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Varieties, production, composition and health benefits of vinegars: A review

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ABSTRACT

Vinegars are liquid products produced from the alcoholic and subsequent acetous fermentation of carbohydrate sources. They have been used as remedies in many cultures and have been reported to provide beneficial health effects when consumed regularly. Such benefits are due to various types of polyphenols, micronutrients and other bioactive compounds found in vinegars that contribute to their pharmacological effects, among them, antimicrobial, antidiabetic, antioxidative, antiobesity and antihypertensive effects. There are many types of vinegars worldwide, including black vinegar, rice vinegar, balsamic vinegar and white wine vinegar. All these vinegars are produced using different raw materials, yeast strains and fermentation procedures, thus giving them their own unique tastes and flavours. The main volatile compound in vinegar is acetic acid, which gives vinegar its strong, sour aroma and flavour. Other volatile compounds present in vinegars are mainly alcohols, acids, esters, aldehydes and ketones. The diversity of vinegars allows extensive applications in food.

Keywords: acetic acid, alcohol, bioactive compounds, composition, fermentation, health benefits, production methods, vinegar

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1.0 INTRODUCTION

Vinegar is a common food product that is widely available in the market. There are two types of vinegar, cider vinegar and normal vinegar. Cider vinegar is made from fruit juices (Madrera et al., 2010), whereas normal vinegar is made from raw plant materials, such as grains, apples, grapes or sugarcane (Junior et al., 2014). In addition to being consumed directly, vinegar plays an important role in the production of food products, as it is applied in a wide variety of products, including sauces, ketchups and mayonnaise. Cider vinegar is a highly beneficial drink, as it helps to promote different kinds of beneficial effects to consumers, such as having antidiabetic effects and lowering cholesterol levels in blood by inhibiting the oxidation of low density lipoproteins (LDLs), among other benefits (Salbe et al., 2009; Laranjinha et al., 1994). There are two main biotechnological processes involved in the production of vinegar, alcoholic fermentation (in the presence of yeast, e.g., *Saccharomyces cerevisiae*) and acetous fermentation (in the presence of acetic acid bacteria) (Budak et al., 2014; Ordoudi et al., 2014). Alcoholic fermentation is the conversion of sugar to alcohol, while acetous fermentation is the conversion of alcohol to acetic acid. There are two types of methods for producing vinegar, the conventional method (Orleans method) and the rapid methods (submerged and generator methods) (Dabija & Hatnean, 2014; Tan, 2005).

There are a few factors (fermentation temperature, strains of yeast, concentrations of sugar and oxygen) that affect the speed of cider vinegar production and the overall aesthetics of cider vinegar.

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1.1 History and Current Issues of Vinegar

Vinegar has been known as a seasoning or preservative agent in salad dressings, ketchup and sauces or has been watered down as a drink by most cultures (Tesfaye et al., 2002). Interestingly, in ancient times, vinegar was considered to be a food by-product from the spoilage of wine due to contact with air.

The earliest known use of vinegar occurred more than 10,000 years ago (Tan, 2005; Johnston & Gaas, 2006). Hippocrates (460 – 377 BC) recommended vinegar for cleaning ulcerations and for the treatment of sores (Johnston & Gaas, 2006). In the 8th century, Samurai warriors of Japan used vinegar as a tonic, as they believed that vinegar tonic gave them power and strength. John Adams, the second president of the United States (1735 – 1826) took apple cider at his breakfast every day. Vinegar was also used medicinally for the healing of wounds (Budak et al., 2014). Sung Tse, who is credited with the development of the field of forensic medicine in the 10th century in China, used sulphur and vinegar as hand washing agents to prevent infection (Chan et al., 1993; Tan, 2005). U.S. medical practitioners used vinegar to treat many ailments, including poison ivy, croup, stomach ache, high fever, and edema in the 18th century (Tan, 2005). In the 18th century, Durande, a French chemist, successfully produced glacial acetic acid by concentrating vinegar. By the 19th century, Schutzenbach, from Germany, developed a method for manufacturing vinegar known as the generator process, which allowed vinegar to be produced within 7 days. In the 20th century, Hromatka, also from Germany, developed an enhanced method of vinegar making, called submerged acetification, which uses improved aeration and stirring to produce vinegar over a shorter period of time (Tan, 2005). In 1999, the International Vinegar Museum was opened on

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the 4th of June in Roslyn, South Dakota, United States of America, which is the first museum dedicated to the subject of vinegar, with exhibits on its manufacture and uses.

In China, more than 3.2 million litres of vinegar are consumed every day due to the nutritional benefits of vinegar, which directly affect the health of consumers. The Chinese government has been paying much attention to the quality of the vinegar produced. The China State Bureau of Quality and Technical Supervision issued a market allowance policy on the quality and safety of vinegar in 2002 (Zhang et al., 2006). Chinese vinegars are used as a traditional condiment derived from grain and are frequently used in cooking and the production of food. Most consumers cannot differentiate between different brands of Chinese vinegar, as they have some similarities in terms of appearance and taste. Chinese vinegars have a high content of volatile compounds, and this is due to the usage of different compositions and concentrations of raw materials and methods of vinegar production (Dong et al., 2016). Across the continent, in European countries, the quality of vinegar is examined through sensory evaluation to maintain the standard of the vinegar (Zhang et al., 2006).

In addition, it has been reported that consuming vinegar regularly contributes to some beneficial effects in terms of digestion, appetite stimulation, antioxidative properties, recovery from exhaustion, lowering lipid content and regulating blood pressure (Chou et al., 2015).

1.2 Definitions of Vinegar

According to the Malaysian Food Act 1983 and Food Regulation 1985, vinegar is defined as a liquid product prepared from the alcoholic fermentation and subsequent acetous fermentation of any suitable food. The act also dictates that the vinegar itself shall not contain less than 4

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percent weight per volume (w/v) of acetic acid and shall not contain any mineral acid. The vinegar may also contain permitted preservatives, caramel as a colouring substance and spices as permitted flavouring substances (Food Regulation, 1985).

According to the Codex Alimentarius Commission, vinegar is a liquid that is fit for human consumption and produced exclusively from suitable products containing starch or sugars or starch and sugars by double fermentation processes, alcoholic and acetous. Vinegar shall not contain more than 0.5% alcohol, and stabiliser is not permitted for use in fermented vinegars according to European law. The vinegar itself shall not contain less than 50 grams per litre (w/v) of acetic acid (Codex Alimentarius Commission, 1987).

The U.S. Food and Drug Administration (FDA) mentions that there are no standards of identity for vinegar established under the Federal Food, Drug and Cosmetic Act. However, the FDA considers that a satisfactory guideline for vinegars that are natural vinegars is that they must contain in excess of 4 grams of acetic acid per 100 mL. Vinegar is made by the alcoholic and subsequent acetous fermentation of fruit juice (USFDA, 1977).

