Fate of Postharvest-Applied Dichlorvos in Stored and Processed Dates

E. Y. El-Behissy,*,† R. D. King,‡ M. M. Ahmed,† and A. M. Youssef†

Food and Environment Control Centre, AbuDhabi Municipality, United Arab Emirates, and Department of Food Science and Technology, Reading University, Reading, United Kingdom

The fate of dichlorvos (DDVP) on dates after storage and processing of postharvest-treated fruits has been investigated. Residues were determined using GC-ECD after extraction of the fruits. A postharvest application was made to fruits at different stages of maturity: khalal fruits (mature full colored stage), rutab fruits (soft brown stage), and the mature tamer fruits (hard raisin-like stage). The fate of the residues was followed during the storage at refrigerated, room, and summer average temperatures (3, 22, and 43 °C). The amount of residues absorbed varied with the level of maturity. The rate of the loss of the residues was found to follow first-order kinetics. First-order rate constants were calculated for the different levels of maturity. The rate of the loss of DDVP increased as the temperature of storage increased. Also, it decreased with increasing maturation of the dates, which was characterized by a decrease in moisture content as well as water activity and an increase in sugar content. The period of storage study was limited by the time of maturation to the next stage. Most common home-cooking methods, including dehydration, jam-making, and syrup-making, resulted in significant decreases in residue levels. Only 0−13% of initial DDVP residues was detected in final products.

Keywords: *Dichlorvos; fate; dates; khalal; rutab; tamer; storage; processing*

INTRODUCTION

In the United Arab Emirates (UAE), as well as in other Arabic and Islamic countries, dates are considered to be one of the most important crops because of their religious and nutritional importance. The per capita daily consumption of dates in Abu Dhabi, UAE, is between 10 and 200 g (*1*) and varies depending mainly on the time of the year and the consumer's age.

Dates are different from most fruits; there are five different stages, of which only three are edible. These development stages according to Ibrahim and Khlif (*2*), Al-Oqaidi (*3*), and FAO (*4*) are hababouk, jimri, khalal, rutab, and tamer stages.

The hababouk or tricarperialate stage starts directly after fertilization, when the fruit bears three carpels, and ends after 4−5 weeks. In the jimri, kimri, or immature green fruit stage, which ends after 9−14 weeks, the fruits appear as smooth small green knots with sour taste because of the presence of a high concentration of tannin. The color of khalal or mature full-colored fruits changes from green to yellow or red according to the variety of the date palm and lasts ∼3−5 weeks. During 2−4 weeks the color of rutab or soft brown fruits becomes dark red to brown or black, while the flesh becomes softer as a result of an increasing concentration of reducing sugars. Dates' dryness and darkness characterize the tamer, tamr, or hard raisin-like fruits. Tamer fruits are the only fruits that may be stored for long periods because the high content of sugar [for example, total sugars in the tamer stage of Hilali Ahmer variety are 64.1% (*5*)] acts as a preservative.

Maturation of khalal to rutab and of rutab to tamer also occurs after harvesting. This maturation increases at higher temperatures. Authors in this study observed that the maturation from khalal to rutab and from rutab to tamer at 43 °C occurred at the first 100 h. At 22 °C, khalal fruits took <10 days to mature to rutab and rutab fruits took ∼10−15 days to mature to tamer. At 3 °C the maturation rate was slower than at other temperatures and required 30 days or more.

As with any agricultural crops, dates are a target for pest attack, so there is a need to treat them with pesticides. Application of pesticides means that potentially high levels of pesticide residues may be consumed. There is a need to set regulations that control the use of pesticides in terms of types and doses in field applications. Khalal and rutab fruits are mostly consumed fresh, whereas tamer fruits may be consumed fresh or after storage or processing. Therefore, Good Agriculture Practice (GAP) for the application of pesticides on date palm trees is required to minimize the risk to human health.

In this study, DDVP was selected because of its wide use on dates in the Emirate of Abu Dhabi. The common use of DDVP in the UAE is as a field insecticide, but in this study it was also used as a postharvest insecticide because dates, especially at tamer stages, are stored for long periods of time and may be attacked by storage pests. DDVP is used as a postharvest insecticide against storage pests that attack, for example, soybean (*6*), rice (*7*), and potatoes (*8*).

MATERIALS AND METHODS

Materials. Insecticide, an emulsifiable concentration of 50% (w/v) of DDVP, was supplied by Denka International as Denkavepon 50, and analytical master standard, 99.8%, was

† Food and Environment Control Centre.
‡ Reading University.

10.1021/jf000812e CCC: $20.00
Published on Web 02/10/2001

supplied by Ciba Giegy, Ltd. Solvents, acetone, petroleum ether (40−60 °C), and isooctane, were of analytical grade. Solvents were used without further purification. Chemicals, sodium chloride and sodium sulfate, which were of reagent grade. They were heated at 550 °C for 12 h.

