

Determination and Application of Acid-Type Preservatives

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Abstract. The global food industry has experienced significant transformation due to urbanization, lifestyle changes, and the demand for long-shelf-life products. Processed foods, including pre-packaged snacks and refrigerated beverages, rely heavily on food additives, including preservatives, which inhibit microbial growth. However, misinformation and concerns about chemical additives have led to widespread public anxiety, with many consumers associating preservatives with health risks, despite scientific evidence. With the improvement of living standards, people has grown increasingly attentive to everyday food safety, turning the spotlight on various additives—preservatives is just one of them. To foster a proper understanding of food additives, this paper conducts an extensive review of academic literature to summarize the physical and chemical properties, safety, and working principles of four acidic preservatives which are frequently appeared in daily life—sorbic acid, benzoic acid, and propanoic acid along with their respective salts. By presenting these findings, the study aims to make people to recognize, accept, and appreciate the role of food preservatives.

Keywords: Preservatives, Classification of Acidic Preservatives, Sorbic Acid and Its Salts, High Performance Liquid Chromatography (HPLC-UV)

1. Introduction

Since ancient times, humans have utilized a range of preservation techniques to maintain the freshness of meat, vegetables, and fruits. In antiquity, salt was used to restrain bacterial growth, or by air-drying to remove moisture—both strategies aimed at extending shelf life. Then, with the development of science and technology, researchers discovered that there are some natural preservatives kept in some species of living organisms (mostly plants), which can be separated and used through artificial extraction [1]. Specific examples include propanoic acid, sorbic acid, and their respective salts, which are the focus of discussion in this paper. Meanwhile, chemically synthesized preservatives emerged and have become the most common commercial agents, and widely applied in food, cosmetics, and pharmaceuticals for their low cost, broad antimicrobial spectrum, minimal required quantity, and high stability. In this paper, the properties and uses is discussed to alleviate people's worries about taking in this type of food additives and to inform people on how to use them properly and safely.

2. Overview of acidic preservatives

Preservatives are substances products used to inhibit and kill microorganisms which cause food spoilage. Since food is rich in nutrients, it is highly susceptible to microbial growth and proliferation, resulting in significant economic losses, food preservatives are widely used in commercial products. There are three main types of food preservatives which can be find in shops-natural preservatives, chemically synthesised preservatives and composite preservatives [2]. Among these, acidic preservatives are common used, and rely on a low pH environment. As the pH decreases, the concentration of undissociated acid increases significantly, and the preservative capacity increases sharply. The antibacterial effect of the acidic preservatives is greatly influenced by its degree of dissociation.

2.1. Natural acidic preservatives

Natural preservatives, also referred to as biological preservatives, can be extracted from animals, plants, and microorganisms [3]. Among these, acetic acid is the earliest natural preservative discovered by humans dating back to around 5000 BC. After that, many other fruits and vegetables were found corrosion resistant. The famous acid used in this area, sorbic acid, was first extracted from unripe fruit of the hawthorn tree by A. W. von Hofmann in 1859. Nearly a century later, scientists discovered its antibacterial and preservative capabilities, and it has since been widely applied in the food, cosmetics, and other industries. Natural acidic preservatives has narrow antibacterial spectrum, slightly poorer stability compared with chemically synthesised preservatives. However, some of its natural ingredients (such as cinnamaldehyde and eugenol) have significantly better antibacterial activity than chemical preservatives and is safer and widely acceptable by consumers.

2.2. Chemically synthesised acidic preservatives

Chemically synthesised preservatives are the most commonly used type in food industries. For instance, potassium sorbate ($C_6H_7KO_2$) exhibits broad-spectrum antibacterial properties under acidic conditions, and can always be found in the food ingredient list, as It is effective and safe to human's body [4]. In general, chemically synthesised preservatives boast low production costs, high yields, and mature manufacturing technologies, coupled with a wide range of applicable scenarios—these advantages make them the preferred choice for commercial food production. However, if food additives are not used in strict accordance with health standards, it will lead to food safety issues and seriously affect the safety of food preservative use.