The European Union defines vinegar as a product that is produced by the double fermentation, i.e., alcoholic and acetic, of substances of agricultural origin. Raw materials such as wine, cider, malt, rice mash, whey, concentrated grape must and various kinds of spirits are utilised (Erbe & Brückner, 1998). In France, vinegar is called *vinaigre*, which literally translates to ‘sour wine’. This *vinaigre* can be made from almost any fermentable carbohydrate source, including but not limited to wines, molasses, dates, apples, pears, berries, beer and honey. It has to be fermented by yeast to convert the natural food sugar to

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alcohol. Next, acetic acid bacteria (*Acetobacter*) convert the alcohol to acetic acid (Johnston & Gaas, 2006).

Furthermore, the Food Standards Australia New Zealand 2.10.1, which is the standard for vinegar and related products, defines vinegar as the sour liquid prepared by the acetous fermentation with or without alcoholic fermentation of any suitable foodstuff and includes blends and mixtures of vinegar. This vinegar must contain not less than 40 g/kg of acetic acid (Food Standards Australia New Zealand Act, 1991).

The Food Safety and Standards Authority of India (2012) states that vinegars are products obtained by the alcoholic and acetic acid fermentation of any suitable medium such as fruit, malt, or molasses, with or without the addition of caramel and spices. They shall not be fortified with acetic acid. The acidity, calculated as the acetic acid content, shall not be less than 3.75% (m/v), the total solids (m/v) shall not less than 1.5%, and the total ash content shall not be less than 0.18% (Food Safety and Standards Authority of India, 2012).

In Korea, the Ministry of Food and Drug Safety (MFDS) establishes food standards and specifications for vinegar production. Vinegar refers to brewed vinegar that is produced by fermenting grains, fruits or alcoholic drinks or by mixing and ripening them with a grain-saccharified solution or fruit juice or to synthetic vinegar that is manufactured by diluting glacial acetic acid or acetic acid with drinking water. The total acid content is quantified as the acetic acid content, which is in the range of 4.0 to 29.0% (w/v), and tar colour should not be detected (MFDS, 2014).

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As a whole, the term "vinegar" is defined as a liquid product that is produced by the fermentation of carbohydrate sources and must contain a minimum of 3.75 to 5.0% (w/v) acetic acid.

2.0 VARIETIES OF VINEGAR

There are a few types of vinegars, classified based on their raw materials and fermentation process. Rice vinegar is the aged and filtered product obtained from the acetous fermentation of sugars derived from rice. It is excellent for flavouring with herbs, spices and fruits due to its mild flavour. It is widely used in Asian dishes because it does not significantly alter the appearance of the food (Yano et al., 1997).

Balsamic vinegar was first produced in Italy. There are two types of balsamic vinegar, namely the traditional and commercial types. Traditional balsamic vinegars are artisanal foods, similar to wines, with long histories and well-developed procedures for their production. Grapes (which are specifically grown in the northern region of Italy near Modena) are left on the vine for as long as possible to increase the sugar level, as ripened grapes contain higher sugar levels. Traditional balsamic vinegar may age up to 25 years. Ageing occurs in a succession of casks made from a variety of woods, such as chestnut, oak and cherry (Daglia et al., 2013).

The commercial version of balsamic vinegar is designated *Aceto Balsamico di Modena* (balsamic vinegar of Modena) and must be aged for a minimum of two months and up to three years to meet the minimum requirements to claim protected geographical indication (IGP). There are a few factors affecting the chemical and organoleptic properties of

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vinegar, such as the acetification system used, the raw material used as the substrate and the amount of time spent ageing in wood (Guerreiro et al., 2014).

Wine vinegar from the Jerez region of southern Spain, also known as sherry vinegar, and the balsamic vinegar from Modena (Italy) are produced using two methods, which are quick acetification methods under strong aeration conditions with large quantities of submerged bacteria and slow acetification processes derived from surface culture fermentation. Therefore, these two vinegars are the most appreciated and prestigious vinegars in the region (Pizarro et al., 2008).

Black vinegar, also known as Kurosu, is produced from unpolished rice with rice germ and bran through stationary surface fermentation and contains higher amounts of organic acids and amino acids than other vinegars (Nishidai et al., 2000). Black vinegar is characterised as a health food rather than only an acidic seasoning because it has been reported to exhibit significant DPPH radical scavenging ability (Chou et al., 2015) and to decrease the size of adipocytes (Tong et al., 2010).

In China, there are a few types of well-known vinegars that have been produced over the years. Sichuan vinegar is one of the most famous vinegars of China, where this vinegar is produced by using as many as 108 medicinal herbs available in China. The liquid extract of smartweed leaves (*Polygonum hydropiper*) is used to initiate the fermentation of the vinegar (Zou et al., 2012). Apart from that, Shanxi old mature vinegar is the most famous vinegar in northern China, where this vinegar is produced using sorghum as its main material for the fermentation process (Zou et al., 2012).

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Research on producing new types of vinegars has been ongoing. Among these studies, research has been carried out on the usage of juice extracted from onions to produce vinegar. The vinegar produced using onion juice has been found to contain high contents of organic acids, amino acids and minerals (Horiuchi et al., 1999). Due to the lower sugar content in onion juice compared to other fruit juices, the addition of sugar is required for alcoholic fermentation to proceed.

Lee et al. (2013) produced tomato vinegar and investigated the benefits of this new vinegar. Tomato juice was obtained by crushing mature tomatoes without stems in a mechanical juicer before undergoing alcohol and acetous fermentation. Tomato-based products are rich sources of important nutrients such as lycopene, carotenoids and polyphenol compounds, and these could have beneficial health effects for humans (Lee et al., 2013). Lycopene is a compound that is associated with decreasing the waist circumference and visceral fat mass of elderly men. Several reports have indicated that regularly consuming tomato lycopene lowers the risk of cardiovascular disease and several types of cancer. In addition, carotenoids are known to be beneficial in preventing atherosclerosis (Lee et al., 2013).

In addition, bamboo vinegar is a brown-red transparent liquid and is composed of nearly 90% water and more than 200 kinds of chemical components. It has a special smoky odour. Bamboo vinegar has been widely used in agriculture and daily life in Japan (Mu et al., 2006). Research shows that bamboo vinegar has a significant effect on the germination and radical growth of seed plants. According to Mu et al. (2003), bamboo vinegar stimulates the hormone-like substances that regulate the germination and radical growth of the seeds.

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3.0 METHODS OF VINEGAR PRODUCTION

There are two fermentation processes required to produce vinegar, which are alcoholic and acetous fermentation, as shown in Figure 1. Alcoholic fermentation proceeds rapidly and usually depletes most sugars within the first 3 weeks. Fermentable sugars are converted into ethanol by the action of yeasts, normally strains of *Saccharomyces cerevisiae*, while in acetous fermentation, the acetic acid bacteria are mainly members of the genus *Acetobacter* and can further oxidise ethanol into acetic acid. Alcoholic fermentation is carried out under anaerobic conditions, whereas acetous fermentation is carried out under aerobic conditions (Budak et al., 2014).

