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Full Length Research Paper

Comparative assessment of picolinic acid with common chemical preservatives in ginger juice during storage

Akinwande, B. A.[1], Adeoye, I. O.[2]* and Anjorin, I. B.[1]

[1]Department of Food Science and Engineering, Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria.
[2]Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria.

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In consideration of the medicinal and health benefit of picolinic acid (PA), this research work compared its effectiveness as a preservative with potassium sorbate and sodium benzoate in ginger juice. Concentration of 0.07, 0.067 and 0.073% of PA, potassium sorbate and sodium benzoate, respectively, were added to ginger juice, packed in polyethylene terephthalate (PET) bottles and stored for 12 weeks at ambient condition. Chemical properties (total soluble solids, total phenolic content, total flavonoids, titratable acidity and ascorbic acid), pH as well as microbiological properties (total viable count and total mould count) of the juice were observed on a fourth night basis. Total phenolic content and total flavonoids were best retained in the sample with PA than others. Higher values for pH and total soluble solids were recorded in the sample preserved with potassium sorbate and sodium benzoate. Proliferation of microbial growth was best controlled by sodium benzoate. PA could be used in preference to the other two preservatives due to its ability to preserve bioactive substances as well as its health and medicinal advantages over others.

Key words: Ginger juice, preservative, picolinic acid, potassium sorbate, sodium benzoate.

INTRODUCTION

Preservatives are the substances that increase the shelf life of foods and beverages. Shelf life is determined by rates of growth of spoilage microorganisms and chemical degradation of food components. Preservatives inhibit one or both of these processes. Several chemical compounds are able to inhibit the growth of microorganisms. One of them, benzoic acid, is a well-known and commonly used food preservative that is present naturally in some materials (Marinova and Yanishlieva, 2003). Its derivatives such as sodium benzoate are also active compounds and are used commercially as food preservatives (Conrad et al., 1994). Potassium sorbate is another established food preservatives, its effectiveness is 5 to 10 times of sodium benzoate and is used in quantities in which there is no known adverse health effect (Westhoff and Franzier, 1998). However, only few of them grant claims for preservatives, which is why the search for ideal antimicrobial agent is continued.

Picolinic acid (PA) is a naturally occurring degradation product of L-tryptophan detected in the human body (Dazzi et al., 2001). It is synthesized in the liver, kidney, and other organs (Fernandez-Pol et al., 2001). PA was found to have a number of biological functions. It is a cheap and safe drug facilitating Zinc/Chromium ion absorption from the intestine because of its metal ion-chelating activity (Evans and Johnson, 1980). Its activity as a metal ion chelator and as a complex group with Chromium makes it useful as a dietary supplement for obese people, since it has a beneficial effect on reducing diabetes risk (Komorow et al., 2008).

Borawska et al. (2008) reported that PA and sodium picolinate show a high antimicrobial activity at pH 5.0 and 7.0 and that PAs and their salts may represent new potential food or cosmetic preservatives.

Ginger (*Zingiber officinale*), one of the oldest spices used worldwide for its peppery taste, preservatives power and typical aroma, has lots of medical benefits. Moreover, ginger contains a number of antioxidants such

*Corresponding author. E-mail: adeoyeid@gmail.com. Tel: (+234) 803 3082 807 or 702 6436 377.

Table 1. pH of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	5.01^{a}	4.93^{b}	4.75^{c}	4.71^{d}	4.74^{cd}	4.74^{c}	4.76^{c}
B	5.10^{a}	5.03^{b}	4.91^{c}	4.87^{d}	4.89^{cd}	4.90^{c}	4.91^{c}
C	5.48^{a}	5.33^{b}	5.24^{c}	5.17^{d}	5.18^{d}	5.19^{d}	5.21^{cd}
D	5.23^{a}	5.14^{b}	5.07^{cd}	5.06^{d}	5.06^{d}	5.07^{cd}	5.08^{c}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

as beta-carotene, ascorbic acid, terpenoids, alkaloids and polyphenols such as flavonoids, flavones glycosides and rutin (Okezie et al., 1997). Ginger with its wide range of antioxidants can be a major source of natural or phytochemical antioxidants. The aim of this study was to carry out a comparative assessment of the preservative effect of PA with sodium benzoate and potassium sorbate in ginger juice during storage.