Instruments. A Varian 3600 GC, equipped with an electron capture detector, was used in the following conditions: column, Chrompack WCOT fused silica, CP-Sil 5 CB stationary phase (100% methyl silicone); length, 10 m; i.d., 0.32 mm; o.d., 0.45 mm; film thickness, 1.20 μm; column oven, programmed from 100 °C (1 min) to 120 °C at 2 °C/min (1 min) and then to 250 °C at 5 °C/min (10 min); electron capture detector, Ni^{63}, set at 320 °C; injector, 230 °C; splitless mode (1 min); carrier gas, helium, at a flow of 2.2 mL/min; makeup gas, nitrogen, at a flow of 20−22 mL/min; data handling, built-in data handling processor, chart speed = 0.3, offset = 20%.

Treatment of Dates with DDVP (Postharvest Treatment). Treatment solution was prepared by dissolving 50 μL of 50% DDVP (w/v) in 2 L of water to give a 0.0025% DDVP solution. Then ∼2 kg of DDVP-free whole dates was dipped into treatment solution in a 5 L dish and mixed well by manual shaking for 2 min to ensure homogeneity. Shaking was repeated every 10 min during the treatment period. After 3−4 h, fruits were removed and dried at room temperature (22−23 °C) for ∼1 h.

Storage Procedures. Treated dates, after time 0 samples had been removed, were put in a 3 L glass dish and then stored in the dark at 3 °C (refrigerator) for up to 30 days for all three stages, at 22 °C (room) for up to 10 days for khalal, 15 days for rutab, and 24 days for tamer, and at 43 °C (incubator) for up to 108 h for khalal and rutab. Samples of 100 g were taken after 1, 3, 5, 7, 10, 12, 15, 20, 25, and 30 days in the case of storage at 3 °C, after 1, 3, 5, 7, and 10 days in the case of storage of khalal at 22 °C, after 1, 3, 5, 7, 10, and 12 days in the case of storage of rutab at 22 °C, after 1, 3, 5, 7, 10, 12, and 15 days in the case of storage of tamer at 22 °C, or after 12, 24, 36, 48, 60, 72, 84, and 108 h in the case of storage at 43 °C from time 0. These samples were placed in tightly closed plastic containers and stored at −18 °C. Three to four subsamples were analyzed within 2−3 days. The sampling was stopped when the dates reached the next stage of maturity; that is, if the experiment was done on khalal stage and the fruits matured to rutab stage during the period of the experiment, the analysis was stopped.

Processing Experiments. *Preparation, Sampling, and Analysis of Processed Products.* Dates were treated with DDVP as mentioned above. One hundred grams was taken as a time 0 sample in tightly closed plastic containers and stored at −18 °C. Four subsamples were analyzed within 2−3 days. The remaining treated fruits were processed. Then 100 g of the processed products was taken and placed in tightly closed plastic containers and stored at −18 °C. Four subsamples were analyzed within 2−3 days. Total solids in fresh and processed dates and the pH values for jam and syrup were measured.

Cooking and Drying Khalal Fruits. A cooked dried khalal was prepared using a modification of the procedures of Sahi (*9*). A 500 g sample of treated dates was placed in a Pyrex dish. Then water at 95−97 °C was added until all fruits were covered in the dish. After cooking for 45 min, the khalal fruits were removed from the cooking water, and a 100 g sample was separated and analyzed. The remaining fruits were spread on a metallic plate and dried in an oven maintained at 70 °C. Dried cooked fruits were packed in 1 kg plastic containers and handling proceeded as mentioned under Preparation, Sampling, and Analysis of Processed Products.

Drying and Packing Tamer Fruits. A packed tamer was prepared using a modification of the procedures of Sahi (*9*). A 500 g sample of treated dates was spread on a plate and placed in an oven at 90 °C for 1 h. Hot dates were cooled and packed in 1 kg plastic containers and treatment proceeded as mentioned under Preparation, Sampling, and Analysis of Processed Products.

Date Jam of Khalal, Rutab, or Tamer Fruits. A date jam was prepared using a modification of the procedures of Sahi (*9*). A 500 g sample of treated dates was used. Seeds, caps, and skins were removed. Fruits were cooked in an equal volume of water for 10−20 min. For each 100 g of fruit flesh, 40 g of sugar and 1 g of citric acid were added. The mixture was cooked to give total soluble solids of 65−68%. Hot jam was filled directly in glass containers, which were capped and then sterilized by dipping in boiled water for 20−30 mi; treatment then proceeded as mentioned under Preparation, Sampling, and Analysis of Processed Products.

Date Syrup. Date syrup was prepared using a modification of the procedures of Sahi (*9*). A 500 g sample of treated dates was used. Seeds, caps, and skins were removed. The dates were placed in dishes, then water was added with the ratio of 3:1 (w/w), and the mixture was cooked in water at ∼70 °C for 1.5 h; a 100 g sample was separated and processed as mentioned under Preparation, Sampling, and Analysis of Processed Products. The solid material was removed by filtration through glass wool. Then the solution was filtered through filter paper, and a 100 g sample was separated and processed as mentioned under Preparation, Sampling, and Analysis of Processed Products. Then the syrup was concentrated to 70−73% total solids by heating at ∼60−70 °C and transferred to glass containers. Finally, the product was sterilized by dipping in boiled water for 20−30 min, and treatment proceeded as mentioned under Preparation, Sampling, and Analysis of Processed Products.