Saccharomyces cerevisiae contains 32 members of the hexose transporter family with respect to transcriptional and posttranscriptional regulation, substrate specificity (only specific substrates can react with the active site of the enzyme of *S. cerevisiae*) and affinity for glucose (Maris et al., 2006). Figure 2 shows the alcoholic fermentation pathway of *S. cerevisiae.* Because glucose is transported via facilitated diffusion, glucose uptake requires the presence of a concentration gradient across the plasma membrane. After this reaction, glucose will dissimilate and proceed through the Embden-Meyerhof glycolytic pathway, where this pathway will oxidise glucose into two pyruvates (Maris et al., 2006). This will cause the formation of two ATP molecules per glucose molecule. Under the anaerobic conditions of alcoholic fermentation, NADH is formed when glyceraldehyde-3-phosphate dehydrogenase is oxidised. This reaction involves pyruvate decarboxylase and alcohol dehydrogenase. There are many forms of carbohydrates present in the hydrolysate; generally, glucose and non-glucose carbohydrates are included. Mannose and fructose are two isomers of glucose that are present in hydrolysates and can be fermented by *S. cerevisiae* strains. Both mannose and

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fructose are transported by all different members of the hexose transporter family. After undergoing phosphorylation catalysed by hexokinase, mannose-6-phosphate is isomerised to fructose-6-phosphate by phosphomannose isomerase. In addition, hexokinase is involved in the phosphorylation of fructose to fructose-6-phosphate, which undergoes glycolysis (Maris et al., 2006). Galactose can also be fermented by *S. cerevisiae* as shown in Figure 2.

On the other hand, acetic acid bacteria are mesophilic obligate aerobes that can oxidise sugars, sugar alcohols and ethanol to allow the production of acetic acid (Raspor & Goranovic, 2008). Therefore, acetic acid bacteria are usually used as the starter cultures for producing vinegars. Examples of *Acetobacter* species used in previous studies are *A. pasterianus* and *A. polyoxogenes* (Raspor & Goranovic, 2008). These bacteria are usually used as the starter cultures for producing vinegars. In acetous fermentation, the biochemical mechanism for the conversion of alcohol to acetic acid starts with the oxidation of alcohol into an acetaldehyde in the presence of alcohol dehydrogenase as shown in Figure 3. These dehydrogenase enzymes consist of quinoproteins and flavoproteins that contain pyrroloquinoline quinone and will form covalent bonds with flavin adenine dinucleotide as prosthetic groups. Alcohol dehydrogenase consists of two or three subunits, including dehydrogenase and cytochrome, which are essential in the enzymatic reaction (Raspor & Goranovic, 2008).

Acetaldehyde will then be converted into hydrate acetaldehyde by adding water. To ensure that acetous fermentation occurs under optimum conditions, it is necessary to achieve and maintain a certain concentration of dissolved oxygen (Dabija & Hatnean, 2014). The oxygen supplied to acetic acid bacteria may influence the speed of the fermentation process as well as the sensory quality of the end product, vinegar. Depending on the rate of the formation

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of acetic acid in vinegar, the acetous fermentation process can be classified into two types of processes: slow (the Orleans method) and fast (the submerged and generator methods) (Dabija & Hatnean, 2014). According to Ubeda et al. (2011), insufficient oxygen during acetous fermentation could lead to the accumulation of acetaldehyde and a lower production of acetic acid.

Aldehyde dehydrogenase (AlDH) plays an important role in converting acetaldehyde to acetic acid. AlDH oxidises acetaldehyde in an NAD-dependent reaction to acetate (Auchter et al., 2009). AlDH metabolises electrophilic aldehydes and can be expressed in all forms of life from simple to complex multicellular organisms (Singh et al., 2013). According to Singh et al. (2013), the elevation of AlDH protects against oxidative damage.

However, according to Ubeda et al. (2011), the loss of a large amount of alcohol compounds could occur during the acetous fermentation stage due to the ability of acetic acid bacteria to use alcohols other than ethanol, such as 3-methyl-1-butanol, isobutanol and 2-methyl-1-butanol, as a substrate. These alcohols are produced during alcoholic fermentation from the amino acid metabolism of yeast (Callejónet al., 2009). According to Callejónet al. (2009), the total volatile compounds will generally increase after acetous fermentation, when acetic acid bacteria have the ability to metabolise other alcohols in a similar way to ethanol and produce their respective fatty acids.

The Orleans method is one of the oldest techniques for producing vinegar. Initially, fermented fruit juice is placed in a vessel with a high diameter/height ratio. After approximately a week, during which acetous fermentation is triggered, the liquid is passed to another vessel. Acetous fermentation is slow, taking effect only at the surface of the liquid,

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where there is sufficient dissolved oxygen, which ensures the conversion of alcohol to acetic acid. This fermentation lasts between 8 to 14 weeks depending on various factors, such as the fermentation temperature, the initial composition of the alcoholic solution, the nature of the microorganisms and the sufficiency of the oxygen supplied (Dabija & Hatnean, 2014).

The submerged method involves the suspension of acetic acid bacteria in the acetifying culture with the application of strong aeration to meet the required oxygen demand in the system. This method consists of stainless steel fermentation tanks with a capacity of 10,000 to 40,000 litres, an air supply system, a cooling system, a foam controlling system, and loading and unloading valves. This method consists of three main steps, which are the loading of raw materials and inocula into the fermentation medium, fermentation and the complete unloading of the fermented medium with the biotransformed product. Part of the finished product is unloaded, and the other part is left in the vessel for the next cycle (Tesfaye et al., 2002).

The generator process is one of the rapid processes for producing vinegars. Fermentation proceeds in this process in a container that consists of two chambers. The larger (upper) chamber is packed with solid materials almost to the top, and this is separated from the lower chamber by a screen. Air is injected and blown upward through the screen and through the solid materials, and the air escapes through the top. The process takes approximately 3 to 7 days to complete the vinegar production. Two-thirds of the final vinegar product is withdrawn from the tank, and a new batch of mash is added slowly to the tank. The optimum temperature for the generator method is 30°C (Tan, 2005).

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To summarise, the Orleans method is slow in terms of producing vinegar compared to the other two methods. However, the Orleans method produces a higher quality vinegar. The submerged method is commonly used in the production of wine vinegars, whereas the generator method is often used in the production of distilled and industrial vinegars. These two methods (submerged and generator) are much faster than the Orleans method in producing vinegars at larger scales (Dabija & Hatnean, 2014).

3.1 Factors Affecting the Production of Vinegar

3.1.1 Yeast Strains

According to Valles et al. (2005), the different strains of yeast used in fermentation could influence the final vinegar produced. Different strains of yeast can produce different amounts of volatile compounds and alcohol contents. This indicates that different kinds of vinegars in terms of aroma, alcohol content and acetic acid content will be produced according to the types of strains used (Valles et al., 2005). *Saccharomyces cerevisiae* r. *bayanus* produces a higher amount of acetic acid compared to *S. cerevisiae* r. *cerevisiae* at 18°C, as shown in a study carried out by Valles et al. (2005).

In addition, according to Ubeda et al. (2011), there are two alcoholic fermentation methods, namely the spontaneously fermented method and the *S. cerevisiae* yeast inoculation method. It was found that alcoholic fermentation in the presence of yeast could produce higher alcohol contents compared to spontaneous fermentation in fruit puree (Ubeda et al. 2011). Ibarz et al. (2005) also noted that yeast plays an important role in producing a higher alcohol content in wines.