2.3. Composite preservatives

Composite preservatives are not a new category of preservatives, but a formulation strategy which combines over 2 types of specific preservatives with performance enhancers. In this way, it can reducing monomer usage through synergistic effects which reduces costs and minimises risks to human health. This type of preservative is more stable and has a broader spectrum of effectiveness, making it suitable for specific preservation applications. A typical example is the composite system of "potassium cinnamate + sodium dehydroacetate + vitamin C," which is commonly applied in the preservation of cooked meat products to extend their shelf life while ensuring safety.

3. Sorbic acid and its salts

Sorbic acid is one of the most common food additive in daily lives, particularly prevalent in packaged food products [5]. It was first discovered in unripe fruit of the hawthorn tree at the end of 19th century, and is widely used in the mid-20th century. Among its derivatives, potassium sorbate is the most commonly used chemical food additive. It inhibits microbial growth and development by suppressing microbial enzyme activity, renowned for its safety, large-scale production capability, and broad spectrum of antimicrobial activity.

3.1. Physical and chemical properties of sorbic acid and its salts

Sorbic acid (chemical formula: $C_6H_8O_2$), also known as 2,4-hexadienoic acid, exhibits inhibitory effects against numerous fungi, including yeasts and molds. It is a white crystalline powder, odourless or with a faint odour, readily soluble in organic solvents such as anhydrous ethanol, acetone, and cyclohexane, but insoluble or slightly soluble in water. Sorbic acid does not decompose at normal temperature and pressure, and contact with strong oxidising agents should be avoided as it is dangerous. Potassium sorbate (chemical formula: $C_6H_7O_2K$), also called potassium 2,4-hexadienoate, is a salt of sorbic acid. It presents as colorless to pale yellow crystalline granules, crystals, or flaky powder, and is either odorless or has a faint scent. When left exposed to air for extended periods, it will absorb moisture and oxidise, causing discolouration. Potassium sorbate is also soluble in ethanol.

3.2. Working conditions of sorbic acid and its salts

The industrial synthesis of sorbic acid employs butyraldehyde, crotonaldehyde and ketones as raw materials, reacting at $0^\circ C$ in a solution containing catalysts such as boron trifluoride. Sorbic acid is always used at a pH condition between 3.0-6.5. It inhibits the growth and reproduction of microorganisms but has virtually no bactericidal effect and is ineffective against anaerobic spore-forming bacteria and lactic acid bacteria. Sorbic acid has a relatively high pH value, so it also works in nearly neutral foods. Potassium sorbate is produced by neutralising sorbic acid with potassium carbonate or potassium hydroxide. It has nearly identical functional properties to sorbic acid, but its salt form allows for easier integration into food products—most notably, its water solubility is significantly higher than that of sorbic acid: at $25^\circ C$, the solubility of potassium sorbate reaches 58 g/100 mL, whereas sorbic acid only has a solubility of 0.16 g/100 mL, and potassium sorbate dissolves much more rapidly.

3.3. Applications and safety of sorbic acid and its salts

Sorbic acid and potassium sorbate are food preservatives with low toxicity and minimal hazards, exhibiting toxicity levels one-quarter that of benzoic acid. Its preservative efficacy is 5 to 10 times that of benzoic acid, with an Acceptable Daily Intake (ADI) of 0 to 25 $mg \cdot kg^{-1} \cdot bw \cdot d^{-1}$. In the food industry, sorbic acid products are used in bakery, soft drinks, meat and pickled vegetables. As one of the safest food preservatives, it is in high demand since 21st centuries, especially in the food processing industries. In the field of materials science, such as synthetic rubber, resins, fibers, and medical applications, sorbic acid also serves as a raw material for various chemical syntheses. These preservatives are technically mature, cost-effective, and highly effective, making them widely adopted by numerous manufacturers.

