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# Highlights

- FIR and hot air drying enhanced lycopene and lutein contents, whereas osmotic treatment preserved sinapic acid and ferulic acid.

# Effect of osmotic treatments and drying methods on bioactive compounds in papaya and tomato

**Running title**: Bioactive compounds in dried papaya and tomato

**Sirithon Siriamornpun[a,*], Jiranan Ratseewo[a], Niwat Kaewseejan[b], Naret Meeso[c,*]**

[a] Research Unit of Process and Product Development of Functional Foods, Department of Food Technology and Nutrition, Mahasarakham University, Kantarawichai, Maha Sarakham 44150, Thailand

[b] Department of Chemistry, Faculty of Science, Mahasarakham University, Kantarawichai, Maha Sarakham 44150, Thailand

[c] Research Unit of Drying Technology for Agricultural Products, Faculty of Engineering, Mahasarakham University, Kuntarawichai, Maha Sarakham 44150, Thailand

*Corresponding authors:

Tel.: +6643 754085 ext. 1822; E-mail: sirithons@hotmail.com (S. Siriamornpun).

Tel.: +66 43 754363; Fax: +66 43 754316; E-mail: n_meeso@yahoo (N. Meeso).



**Abstract**

We determined the retention of bioactive compounds including phenolic acids, flavonoids and carotenoids in papaya and tomato as affected by osmotic treatment and drying methods. Two drying methods namely combined far-infrared radiation and air convection (FIR-

HA) drying and hot air (HA) drying were used for drying the untreated and osmotically-treated samples. Five treatments were studied including untreated sample and dried with FIR, untreated sample and dried with HA, osmotically treated, osmotically treated and dried with FIR, and osmotically treated and dried with HA, compared with a fresh sample. The results showed that non-osmotically treated samples and dried with FIR had the highest values of total phenolic content, DPPH and FRAP among all samples including fresh papaya and tomato. Chlorogenic acid was increased by FIR and HA drying in an untreated sample while sinapic and ferulic acids were most preserved by osmotic treatment. It was found that lycopene and lutein contents were significantly increased by both FIR and HA methods in papaya without osmotic treatment. However, the contents of beta-carotene and total flavonoids were decreased by all treatments.

**Keywords:** drying; antioxidants; lycopene; lutein; phenolic acids; flavonoids

## 1. Introduction

Fruits contain many kinds of bioactive compounds including flavonoids, phenolics, carotenoids and vitamins, which are all considered beneficial to human health, for decreasing the risk of non-communicable diseases [1,2] such as cardiovascular diseases [3] and certain cancers. [3,4] In recent years, studies of bioactive compounds in fruit species have been popular for intensive investigations. [5] However, the bioactive compounds and antioxidant properties of fruits could be affected by processing. In this study, we selected two popular fruits namely papaya and tomato which are considered to contain high antioxidants, to be investigated. Papaya (*Carica papaya* L.) is a popular and economically important fruit of tropical and subtropical countries. It can be consumed fresh, dried, as juice and as other processed products. Papaya has been reported to

exhibit antioxidant activity containing high levels of phenolic compounds and carotenoids. [6,7] Tomato is one of the most widely used and versatile vegetable crops. They are consumed fresh and are also used to manufacture a wide range of processed products. [8] Tomatoes and tomato products are rich in health-related food components as they are good sources of carotenoids (in particular, lycopene), ascorbic acid (vitamin C), vitamin E, folate, flavonoids and potassium. [9,10] Drying is an important process for preserving biomaterials in order to extend shelf life, because the drying process inhibits enzymatic degradation and limits microbial growth. Furthermore, drying reduces the weight of raw materials thus saving the cost of transportation. [11] Among many drying techniques, hot-air drying (HA) is the most commonly employed commercial technique for drying vegetables and fruits. Heated air is driven from various directions, depending on the nature of the products being dried.[12] The major disadvantage associated with HA drying is that the long drying time needed causes degradation of food quality[12] and nutritional losses.[13, 14] Far-infrared radiation (FIR) has been reported to be successfully applied in the drying of fruit, vegetable and agricultural products since it can preserve the color and retain bioactive compounds in plant preparations such as potato[15], onion[16], apple[17], rice[18] and mulberry tea.[19] In addition to drying, the osmotic process has received considerable attention as a pre-drying treatment so as to reduce energy consumption and improve food quality.[20] Although dried papaya and tomato products have long been consumed and available in the markets either with or without osmotic treatment, so far, there have been limited published reports on the effects of drying on bioactive compounds and on the antioxidant properties of papaya. Therefore, the main aim of this study was to investigate the effect of two different drying methods, namely FIR-HA and HA drying, on changes in the antioxidant properties and bioactive compounds in untreated

and osmotic-treated papayas. We expect the results to lead to establishing an appropriate method of dried papaya and tomato with respect to bioactive compounds and antioxidant activity.

## 2. Materials and Methods

### *2.1 Chemicals and reagents*

Folin–Ciocalteu reagent, phenolic acids standards, namely gallic, protocatechuic, *p*-hydroxybenzoic, vanilic, chorogenic, caffeic, syringic, *p*-coumaric, ferulic and sinapic acids, standards flavonoids such as catechin, rutin, myricetin, quercetin, apigenin and kaempferol, 2,4,6-tripyridyl-S-triazine (TPTZ), 2,2-diphenyl-1-picrylhydrazyl (DPPH), lycopene, beta-carotene and lutein were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Methanol, acetonitrile and other reagents used in the HPLC analysis were purchased from Merck (Darmstadt, Germany). All other solvents were purchased from Fisher Scientific (Leicester, UK) and were of analytical grade.