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3.1.2 pH

The optimum pH for the growth of acetic acid bacteria is from pH 5.5 to pH 6.3 (Raspor & Goranovic, 2008). However, several studies have found that acetic acid bacteria can still survive at pH 3.0, and some strains have been isolated from aerated media with a pH as low as 2.0. Three different groups of strains may be involved in the production of vinegar, which are acetophilic strains (grow at pH 3.5), acetotolerant strains (grow at pH 3.5 to 6.5) and acetophobic strains (grow at pH levels higher than 6.5). There might be a gradual development from acetophobic to acetotolerant strains followed by acetophilic strains due to the longer period of exposure to low pH and high acetic acid concentrations (Raspor & Goranovic, 2008).

3.1.3 Temperature

The optimum temperature for the growth of acetic acid bacteria is 25°C to 30°C. Thermotolerant acetic acid bacteria are able to grow at up to 40°C. These bacteria may oxidise ethanol at 38°C to 40°C, and the rate of ethanol oxidation could be more rapid compared to that of mesophilic strains in this temperature range. However, another study has shown that acetic acid bacteria are still active at 10°C but have a slower growth rate (Raspor & Goravonic, 2008).

3.1.4 Production Methods

As mentioned in the section on production methods, the use of different methods, such as the Orleans, submerged or generator methods, will affect the quality of vinegars. Because the

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Orleans method requires the longest amount of time for vinegar production compared to the submerged and generator methods, it ensures that the substrates are almost fully used up to maximise the ethanol and acetic acid content in the final product, vinegar (Dabija & Hatnean, 2014). Ordoudi et al. (2014) reported that the total phenolic content of pomegranate vinegar was not affected by the 2-stage fermentation process, while the total anthocyanin content was greatly reduced (10-fold) during alcoholic fermentation and the end product (vinegar) had a similar total anthocyanin content compared to that of fresh pomegranate juice.

4.0 VOLATILE COMPOUNDS AND ORGANIC ACIDS IN VINEGARS

The unique flavour and aroma of vinegar are mainly attributed to the acetic acid fermentation process. The strong aroma and flavour in vinegars are due the presence of acetic acid. However, aside from acetic acid, other fermentation products in vinegars, such as organic acids, esters, ketones and aldehydes, also contribute to the organoleptic properties of vinegars (Ozturk et al., 2015). These compounds are produced during the fermentation and ageing process, in which acetic acid acts as the precursor for the formation of these products (Yu et al., 2012). These volatile compounds could be influenced by the initial raw materials used, the methods of vinegar production and the time taken for acetification (Pizarro et al., 2008).

In a study conducted by Ozturk et al. (2015), who studied the volatile compounds found in Turkish traditional homemade vinegars and industrial vinegars, a total of 61 and 38 volatile compounds were found in the traditional and industrial vinegar samples, respectively. Among the volatile compounds identified, α-terpineol (25%) and ethyl acetate (15%) were the major volatile compounds in the traditional vinegars. Interestingly, ethyl acetate was mainly found in the vinegars produced from grape, while α-terpineol was not observed in any of the

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grape vinegar samples. In the industrial samples, octanoic acid (15.6%) and isoamyl acetate (18.6%) (banana odour) were found to be the major volatile compounds in grape and pomegranate vinegars, respectively (Ozturk et al., 2015).

Su and Chien (2010) reported that vinegar produced using rabbiteye blueberry had the following as its most important aroma-active compounds: acetic acid (vinegar odour), 2/3-methyl-butanoic acid (sweaty odour), phenethyl acetate (sweet, honey odour), 2-phenylethanol (rosy, sweet odour), octanoic acid (sweaty odour), eugenol (clove odour) and phenylacetic acid (floral odour). Some compounds such as 2,3-butanedione (buttery odour), (E,Z)-2,6-nonadienal (cucumber odour), ethyl butanoate (apple, fruity odour) and linalool (floral, cut grass odour) had low concentrations or were not detected by GC-MS but showed some odour impact in the samples due to the low odour thresholds of these compounds.

Del Signore (2001) conducted a study on the volatile compounds in 56 samples of balsamic vinegars, traditional balsamic vinegars (aged – some for 25 years) and common vinegars from Modena and Reggio Emilia, Italy. This study showed that the common and balsamic vinegars contained more esters and propionic acid than traditional balsamic vinegars. The one exception was 2,3-butanediol diacetate, which is present in larger concentrations in traditional balsamic vinegar. Among the aldehydes, diacetyl, hexanal and heptanal were found in larger quantities in traditional balsamic vinegars compared to balsamic (three times smaller quantity) and common vinegars (five times smaller quantity). For alcohol, octanol was present in larger concentrations in traditional balsamic vinegar, while 1-propanol, isobutyl alcohol, isoamyl alcohol and 1-hexanol were found in higher quantities in balsamic vinegar. In the common vinegar, 2-propanol and ethanol were present in higher quantities (Del Signore, 2001).

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Madrera et al. (2010) reported that the organic acids (lactic, acetic and succinic) and volatile compounds (2-butanol, 2-propen-1-ol, 4-ethylguaiacol and eugenol) of vinegars are significantly influenced by the maturation of the vinegar. It was found that vinegars with higher levels of maturation have higher concentrations of these compounds. According to Ubeda et al. (2011), the formation of esters during alcoholic fermentation is very high through spontaneous fermentation compared to inoculated fermentation. This might be due to the presence of enzymatic activities from the different yeast strains. In their study, persimmon vinegar showed higher contents of volatile compounds compared to strawberry vinegar, except for acetaldehyde, 1-propanol and isobutanol. Different methods of alcoholic fermentation could lead to different qualities of the vinegar that is produced. Overall, for persimmon vinegar, inoculated alcoholic fermentation results in higher amounts of volatile compounds, whereas in strawberry vinegar, spontaneous alcoholic fermentation results in higher amounts of volatile compounds.

Yu et al. (2012) reported on the volatile compounds present in aromatic vinegar samples produced from cereals (sticky rice, wheat bran and rice husks) from Zhenjiang, China. The headspace solid-phase microextraction (HS-SPME) method was employed to extract the volatile compounds, and the samples were found to contain alcohols, acids, esters, aldehydes, ketones and heterocycle compounds. Among them, esters were the major volatile compounds found, among which ethyl acetate, acetic acid 2-phenylethyl ester and dihydro-5-pentyl-2(3H)-furanone were found to be responsible for fruit flavour and peach and intense coconut aromas, respectively. Aside from acetic acid, 3-methyl-butanoic acid was found in the samples, which is attributed to a strong, pungent cheesy or sweaty smell. Among the carbonyl compounds found in these Zhenjiang aromatic vinegars were 2,3-butanedione and 3-

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hydroxy-2-butanone. These compounds were responsible for a buttery flavour as well as caramel and fruity odours. There were also alcohols that were responsible for the sweet and fruity aroma of the Zhenjiang aromatic vinegars, namely, 3-methyl-1-butanol, 2,3-butanediol, ethanol and phenyl ethyl alcohol. Yu et al. (2012) also reported on the presence of heterocycle compounds, among which alkylpyrazines including 2,3,5-trimethyl pyrazine, 2,3-dimethyl-5-ethylpryazine, tetramethyl-pyrazine and 2,3,5-trimethyl-6-ethylpyrazine were the major compounds. These compounds give the nutty, roasty and toasty tones to vinegars.