Date Paste. A date paste was prepared using a modification of the procedures of Ibrahim and Khlif (*2*). A 500 g sample of treated dates was used. Seeds, caps, and skins were removed. Dates were dried using an oven at 90 °C for 1 h. Then the dates were chopped to a paste and packed in plastic containers, and treatment proceeded as mentioned under Preparation, Sampling, and Analysis of Processed Products.

Measurement of Moisture Content. Six subsamples of ∼2−3 g of fresh chopped dates or two subsamples of ∼2−3 g of processed dates were spread out in dried and weighed metallic dishes. Samples were then dried in an oven maintained at 100 °C under vacuum for 12 h (which by practice was enough time to achieve constant weight). Hot dried dishes were removed from the oven and placed into a desiccator, cooled, and weighed. Moisture content was calculated as a percentage of the wet sample.

Measurement of pH. The pH meter was calibrated using pH 4 (potassium biphthalate buffer) and pH 7 (potassium phosphate monobasic sodium hydroxide buffer) buffer solutions supplied by Fisher Scientific. pH values were measured directly by dipping the electrode in a 20% (w/v) suspension of the sample.

Analysis of Dichlorvos Residues. *Preparation of Date Samples.* Seeds and caps were removed manually and dates were chopped using a knife. Chopped dates were mixed using a mortar to produce a homogenized paste.

Measurement of Moisture Content. Six subsamples of ∼2−3 g each were spread out in a dried and weighed metallic dish. Samples were then dried in an oven maintained at 100 °C under vacuum for 12 h (practically was enough time to achieve constant weight). Hot dried dishes were removed from the oven and placed into a desiccator, cooled, and weighed. Moisture content was calculated as a percentage of the wet sample.

Extraction of Dichlorvos Residues. The residues were extracted using the methods of Miller (*10*) and Nakamura et al. (*11*) with modifications. Dates (20 ± 1 g) were blended with 100 mL of acetone and 20 mL of water for 2 min. The mixture was filtered through a fast filter paper (Whatman No. 4), and then the retained residues were blended again with another 50 mL of acetone and 20 mL of water. Then the combined extract was transferred to a separating funnel. About 5−6 g of sodium chloride was added and extracted by 100 mL of petroleum ether. The aqueous layer was transferred to another separating funnel and extracted with another 50 mL of petroleum ether. The organic fraction was then filtered through 20 g of anhydrous sodium sulfate on medium-fast filter paper (Whatman No. 1) and evaporated at 35 °C using a rotary evaporator under vacuum to ∼5 mL. About 2−3 mL of isooctane was then added and the evaporation of petroleum ether completed. The extract was filtered into a measuring

Table 1. Recovered DDVP from Each Maturity Stage

stage	added DDVP (ng/g)	n^a	mean recovery %
khalal	292.1	3	82.8 ± 1.3
rutab	2720	3	79.5 ± 0.9
tamer	3807	3	84.0 ± 0.67
tamer	3148	3	78.5 ± 0.15
mean			81.2 ± 1.01

[a] n = number of replicates.

cylinder fitted with a glass stopper using slow filter paper (Whatman No. 5), and then the solution was completed to a total volume of 20 mL using isooctane. Aliquots of 0.5−1 μL were injected onto the GC-ECD injector.

Recovery Experiment. Treatment solution was prepared by dissolving 50 μL of 50% DDVP (w/v) in 2 L of water to give a 0.0025% DDVP solution Then ∼2 kg of DDVP-free whole dates was dipped into treatment solution in a 5 L dish and mixed well by manual shaking for 2 min to ensure homogeneity. Shaking was repeated every 10 min during the treatment period. After 3−4 h, fruits were removed and dried at room temperature (22−23 °C) for ∼1 h. DDVP was extracted using the above method to determine exactly the applied concentration. Remaining treated dates were stored for 24 h at 4 °C. After 24 h, DDVP residues were recovered by extracting and measuring them using the procedures as described above.

Detection Limit of the GC-ECD. The detection limit of the GC system was estimated by observing the detector response for decreasing amounts of standard solutions of DDVP in isooctane. It is considered as the nanograms that give response after the injectiion of 2 μL of the standard solution into the GC-ECD. Two microliters is the maximum volume that could be injected into the detection instrument.

RESULTS AND DISCUSION

Analytical Methodology. The DDVP was estimated by GLC using a Chrompack WCOT fused silica, CP-Sil 5 CB column and ECD detector. A linear calibration curve was obtained with product moment correlation coefficients of 0.9947−1.00 for concentrations up to 2267 ng/mL.

