Laboratory Analysis of pH and Neutralizable Acidity of Commercial Citrus Fruits in Nigeria

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Abstract: This is an in vitro study to evaluate five different commercially available citrus fruits: viz., Sweet orange (Citrus sinensis Osbeck), Grape (Citrus maxima (J. Buruan) Merrile), Lemon (Citrus limon (Burn F.) and Lime (Citrus aurantifolia) Swingle. Evaluation of their pHs and neutralizable acidity were made. A 50 mL of each fruit was prepared by juice press. Initial pH was measured in triplicate for the five fruits. The neutralizable acidity was assessed by measuring the volume of 0.10 N sodium hydroxide required to raise the pHs of each fruit to a neutral pH of 7.0. Results showed that all the evaluated drinks were acidic with pHs that ranged from 2.4 to 4.1. Lime produced the lowest mean pH of 2.4 and tangerine yielded the highest of 4.1. The mean volume of sodium hydroxide to neutralize the fruits ranged from 5.1mL to 104mL. Regarding neutralizable acidity, Lime required the highest NaOH to neutralize thus possessing the strongest potential to erode enamel. Tangerine required the least base to neutralize. All the 5 evaluated citrus fruits are acidic with pHs well below the critical pH (5.5) of enamel demineralization. Inappropriate consumption of these fruits especially lime may incite toothwear.

Key words: Citrus - Acidity - Dental erosion

INTRODUCTION

Citrus fruits have long been valued as part of a nutritious and tasty diet. The flavours provided by citrus are among the most preferred in the world and it is increasingly evident that citrus not only tastes good, but is also good for people. It is well established that citrus and citrus products are a rich source of vitamins, minerals and dietary fibre (non-starch polysaccharides) that are essential for normal growth and development and overall nutritional well-being. However, it is now beginning to be appreciated that these and other biologically active, non-nutrient compounds found in citrus and other plants (phytochemicals) can also help to reduce the risk of many chronic diseases [1].

There has been a steady rise in citrus production globally due mainly to increase in hectarage, consumer preference for more health or convenience food and rising incomes [2]. Although about 140 counties are known to be involved in citrus production. Brazil and the United States alone were credited with contributing up to 45% of global orange production [3]. Year 2007 estimate indicates that the top 10 citrus producing counties are Brazil, China, United States, Mexico, India, Spain, Iran, Italy, Nigeria and Turkey. Citrus production in West Africa is on a small scale and unorganized, [4] the ranking of Nigeria on the 9th position among the world top 10 producers of the commodity signify that the situation might be changing. This is in consideration of the fact that previous statistics did not feature Nigeria or any of the West African countries [5]. In any case, most of the citrus fruit produced in the country is consumed locally [4] and does not seem to feature at all in international trade [2]. Sweet orange (Citrus sinensis) production in Nigeria is significant, with heavy direct consumption due primarily to few and small capacity processing industries to convert the fruit to juice, concentrate and canned fruit [6].
Citrus fruits contain N (1–2 g/kg on a wet basis), lipids (oleic, linoleic, linolenic, palmitic, stearic acids, glycerol and a phytosterol), sugars (glucose, fructose, sucrose), acids (primarily citric and malic, but also tartaric, benzoic, oxalic and succinic), insoluble carbohydrates (cellulose, pectin), enzymes (pectin esterase, phosphatase, peroxidase), flavonoids (hesperidin, naringin), bitter principles (limonin, isolimonin), peel oil (d-limonene), volatile constituents (alcohols, aldehydes, ketones, esters, hydrocarbons, acids), pigments (carotenes, xanthophylls), vitamins (ascorbic acid, vitamin B complex, carotenoids) and minerals (primarily calcium and potassium). Citrus fruits are classified as acid fruits, since their soluble solids are composed mainly of organic acids and sugars [7].

The erosive capabilities of citrus juices have been demonstrated repeatedly on rat molar teeth. McClure [8] noted erosion with cranberry and grape-fruit juices. Bieri et al. [9] showed that rats fed orange juice for one week had tooth surface loss comparable with that seen with citric and acetic acids. Many animal studies have been carried out to evaluate the erosive properties of different juices [10-13]. Wynn and Haldil [14] reported that a wide range of juices, including grape juice, caused a similar effect to citric or acetic acid on rat molar teeth. Miller [15] noted similar results when he investigated several fruit juices. Holloway et al. [13] found diluted lemon juice diminished enamel in three weeks. Darby, [16] in what is apparently the first report of dietary erosion in humans, described changes in the teeth in two women who regularly sucked lemons; another two were reported to have undertaken the grape cure’ in Switzerland; a practice that involved a high consumption of grapes. Many authors have since described the effect of citrus fruits and their juices on the human dentition [17-23].