MATERIALS AND METHODS

Ginger (*Z. officinale*) root and sweetener were obtained from an open market in Ogbomoso. Polyethylene terephthalate (PET) bottles (50 ml size) were sourced from CASCADE Nigeria Limited (private company), Lagos State, Nigeria. PA, potassium sorbate and sodium benzoate were Sigma analytical reagents and were obtained from the Inorganic Chemistry Laboratory of Ladoke Akintola University of Techonology, Ogbomoso, Oyo State, Nigeria.

The ginger was sorted, cleaned, washed and crushed with mortar and pestle to extract the juice. The extracted juice was sieved with muslin cloth and diluted with portable water before the addition of sweetener. The ginger juice was divided into four portions. The first portion served as control without any preservative, 0.070% PA was added to the second portion, 0.067 potassium sorbate was added to the third portion, while 0.073% sodium benzoate was incorporated to the last portion. Each portion was pasteurized at 75°C for 30 min and hot fill into sterilized PET bottles. Sterilization of the bottles was carried out by immersing them in 7 ppm of chlorine solution for about 5 min. The filled bottles were kept on the shelf at room temperature and were sampled for analyses on fourth night basis in three replicates.

Chemical analysis

The pH and total soluble solids of the processed ginger juice were measured according to the method of AOAC (2000). Ascorbic acid content was also determined according to the procedures in the same method. The standard solution was prepared with 50 ml ascorbic and diluted to 100 ml with water. The sample and standard solution were titrated against dichloroindophenol solution to a pink endpoint lasting at least 10 s before the reading was taken. The result was expressed as mg ascorbic acid/ml sample. Titratable acidity was measured by addition of 10 ml of sample to 100 ml distilled water and titrating the solution with 0.1 N sodium hydroxide to an endpoint of light pink with 3 drops of phenolphthalein indicator (Height and Gump, 1995). The result was expressed as gram tartaric acid/100 ml.

The total phenolic content was determined by the Folin-Ciocalteu method. To 3.90 ml of water, 0.1 ml of the sample (10% v/v ginger juice) was added followed by addition of 0.5 ml of Folin-Ciocalteu reagent. After 3 to 6 min, 0.5 ml of saturated sodium carbonate (20 g of Na_2C0_3 in 100 ml of H_20) was added. After 30 min of vigorous mixing with a vortex mixer, a reading was taken at 725 nm (2120UV spectrophotometer). The result was expressed as gallic acid equivalents using a calibration curve with gallic acid as the standard (mg/L).

Total flavonoid content was determined according to the procedures outlined by Zhishen et al. (1999). 1 ml of diluted sample 1 ml sample/5 ml distilled H_20) was placed in a 10 ml flask. 4 ml distilled water was added, then 0.3 ml of $NaN0_2$ (5 g/100 ml distilled water) was added. After 6 min, 2 ml of 1 N NaOH was added and the solution was diluted to a total volume of 10 ml with distilled water. The absorbance of the solution was measured at 510 nm and flavonoid concentration was determined using a catechin calibration curve.

Microbiological analysis

The total mould count was determined according to the method of Adams and Moss (2008). 1 ml of the sample was pipetted into a sterile Petri dish and mixed with an appropriate volume of molten agar (potato dextrose agar) using pour plate method with incubation period of 48 h at 25°C. The plate was observed under electronic colony counter for microbial growth. The total bacteria count was also determined using the same method. 1 ml of the sample was pipetted into a sterile Petri dish and mixed with an appropriate volume of molten agar (plate count agar) using pour plate method with incubation period of 48 h at 35°C. The plate was observed under electronic colony counter for microbial growth.

Statistical analysis

All the analyses were done in three replicates. Statistical analysis of all the data was done with the Statistical analysis system (SAS) package (version 8.2 of SAS institute Inc., 1999). Statistically significant differences ($p < 0.05$) in all data were determined by analysis of variance (ANOVA) procedure, while Fisher's test was used in determining the least significant difference (LSD) for separation of the means.