Table 1 shows the recoveries of the extraction method. Mean recovery is 81.2%. Between 87 and 97% of DDVP was recovered from six different types of fortified vegetables and fruits and detected by GC-FPD as reported by Nakamura et al. (*7*). Nakamura et al. (*11*) also reported that between 83.6 and 113.0% of DDVP was recovered from various fruits and vegetables and detected by GC-NPD.

The detection limit of the GC-ECD system was 2.2 ng/mL (4.4 pg of DDVP), which is nearly similar to the detection limit of DDVP reported by Nakamura et al. (*7*) using GC-FPD (2 ng/g).

Fate of DDVP during Storage of Postharvest-Treated Dates. *Fate of DDVP during Storage.* The fate of DDVP in postharvest-treated dates during storage was investigated. Medium mature khalal and rutab fruits were stored at 3, 22, and 43 °C and tamer fruits at 3 and 22 °C. Storage of the more mature tamer fruits at 43 °C was not carried out because of the loss of moisture that would have resulted in inedible fruits. The storage of khalal and rutab fruits at 43 °C causes early maturity and the transitions from khalal to rutab and from rutab to tamer in a very short time. This limits the effective length of the storage trials. The accelerated maturation also occurs at other temperatures but is not so significant as at 43 °C. At 22 °C, khalal fruits took <10 days to mature to rutab and rutab fruits took ∼10−15 days to mature to tamer. The maturation at 3 °C was slower than at other temperatures so it was possible to follow the decay of DDVP until day 30. Results are summarized in Table 2.

It is clear from the results that DDVP was lost rapidly, with >90% loss of the initial deposit by the end of storage period (except tamer stored at 3 °C). Increasing storage temperature would normally increase the rate of evaporation of the highly volatile DDVP, and it would accelerate the rate of enzymatic and nonenzymatic degradation reactions of DDVP. Storage at 43 °C may not necessarily result in increased enzymatic activity. Enzyme-catalyzed processes usually have optimum temperatures, and high temperatures may inactivate or deform enzymes.

Hesagawa et al. (*12*) found that 46.4 and 5.81% of the initial concentration of DDVP remained in postharvest-treated potatoes after 4 weeks of storage at refrigeration and room temperatures, respectively, whereas 24.0 and 0.03% of the initial deposit remained after 13 weeks of storage at both temperatures, respectively.

The rate of loss of DDVP differed in different maturity stages. It is clear from the results that the rate of loss of DDVP was in the order khalal > rutab > tamer. This order is equivalent to the order of moisture content of these maturity stages (see Table 3). The higher the moisture content, the faster is the expected rate of hydrolysis of DDVP. Kawar et al. (*13*) reported that after 11 months of storage at −15 °C of wheat samples with moisture contents in the range of 9.3−13.7% and treated with 50 mg/kg DDVP, losses of between 2 and 22% of the initial DDVP occurred at different moisture contents.

The rate of DDVP loss in potatoes (which contain ∼80% moisture) reported by Tsumura-Hasegawa et al. (*8*) (48.6% loss after 86 days) was less than that observed for khalal fruits, which was 97.71% after 30 days. This suggests that other factors besides water content are important. In the case of dates the main other variance is the sugar content. Total sugar content for Khunaizy variety, for example, are 23.4, 46.2, and 53.9% in khalal, rutab, and tamer fruits, respectively (*5*). During the maturation of khalal fruits to rutab and from rutab fruits to tamer, the moisture content decreases and the sugar content increases, which means that the water activity decreases and hence the enzyme reaction rates such as for the enzymatic degradation of DDVP can be expected to decrease. The water activity of tamer stage fruits of the Ruzeiz cultivarr, which have a moisture content of 12.38%, was 0.43 (*14*). This also explains why tamer is the only stage that may be stored for very long time without any preservation.

It was observed that treating the fruits at different levels of maturity with DDVP resulted in a large variation in initial residue concentration, although all stages were dipped in the same concentration of DDVP (0.0025% DDVP). The rate of penetration of DDVP varied among three stages, in the order rutab ≈ tamer ≫ khalal. The skin of the khalal fruits is thicker than that of theothers, which may reduce the penetration rate. Also, the cap of the fruit is loose in the rutab and tamer fruits compared to the khalal fruits. As a result, there is a pore in the fruit, which may let the treatment solution enter the fruits without the need for absorption through the skin.

Kinetic Study of the Fate of DDVP. Plotting the fraction of DDVP remaining against time for khalal,

Table 2. Summarized Results of Storage Experiments of Different Maturity Stages of Dates at Different Temperatures

stage	storage temp (°C)	storage period (h)	initial concn (mean ± SD, ng/g)	concn at end of storage period (mean ± SD, ng/g)	loss % (mean ± SD)
khalal	3	720 (30 days)	292.1 ± 3.3	6.69 ± 0.99	97.7 ± 0.34
	22	240 (10 days)	467.7 ± 7.3	8.77 ± 0.47	98.1 ± 0.10
	43	108	292.1 ± 3.3	21.92 ± 0.88	92.5 ± 0.30
rutab	3	720 (30 days)	2720 ± 63	226.1 ± 4.8	91.7 ± 0.18
	22	360 (15 days)	1852 ± 12	26.53 ± 0.67	98.6 ± 0.04
	43	108	1937 ± 17	55.05 ± 0.53	97.5 ± 0.03
tamer	3	720 (30 days)	4532 ± 10	1378 ± 23	69.6 ± 0.50
	22	600 (25 days)	3148 ± 3.04	175.3 ± 6.2	94.4 ± 0.20
	43				