### *2.2 Sample preparation*

Samples of papaya (*Carica papaya* L.), cultivar Khaek Dam and tomato (plum tomato), were purchased from a local market in Maha Sarakham Province, Thailand. At each market, approximately 2 kg of samples were sampled from three representative outlets. Single composite samples for each representative market were prepared by combining about 500 g of sample. The ripe fresh papaya samples were peeled manually and the seeds removed before process. Fresh plum tomatoes were cleaned. Then, all samples were cut into cubes of 1.5 $cm^3$ and divided into two groups. The first was pretreated by soaking in 60% sucrose as an osmotic agent (see below)

prior to being dried, while the latter was directly dried by FIR-HA and HA methods without pretreatment. The samples were stored at refrigerator (4±1°C) before use.

*2.3 Osmotic dehydration*

Sucrose (food grade) dissolved in distilled water was used as the osmotic agent. The sucrose concentration used were 40, 50 and 60% (w/w) containing appropriate amounts of 0.1 M calcium chloride and 0.1 M lactic acid. These salts and acids concentrations were selected in previous tests of 30 min of osmotic dehydration. The samples cubes, previously weighed and identified, were placed into 250 mL beakers, containing the osmotic solution. A fruit/solution ratio of 1:10 was used. The samples were immersed for 24 h in each of the following succession of sucrose solutions: starting from 40, 50 and 60%. After 72 h of dehydration in sucrose solutions, the samples pieces were drained, rinsed with distilled water and placed on absorbent paper to remove excess solution. Afterwards, the papaya pieces were dried with hot-air (HA) and FIR-HA.

*2.4 Drying processes*

*2.4.1 Hot air drying*

Hot air (HA) drying was done using a laboratory-scale dryer. The sample tray (25.4 × 37 $cm^2$), the sample tray was placed midway between, and parallel to, the top and bottom heaters, and the distance between each set of heaters and a tray was fixed at 15 cm. The sample tray was supported on a balance which enabled continuous recording of the mass the product throughout the test.[19] Drying temperature was set at 60 °C and air velocity at 1.5 m/s for 18 h (untreated) and for 32 h (osmotic treated) to achieve moisture content of 17% dry basis. Moisture content of

samples was determined according to the AOAC method in a vacuum oven (Shellab, model 1410) at 103±1 °C and the dry weight of samples was calculated from % moisture.[21]

*2.4.2 Combined far-infrared radiation and air convection (FIR-HA) drying*

A laboratory-scale dryer using in this study was developed in the Research Unit of Drying Technology for Agricultural Product, Faculty of Engineering, Mahasarakham University, Thailand. We used the FIR drying method of Wanyo *et al*.[19] Briefly, the papaya and tomato samples were placed onto a mesh tray and irradiated with a combination of far-infrared radiation with hot air convection at FIR intensities of 5 kW/m$^2$, HA temperature of 40 °C, HA velocities of 1 m/s and a drying time of 4 h to provide the moisture content of 17% dry basis.

*2.5 Sample extraction*

The sample extraction for determination of total phenolic content, total flavonoid content and antioxidant activity was performed using the method described previously.[5] Fresh and dried samples (1 g, on dry weight basis) were extracted three times with 10 ml of 80% methanol at room temperature for 2 h on an orbital shaker at 180 rpm. Then, the mixture was centrifuged at 1400 × g for 20 min and the supernatant was transferred into a 30 mL of vial and stored at -20 °C until analysis.

*2.6 Determination of total phenolic content*

Total phenolic content (TPC) was determined using a Folin–Ciocalteu reagent as described by Kubola and Siriamornpun[22] and as adapted from Velioglu *et al.*[23] Briefly, 300 µL of the extract was mixed with 2.25 ml of Folin–Ciocalteu reagent (previously diluted 10-fold with

distilled water) and allowed to stand at room temperature for 5 min; 2.25 mL of sodium carbonate (60 g/L) solution were added to the mixture. After 90 min at room temperature, absorbance was read at 725 nm using a spectrophotometer. The TPC in samples was calculated based on the linear regression equation of the gallic acid standard curve ($y = 0.002x + 0.008$; $R^2 = 0.998$). Results were expressed as mg gallic acid equivalents per g of dried weight (mg GAE/g dry weight).

*2.7 Determination of total flavonoid content*

Total flavonoid content (TFC) was determined using the colorimetric method described by Bakar *et al*[5] and as adapted from Dewanto *et al.*[24] Briefly, 0.5 mL of the extract was mixed with 2.25 mL of distilled water in a test tube followed by the addition of 0.15 mL of 5% $NaNO_2$ solution. After 6 min, 0.3 mL of a 10% $AlCl_3 \cdot 6H_2O$ solution was added and allowed to stand for another 5 min before 1.0 mL of 1 M NaOH was added. The mixture was mixed well by vortex. The absorbance was measured immediately at 510 nm using a spectrophotometer. The TFC in sample was calculated using the linear regression equation of the rutin standard curve ($y = 0.001x$; $R^2 = 0.999$) and expressed as mg rutin equivalents per g dried weight (mg RE/g DW).