RESULTS AND DISCUSSION

Chemical properties

Variation in pH values was observed in all the samples before storage as shown in Table 1. Highest value of

Table 2. Total soluble solids (%) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	18.00^{f}	18.25^{e}	18.30^{de}	18.35^{d}	18.50^{c}	18.60^{b}	18.70^{a}
B	17.10^{e}	17.20^{d}	17.20^{d}	17.30^{c}	17.50^{b}	17.60^{a}	17.65^{a}
C	18.50^{e}	18.75^{d}	18.90^{c}	18.95^{c}	19.15^{b}	19.25^{a}	19.30^{a}
D	17.50^{f}	17.55^{f}	17.70^{e}	17.80^{d}	17.90^{c}	18.00^{b}	18.10^{a}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

Table 3. Ascorbic acid content (mg/100 ml) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	9.75^{a}	8.75^{b}	7.50^{c}	6.50^{d}	5.50^{e}	4.75^{f}	4.50^{f}
B	12.65^{a}	10.1^{b}	9.00^{c}	8.25^{d}	7.50^{e}	7.00^{f}	6.25^{g}
C	12.65^{a}	10.5^{b}	8.75^{c}	8.00^{d}	7.50^{de}	7.00^{ef}	6.50^{f}
D	10.25^{a}	9.50^{b}	8.25^{c}	8.00^{d}	7.50^{e}	7.25^{f}	7.00^{g}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

5.23 was obtained in sample preserved with sodium benzoate, while least value of 5.01 was recorded in the control sample. The pH of all the samples decreased with increase in storage period till 6 weeks (with significant difference at $p < 0.05$) and increased thereafter till 12 weeks. Oroniran et al. (2011) also reported increase in pH value in soymilk that was preserved with spices during storage. Percentage reduction in pH at 6 weeks after storage was highest in control sample (5.99%), while values of 4.51, 5.66 and 3.25% were obtained in samples preserved with PA, potassium sorbate and sodium benzoate, respectively.

Total soluble solids content increased steadily, but with significant difference, in all the samples as storage progressed as shown in Table 2. This could be due to depolymerization, or cleavage of glycosidic linkages of the polysaccharides as storage continued. All the samples showed gradual decrease in the ascorbic acid content as storage time increased as shown in Table 3. Samples preserved with PA and potassium sorbate had highest value of 12.65 mg/100 ml at the beginning of the storage period, while control sample had the least value of 9.75 mg/100 ml. The percentage reduction from initial concentration ranged from 31.7% in the sample preserved with sodium benzoate to 53.8% in the control sample.

According to Zvaigzne et al. (2009), the content of Vitamin C in citrus fruit juices substantially decreased after 1 day of storage in a refrigerator. Osundahunsi (2008) reported similar degradation of ascorbic acid content in orange juice at both refrigerated and ambient storage conditions. Citrus juice concentrates that were stored at different temperatures for 8 weeks were also indicated to exhibit loss of ascorbic acid content (Burdulu et al., 2006). It was also indicated that change in the ascorbic acid content was observed at the end of Week 2 under both storage conditions and 40% reduction was observed after storage for 17 weeks at ambient condition.

The total titratable acidity of the samples were in the ranged of 1.60 g/100 ml in sample with sodium benzoate and 2.28 g/100 ml in sample preserved with PA (Table 4). Control sample and sample with potassium sorbate were in the range of 1.88 and 1.63 g/100 ml, respectively. It was observed that in all the samples, the total titratable acidity has a uniform increasing trend although sample that was preserved with PA recorded highest value at all sampling periods. Similar increasing trend was observed in soymilk sample that was preserved with local spices (Oroniran et al., 2011). The samples were significantly different from each other at $p < 0.05$.

Table 5 shows the results obtained for the total phenols in the samples. Except between Weeks 4 and 6, sample preserved with PA had highest values at the sampling times. Highest value of 12.50 mg/100 g was obtained in PA preserved sample at the end of the storage period, while least value of 9.50 mg/100 g was obtained in the control sample. There was a general decrease in the values obtained in all the samples with increase in storage time. Highest loss (24.0%) was recorded in control sample, while the sample preserved with sodium sorbate had least value (13.8%) for percentage loss followed by that preserved with PA (16.7%).