In recent years, Citrus fruits are increasingly found in the daily diet of many people. Some of the more common being orange, lemon, tangerine and grapefruit and it is noteworthy that a number of these acidic fruit juices have consistently been implicated as important causes of erosion of tooth structure [24, 25]. Over the last decades, the decline in the prevalence of dental caries in the world population has been accompanied by a remarkable increase in the incidence of non-carious lesions, such as dental erosion [26]. Avalanche of current evidence has shown that dental erosion alone or in combination with attrition or abrasion is a predominant cause of toothwear [27] and the most important sources of erosive acids are those found in the diet.

MATERIALS AND METHODS

A 5 popular and commercially available citrus fruit were evaluated. Sweet orange; Citrus sinences Osbeck, Grape; Citrus maxima (J.Buruan) Merrile, Lemon; Citrus limon Burn F. and Lime; Citrus aurantifolia Swingle. The erosive potential of each fruit was assessed by measuring its initial pH and neutralizable acidity in vitro.

Sample Preparation: Each sample of the citrus fruit was cut in half and the juice squeezed out with a juice-press. About 50mL of each sample was obtained and gently mixed. The skin and solids were not included; the solids being filtered out through a fine filter extracting as much juice as possible. A clean and dry safety 10ml pipette was used to draw up 10ml of juice and discharge it into a 250ml beaker.

Measurement of Initial pH: The initial pH of each fruit was measured using a pH meter (Hanna Instrument; Serial number S358236). A 20mL of each freshly prepared fruit juice was put in a glass beaker placed on a thermostatically controlled electric hotplate at 37°C. Before reading its pH, each sample was agitated (using a magnetic stirrer) for 1 min until a stable reading was obtained. Each fruit was tested three times to give a mean measurement. Between readings, the electrode was rinsed in distilled water to ensure that no cross-contamination occurred.

Measurement of Neutralizable Acidity: A 20 mL of the freshly prepared fruit juice was put in a glass beaker placed on a thermostatically controlled electric hotplate at 37°C. This was titrated with 0.1N NaOH added in 0.2ml increments until the pH of 7 is reached. This was done by using a non heating magnetic stirrer until a stable pH reading was obtained after each increment (0.2ml) of NaOH. This was done to measure the total neutralizable. Titrations were repeated in triplicate for each fruit to check for reproducibility and to give a mean value for that fruit. Neutralizable acidity of a solution is usually measured by reacting the acids present with a base such as sodium hydroxide (NaOH) to a chosen end point, close to neutrality. The amount of NaOH required to raise the pH to 7 is then noted for each fruit juice.
RESULTS

Evaluation of the pH: The pH and standard deviation values of the fresh fruit juices were shown in Table 1. All the tested fruits were acidic and had pH well below 5.5. The mean pH was lowest for lime (2.4), followed by lemon (3.1) and highest for tangerine (4.1).

Evaluation of Neutralizable Acidity: Results showed that the mean volume of sodium hydroxide base needed to raise the pH of the fruits to 7.0 ranged from 5.3mL to 104mL (Table 2). Lime needed the most base (104mL) to raise its pH to 7.0 while Tangerine needed the least volume of base to raise its pH to 7.0. It was observed that Lime had the lowest pH and also the highest neutralizable acidity, signifying it to be the most acidic. Conversely, Tangerine had the highest pH (4.1) and the smallest amount of neutralizable acidity, making it the least acidic of the tested samples.

DISCUSSION

The initial pH of all the citrus fruit juices evaluated in the study ranged from 2.4 to 4.1, which is consistently below that considered to be the threshold for the initiation of enamel dissolution (pH 5.5). Lussi and Jaeggi in their review submitted that pH value of a drink or foodstuff among other factors is undoubtedly important in explaining erosive attack [28]. This was also pointed out by Jensdottir et al. that the pH of drinks determines their erosive potential within the first minutes of exposure [29].

On the other hand, acidity of a drink is believed to be the primary factor in the development of dental erosion; this total acid level (known as titratable acid), rather than the pH, is thought to be an important factor in erosion because it determines the actual hydrogen ion availability for interaction with the tooth surface [25, 30]. Subsequently, various workers have suggested that measurement of a beverage’s total acid content is a more realistic and more accurate method for predicting erosive potential [31-33]. This study showed that tangerine had the highest pH and required the least base to neutralize while lime had the lowest pH and needed the most base (104mL) to neutralize thereby having the strongest potential to erode teeth than the other citrus fruits evaluated. This is similar to that of Baldwin who reported that tangerines and oranges have the lowest acidity, while lemons, limes and sour oranges have the highest acidity among citrus fruits [34].