*2.8. Determination of antioxidant activity*

*2.8.1 DPPH$^{\bullet}$ scavenging activity*

Antioxidant activity of each sample was measured in terms of radical scavenging ability or hydrogen donating using the DPPH method.[25] The sample was diluted in methanol and then 0.1 ml of diluted sample was added to 3 ml of 0.1 mM DPPH solution dissolved in methanol. The mixture was shaken and placed in the dark at room temperature for 30 min. The absorbance

of the resulting solution was measured at 517 nm using a spectrophotometer against a control. DPPH$^{\bullet}$ scavenging activity was calculated using the following equation:

$$\text{DPPH}^{\bullet}\ \text{scavenging activity (\%)} = [1 - (A_{(\text{sample})} - A_{(\text{control})})] \times 100$$

*2.8.2 Ferric reducing antioxidant power (FRAP)*

The FRAP assay is based on the reduction of $Fe^{3+}$–TPTZ to a blue colored $Fe^{2+}$–TPTZ using the method of Benzie and Strain with slight modification.[26] The antioxidant potential of the extract was determined against a standard curve of ferrous sulphate (Fe(II), 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM) in distilled with 0.1% (v/v) HCl. The FRAP reagent was freshly prepared by mixing 100 mL of 300 mM acetate buffer (pH 3.6), 10 mL of 10 mM TPTZ solution in 40 mM HCl, 10 mL of 20 mM $FeCl_3$ at a ratio of 10:1:1 (v/v/v) and 12 mL distilled water, at 37 °C. To perform the assay, 1.8 mL of FRAP reagent, 180 µL of distilled water and 60 µL of sample were added to the same test tubes and then incubated at 37 °C for 4 min. The absorbance of the mixture was read at 593 nm, using the FRAP working solution as a blank. Data were calculated according to the following linear regression equation of $FeSO_4$ standard curve ($y = 0.874x + 0.092$; $R^2 = 0.995$) and then expressed as µmol Fe(II) per g dry weight (µmol Fe(II)/g DW).

*2.9 Determination of phenolic compounds by HPLC*

*2.9.1 Phenolic compounds extraction*

The phenolic compounds in samples were extracted using the method described previously by Uzelac *et al.*[27] A sample (5 g) was mixed with 50 mL methanol/HCl (100:1, v/v) which contained 2% tert-butyl hydroquinone, in an inert atmosphere ($N_2$) during 12 h at 35 ◦C in the dark. After that, the extract was centrifuged at 1400 × g and the supernatant was evaporated

to dryness using a rotary evaporator under vacuum at 40 ◦C. The residue was redissolved in 25 mL of water/ethanol (80:20, v/v) and extracted three times with 25 mL of ethyl acetate. The organic fractions were combined, dried for 30–40 min with anhydrous sodium sulphate, filtered through a Whatman-40 filter, and evaporated to dryness as described earlier. The residue was redissolved in 5 mL of methanol/water (50:50, v/v) and filtered through a 0.45 μm filter before injection (20 μL) into the HPLC instrument.

*2.9.2 Analysis of phenolic acids and flavonoids using RP-HPLC*

The content and composition of phenolic acids and flavonoids were determines using RP-HPLC as described previously.[28] RP-HPLC instrument consists of Shimadzu LC-20AC pumps, SPD-M20A diode array detection (DAD) and column Inetsil ODS-3, C18 (4.6mm x 250 mm, 5 μm) (Hichrom Limited, Berks, UK). The mobile phase consisted of 1% acetic acid in water (solvent A) and acetonitrile (solvent B) at a flow rate of 0.8 mL/min. Gradient elution was performed as follows: from 0 to 5 min, linear gradient from 5% to 9% solvent B; from 5 to 15 min, 9% solvent B; from 15 to 22 min, linear gradient from 9% to 11% solvent B; from 22 to 38 min, linear gradient from 11% to 18% solvent B; from 38 to 43 min, linear gradient from 18% to 23% solvent B; from 43 to 44 min, linear gradient from 23 to 90% solvent B; from 44 to 45 min, linear gradient from 90 to 80% solvent B; from 45 to 55 min, isocratic at 80% solvent B; from 55 to 60 min, linear gradient from 80% to 5% solvent B and a re-equilibration period of 5 min with 5% solvent B used between individual runs. Operating conditions were as follows: column temperature, 38 °C, injection volume, 20 μL and UV-diode array detection at 280 nm for phenolic acids and at 370 nm for flavonoids. Phenolic acids and flavonoids in the samples were

identified by comparing their relative retention times and UV spectra with those of authentic compounds and were detected using an external standard method.

*2.10 Extraction and determination of carotenoids*

Carotenoids (lycopene, beta-carotene and lutein) contents in samples were extracted and quantified according to the method described previously.[29, 30] For extraction, each dried sample (5 g) was extracted three times with 50 mL of methanol and stored at room temperature and evaporated under reduced pressure at 25 °C. The contents of lycopene, beta-carotene and lutein were determined using RP-HPLC (LC-20AC, Shimadzu, Japan), SPD-M20A diode array detection and chromatographic separations on a column Inetsil ODS-3, C18 (4.6 mm x 250 mm, 5 µm, Hichrom Limited, Berks, UK). The mobile phase used was acetonitrile/dichlorometane/ methanol (70:20:10) at a flow rate of 1.3 mL/min and the isocratic elution conditions were described previously by Siriamornpun *et al.*[30] Operating conditions were as follows: column temperature 40 °C, injection volume 20 µL and UV-diode array detection at 454 nm. The carotenoids content in the samples were calculated using the linear equation obtained from a calibration curve of the external standard.