Total flavonoids in the samples reduced as the storage

Table 4. Total titratable acidity (g/100 ml) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	1.33^{e}	1.60^{d}	1.78^{c}	1.85^{ab}	1.83^{b}	1.85^{ab}	1.88^{a}
B	1.94^{e}	2.08^{d}	2.25^{ab}	2.23^{bc}	2.20^{c}	2.23^{bc}	2.28^{a}
C	1.35^{b}	1.40^{b}	1.60^{a}	1.60^{a}	1.58^{a}	1.60^{a}	1.63^{a}
D	1.39^{c}	1.41^{c}	1.55^{b}	1.60^{a}	1.55^{b}	1.58^{ab}	1.60^{a}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

Table 5. Total phenolic content (mg/100 g) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	12.50^{a}	12.00^{b}	11.50^{c}	11.00^{d}	10.50^{e}	10.00^{f}	9.50^{g}
B	15.00^{a}	15.00^{a}	14.00^{b}	14.00^{b}	13.25^{c}	13.00^{c}	12.50^{d}
C	14.50^{a}	14.75^{a}	14.50^{a}	14.00^{b}	13.00^{c}	12.75^{c}	12.25^{d}
D	13.00^{a}	13.00^{a}	12.25^{b}	12.00^{b}	11.25^{c}	11.00^{c}	10.50^{d}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

Table 6. Total flavonoids (mg/100 g) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	22.00^{a}	18.50^{b}	16.25^{c}	16.50^{c}	15.00^{d}	14.50^{d}	13.50^{e}
B	28.50^{a}	25.50^{b}	24.50^{c}	24.25^{cd}	24.00^{d}	23.00^{e}	22.00^{f}
C	25.00^{a}	23.50^{b}	22.00^{c}	22.25^{c}	21.25^{d}	21.00^{d}	21.00^{d}
D	20.25^{a}	18.75^{b}	17.50^{c}	17.25^{c}	16.25^{d}	16.00^{d}	15.50^{e}

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

Table 7. Total mould count (cfu/ ml) of ginger juice during storage.

*Sample	Weeks						
	0	2	4	6	8	10	12
A	3.0×10^2	4.0×10^2	1.1×10^3	1.9×10^3	2.6×10^3	2.9×10^3	3.2×10^3
B	1.0×10^2	2.4×10^2	3.5×10^2	4.7×10^2	7.3×10^2	1.0×10^3	1.8×10^3
C	1.0×10^2	2.0×10^2	4.2×10^2	5.5×10^2	7.9×10^2	1.2×10^3	1.5×10^3
D	1.0×10^2	1.3×10^2	2.4×10^2	4.8×10^2	5.6×10^2	7.0×10^2	1.0×10^3

Means followed by different letters across the rows are significantly different ($p < 0.05$) from one another. *A, Control sample; B, sample preserved with PA; C, sample preserved with potassium sorbate; D, sample preserved with sodium benzoate.

time progressed as shown in Table 6. At the end of storage time, the content ranged from 13.50 mg/100 g in control sample to 22.00 mg/100 g in sample preserved with PA. A similar decline has been reported (Zvaigzne et al., 2009) in another colour pigment (β-carotene) in citrus juices after 1 day of storage in a refrigerator. The decline was attributed to be due to the effect of light and oxygen on the juice during preparation process as well as during storage.

Antimicrobial properties

Lower count for total mould was obtained in all the samples with preservatives (range of 1.0×10^2 to 1.8×10^3 cfu/ml) as compared to the control sample (range of 3.0×10^2 to 3.2×10^3 cfu/ml) at each sampling period (Table 7). There was a general increase in the count in all the samples with increase in storage time. Highest values were obtained at the end of the 12 weeks storage period

in all the samples. Sodium benzoate preserved sample had least mold count at all times except at Week 6 when least amount was obtained in PA preserved sample. PA was observed to have better preservative effect than potassium sorbate up to week 10.

The prominent organisms that were isolated from the samples include *Pseudomonas* spp., *Bacillus* spp., *Staphlococcus* spp., *Geotricum* spp. and *Saccharomyces* spp. at the end of storage period.

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