The effects of ethephon on the ripening of carambola (*Averrhoa carambola* L.)

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**Abstract**

Today, there are a lot of types of chemicals that have the ability to mature and affect the quality of fruit. They can help us to gain actively in fruit processing, especially ethephon (ethrel or 2-cloroethyl phosphonic acid). The purpose of this study is to investigate the influence of ethephon on the ripening of carambolas (star fruit). Carambolas are the most common fruit in Vietnam, Asian and South American countries; they are the most nutritious fruits in vitamins and minerals, especially ascorbic acid (Vitamin C). The samples were soaked into ethephon at different concentration of 0, 5, 10, 15, 20, and 25% (v/v), were stored in plastic basket covered with canvas at 30±3°C, humidity of 71±10%. The evaluation criteria used in this study were ripe ratio, weight loss, reducing sugar content, total acidity, sensory evaluation, color and residual ethephon content. The results showed that carambolas were soaked in ethephon at the rate of 15 ml/l have the ability to ripen quickly, equally and have beautiful colors on the surface of the peel, and low residual ethephon content. Currently, in Vietnam, there is no regulation for the maximum content of ethephon permitted in carambola. We hope that the Ministry of Public Health will issue the maximum amount of permitted residues of ethephon in carambola for setting customer’s mind at rest, easy to manage and control for government agency.

**Introduction**

Vietnam consists of the tropical area, is suitable for the cultivation of the fruit trees and vegetables, especially the carambolas (star fruit) which originated of the South – East Asian Nations, China and India. In Vietnam, there are two main types of carambolas: the sour and the sweet carambolas which have the green or yellow colour, thin skin and ripe fruit turns to dark yellow colour. The nutrient value of carampolas is high, especially vitamin C (20 – 50 mg/100g edible part) and the others such as oxalic acid, the minerals (Vũ, 1999). The carambolas are used widely in food industry (for instant beverage, jam or fresh fruit), as well as in medicine. Although, carambola was not the main role in agriculture but it contributed to the farmer’s living gradually improves, then the control of its maturation is very important in the storage process and gain actively in fruit processing.

The fruit produces ethylene during the maturation, which stimulates its ripening but gas generated less than the chemicals used as ethephon, calcium carbine, etc. They were widely used in post-harvest technology, especially the climacteric fruits (Phạm, 2003; Korsak and Park, 2010). These chemicals can reduce the storage time. Among them, Ethephon (or ethrel) is used in agriculture for stimulate the flowering, the sprouting, shorten the period of defoliation and increase the crop yield (Phạm, 2003). Ethylene from chemicals was more than endogenous ethylene from fruit during the respiration and it can soften the peel, decomposes the chlorophyll and makes yellow peel (Campbell *et al.*, 1985). Although, there were the circular prescribed maximum residue of ethephon in some fruits in 2010 but still limited for a lot of type of fruit. Furthermore, the use of ethephon has not specific guidance process yet for each group of fruit (Nguyễn *et al.*, 1999) because ethephon can affect the skin and eyes when contacts directly but it not a carcinogen (Bùi, 2007). ADI standards of FAO allows for ethephon at 0.05 mg/kg body weight/day.

Currently, the use of ethephon in Vietnam is relatively new and interesting issue. The standards of residue in each type of fruit is quite limited, especially carambolas. Therefore, the object of this study was to find out the effects of ethephon on ripening of carambolas, control the preservation process and help the authorities to administer the ethephon use for this fruit.

**Materials and Methods**

**Materials**

The sour carambola (*Averrhoa carambola* L.) was harvested in Ba Diem – Hoc Mon province, Vietnam, from 40 – 45 days after start fruited. The fruit are...
green and light yellow, light characteristic odour. The maturation achieved level 2, have the uniform shape and size, non–physical damage, non–insect (Omar et al., 2004). The fruit has about 9–11 cm of length, 5–7 cm of diameter and weight from 85–110 g/fruit. Ethephon is liquid form, transparent, light yellow, 500 ml/bottle, made in China and imported by the company HPC. The ingredient includes the ethephon and the stable additive 10%.