4.1 Bioactive Compounds of Vinegars

Bioactive compounds are extra-nutritional constituents in foods (Etherton et al., 2002). The antioxidative activities of vinegar derived mainly from its bioactive compounds including carotenoids and phytosterols as well as phenolic compounds and vitamins C and E (Charoenkiatkul et al., 2016). Antioxidants have been used to control oxidation and retard food from spoilage; however, many are used today because of their putative health benefits (Finley et al., 2011). Bioactive compounds can act as antioxidants, enzyme inhibitors and inhibitors of gene expression (Etherton et al., 2004).

By comparing the data obtained from Qiu et al. (2010) and Verzelloni et al. (2007), oat vinegar (OV) contained the highest amount of catechin (5.29 mg/mL), followed by Zhenjiang vinegar (ZV) (4.18 mg/mL) and traditional balsamic vinegar (3.72 mg/mL). In addition, the flavonoid compounds in OV (2.04 mg/mL) were found at a much higher concentration compared to those in ZV (1.10 mg/mL) and other vinegars shown in Table 1. It is very important to determine the contents of flavonoids and polyphenols, as these play an important role in antioxidant activity. Polyphenols have antioxidative properties, as they have

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an aromatic phenolic ring, which can stabilise and delocalise the unpaired electrons within the aromatic ring (Qiu et al., 2010). It is worth mentioning that Ubeda et al. (2013) reported that strawberry vinegar (SV) has a significantly higher amount of total phenolic contents at 1.61 ± 0.10 mg GAE/mL compared to the others in Table 1.

Anthocyanin breakdown is dependent on the pH in the presence of oxygen and is directly related to the level of pseudobase (colourless) and inversely related to the concentration of cations. A study carried out by Su and Chien (2007) indicates that when the temperature increases, there will be an increase in the rate of anthocyanin monomer losses in the products. According to Su and Chien (2007), the anthocyanin content in wine vinegars is lower than in other products, especially the vinegars shown in Table 1, because the breakdown of anthocyanin is dependent on the pH and the availability of oxygen. The overall result shows that skin-contact (including the skin of blueberry) fermentation of vinegar results in a higher amount of antioxidant activity in blueberry products compared to non-skin-contact fermentation (Su & Chien, 2007). Blueberry wine vinegar with skin has the highest amount of gallic acid, followed by blueberry vinegar and blueberry wine vinegar without skin.

According to Jang et al. (2015), traditional vinegars, for example, rural lacquer vinegar and rural Korean black raspberry vinegar, contain high concentrations of total phenolic compounds and show high activities in ABTS and DPPH assays. Rural Korean black raspberry vinegar contains higher levels of quercetin and cyanidin, which are metabolites associated with antioxidant activity, and it thus showed the highest antioxidant activity among all of the samples used in the study. The saccharide contents in commercial vinegars are higher than those in traditional vinegars, and this might due to the addition of artificial

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sweeteners and saccharide during the fermentation processes, as alcoholic fermentation uses sugars as a substrate for the biochemical saccharification to alcohol (Jang et al. 2015).

Sakanaka and Ishihara (2008) reported that unpolished rice vinegar contains higher total phenolic compounds compared to polished rice vinegar, as shown in Table 2, because unpolished rice contains rice bran, which has phenolic compounds, such as dihydroferulic acid, dihydrosinapic acid, sinapic acid, vanillic acid and p-hydroxycinnamic acid (Sakanaka & Ishihara, 2008).

In the same study, apple cider vinegar was found to contain significantly lower contents of total phenolic compounds, which might be due to the raw material used (Sakanaka & Ishihara, 2008). A comparison of the results obtained for unpolished rice vinegar and rice vinegar by Shimoji et al. (2002) indicated that unpolished rice vinegar contains more phenolic compounds compared to rice vinegar, as shown in Table 2.

In addition, traditional balsamic vinegar contains a higher amount of ferulic acid (Plessi et al., 2006) compared to unpolished rice vinegar and rice vinegar (Shimoji et al., 2002), as shown in Table 2. Cerezo et al. (2008) studied the effects of different types of barrels (acacia, cherry, chestnut and oak) on the phenolic composition of red wine vinegar, finding that catechin and resveratrol glycoside showed significant decreases during acetification, while gallic acid and gallic ethyl ester increased substantially for those vinegars produced in chestnut wood barrels.

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5.0 BIOACTIVITIES AND HEALTH BENEFITS OF VINEGAR

According to Etherton et al. (2004), bioactive compounds affect physiological or cellular activities, resulting in beneficial health effects. Bioactive compounds promote better and more effective health benefits compared to nutrients (Etherton et al., 2004). Bioactive compounds are claimed have the ability to modify the risk of disease rather than prevent diseases. In addition, there is great interest in polyphenolic compounds as quality determinants because, in addition to their antioxidant activity, they are also responsible for the colour and astringency of vinegar (Mas et al., 2014).

Several epidemiological studies have suggested that consuming natural antioxidants, such as polyphenol-rich foods containing flavonoids, anthocyanins and other phenolic compounds, has a protective effect against the aforementioned diseases (Almeida et al., 2011). Furthermore, antioxidants can minimise the postprandial increase in lipid hydroperoxides, which are generated during the digestion of food. Dietary antioxidants help prevent the formation of peroxides and their assimilation in the digestive tract (Verzelloni et al., 2007). Several studies have shown that higher oxidant and lower antioxidant levels in the human body could cause oxidative stress, which leads to the acceleration of the ageing process and the development of some chronic, inflammatory and degenerative diseases (Candido et al., 2015). Vinegar has high antioxidant activity, antimicrobial properties, antidiabetic effects and therapeutic properties (Budak et al., 2014), which could offset the development of the above mentioned diseases.

Juice and wine products derived from blueberry show a high capacity for inhibiting linoleic acid peroxidation in ferric thiocyanate assays. Blueberry wine vinegar with the skin of

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blueberry has the highest antioxidative activities compared to blueberry wine vinegar without the skin of blueberry and blueberry vinegar in both beta-carotene bleaching assays and ferric thiocyanate assays (Su & Chien, 2007). According to Verzelloni et al. (2007), traditional balsamic vinegar has a higher amount of catechin compared to mass-produced balsamic vinegar and red wine vinegar. The values obtained in the peroxidase assay were lower than the values of total phenolic compounds, as reducing sugars such as glucose and fructose will react with the total phenolic compounds but do not react in the peroxidase assay (Verzelloni et al., 2007).