*2.11 Statistical analysis*

All experiments were performed in triplicate and the results were expressed as mean ± standard deviation (SD). Analysis of variance (ANOVA) was carried out to determine any significant differences of measurements using the SPSS statistical software (SPSS 11.5 for Windows; SPSS Inc., Chicago, IL, USA), and considering the confidence level of 95%. The

227 significance of the difference between the means was determined using the Duncan test and the
228 differences were considered to be significant at $p < 0.05$.
229
230 **3. Results and discussion**
231 We investigated the effects of pretreatment with and without the osmotic process
232 followed by drying with two different methods: using hot air (HA) and combined far-infrared
233 radiation and air convection drying (FIR-HA), on retention of bioactive compounds in papaya
234 and tomato. Five treatments of two samples were studied and the details with abbreviations are
235 provided in Table 1.
236
237 *3.1. Effect of drying methods and osmotic treatments on TPC, TFC and antioxidant activity*
238 The TPC of these different methods of samples ranged from 63 to 551 µg GAE/g DW in
239 papaya and 43 to 341 µg GAE/g DW in tomato. The highest value of TPC was found in U-FIR-
240 HA, followed by U-HA and fresh papaya (FP), while OTT-HA contained the lowest TPC
241 compared to other samples for both papaya and tomato. Similar trends were found for FRAP and
242 DPPH, the results showed U-FIR-HA had the highest values compared to other treated samples
243 including fresh samples. Unlike others, TFC was found to be highest in fresh sample for papaya
244 and was decreased after being processed (Table 2). Whilst the level of the TFC of tomato varied
245 significantly between 7 in OT-HA and 36 µg RE/g DW in U-FIR-HA. It was observed that the
246 osmotic-treated samples contained significantly ($p < 0.05$) lower contents of phenolic
247 compounds and antioxidant activities than did the samples without osmotic treatment; of these,
248 osmotic treated and dried with HA of papaya and tomato had the lowest values for all parameters
249 tested. Our findings were in agreement with previous work of Bchir *et al* who reported that the

total phenolic content and antioxidant activity of pomegranate seeds were significantly decreased during osmotic and osmotic-drying processes.[31] These results indicated that osmotic treatment is influenced against degradation or decomposition of bioactive compounds, especially phenolics. Degradation of certain bioactive compounds in fruit tissues might lead to a decrease in the biological activity of the dried products. As during osmotic treatment, a cell placed in a hypertonic solution which possesses a higher osmotic pressure than that of the cell, causes to the loss of water within the cell and that could provoke changes in the biochemical properties of the fruits.[32] Additionally, previous study has reported that losses of phenolic compounds during osmotic process could partial happen from enzymatic oxidation of polyphenoloxidase (PPO).[33] Previous works showed that dehydration or drying process of plants stimulates changes in chemical compositions, bioactive compounds and functional properties as well as physical characteristic.[19, 22, 30, 34] In addition, rehydration process is also important role for evaluation of sensory properties.[35] The difference in rehydration characteristics could be caused by the different surface hardening, the degree of structural damage, and cell shrinkage induced by dehydration.[36-38] The rates of rehydration of dehydrate materials using rotating tray drying showed the highest with the values of rehydration ratio (RR) ranged from 3.7-4.8[39], followed by hot-air drying (RR < 4.5)[40] and sun drying (RR 2.7-3.2).[41] In our present study, it was observed that the dried samples using FIR provided higher rehydration capacity than that of HA dried materials (data not shown). For FIR, the rehydration ratio was decreased when FIR intensity increased.[42]

In the case of HA, with longer drying times, HA drying causes the damage to sensory characteristics, nutritional properties of foods, oxidation of pigments and destruction of vitamins, and solute migration from the interior of the food to the surface.[43] Apart from losses of phenolic

compounds, degradation of vitamin C (ascorbic acid) should be considered with respect to decreases in antioxidant activities as reported by Demarchi *et al* who studied apple leather.[44] Demarchi *et al* suggested that less-severe drying technology should be studied to replace HA drying as the functional compounds in the dried products may not be preserved by this means.[44] Conversely, an increase of antioxidant activities by FIR may be explained by the fact that FIR creates internal heating with molecular vibrations of materials; thus it may break down covalent complex molecular structures and release some antioxidant compounds such as flavonoids, carotene, lycopene, tannin, ascorbate, flavoprotein or polyphenols from repeating polymers, hence increasing antioxidant activities.[30, 45] Many antioxidant phenolic compounds in plants are most frequently present in a covalently bound form with insoluble polymers.[45] FIR treatment could liberate and activate low-molecular-weight natural antioxidants in plants if this bonding is weak.[46] Previous studies found that antioxidant activities and total phenolic contents increased after exposure of rice hulls to FIR radiation[46], peanut hull [47] and mulberry tea.[19] Since a cell is placed in a hypertonic solution during the osmotic process and osmotic dehydration, it will lose water and this may lead to decreases in phenolic compounds and in a subsequent antioxidant activity.[48] Nunez-Mancilla *et al* reported that total antioxidant activity was decreased in all osmotic treated strawberries compared with fresh samples.[49] This is also supported by a previous study that anthocyanin content and antioxidant activity decreased in osmo-dehydrated dried blueberries.[50] According our results (Table 2) in this studies, TPC seemed to be responsible for antioxidant activities assessed by FRAP and DPPH assays as antioxidant activities increased with increasing of TPC for both papaya and tomato.