Process of maturity
Carambolas are separated, cleaned with the tap water, dried at the condition room, dipped into ethephon solutions (0, 5, 10, 15, 20 and 25 ml/l) during 1 minute and dried for 20 min at room temperature (rate of fruit/solution about 1/2 (w/v)). Then the fruits are stored and analyzed the parameters each 24 hours. Carambolas were stored in a basket covered by cloth at 30±3°C and relative humidity 72±10%.

Analysis methods
The percentage of mature fruits is determined by the color level from 5–6. The fruit is yellow to orange and has only green at rib (Omar et al., 2004).

The loss of weight (%) measured each 24 hours was compared with the first weight.

The content of glucose (%) was determined by glucometer apparatus Cleverchek (Germany) and calculated according to the formula:

\[
\text{% Glucose} = \frac{a \times 10^{-3} \times 180 \times \frac{V_p}{1000} \times 100}{m} \quad (\text{Tan et al., 2013)}
\]

\(a\): concentration of glucose measured by the glucometer (mmol/L)
\(180\): mass of molecule glucose
\(m\): mass of fruit (g)
\(V_p\): volume of dilution (ml)

Total acidity (g/l) determined by AOAC method (2000), converted into oxalic acid.
Residues of ethephon (mg/kg): determined by gas chromatography-mass spectrophotometer (GC–MS) (TCVN 8668, 2011).
The system of colour of carambolas was measured by a Chroma Minota CR-410 based on values of \(L^* C^* h\) (Rich, 2000).
Sensory evaluation was performed by the method of pairing test (Lawless and Heymann, 2010) between the best sample soaked in ethephon solution and the control sample in the same maturity with 24 tester not trained.

Data analysis
Each sample of 850-1000g (~10 fruits) for preservation and repeated 3 times. Data would be analyzed by Statgraphics software (Centurion XV) with pvalue=0.05.

Results and Discussion
Effect of ethephon concentration solution on maturity and weight loss of Carambola versus preservation time
Figure 1 shows fruit samples which were not yet ripe after 48 hours with different ethephon concentration. In the period from 72 to 120 hours, the samples soaked in ethephon solution that was significant difference with the sample non ethephon treatment samples (control sample) (p<0.05). After preservation time from 144 to 168 hours, the rate of mature fruits in the different concentration of ethephon was not significant difference that means fruit ripe quite equally. From 192 hours, the percentage of the ripe fruit of the samples was significantly different in the level of 5%.

The rate of mature fruits in the different samples increases correspondence with preservation time. Among them, the samples soaked in ethephon solution had the ripe time that shortened. The ripe fruit with ethephon treatment increased rapidly during the period from 96 hours to 144 hours while the control sample increased slowly. Thus, the ethephon has the role of promoting the process of fruit ripening faster and has the ability to result in a more uniform ripening which enhance the productivity of fruit ripening (Trần, 2000). At 120 hours, the sample at 25 ml/l ethephon concentration reached the highest rate of mature fruit was 70% then decreased because of the damages. From 144 hours to 168 hours, the sample at 15 ml/l ethephon concentration has the rate of maturity which was from 57% to 60% and reached the highest, the most stable and the rate of damage occurred at least. After 216 hours storage, the control simple was 27%, when compared to the other, the sample of the concentration ratio of 15 ml/l which had a very low damaged rate and the equivalent of a blank simple was 23% in Figure 1. The maturity stage is also the stage began to appear damaged. Protopectin was hydrolyzed into pectic acid and methanol; fruit became softly and degraded the structure (Tôn et al., 2008). The carambolas ripening were uniform yellow and had specific odour. Tannin content decreased during ripening stage and changed the acerbity of fruit. The aroma which include aldehydes, alcohol, esters, lactones, terpenes and sulfur compounds is produced by evaporating compounds which were synthesized in the ripening of the fruit (Nguyễn et
The weight loss of the samples from 0–96 hours was not significant difference with the all sample (p<0.05). Figure 2 shows that the weight of fruit in all samples decreased with preservation time. The carambola had thin skin which conduced to a result that loss easily the mass during storage, the loss of water and the metabolism of starch into sugar. In particular, the process of evaporation is the primary cause which reduces naturally the weight of vegetables (75-85% of total loss).