4. Benzoic acid and its salts

Benzoic acid-based preservatives are widely used globally, primarily in the production of food and pharmaceuticals [6]. Benzoic acid was first discovered by the French in 1618 and until the mid 19th century, it was used in pharmaceuticals. This preservative acts through its undissociated molecules. These molecules enter cells and interfere with the permeability of microbial cell membranes, thereby hindering the absorption of amino acids by the cell membranes. The benzoic acid molecules which enter the cell can acidify stored alkali, inhibit the activity of microbial respiratory enzyme systems, and block the acetyl-CoA condensation reaction, thereby achieving a preservative effect.

4.1. Physical and chemical properties of benzoic acid and its salts

Benzoic acid (chemical formula: $C_7H_6O_2$) is a white, crystalline organic compound belonging to the carboxylic acid family. It has a chemical formula of $C_7H_6O_2$. Benzoic acid possesses a faint scent of benzaldehyde or benzoin and has a stable chemical structure which is difficult to oxidize. It is slightly soluble in cold water and hexane and is soluble in hot water, ethanol, benzene, carbon disulfide, and other solvents. Benzoic acid is lightweight, and its vapors are highly irritating. Sodium benzoate (chemical formula: $C_7H_5O_2Na$) is one of the most common derivatives of benzoic acid. It appears as a white granular or crystalline powder, either odorless or with a faint benzoin-like scent, and is highly soluble in water. Sodium benzoate is typically produced by the reaction of benzoic acid with alkaline sodium bicarbonate.

4.2. Working conditions of benzoic acid and its salts

The liquid-phase air oxidation method for toluene is the most widely used production method of benzoic acid. During the process, toluene serves as the raw material, heavy metal salts act as the primary catalyst, bromides function as the co-catalyst, and air provides the oxidizing agent. Benzoic acid exhibits antibacterial activity only in its undissociated state: when the pH of the environment exceeds 4.5, its preservative efficacy decreases significantly. It has good heat resistance, but it may volatilize or degrade when the temperature exceeds $100^\circ C$. During food production, benzoic acid preservatives should not be mixed with Vitamin C, iron ions, copper ions to avoid formation or discoloration of benzene which is a type of carcinogen. Sodium benzoate is more water-soluble, making it suitable for liquid formulations, and it does not readily volatilize with water vapor, but has the same effect as benzoic acid.

4.3. Applications and safety of benzoic acid and its salts

For adults, long-term intake within the ADI range (0–5 mg/kg bw) poses a negligible health risk to adults. However, excessive consumption or for specific groups, benzoic acid products are risky—for example, toxic effects such as metabolic acidosis, chromosomal breaks, and neurobehavioral alterations.

Benzoic acid boasts the lowest production cost among acidic preservatives and offers the best cost-performance ratio, so benzoic acid preservatives are most commonly used in acidic products. Benzoic acid has a low solubility (0.34 g/100 mL, $20^\circ C$), so it will dissolve in hot water or ethanol before adding the material. At a pH level of 2.5–4, it is most effective at inhibiting yeast and mold.

Sodium benzoate, due to its high solubility (58g/100 mL,), is commonly used in liquid products such as soy sauce, carbonated beverages, and jams. In the food industry, it is often blended with

potassium sorbate in a 1:1 ratio to form a composite preservative. This combination reduces the total preservative dosage by approximately 30%, broadens the spectrum of microorganisms inhibited, and minimizes the potential adverse effects of preservatives. Beyond the food sector, sodium benzoate is also added to pharmaceutical products (e.g., syrups, oral liquids, and eye drops) at a dosage of less than 1 mg/mL to inhibit bacterial growth, ensuring the products pass the Antimicrobial Effectiveness Test (AET).