The traditional Japanese rice vinegar Kurosu has been reported to contain ethyl acetate, which has superior antioxidative activities compared to apple vinegars and wine. According to Nanda et al. (2004), Kurosu has the ability to inhibit the growth of human cancerous cells. In their study, Kurosu vinegar, which is derived from traditional Japanese vinegar produced from unpolished rice, contains rice bran, possibly to inhibit the growth of human cancer cell lines (Nanda et al., 2004).

Maillard reaction product (MRP) standards react in a concentration-dependent manner in the Folin-Ciocalteu assay, while the peroxidase assay will not involve any reactions. On the other hand, glucose and fructose are the examples of reducing sugars, which will react in the Folin-Ciocalteu assay but not in the peroxidase assay (Verzelloni et al., 2007). According to Verzelloni et al. (2007), MRPs are adsorbed at the hydrophobic stationary phase of the columns.

In addition, according to Lee et al. (2013), tomato vinegar has powerful anti-visceral obesity properties in HFD-induced obese rats. The intra-abdominal deposition of visceral

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adipose tissue is known as a general type of obesity that is associated with conditions such as type 2 diabetes mellitus, hyperlipidemia, hypertension and coronary heart disease. They found that consuming tomato vinegar regularly can reduce the total visceral fat and the epididymal adipocyte size (Lee et al., 2013).

Vinegar is widely used as an acidic seasoning and has been reported to have health benefits, such as providing improved digestive system function, appetite stimulation, antioxidant properties, exhaustion recovery effects, lower lipid levels and the regulation of blood pressure (Fushimi et al., 2001; Qui et al., 2010). In addition, vinegar also contains polyphenols, which have been shown to prevent lipid peroxidation, hypertension, hyperlipidemia, inflammation, DNA (deoxyribonucleic acid) damage and cancer (Osada et al., 2006; Prior & Cao, 2000; Chou et al., 2015).

According to Kondo et al. (2001), the residues of rice vinegar have the ability to inhibit ACE (angiotensin converting enzyme) activity and have reduced blood pressure *in vitro*. The mechanism of blood pressure reduction by acetic acid could be mediated by a different mechanism from that of ACE inhibitory activity. In addition to reducing blood pressure, vinegar shows a decrease in rennin activity upon the ingestion of acetic acid. Rennin plays an important role in the initial reaction of the rennin-angiotensin system, where the reduction of blood pressure could take place. The consumption of acetic acid could reduce plasma rennin activity as well as blood pressure.

Vinegars are also commonly used for the pickling of fruits and vegetables and in the preparation of mayonnaise, salad dressings and other food condiments (Tan, 2005; Pooja &

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Soumitra, 2013). Moreover, vinegars have been traditionally used as a food preservative by many countries due to their ability to retard microbial growth (Pooja & Soumitra, 2013).

The various types of organic acids in vinegar, and mainly acetic acid, can diffuse through the cell membranes of microorganisms, leading to bacterial cell death (Booth & Kroll, 1989). Reactive oxygen species such as superoxide, hydrogen peroxide and the hydroxyl radical have been reported to negatively affect lipids, proteins and DNA, resulting in accelerated ageing, cancer and brain degenerative disorders (Maes et al., 2011). Recent studies have suggested that bioactive compounds such as polyphenols and vitamins (also highly available in vinegars) may minimise the incidences of these degenerative illnesses by providing antioxidative effects (Pandey & Rizvi, 2009).

Vinegar may also improve the insulin sensitivity of humans, and this contributes to its antidiabetic effects. Recent studies have shown that vinegar could be used for diabetic treatments (Salbe et al., 2009). In humans, the insulin response curve is decreased by 20% after consuming sucrose co-administered with vinegar. Several studies have shown that the acetic acid in vinegar may prevent the complete digestion of complex carbohydrates by increasing the uptake of glucose by tissues, resulting in reduced blood glucose levels (Fushimi et al., 2001).

Polyphenols such as chlorogenic acid, which is present in high levels in apple cider vinegar, could inhibit the oxidation of low-density lipoproteins (LDLs) and potentially improve health by preventing cardiovascular disease (Laranjinha et al., 1994). Fushimi et al. (2006) reported that consuming 0.3% of dietary acetic acid from foods may help in reducing the serum cholesterol and triglyceride levels in the serum. Acetic acid has also been reported

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to enhance lipid homeostasis and helps to lower cholesterol level *in vivo*. A study by Fukami et al. (2010) indicates that acetic acid bacteria produce alkali-stable lipids (ASL). ASL have a significant effect in improving cognitive ability, as they contain highly pure free dihydroceramide, a precursor to various sphingolipids such as gangliosides (Fukami et al., 2010), which are composed of sialic acid- and ceramide-conjugated oligosaccharides (Svennerholm, 1994). These sialic acid- and ceramide-conjugated oligosaccharides have been shown to be effective in improving the symptoms of Alzheimer patients (Svennerholm, 1994). Additionally, cider vinegar has been reported to have the ability to balance pH levels in the body if taken regularly (Brown & Jaffe, 2000).

5.1 Other Non-Food Uses of Vinegar

Aside from food applications, vinegar may be used as an extraction agent of chromium, copper and arsenic from chromate copper arsenate (CCA)-treated wood using wood vinegar (Ahn et al., 2012). This shows that wood vinegar could be an alternative to synthetic chemicals for removing metal elements from treated wood waste.

In addition, vinegar has been used to improve the performance of solar disinfection (SODIS) systems by lowering the pH. This result has shown that the choice of catalyst (vinegar) was an important factor in addition to low pH in disinfection using sunlight (Amin & Han 2011).

According to Baimark and Niamsa (2009), vinegars can act as antifungal agents in natural rubber. Due to the high moisture content of natural rubber, fungi can grow easily, which might cause a major problem in natural rubber production, as it influences the quality

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of the final products. Commercial antifungal agents are highly toxic and not friendly to the environment, which causes some environmental issues (Baimark & Niamsa, 2009). However, adding vinegar during natural rubber production could minimise this problem effectively. The presence of acetic acid and phenolic compounds can act an anti-germination agent and a termiticide (Baimark & Niamsa, 2009).

6.0 CONCLUSION

Vinegar is an acidic liquid product prepared from alcoholic fermentation by yeast followed by acetous fermentation by acetic acid bacteria of any suitable food. In the past few decades, the production of agriculture products is increasing worldwide for human consumptions at a level at which there are production surpluses. To reduce waste, the use of these crops as initial raw materials for the conversion into other products such as vinegar is vital. There are generally two types of methods to produce vinegar, the slow method (Orleans method) and the rapid methods (submerged and generator methods). Aside from the main compound, i.e., acetic acid, vinegar contains various organic acids, esters, ketones and aldehydes, which contribute to its organoleptic properties. It can provide many health benefits to consumers when they take vinegar regularly. Vinegars also contain diverse bioactive compounds including, but not limited to, carotenoids, phytosterols, phenolic compounds, and vitamins C and E, which contribute to their various bioactivities. Vinegar promotes digestion, stimulates the appetite, exhibits antioxidant activity, has antidiabetic effects, and presents antimicrobial properties. Therefore, consumers are encouraged to consume vinegar regularly for the benefit of their health, naturally.

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8.0 CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest in this review article.