Table 3. Moisture Content of Fresh Jimri, Khalal, Rutab, and Tamer Fruits[a]

commodity	*n*	moisture content (% ± SD)
jimri	6	83.5 ± 1.6
medium mature khalal	6	57.4 ± 1.3
rutab	6	36.6 ± 0.8
tamer	6	22.7 ± 1.0

[a] Moisture content of fresh fruits for all four stages was measured in mixed-variety date samples.

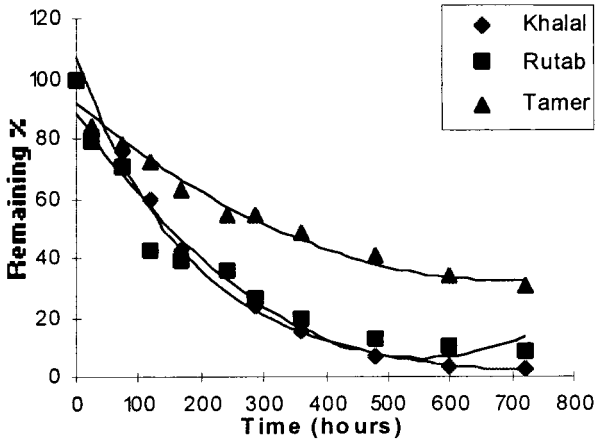

Figure 1. Decay of DDVP during the storage of khalal, rutab, and tamer fruits at 3 °C.

rutab, and tamer fruits stored at 3 °C (Figure 1), 22 °C (Figure 2), and 43 °C (Figure 3) shows a smooth curve with the rate decreasing with time, suggesting a first-order reaction for the loss stage. This was confirmed by plotting the natural logarithm of the fraction remaining against time. A straight line was obtained, confirming that the rate-determining step followed first-order kinetics at all of the temperatures studied (regression line equations are shown in Table 4).

The rate constants and half-lives calculated for each of the fruits at the different temperatures studied are shown in Table 4. Tsumura-Hesagawa et al. (*8*) studied the kinetics of DDVP loss in potatoes stored at 5 °C and found the loss rate followed first-order kinetics with a rate constant of 0.0155, which is similar to the rate constants observed in this study.

Rate constants observed for the loss of DDVP differed in different maturity stages. They were in the order khalal > rutab > tamer at 3 and 22 °C, whereas the order was rutab > khalal at 43 °C. The variations in rate constants among different maturity stages may be correlated to the moisture contents of each stage, which were in the order khalal > rutab > tamer (see Table 3). Also, the rate constants may be correlated to sugar

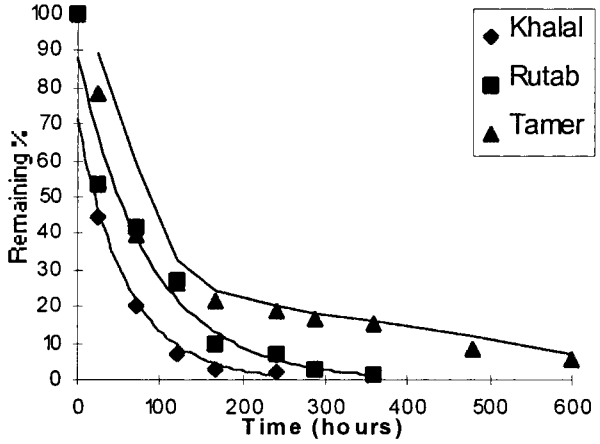

Figure 2. Decay of DDVP during the storage of khalal, rutab, and tamer fruits at 22 °C.

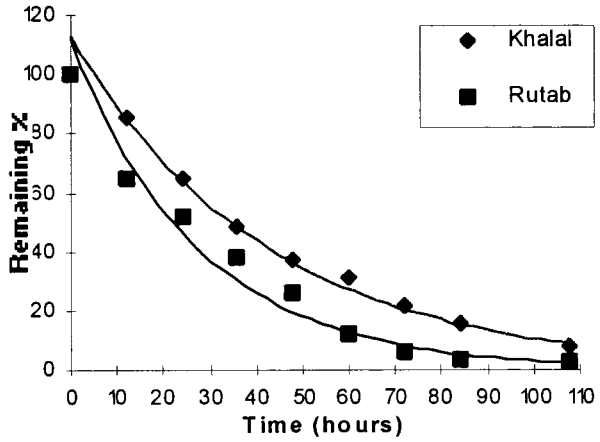

Figure 3. Decay of DDVP during the storage of khalal and rutab fruits at 43 °C.

content, which is in the order tamer > rutab > khalal, as a high sugar content means lower water activity, which affects the rate of enzymatic reactions.