*3.2. Effect of drying methods and osmotic treatments on phenolic acids*

The phenolic acids composition and content in papaya and tomato were detected and quantified using HPLC–DAD and are shown in Tables 3. According to our available ten authentic standards namely gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, chlorogenic acid, vanillic acid, caffeic acid, syringic acid, *p*-coumaric acid, ferulic acid and sinapic acid, it was possible to identify five phenolic acids, namely chlorogenic acid, caffeic acid, *p*-coumaric acid, ferulic acid and sinapic acid in fresh papaya and all untreated dried papayaand tomato. On the other hand, *p*-coumaric acid, caffeic acid and chlorogenic acid had disappeared from all osmotic-treated samples. Nevertheless, the levels of ferulic acid and sinapic acid could be preserved by osmotic treatment which did not produce any significant difference ($p < 0.05$) from that of the two fresh samples. The results showed that *p*-coumaric acid, caffeic acid and chlorogenic acid all increased as a result of FIR-HA for the untreated samples while these compounds were not detected in all the osmotic-treated papayas and tomatoes. We observed that caffeic acid was found in U-FIR-HA and U-HA while this compound was not detected in fresh and osmotic-treated tomato. UP-HA also caused a significant increase in the level of chlorogenic acid compared to that of the fresh ripe papaya and tomato. It could be said that caffeic acid, *p*-coumaric acid and chlorogenic could be enhanced by heat treatment. Changes of individual phenolic acid levels, as affected by different drying processes, have been reported in mulberry leaf tea[19] and marigold flower.[30] However, phenolic acids may differ in regards to chemical structures including their linkages or bindings. Therefore the responses to various processes may be different. For example, there were greater amounts of all phenolic acids in mulberry leaf dried by HA and FIR, compared to fresh samples. Of those, nine out of eleven phenolic acids were found to be higher in FIR dried samples, only chlorogenic and syringic were found to be higher in HA dried mulberry leaf.[19] For marigold flowers, FIR and HA were shown to enhance the

release of phenolic acids but freeze drying did not.[30] Thermal processing disrupts the cell wall of fruits and vegetables resulting in the release of oxidative and hydrolytic enzymes such as PPO that can damage some antioxidants especially phenolic compounds.[51, 52] However thermal processing can break down the cellular constituents thus releasing more bound and small molecules of phenolic acids.[51]

According to the literature, changes of phenolic acids as resulting from osmotic treatment have not been previously reported. Rózek *et al* demonstrated that the content of phenolic compounds such as gallic acid, protocatechuic acid and catechin in grape seed extract were significantly lost by processes of osmotic and osmotic-air drying.[53] Although most phenolic acids were destroyed by osmotic treatment, ferulic acid and especially sinapic acid could even be preserved by osmotic treatment as these compounds were not significantly altered ($p < 0.05$) from the respective levels for fresh or dried samples. Although the five phenolic acids identified in the samples are hydroxybenzoic acids, the difference between ferulic and sinapic acids on the one hand, and the remainder on the other hand is the presence of a methoxyl group as indicated in Fig. 1. Sinapic acid contains two methoxyl groups, and ferulic has one while the others do not. The plausible explanation of how these two phenolic acids could be preserved by osmotic treatment. This may involve the linkages or bindings of the osmotic solution (sucrose) and the methoxyl groups or may be caused by hydrophobicity of methoxyl groups against water solubility. However, this must be studied further.

*3.4. Effect of drying methods and osmotic treatments on flavonoid compounds*

The drying methods and osmotic treatments of papaya and tomato were quantified and identified for their flavonoids by comparing their HPLC–DAD retention times with available

342 authentic standards, namely rutin, myricetin, quercetin, apigenin and kaempferol. The flavonoid
343 contents of the evaluated samples are presented in Table 4. It was possible to identify all
344 flavonoids in both fresh samples except for apigenin which was not detected in fresh tomato.
345 The results showed that rutin, quercetin and keampferrol were the most predominant flavonoids
346 in all samples. It was found that U-FIR-HA dried tomato had the remarkably significantly
347 highest content of rutin and quercetin with the values of 621 and 263 μg/g DW, respectively. On
348 the other hand, OT-HA dried papaya contained the highest rutin compared to other treated
349 samples including fresh papaya. Myricetin was found the highest in fresh and untreated dried
350 papayas, while this compound was not detected in osmotic treated and dried papayas. This may
351 be caused by a higher number (six) of hydroxyl groups in the molecular structure compared with
352 other flavonoids, leading to water solubility of myricetin in fresh and untreated dried papayas
353 greater than that of osmotic treated. Apigenin was increased in dried untreated osmotic samples
354 (U-FIR-HA, U-HA) while this compound was not detected in all the osmotic-treated papayas and
355 tomatoes except for OT-FIR dried papaya. In our present study, it was observed that kaempferol
356 was the most stable flavonoid to processing for these two fruits. Thermal processing can provide
357 positive and negative effects on phenolic compounds and antioxidant activity. For example, the
358 cell wall of fruits and vegetables were disrupted by thermal processing resulting in the release of
359 oxidative and hydrolytic enzymes[51] such as PPO (polyphenoloxidase) that can damage some
360 antioxidants especially phenolic compounds.[52] On the other hand, thermal processing can break
361 down the cellular constituents thus releasing more bound and small molecules of phenolic acids,
362 resulting in an increase of more active molecules consequently more antioxidant activities.[51]
363 Unlike phenolic acids in Table 3, there were different trends of flavonoids as affected by
364 treatments between papaya and tomato samples. Therefore, apart from treatments or processing

methods, the retention of flavonoids or other bioactive compounds may also be dependent on the nature of plant matrix and chemistry of bioactive compounds.