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Yu, Y.J., Lu, Z.M., Yu, N.H., Xu, W., Li, G.Q., Shi, J.S., & Xu, Z.H. (2012). HS-SPME/GC-MS and chemometrics for volatile composition of Chinese traditional aromatic vinegar in the Zhenjiang region. *Journal of the Institute of Brewing,* 118: 133–141.

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Table 1 Comparison of bioactive compounds between various types of vinegars

Analysis \ Vinegars	TBV[a]	BV[a]	RWV[a]	OV[b]	ZV[b]	BV1[c]	BV2[c]	BV3[c]	URV[d]	PV[d]	TV[e]	SV[f]
Total phenolic compounds (mg catechin / mL)	3.72	1.99	0.71	5.29	4.18	-	-	-	-	-	-	-
Total flavonoid content (mg / mL)	0.58	0.33	0.23	2.04	1.10	-	-	-	-	-	-	-
Total phenolic compounds (mg gallic acid / mL)	-	-	-	-	-	0.89 ± 0.02	1.11 ± 0.03	0.98 ± 0.02	0.73 ± 0.10	0.80 ± 0.11	0.37 ± 0.001	1.61 ± 0.10
Total anthocyanins (mg cyaniding-3-glucoside) / 100mL)	-	-	-	-	-	0.97 ± 0.06	1.37 ± 0.09	3.22 ± 0.13	-	-	-	-

[a]: Verzelloni et al. (2007)
[b]: Qiu et al. (2010)
[c]: Su & Chien (2007)
[d]: Sakanaka & Ishihara (2008)
[e]: Lee et al. (2013)
[f]: Ubeda et al. (2013)

TBV: Traditional Balsamic Vinegar
BV: Balsamic Vinegar
OV: Oat Vinegar
ZV: Zhenjiang Vinegar
BV1: Blueberry Wine Vinegar (without skin contact)

BV2: Blueberry Wine Vinegar (with skin contact)
BV3: Blueberry Vinegar
URV: Unpolished Rice Vinegar
PV: Persimmon Vinegar (Saijo)
TV: Tomato Vinegar
SV: Strawberry Vinegar

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Table 2 Comparison of phenolic compounds concentration between various types of vinegars

Vinegar / Compounds	URV[a]	Rice Vinegar [a]	TBV [b]	Acacia RWV. [c]	Cherry RWV.[c]	Chestnut RWV. [c]	Oak RWV.[c]
Dihydroferulic acid	24.8	0.09	-	-	-	-	-
Dihydrosinapic acid	4.68	-	-	-	-	-	-
Ferulic acid	0.95	0.03	8.8	-	-	-	-
Sinapic acid	1.15	-	-	-	-	-	-
Vanillic acid	1.44	-	8.1	1.31	1.78	1.55	1.67
p-hydroxycinnamic acid	0.17	-	-	-	-	-	-
Protocatecuic acid	-	-	18.8	11.29	5.80	7.91	5.79
Syringic acid	-	-	13.8	2.66	4.31	4.14	4.21
Isoferulic acid	-	-	2.2	-	-	-	-
Gallic acid	-	-	18.0	32.65	29.52	162.72	33.97
Caffeic acid	-	-	10.9	5.68	6.00	5.76	5.67

[a]: Shimoji et al. (2002)
[b]: Plessi et al. (2006)
[c]: Cerezo et al. (2008)

URV: Unpolished Rice Vinegar
TBV: Traditional Balsamic Vinegar
Acacia RWV.: Acacia Red Wine Vinegar*
Cherry RWV.: Cherry Red Wine Vinegar*
Chesnut RWV.: Chestnut Red Wine Vinegar*
Oak RWV.: Oak Red Wine Vinegar*

* Acacia, cherry, chestnut and oak are the type of barrels used for the fermentation

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Figure 1

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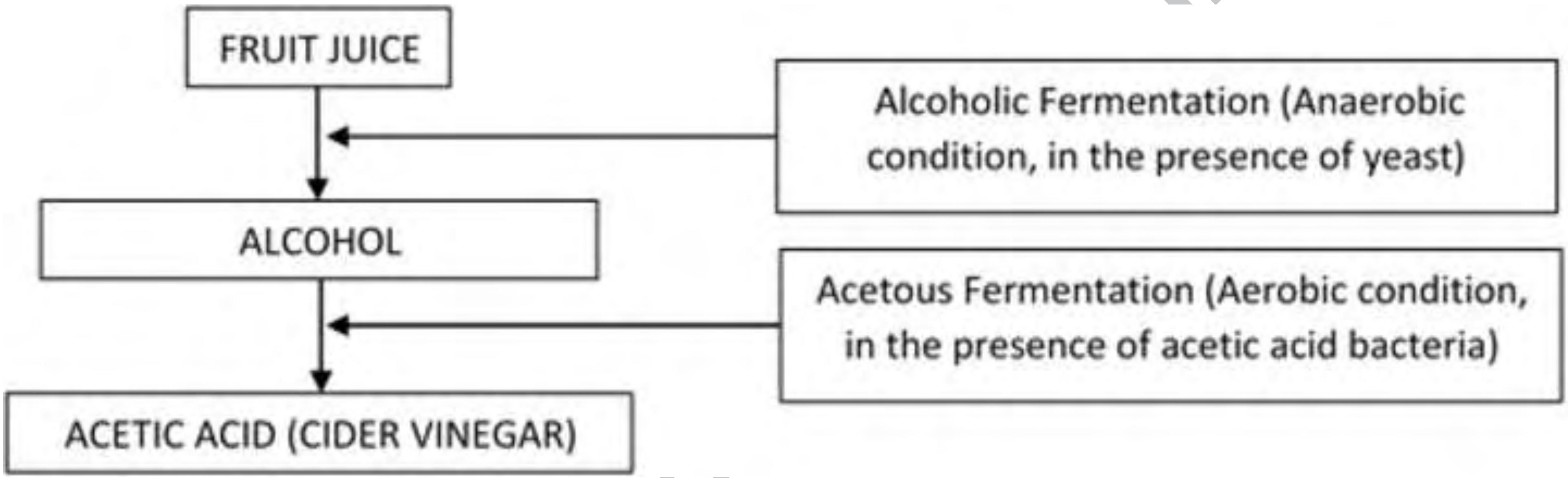