Because the ripening process can increase the volume, the air penetrates the cells and it change density of fruit, as well as the damage decreased the weight. The speed of evaporation during ripening was very different: in the first phase (immediately after harvest) dehydration is quite strong, then decreased and at last increased when the damage of vegetables was started. The natural decrease of weight is inevitable in any conditions of storage (Nguyễn et al., 1982).

In all samples, the amount of weight loss has increased versus preservation time and in the early stages changed insignificantly. At 120 hours, the weight loss of carambolas increased quickly. In the period from 216 to 240 hours, it increased suddenly; this is also the time of the most damage. The respiration of fruit increases strongly and used a lot of dry materials. This is a cause for making rapid reduction of weight and this results was similar the studies of the other fruits. There are many factors that affect the reduction of weight, among them, the method of packaging is the most important factor (Tôn et al., 2008). However, the carambola was stored in the room condition, thus the weight also decreased naturally about 5% after 5 days of storage.

**Effect of ethephon concentration solution on glucose content and total acidity of Carambola versus preservation time**

Figure 3 shows that the glucose content in all samples increased at 24–72 hours and decreased versus next preservation time. At ethephon concentration of 25 ml/l, glucose content in fruit increased quickly at 48 hour, after that decreased rapidly. The sample of 5 ml/l and 10 ml/l ethephon concentration compared with control samples changes slightly. The sample of 15 ml/l has glucose content didn’t increase as fast as the sample 25 ml/l and slow reduction.

The cause of the change is due to the substrate in the process of respiration which is glucose and acid. In the first phase, the process of respiration increases, glucose and acids content used for the respiration but sugar content didn’t reduce because there is the creation of glucose from hydrolyzed starch, a fraction from the hydrolysis of cellulose, hemicellulose,
lignin … which soften the fruit and digests easily (Tôn et al., 2008)

After 72-96 hours storage, the reducing sugar content tends to decrease versus preservation time. At the moment, it reduced quickly or slowly depending on the ripeness of each sample. During ripening, the sugar content in the fruit is inclined to increase by the help of the mother plant or due to hydrolyze the starch in the fruit into different sugars depending on the maturity of fruits and each type of fruit (Lê et al., 2008). However, at the end of the process of preservation, glucose content would be reduced because it is decomposed totally by the respirations and there is not the hydrolysis of starch into sugar.

During the period of storage, total acid content in ethephon treatment samples tends to increase slightly from 48 to 120 hours and then decrease. The control sample has the total acid content which also increases slowly and reaches the highest value at 192 hours then decreases. This means that the metabolism of acid was quite slow in the control sample and the carambola soaked in ethephon solution accelerated the process of respiration.

Establishing the correlation between the level of ripening with the optical parameters of color for the carambolas (sour star fruit) in Vietnam

Carambola was mature and ripe, it will go through 6 stages from green to orange (Omar et al., 2004). However, currently there is no scientific publication shows that the correlation between the level of ripening with the optical parameters such as \( L^* \) (lightness), \( C^* \) (chromaticity colors) and \( h^o \) (hue angle) of the sour carambola (star fruit). Therefore, the measurement of the optical parameters built in Table 1 will be facile for the comparison.

