snacks. Cranberry pastille is a special type of confectionery made from puree, sugar, and gelatin. It has a smooth texture and sweet taste, containing vitamins and beneficial substances. Pastille can be enjoyed as a dessert or simply as a tasty and healthy low-calorie snack.

The energy value, or caloric content, is the amount of energy produced during the biological oxidation of fats, proteins, and carbohydrates contained in the raw material, expressed in kilocalories (kcal) or kilojoules (kJ).

According to the chemical composition, fresh cranberries contain on average: fat – 0 g, protein – 0.5 g, carbohydrates – 4.8 g, while in dried cranberries, respectively: fat – 0.16 g, protein – 0.38 g, carbohydrates – 8.2 g.

To determine the theoretical caloric content, we considered the energy value coefficient of nutrients and their content in cranberries. Therefore, for fresh cranberries, the theoretical caloric content is: 2.0 kcal (carbohydrates)+18.0 kcal (proteins)= 20.0 kcal; for dried cranberries, the theoretical caloric content is: 1.44 kcal (carbohydrates)+1.52 kcal (proteins)+30.75 kcal (carbohydrates)= 33.71 kcal.

Knowing the theoretical caloric content, we determined the actual caloric content taking into account digestibility, expressed as the digestibility coefficient.

For mixed nutrition, the digestibility is: 84.5 % for proteins, 94 % for fats, and 95.6 % for carbohydrates.

For fresh cranberries:

$$(2.0 \cdot 84.5) / 100 + (18 \cdot 95.6) / 100 = 18.9 \text{ kcal.}$$

For dried cranberries:

$$(1.44 \cdot 94.0) / 100 + (1.52 \cdot 84.5) / 100 + (30.75 \cdot 95.6) / 100 = 32.04 \text{ kcal.}$$

Therefore, the actual caloric content per 100 grams of fresh cranberries is 18.9 kcal, and for dried cranberries, it is 32.04 kcal, taking into account the digestibility coefficient.

To obtain the energy value in the International System of Units (SI), which is kilojoules, we used the conversion factor: 1 calorie = 4.186 kilojoules. Therefore, the energy value of fresh cranberries was 18.9 calories (79.19 kilojoules), and for dried cranberries, it was 32.04 calories (134.25 kilojoules) per 100 grams of edible portion.

## Conclusions

The benefits of using the sublimation method for preserving the antioxidant properties of cranberries have been studied. Cranberries are known for their antioxidant properties, which help combat infections, reduce the risk of heart disease, and improve arterial pressure. This berry is particularly beneficial in prostate cancer.

Most of the beneficial compounds in cranberries are found in their skin, which may lose its properties during traditional juice extraction. Drying is an alternative method for preserving antioxidants, but traditional methods can lead to a loss of product quality.

Sublimation drying has proven to be the most efficient and innovative method, as it ensures the preservation of cranberry antioxidant properties. After the sublimation cycle, the final moisture content of the material is only 2–5 % of the initial content, guaranteeing the maximum retention of beneficial properties and the production of a high-quality product. This method is promising for maintaining the quality of raw materials during drying and preserving their medicinal properties.

The obtained results indicate that the application of sublimation drying allows preserving the bioactive compounds and quality indicators in cranberries. The excellent sweet taste and rich delicate aroma of the berries remain even after the drying

process. The caloric content of dried cranberries is approximately 32 calories per 100 grams of berries.

### Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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