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Figure 2

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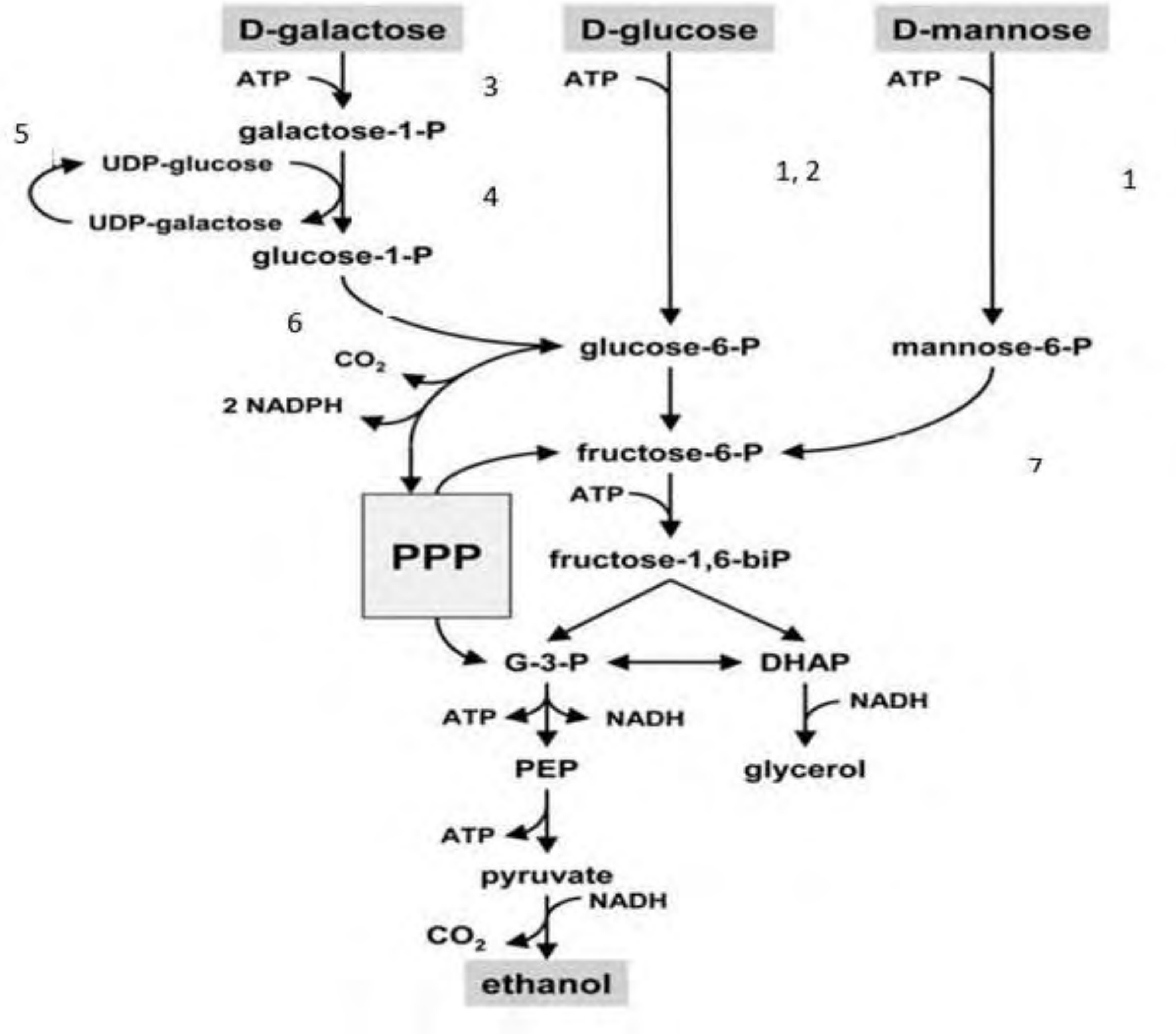

Figure 3

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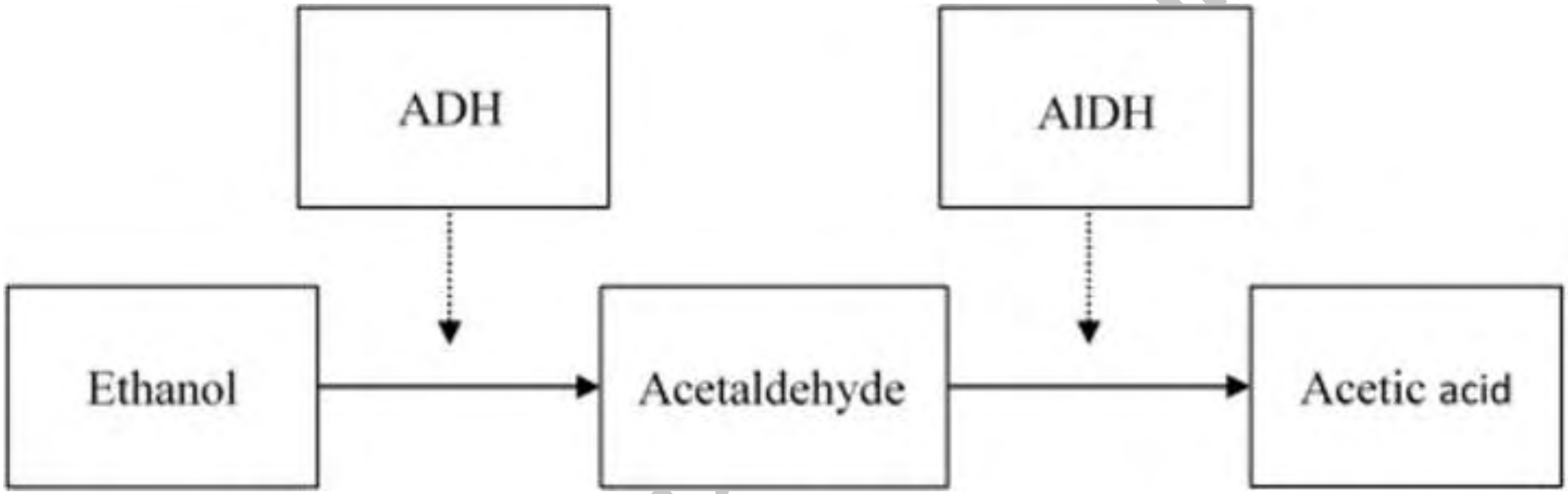

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Figure 1 The process of cider vinegar-making from fruit juice

Figure 2 Alcoholic fermentation by yeast under anaerobic condition. The gene names encoding the various enzymes. Glucose catabolism: 1: hexokinase; 2: glucokinase. Galactose catabolism: 3: galactokinase; 4: galactose-1-phosphate uridylytransferase; 5: UDP-glucose 4-epimerase; 6: phosphoglucomutase. Mannose catabolism: 1, hexokinase I; 7: mannose-6-phophate isomerase. G-3-P, Glyceraldehyde-3-phosphate; DHAP, dihydroxy-acetone-phosphate; PEP, phospho-enol pyruvate; PPP, Pentose phosphate pathway. (Source: Maris et al. 2006)

Figure 3 Acetous fermentation in the presence of acetic acid bacteria. Alcohol dehydrogenase (ADH) and (AlDH) aldehyde dehydrogenase catalyse the oxidation of ethanol to acetaldehyde and acetaldehyde to acetic acid respectively.

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Highlights

- Vinegar is liquid product from alcoholic and acetous fermentation of suitable food
- Vinegar varieties: black vinegar, rice vinegar, balsamic vinegar, white wine vinegar
- Vinegar contains various bioactives: polyphenols, micronutrients and antioxidants
- Bioactivities of vinegars include antimicrobial, antioxidative and antidiabetic

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Accepted Manuscript

Varieties, production, composition and health benefits of vinegars: A review

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