Fate of DDVP Residues during Processing. The loss of DDVP during processing was studied. Processing methods used were modified to be suitable for in-laboratory work and represent typical processes applied to dates. The work was concentrated on the effect of cooking whole and minced fruits and the effect of dehydrating whole and minced fruits on the levels of DDVP. The rate of loss of DDVP residues differed in different processes (cooking and dehydration) as well as in different stages of maturity of dates.

Effect of Cooking on DDVP Residue Levels. Date fruits were subjected to various thermal treatments by cooking for different periods of time with various quantities of

Table 4. Regression Line Equations, Rate Constants, Half-Lives, and Activation Energies of DDVP Degradation Reactions at Different Temperatures for Different Stages of Dates

stage	temp (K)	regression line eq	rate constant (h^{-1})	$t_{1/2}$ (h)
khalal	276	$y = -0.0054x + 4.6687$	0.0054	128.3
	295	$y = -0.0168x + 4.2676$	0.0168	41.25
	316	$y = -0.0238x + 4.7296$	0.0238	29.12
rutab	276	$y = -0.0034x + 4.3703$	0.0034	203.8
	295	$y = -0.0115x + 4.4823$	0.0115	60.26
	316	$y = -0.0365x + 4.717$	0.0365	18.99
tamer	276	$y = -0.0016x + 4.4606$	0.0016	433.1
	295	$y = -0.0043x + 4.1645$	0.0043	161.2
	316			

Table 5. Effect of Cooking on the DDVP Residue Levels

type of processing	maturity stage	whole or minced	initial concn (mean ± SD, on dry wt, ng/g)	remaining % (mean ± SD)
cooked khalal	khalal	whole	576.0 ± 12	20.7 ± 1.1
jam making	khalal	minced	576.0 ± 12	19.7 ± 1.3
	rutab	minced	5427 ± 24	4.88 ± 0.36
	tamer	minced	5393 ± 39	12.8 ± 0.29
cooked syrup	tamer	minced	3569 ± 33	40.9 ± 0.37
concentrated syrup	tamer	minced	3569 ± 33	9.16 ± 0.39

Table 6. Moisture Content and pH Values for Cooked Products

commodity	n^a	moisture content (% ± SD)	pH (± SD)
cooked khalal	2	67.3 ± 0.1	5.20 ± 0.11
dried cooked khalal	2	22.4 ± 0.2	
khalal jam	2	34.9 ± 0.1	4.07 ± 0.11
rutab jam	2	36.6 ± 0.2	4.30 ± 0.02
tamer jam	2	35.1 ± 0.2	3.90 ± 0.01
tamer syrup	2	31.7 ± 0.1	4.82 ± 0.10
dried whole tamer	2	23.7 ± 0.1	
tamer paste	2	15.9 ± 0.2	

[a] n = number of replicates.

water and other additives, according to the requirement of the type of processing (e.g., jam making). The cooking was done for whole (khalal) and minced (khalal, rutab, and tamer) fruits. Remaining DDVP residues are shown in Table 5.

Results show that between 60 and 95% of the initial deposit of DDVP was removed by cooking. The high vapor pressure of DDVP (2.1 Pa at 25 °C, *15*) suggested that most of the DDVP was lost by evaporation during cooking. According to *The Pesticide Manual* (*15*), DDVP is stable to heat, so some loss may result from nonenzymatic hydrolysis, which would be accelerated by heating (high temperatures usually deactivate enzymatic systems). The pH values of the cooking solutions of all products were slightly acidic (see Table 6). Fest and Schmidt (*16*) reported that acid hydrolysis of enol phosphates such as DDVP is favored compared to trialkyl phosphates and consists largely in the cleavage of the P−O bond. This suggests that some of the DDVP may be lost by acid-catalyzed hydrolysis.

The efficiency of cooking in removing DDVP was better in other studies. Tsumura et al. (*17*) reported that no DDVP residues were detected either in boiled buckwheat noodles or in boiling water.

Different types of cooking of dates required between 45 and 90 min (*9*). These relatively long periods may increase the chance of the loss of DDVP. Miyahara and Saito (*18*), in contrast with that, reported this after cooking soybeans in soybean milk. Soybeans were washed, ground with water, and then heated at 100 °C for only 5 min to produce soybean milk, which would be used later in producing soybean tufo. This process resulted into 96% loss in DDVP residues.

Table 7. DDVP Remaining after Syrup-Processing Procedures Were Applied on Real Tamer and on Water Only

	control syrup (water only)			real tamer syrup		
stage	n^a	remaining %	total solids	n	remaining %	total solids
0 time		100	0	4	100	7.5
cooked syrup	3	12.3	0	3	40.9	27.7
filtered syrup				4	17.7	46.4
concentrated syrup	3	5.88	0	4	9.16	68.3

[a] n = number of replicates.