*3.3. Effect of drying methods and osmotic treatments on carotenoid content*

Changes in the carotenoid content of samples after treatment are shown in Table 5. Among the different drying methods, HA was found to provide the highest content of lycopene (507 μg/g DW) in tomato whereas FIR-HA gave the highest value (256 μg/g DW) in papaya. For lutein, it was found the highest content in U-FIR-HA samples, followed by U-HA and fresh samples respectively for both papaya and tomato. While beta-carotene contents were decreased in all treated and dried samples. Obviously, all osmotic treated samples including both with and without drying had comparatively low concentration of all carotenoids tested. Our previous studies reported on changes of lutein, lycopene and beta-carotene in marigold flower resulting from different drying methods, namely freeze drying, HA and FIR. We found that all carotenoids tested were enhanced by all means of drying.[30] Lutein was found to be highest in freeze dried and FIR dried. While beta carotene and lycopene contents were highest in FIR and HA dried marigold petals. In contrast, HA gave the highest lycopene content in gac arils among the three drying methods used, namely HA, FIR and low relative humidity air drying (LRH).[34] In addition, they found that beta-carotene content was reduced by all means of drying, the greatest loss being due to FIR.[34] Accordingly, it is obvious that individual carotenoids react differently in their susceptibility to heat and other treatments. It has been reported that lycopene is relatively stable to thermal processes.[54] On the other hand, beta-carotene seemed to be sensitive to thermal processes as demonstrated in the results of our present study and a non-thermal process such as freeze drying, as reported by Kubola *et al.*[34]

## 4. Conclusion

Drying and osmotic processes have varying effects on the contents of bioactive compounds including phenolics, flavonoids and carotenoids, leading to degradation of phytochemicals, there by affecting the total antioxidant activity of papaya and tomato. Besides treatments or processing methods, we also found that the retention of bioactive compounds may also be dependent on the nature of plant matrix and chemistry of bioactive compounds. Interestingly, ferulic acid, sinapic acid and keampferol contents in both papaya and tomato during osmotic treatments were similar to or even higher than those of all conditions tested, whereas the amounts of other compounds were significantly decreased; indicating that the osmotic process can be protected against these compounds degradation during further drying. The drying process using FIR enhanced content of some bioactive compounds such as phenolic compounds along with antioxidant properties. According to our present results, we suggest that FIR drying should be considered as a good drying method for papaya and tomato based on a consideration of preserving its bioactive compounds and antioxidant properties. However, combination with an appropriate process or pretreatments is needed for food manufacture with respect to maintaining not only bioactive compounds but also sensory properties.

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**Table 1** Description of samples.

| Sample codes | Description of treatments |
|---|---|
| Fresh | Fresh papaya (half ripen, green and yellow (peel), orange (pulp), 11-12 ºBrix, 150-180 days after blooming)<br>Fresh ripe tomato (ripe, red colour ( peel) pink (pulp), 7-8 ºBrix, 35-45 days after blooming) |
| U-FIR-HA | Untreated and dried with FIR-HA |
| U-HA | Untreated and dried with HA |
| OT | Osmotic treated |
| OT-FIR-HA | Osmotic treated and dried with FIR-HA |
| OT-HA | Osmotic treated and dried with HA |

**Table 2** Changes of TPC, TFC, FRAP and DPPH in samples as affected by different treatments.

| Samples | TPC (µg GAE/g DW) | TFC (µg RE/g DW) | FRAP (µmol $FeSO_4$/g DW) | DPPH (% inhibition) |
|---|---|---|---|---|
| **Papaya** | | | | |
| Fresh | 443.23 ±24.32$^{c}$ | 92.15±2.00$^{a}$ | 190±4.08$^{b}$ | 42.51±0.61$^{b}$ |
| U-FIR-HA | 551.21 ±10.31$^{a}$ | 76.21±3.34$^{b}$ | 230±10.11$^{a}$ | 47.21±2.25$^{a}$ |
| U-HA | 512.91 ±20.62$^{b}$ | 57.91±1.82$^{c}$ | 180±4.21$^{c}$ | 42.55±1.52$^{b}$ |
| OT | 94.42 ±5.21$^{e}$ | 52.35±2.3$^{d}$ | 110±6.78$^{e}$ | 22.79±0.15$^{d}$ |
| OT-FIR-HA | 122.32±12.11$^{d}$ | 49.44±0.64$^{e}$ | 140±6.88$^{d}$ | 26.73±0.52$^{c}$ |
| OT-HA | 63.22±9.12$^{f}$ | 47.41±0.59$^{f}$ | 90±9.98$^{f}$ | 22.11±1.76$^{d}$ |
| **Tomato** | | | | |
| Fresh | 231.14 ±4.04$^{b}$ | 15.75±0.36$^{d}$ | 290±4.08$^{c}$ | 52.54±2.15$^{c}$ |
| U-FIR-HA | 341.34 ±10.23$^{a}$ | 35.72±2.11$^{a}$ | 350±12.36$^{a}$ | 62.91±2.06$^{a}$ |
| U-HA | 330.11 ±10.80$^{a}$ | 33.36±4.90$^{b}$ | 302±1.12$^{b}$ | 57.45±2.12$^{b}$ |
| OT | 54.56 ±3.11$^{d}$ | 10.32±1.3$^{e}$ | 130±6.78$^{e}$ | 32.79±0.11$^{e}$ |
| OT-FIR-HA | 62.34±7.01$^{c}$ | 20.44±0.64$^{c}$ | 160±6.88$^{d}$ | 36.73±0.52$^{d}$ |
| OT-HA | 43.32±2.19$^{e}$ | 7.41±0.59$^{f}$ | 110±9.98$^{f}$ | 25.11±1.76$^{f}$ |

Results are expressed as mean ± SD (n = 3). Values with different letters in the same column represent significant differences at $p < 0.05$.