5. Propanoic acid and its salts

Propanoic acid is used as a food preservative and anti-mold agent [7]. Its salts served as a safer alternative to the more toxic benzoate preservatives and costly sorbate preservatives. Notably, propanoic acid itself is a corrosive liquid with an unpleasant rancid, pungent odor, making it unsuitable for direct use in food. By contrast, it is always used in the form of calcium salts and sodium salts, which enhance the preservative's stability, solubility, and eliminate its pungent odor. Similar to other acidic preservatives, undissociated propionic acid molecules penetrate the cell membranes of microorganisms such as molds and bacteria. They lower the intracellular pH, disrupt the energy metabolism system, and inhibit enzyme activity, thereby suppressing microbial growth and reproduction.

5.1. Physical and chemical properties of propanoic acid and its salts

Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) is a short-chain saturated fatty acid. It is highly corrosive, it possesses an unpleasant rancid, pungent odor and is generally not used in food products. Therefore, sodium propionate and calcium propionate are more frequently used in preservatives.

Sodium propionate ($\text{CH}_3\text{CH}_2\text{COONa}$) transparent granules or crystals with a peculiar odor, deliquescent in moist air, readily soluble in water and slightly soluble in alcohol. It is Incompatible with strong oxidizing agents. To keep it, sodium propionate products are always put in places dry, sealed, at room temperature in an inert atmosphere.

Calcium propionate ($(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca}$) appears as white crystals, crystalline powder, or granules, odorless or with a faint propionic acid odor. The form used as a food additive is the monohydrate salt, which is stable to water and heat, hygroscopic, and readily soluble in water at 39.9 g/100 mL (20°C). It is almost insoluble in ethanol and ethers. It is typically stored in a dry, sealed environment at $\leq 30^\circ\text{C}$.

5.2. Working conditions of propanoic acid and its salts

Calcium propionate and sodium propionate works at almost the same conditions. Both of them work at a pH range between 3.5-5.5. When the pH of the environment exceeds 8, they become difficult to achieve the desired effect. Additionally, both substances remain stable at room temperature, but they should not be used alongside strong oxidizing agents—this prevents chemical reactions that could lead to decomposition and loss of efficacy. Despite their similarities, there are key differences between the two salts. A notable one is that calcium propionate reacts with sodium bicarbonate (a common component in chemical leavening agents, used in baked goods to help dough rise) to form calcium carbonate (CaCO_3). This reaction not only reduces the efficacy of both the preservative and the leavening agent but may also affect the texture and quality of the final food product—an important consideration for its application in bakery products.

6. Determination of the acidic preservatives

Liquid chromatography and gas chromatography are mainly employed for the detection of sorbic acid and benzoic acid [8]. A critical pretreatment step is required before any chromatographic analysis: 1 mL of hydrochloric acid solution (1:1, v/v) should be added to the sample to adjust its pH to approximately 2. This converts sorbic acid to its molecular form, facilitating extraction. High Performance Liquid Chromatography (HPLC-UV) is widely used in the determination of benzoic acid, sorbic acid and sodium saccharin in China. This method is primarily used for testing beverages, jams, dairy products, and the like. Methanol, ethanol, acetonitrile and water are routinely employed for the extraction of various sample types prior to testing. For example, when testing vinegar and soy sauce, water is mutually soluble with the samples, resulting in chromatograms with the highest number of interference peaks. Methanol extraction yields the most effective separation, producing a clear, well-separated mixture upon settling. Chromatograms obtained from this sample exhibit the fewest impurity peaks during instrumental analysis [9,10].

7. Conclusion

This paper systematically explores three common acidic preservatives—sorbic acid, benzoic acid, propanoic acid, and their salts—covering their classifications, physicochemical properties, working conditions, applications, and detection methods. It confirms that these preservatives, when used in compliance with ADI standards, are safe and effective for extending food shelf life, with their salts often addressing limitations like low solubility of parent acids. HPLC-UV emerges as a reliable detection tool for ensuring proper usage. While natural preservatives have consumer appeal, chemically synthesised and composite ones remain vital for commercial needs. This study aims to ease public concerns and provide references for rational application of acidic preservatives in the food industry.

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