Table 8. Effect of Drying on DDVP Residue Levels

type of processing	stage	whole or minced	initial concn (mean ± SD, on dry wt, ng/g)	remaining % (mean ± SD)
dehydrated cooked khalal	khalal	whole	576.3 ± 12.2	0.0
packed tamer	tamer	whole	5393 ± 39	14.4 ± 0.14
tamer paste	tamer	minced	5393 ± 39	7.96 ± 0.14

Cooking khalal in water for 45 min removed lesser amounts of residues (79.3 ± 1.1% of initial residues) compared to that caused by blanching postharvest-treated potatoes (96.4% of initial DDVP) (*12*). Potatoes were blanched in three steps with different temperatures and periods (80 °C for 7 min, 60 °C for 12 min, and 85 °C for 8 min). These differences demonstrate that the nature of the crop has an effect on the rate of loss of DDVP during the processing. The main difference between dates and rice, potatoes, and soybeans is that the former contains >60% sugars. This suggests that the sugar content of raw fruits may influence the rate of loss. Other components in dates may influence the rate of removal of DDVP residues during cooking. Further studies are needed to identify these.

The cooking step involved in syrup production was less efficient (∼60% loss) compared to other processing methods involving cooking. The removal rate increased when cooking was combined with filtration (∼82% loss) and concentration (∼92% loss). It is expected that some DDVP residues removed by filtration were associated with the waste, whereas the concentration step involved more exposure to heat.

In a syrup control experiment (see Table 7), DDVP was less stable to heat in water than in treated tamer. About 88% of the initial deposit were removed by cooking treated plain water, whereas ∼60% was removed by cooking treated tamer. This difference suggests that there is a protective effect from one of the constituents, probably the sugar. The nature of this protective effect needs further investigation.

Effect of Drying on DDVP Residue Levels. Date products were dried in an oven at 80 °C and the DDVP levels determined. The results are shown in Table 8.

Results show that no residues were detected in the dried cooked khalal, whereas ∼8−14% of DDVP remained in dried whole tamer and tamer paste. Loss of

DDVP by dehydration is expected to be mainly the result of evaporation.

In the case of dried cooked khalal, most of the residues were removed during the cooking step; the additional step of drying resulted in the removal of all DDVP residues.

In the case of tamer, no cooking step was used before drying, but the efficiency of removal during drying tamer (whole and paste) was high. It was slightly higher in the paste product. The greater loss of residues in the paste could result from the removal of the date skin during paste production.

Similar work carried out on unwashed whole figs treated with fenitrothion reported that 71.1% of fenitrothion residues were lost (*19*).

Conclusions. *Fate of DDVP during Storage of Dates.* Postharvest-applied DDVP was found to be absorbed to different extents depending on the maturity of the fruits, the maturer tamer and rutab fruits absorbing greater amounts than the less mature khalal.

The rate of loss of DDVP was found to follow first-order kinetics at the three storage temperatures used. It was predicted by the first-order rate model that the rate of loss of residues is higher at elevated temperatures, which can result in quality changes in the fruits. High temperatures will promote the maturation of the immature fruits and loss of moisture content. The problem of the growth of spoilage organisms is most apparent in immature fruits that have a higher moisture content. Storage at low temperatures can also result in a loss of quality as the moisture content is reduced in open systems. Storage in closed containers maintains the moisture levels but reduces the rate of loss of DDVP by evaporation.

Storage at room temperature may be considered the best in terms of the rate of degradation reaction as well as improving the quality of the fruits, but it is necessary to treat the fruits with a suitable fungicide to prevent fungal growth and fermentation.

The treatment rate of DDVP for postharvest application to dates that will be stored needs to be established. Three factors need to be considered. First, the treatment rate must be effective against storage insects. Second, the method of application, whether it is fumigation or dipping in pesticide solution, may lead to different initial concentrations of residues. Fumigation in closed rooms, as is done with methyl bromide, is likely to be preferred as it will reach most insects while at the same time the residues absorbed by the fruits would be less. Finally, at the end of the storage period residue levels must be acceptable and not harmful to consumers.

Further studies are required to estimate the effect of date compositions, other than moisture content, on DDVP degradation.

Fate of DDVP during Processing. All of the processes investigated resulted in significant reductions in DDVP levels. The principal mechanisms for the loss are expected to be evaporation and hydrolysis. Further studies are required to evaluate the effect of sugar content and other components on the degradation of DDVP during processing. The treatment rate for postharvest applications to dates that undergo processing needs to be established as with storage. In date-processing factories, dates are stored in large refrigerators after fumigation with suitable pesticides before processing.

ACKNOWLEDGMENT

We thank our colleagues Mr. Mohammed Osman Hashem and Dr. Naeem Aktar Rabbi for technical help.

LITERATURE CITED

(1) El-Behissy, E. Y. The Fate of Dichlorvos (DDVP) in Field-Treated and in Stored and Processed Post-Harvest Treated Edible Maturity Stages of Dates (Khalal, Rutab and Tamer). M.Phil. Research, Reading University, U.K., 1998; pp 91, 130.