TPC, Total phenolic content; TFC, total flavonoid content; FRAP, ferric reducing antioxidant power and DPPH, 2,2-difenyl-1-picrylhydrazyl radical scavenging activity.

**Table 3** Concentration of phenolic acids in samples as affected by different treatments.

| Samples | Phenolic acids (mg/100g DW) | | | | |
|---|---|---|---|---|---|
| | Chlorogenic acid | Caffeic acid | *p*-Coumaric acid | Ferulic acid | Sinapic acid |
| **Papaya** | | | | | |
| Fresh | 2.19±0.07$^{b}$ | 2.59±0.01$^{c}$ | 3.16±0.05$^{b}$ | 65.34±4.11$^{a}$ | 15.44±2.90$^{a}$ |
| U-FIR-HA | 3.03±0.31$^{a}$ | 2.63±0.01$^{a}$ | 5.68±0.09$^{a}$ | 33.53±1.79$^{b}$ | 3.75±0.08$^{c}$ |
| U-HA | 3.18±0.14$^{a}$ | 2.60±0.01$^{b}$ | 2.33±0.01$^{c}$ | 28.92±2.65$^{d}$ | 3.64±0.41$^{c}$ |
| OT | nd | nd | nd | 64.56±3.28$^{a}$ | 15.83±1.72$^{a}$ |
| OT-FIR | nd | nd | nd | 31.87±1.23$^{c}$ | 14.12±1.18$^{b}$ |
| OT-HA | nd | nd | nd | 35.23±1.13$^{b}$ | 14.92±1.34$^{b}$ |
| **Tomato** | | | | | |
| Fresh | 3.35±0.11$^{b}$ | nd | 2.50±0.13$^{b}$ | 63.44±2.46$^{a}$ | 16.50±1.73$^{b}$ |
| U-FIR-HA | 13.53±1.65$^{a}$ | 3.52±0.07$^{a}$ | 3.02±0.12$^{a}$ | 61.36±1.29$^{a}$ | 31.84.±1.36$^{a}$ |
| U-HA | 14.59±2.09$^{a}$ | 2.65±0.03$^{b}$ | 3.03±0.05$^{a}$ | 34.38±3.01$^{c}$ | 16.53±1.91$^{b}$ |
| OT | nd | nd | nd | 62.93±2.94$^{a}$ | 15.91±1.21$^{b}$ |
| OT-FIR-HA | nd | nd | nd | 41.65±2.11$^{b}$ | 15.12±1.04$^{b}$ |
| OT-HA | nd | nd | nd | 34.19±1.61$^{c}$ | 14.87±1.12$^{b}$ |

Results are expressed as mean ± SD (n = 3). Values with different letters in the same column represent significant differences at $p < 0.05$.
nd: not detected

**Table 4** Concentration of flavonoid compounds in samples as affected by different treatments.

| Samples | Flavonoid compounds (μg/g DW) | | | | |
|---|---|---|---|---|---|
| | Rutin | Myricetin | Quercetin | Apigenin | Keampferol |
| **Papaya** | | | | | |
| Fresh | 5.0±0.01$^{b}$ | 19.72±0.04$^{b}$ | 26.46±0.05$^{a}$ | 5.14±0.11$^{d}$ | 12.44±1.00$^{a}$ |
| U-FIR-HA | 4.2±0.20$^{c}$ | 23.96±0.30$^{a}$ | 12.75±0.20$^{c}$ | 12.3±0.19$^{b}$ | 10.32±0.90$^{b}$ |
| U-HA | 3.18±0.14$^{d}$ | 12.40±0.01$^{c}$ | 8.33±0.01$^{d}$ | 28.92±2.05$^{a}$ | 10.64±0.41$^{b}$ |
| OT | 4.48±0.30$^{c}$ | nd | 21.35±2.40$^{b}$ | nd | 12.01±1.02$^{a}$ |
| OT-FIR-HA | 4.31±0.21$^{c}$ | nd | 12.05±0.67$^{c}$ | 7.32±0.60$^{c}$ | 10.26±1.18$^{a}$ |
| OT-HA | 7.24±0.63$^{a}$ | nd | 22.33±2.96$^{b}$ | nd | 12.01±1.34$^{a}$ |
| **Tomato** | | | | | |
| Fresh | 97.61±5.21$^{c}$ | 21.25±4.00$^{a}$ | 12.94±0.13$^{e}$ | nd | 12.65±1.22$^{a}$ |
| U-FIR-HA | 620.61±12.40$^{a}$ | nd | 262.99±10.38$^{a}$ | 10.80±1.03$^{b}$ | 11.56.±1.22$^{a}$ |
| U-HA | 12.94±5.10$^{f}$ | nd | 81.79±9.40$^{b}$ | 34.38±3.01$^{a}$ | 11.79±1.01$^{a}$ |
| OT | 28.52±2.08$^{e}$ | nd | 14.21±1.93$^{e}$ | nd | 10.18±1.21$^{b}$ |
| OT-FIR-HA | 69.02±3.65$^{d}$ | nd | 30.21±4.02$^{d}$ | nd | 11.39±1.00$^{b}$ |
| OT-HA | 121.75±9.32$^{b}$ | 20.29±2.10$^{a}$ | 52.97±5.22$^{c}$ | nd | 10.61±1.12$^{b}$ |

Results are expressed as mean ± SD (n = 3). Values with different letters in the same column represent significant differences at $p < 0.05$.
nd: not detected.