Erosive potentials of citrus have been demonstrated with animal experiments. In the rat molar teeth, McClure [8] noted erosion with cranberry and grape-fruit juices. Bieri et al. [9] showed that rats fed orange juice for one week had tooth surface loss comparable with that seen with citric and acetic acids. Many other animal studies have been carried out to evaluate the erosive properties of different juices [10-13]. Wynn and Haldil [14] reported that a wide range of juices, including grape juice, caused a similar effect to citric or acetic acid on rat molar teeth. Darby [16] was the first to report dietary erosion in humans, he described changes in the teeth in two women who regularly sucked lemons; another two were reported to have undertaken the grape cure’ in Switzerland; a practice that involved a high consumption of grapes. Many authors have since described the effect of citrus fruits and their juices on the human dentition [17-23].

As indicated by some researchers [35, 36] citric acid is the main organic acid found in citrus juices. Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is a weak

<p>| Table 1: The pHs of the tested fruits |</p>
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Citrus fruit</th>
<th>1st Reading</th>
<th>2nd Reading</th>
<th>3rd Reading</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Grape</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>.0000</td>
</tr>
<tr>
<td>2</td>
<td>Sweet orange</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>.0000</td>
</tr>
<tr>
<td>3</td>
<td>Tangerine</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>.0000</td>
</tr>
<tr>
<td>4</td>
<td>Lime</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>.0000</td>
</tr>
<tr>
<td>5</td>
<td>Lemon</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>.0000</td>
</tr>
</tbody>
</table>

<p>| Table 2: The amount of NaOH needed to raise the pH of the fruits to 7. |</p>
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Citrus fruit</th>
<th>1st Titration (ml)</th>
<th>2nd Titration (ml)</th>
<th>3rd Titration (ml)</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Grape</td>
<td>20.1</td>
<td>20.2</td>
<td>20.2</td>
<td>20.2</td>
<td>.0577</td>
</tr>
<tr>
<td>2</td>
<td>Sweet orange</td>
<td>11.5</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
<td>.0577</td>
</tr>
<tr>
<td>3</td>
<td>Tangerine</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>.0000</td>
</tr>
<tr>
<td>4</td>
<td>Lime</td>
<td>103.8</td>
<td>104.0</td>
<td>104.1</td>
<td>104.0</td>
<td>.1528</td>
</tr>
<tr>
<td>5</td>
<td>Lemon</td>
<td>37.9</td>
<td>38.0</td>
<td>38.1</td>
<td>38.0</td>
<td>.1000</td>
</tr>
</tbody>
</table>
tricarboxylic acid that is naturally concentrated in citrus fruits. Among fruits, citric acid is most concentrated in lemons and limes, comprising as much as 8% of the dry fruit weight [37]. Lemon and lime juice, both from the fresh fruit and from juice concentrates, provide more citric acid per liter than ready-to-consume grape fruit juice, ready-to-consume orange juice and orange juice squeezed from the fruit [38].

In a study to determine the pH, ascorbic, citric and total organic acid content of some local fruits in Nigeria, Orange juice had the highest level of ascorbic acid but low in citric acid while lime juice is very rich in citric acid [39]. Meurman et al. reported that nine out of 13 sports drinks evaluated contained citric acid, two contained malic acid and two contained an unknown acid. Furthermore, the citric acid based drinks were more erosive than the malic acid containing drinks [40]. Pure fruit juice is now often advocated as a healthy drink which actually contains a lot of acid and can have a very low pH. Orange juice that is commonly served contains citric acid and its acidity is said to be comparable to that of soft drinks [31].

Etiology of dental erosion is multi-faceted; the results of the study would have to be applied with caution. This is also based on the fact that fruits generally have variable nutrient content depending on the stage of maturity. At the beginning of the ripening process the sugar/acid ratio is low, because of low sugar content and high fruit acid content, this makes the fruit taste sour. During the ripening process the fruit acids are degraded, the sugar content increases and the sugar/acid ratio achieves a higher value. Overripe fruits have very low levels of fruit acid and therefore lack characteristic flavour. Finally, this study will provide good baseline information on acidity of common citrus fruits in Nigeria and their potential to incite dental erosion. It also forms a good background data to formulation of further epidemiological and more advanced in vitro studies on these samples.

CONCLUSIONS

This study showed that all the commercially available citrus fruits evaluated are acidic with significant dental erosive potential. All the pHs were below the critical pH of enamel dissolution. Inappropriate consumption of these fruits especially lime could incite erosive toothwear.

REFERENCES