\[ \chi^2 = 0.168 < \chi^2_{crit} = 2.71 \] This shows that two samples didn’t have the significant difference. Thus, the sample soaked ethephon was totally similar with control sample; the consumers unrecognized completely the differences between two samples.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Description</th>
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<th>Description</th>
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<tbody>
<tr>
<td>1</td>
<td>The whole fruit is dark green, ( L = 44.5 \pm 0.2 )</td>
<td>( L = 57.0 \pm 0.2 )</td>
<td>4</td>
<td>Mature fruits, Yellow colour ( C^* = 42.29 \pm 0.18 )</td>
<td>( h^o = 85.36 \pm 0.56 )</td>
</tr>
<tr>
<td>2</td>
<td>Partially ripe fruit, ( L = 48.27 \pm 0.28 )</td>
<td>( L = 53.05 \pm 0.68 )</td>
<td>5</td>
<td>Ripe fruit, ( L = 50.0 \pm 0.15 )</td>
<td>( h^o = 79.25 \pm 0.72 )</td>
</tr>
<tr>
<td>3</td>
<td>Mature fruits have alternately a green and yellow, ( L = 56.35 \pm 0.64 )</td>
<td>( L = 56.35 \pm 0.84 )</td>
<td>6</td>
<td>Ripe fruit, ( L = 51.59 \pm 0.89 )</td>
<td>( C^* = 43.05 \pm 0.63 )</td>
</tr>
<tr>
<td>4</td>
<td>Unsuitable for harvesting</td>
<td>( h^o = 114.9 \pm 0.24 )</td>
<td>5</td>
<td>Suitable for harvesting</td>
<td>( h^o = 108.97 \pm 0.53 )</td>
</tr>
<tr>
<td>5</td>
<td>( h^o = 68.82 \pm 0.66 )</td>
<td>( h^o = 68.82 \pm 0.66 )</td>
<td>6</td>
<td>( h^o = 73.79 \pm 0.66 )</td>
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The sensory evaluation

The result shows the ethephon treatment sample of 15 ml/l that has the short time of maturation, high rate of ripe fruit, less damaged, fairly uniform ripeness, the low weight loss. We carried out the sensory evaluation between the sample soaked (15 ml/l ethephon concentration) and the control sample with the same maturity (At level 5-6) (Omar et al., 2004). Using the method of pairing test has the result below.

\[ \chi^2 = 0.168 < \chi^2_{crit} = 2.71 \] This shows that two samples didn’t have the significant difference. Thus, the sample soaked ethephon was totally similar with control sample; the consumers unrecognized completely the differences between two samples.
Residue of ethephon content on carambola during storage

The ethephon treatment sample of 15 ml/l was measured residues of ethephon during preservation time by GC-MS method. The results showed that residues of ethephon in this samples decreased quickly during preservation time. They are 0.18, 0.074, 0.015 and 0 mg/kg at the 1st, 3rd, 5th and 7th day during the preservation time, respectively. This result is similar to several studies about the effect of ethephon on some fruits for instant acerola (Quoc et al., 2012), ambarella (Tan et al., 2013), bananas (Tan et al., 2014) and. The residues of ethephon was not detected the ethephon after the 7th day. This can be explained that the combination of ethephon and structure of fruit is loose, further there is the process of respiration occurred, so ethephon reacts with water in the air during preservation time and releases ethylene (Trần, 2000) follow chemical equation bellows:

\[
\text{CICH}_2\text{-CH}_2\text{-P-OH} + H_2O \rightarrow CH_2 = CH_2 + H_3PO_4 + HCl
\]

Thus, residues of ethephon will decrease during preservation time and the fruits will mature faster with the support of exogenous ethylene. Therefore, the use of this chemical to soak the fruit is easy, effective and less harmful to consumers.

Conclusion

Carambola soaked into ethephon solution of 15 ml/l has the very fast maturity, high quantity of ripe fruits fairly uniform and beautiful colors only after 5 days storage. The carambola soaked at this ethephon concentration was insignificant difference about color or taste with the control sample. This is also the best properties of ethephon. At the same time, the residue of this substance is very low and absolutely not affects the health of consumers. Based on this study, we also recommend the authorities soon add ethephon residue standards for each type of fruit assure to health of the consumers and facilitate the management, evaluate food safety.

References

Pham, V.C. 2003. Controlling the growth, development and flowering of fruit plant. Ha Noi: Agricultural Publisher. (in Vietnamese)