**Table 5** The contents of lycopene, beta-carotene and lutein in fresh and treated samples.

| Samples | Carotenoid contents (μg/g DW) | | |
|---|---|---|---|
| | Lycopene | Beta-carotene | Lutein |
| **Papaya** | | | |
| Fresh | 126.16±2.01$^{c}$ | 9.36±0.65$^{a}$ | 14.4±0.41$^{c}$ |
| U-FIR-HA | 256.13±1.87$^{a}$ | 5.45±0.35$^{c}$ | 37.11±3.24$^{a}$ |
| U-HA | 208.30±1.55$^{b}$ | 6.80±0.48$^{b}$ | 18.90±2.08$^{b}$ |
| OT | 39.11±2.88$^{f}$ | 4.59±0.22$^{d}$ | 7.4±0.41$^{f}$ |
| OT-FIR-HA | 49.38±1.02$^{d}$ | 4.73±0.19$^{d}$ | 13.11±0.29$^{d}$ |
| OT-HA | 46.81±0.86$^{e}$ | 3.87±0.19$^{e}$ | 10.17±1.03$^{e}$ |
| **Tomato** | | | |
| Fresh | 301.11±1.42$^{c}$ | 54.4±0.14$^{a}$ | 41.35±0.07$^{c}$ |
| U-FIR-HA | 435.55±1.58$^{b}$ | 38.5±0.20$^{b}$ | 100.71±1.91$^{a}$ |
| U-HA | 506.60±8.74$^{a}$ | 19.2±0.15$^{c}$ | 52.2±0.09$^{b}$ |
| OT | 63.11±3.63$^{f}$ | 10.44±0.22$^{d}$ | 22.4±0.41$^{d}$ |
| OT-FIR-HA | 70.38±1.45$^{e}$ | 7.18±0.19$^{e}$ | 17.11±0.29$^{e}$ |
| OT-HA | 80.81±4.56$^{d}$ | 5.72±0.19$^{f}$ | 13.17±1.03$^{f}$ |

Results are expressed as mean ± SD (n = 3). Values with different letters in the same column represent significant differences at $p < 0.05$.

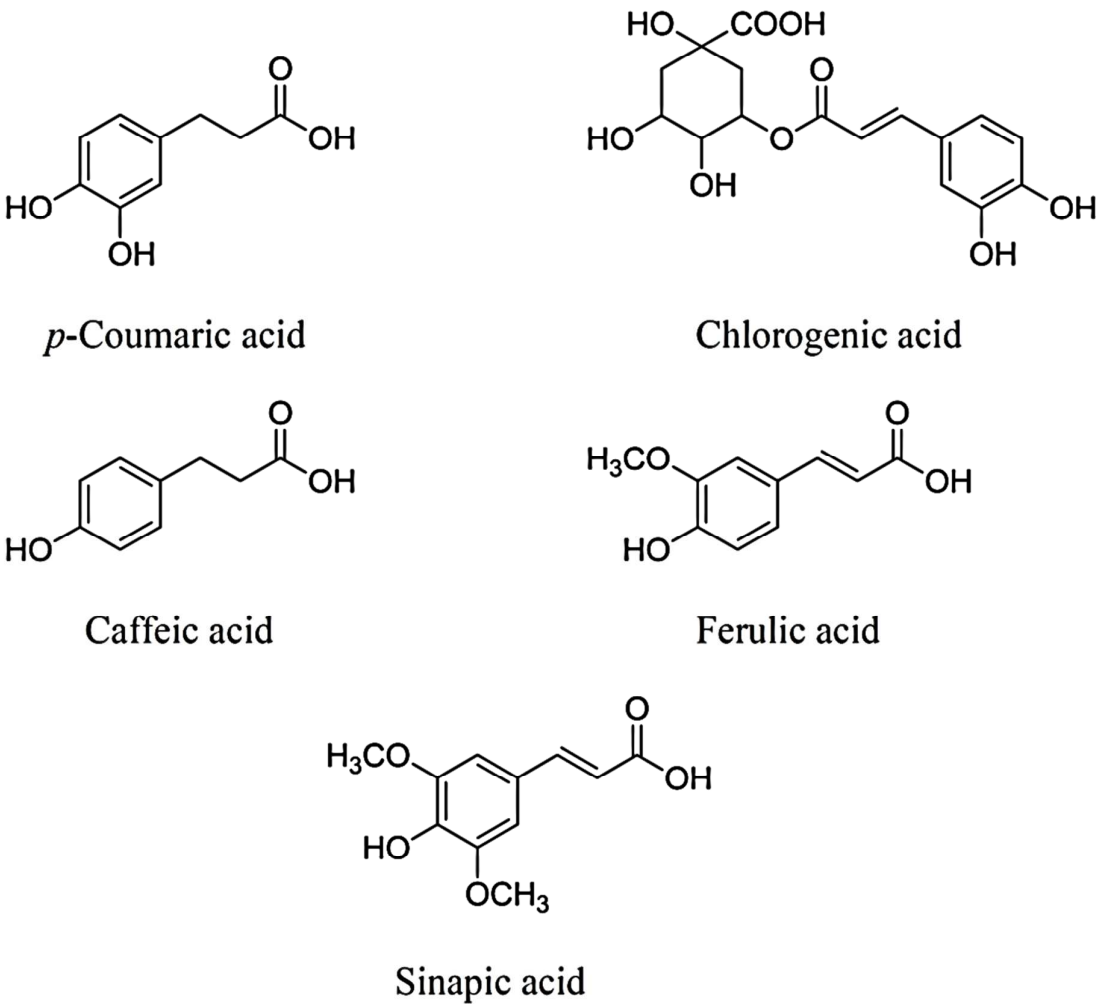


**Fig. 1** Chemical structures of standard phenolic acids.