(2) Ibrahim, A. M.; Khlif, M. N. H. *Date Palm, its Plantation, Care and Production in the Arabian Countries*; Al-Eskandaria, Egypt, 1993; p 598 (in Arabic).

(3) Al-Oqaidi, K. H. *Dates and Microbial Biotechnology*; Al-Watan Press: Beirut, Lebanon, 1987; pp 113−127, 136 (in Arabic).

(4) FAO. *Plant Production and Protection, Paper 35. Date Production and Protection*; FAO: Rome, Italy, 1982; pp 190, 192, 199, 209, 228, 235, 236, 239.

(5) Ahmed, I. A.; Ahmed, A. K.; Robinson, R. K. Chemical composition of date varieties as influenced by the stage of ripening. *Food Chem*. **1995**, *4*, 305−309.

(6) Miyahara, M.; Saito, Y. Pesticide Removal Efficiencies of Soybean Oil Refining Processes. *J. Agric. Food Chem*. **1993**, *41*, 731−734.

(7) Nakamura, Y.; Sekiguchi, Y.; Hasegawa, S.; Tsumura, Y.; Tonogai, Y.; Ito, Y. Reductions in Postharvest-Applied Dichlorvos, Chlorpyrifos-methyl, Malathion, Fenitrothion and Bromide in Rice during Storage and Cooking Processes. *J. Agric. Food Chem*. **1993**, *41*, 1910−1915.

(8) Tsumura-Hasegawa, Y.; Tonogai, Y.; Nakamura, Y.; Ito, Y. Residue levels of dichlorvos, chlorpropham and pyrethrins in postharvest-treated potatoes during storage and processing into starch. *J. Agric. Food Chem*. **1992**, *40*, 1240−1244.

(9) Sahi, A. A. *Laboratory Book in Date Technology*; Al-Basra University: Al-Basra, Iraq, 1986; pp 71−75, 137−139, 143−145 (in Arabic).

(10) FAO. *Food and Nutrition Paper 14/13, Manuals of Food Quality Control, 13: Pesticide Residue Analysis in the Food Control Laboratory*; Miller, G.; FAO: Rome, Italy, 1992; pp 65−67.

(11) Nakamura, Y.; Tonogai, Y.; Sekiguchi, Y.; Tsumura, Y.; Nishida, N.; Takakura, K.; Isechi, M.; Yuasa, K.; Nakamura, M.; Kifune, N.; Yamamoto, K.; Terasawa, S.; Oshima, T.; Miyata, M.; Kamakura, K.; Ito, Y. Multiresidue analysis of 48 pesticides in agricultural products by capillary gas chromatography. *J. Agric. Food Chem*. **1994**, *42*, 2508−2518.

(12) Hesagawa, Y.; Tonogai, Y.; Nakumura, Y.; Ito, Y. Reduction of Post-harvest Applied Pesticides in Potatoes during Storage and the Process of Preparing French fries. *J. Food Hyg. Soc. Jpn*. **1991**, *32* (3), 128−136 (in Japanese).

(13) Kawar, N. S.; de Batista, G. C.; Gunter, F. A. Pesticide stability in cold-stored plant parts, soil, and dairy products, and in cold-stored extractive solutions. *Residue Rev*. **1973**, *48*, 45−77 (cited on p 317 in *FAO/WHO [I], Pesticide Resisues in Food*, sponsored jointly by FAO and WHO, No. 124, Evaluations, Part I, Residues, 1993).

(14) Yousif, A. K.; Morton, I. D.; Mustafa, A. I. Studies On Date Paste. In *Proceedings of The Second Symposium on the Date Palm*; Mars Publishing House: Al-Riyad, Saudia Arabia, 1986; Vol. II, pp 85−91.

(15) *The Pesticide Manual*, 10th ed.; Tomlin, C., Ed.; BCPC: Surrey, U.K., 1994; pp 313, 314.

(16) Fest, C.; Schmidt, K.-J. *The Chemistry of Organophosphorus Pesticides*, 2nd revised ed.; Springer-Verlag: Berlin, Germany, 1982; p 27.

(17) Tsumura, Y.; Hasegawa, S.; Sekiguchi, Y.; Nakamura, Y.; Tonogai, Y.; Ito, Y. Residues of Post-harvest Application Pesticides in Buckwheat after Storage and Processing into Noodles. *J. Food Hyg. Soc. Jpn*. **1994**, *32* (3), 1−7 (in Japanese).

(18) Miyahara, M.; Saito, Y. Effect of the Processing steps in Tofu Production on Pesticide Residues. *J. Agric Food Chem*. **1994**, *42*, 369−373.

(19) Solaiman, Y. A. A. Pesticide residues as influenced by processing steps in foods. Ph.D. Thesis, The University of Ain Shams, Egypt, 1990; pp 63, 65, 101, 113, 121, 130.

Received for review July 5, 2000. Revised manuscript received December 16, 2000. Accepted December 17, 2000.

JF000812E