Loss of Fatty Acid Esters from Grape Surfaces during Drying

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ABSTRACT

Fatty acid esters have been shown to reduce the drying time of grapes by interacting with the waxy surface of the grapes. Laboratory scale procedures were developed to determine the fate of esters during dehydration. Thompson seedless grapes were dipped in a water emulsion containing 2% fatty acid ester, 2% potassium carbonate and an emulsifier. Grapes were dried at ambient, 43 C and 71 C. Drying rates vs. fatty acid ester concentration on the grape surfaces were plotted. The fate of fatty acid esters during dehydration was determined by running the dryer exhaust through a cold trap and extracting the condensate. These studies showed that the large loss of esters during drying lowered the drying rate considerably. An additional dip during drying reduced the drying time significantly. The ester losses appeared to be caused by vapor distillation of the esters during drying.

INTRODUCTION

Fatty acid esters are used in Australia to provide as much as a three-fold increase in the drying rate of grapes (1). Possingham (2) reports that the fatty acid esters interact with the waxy cuticle of the grape skin, which acts as a water barrier, allowing an increased rate of water loss during drying. The reduced drying time would lessen the exposure of sun-dried raisins to rain and reduce energy requirements for tunnel dehydrated raisins. The rapid initial drying of ester-treated grapes produces an amber-colored raisin in contrast to the blue-black color of untreated sun-dried raisins (3).

Fatty acid esters suitable for raisin drying can be manufactured from various fats and oils of both plant and animal origin. For the work reported here we used methyl or ethyl esters of acids from high oleic safflower oil. Other potential sources include fractionated tallow, partially hydrogenated soybean oil, cottonseed oil and palm oil, all of which produce C_{14}-C_{18} ester mixtures which are liquid at ambient temperatures.

In California, over 90% of the raisin grapes are sun-dried in the vineyards with the remainder dehydrated in gas-fired tunnel dryers. Laboratory experiments to determine the effect on drying rate of dipping various waxy-skinned fruits in water emulsions of ethyl esters of fatty acids prior to forced air dehydration were conducted by Ponting and McBean (4). Field studies of forced air dehydration and sun drying of Thompson seedless grapes were conducted by Petrucci et al. (5) to adapt these laboratory procedures to methods commercially feasible in California. This research has brought about a limited commercial use of fatty acid esters for drying raisins in California. Some problems remain to be overcome, however, including variable drying rates that have occurred in commercial practice and marketing problems associated with the lighter and more variable color of the ester-treated raisins.

While considerable research has been conducted on the effects of methods and levels of application of fatty acid esters on the drying rate of raisins, nothing is known about the fate of esters during drying or how changes in their concentration on the surface of grape skins affects the drying rate throughout the entire drying period. This study was undertaken to determine changes in ester concentration and the effect on drying rate.

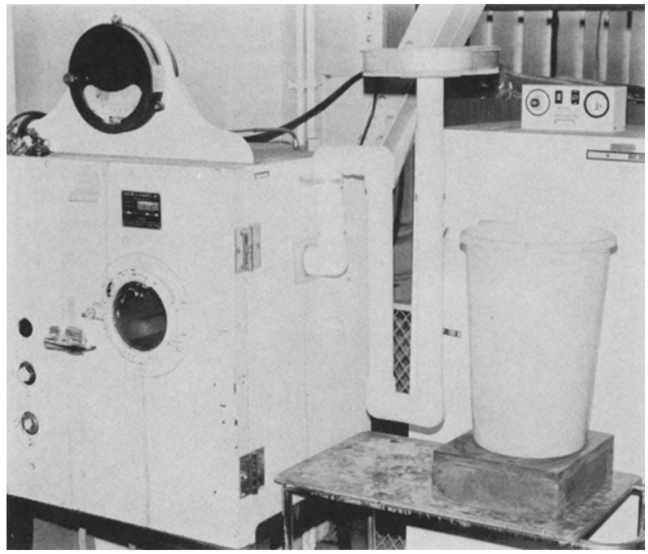

FIG. 1. Front view of Proctor Schwartz cabinet dryer with u-tube collector attached. Plastic container holds dry ice and ethanol. When collector is in operation, container is placed around u-shaped section of collector.

MATERIALS AND METHODS

Thompson seedless grapes used in these experiments were obtained from Fresno, California, and stored at 1 C until needed. Grapes were cut from the bunches and mixed prior to treatment.

Samples were prepared for drying by dipping the controls in water and the test samples in a water emulsion containing 2.0% fatty acid ester, 2.0% potassium carbonate and 0.1% emulsifier (Tween 60). The samples were drained for 30 min and weighed into previously tared drying trays. Approximately 50 and 100 g samples were used in these experiments.

A Procter Schwartz cabinet dryer was used for all forced-air dehydration experiments. The exhaust port of

TABLE I

Recovery of Methyl Esters During Dehydration at 71 C

Run Number	I	II
Weight of fresh grapes	50.7 G	51.2 G
Methyl oleate applied to grapes	24.9 MG	22.2 MG
	After 3 hr Drying at 71 C	
Weight of grapes	35.5 G	33.1 G
Moisture loss	15.2 G	18.1 G
Methyl esters on grapes	8.3 MG	7.4 MG
Methyl esters lost	16.6 MG	14.8 MG
Methyl esters recovered from collector	8.1 MG	7.6 MG

the cabinet dryer was fitted with a PVC pipe collector (Fig. 1) for the recovery of evaporated volatiles. A small squirrel cage fan was mounted inside the dryer to increase the air flow through the collector to 430 cfm. A 50 g sample of grapes was placed inside the first part of the collector tube on a perforated metal screen. To supplement recovery in the U-tube, a 12 in. aluminum dish collector was mounted ¼ in. above the exhaust port of the collector. Dry ice and ethanol were used to cool the collector surfaces.

Volatiles collected in the U-tube and dish collector were combined and extracted with distilled Skellysolve B, and a known amount of internal standard, methyl margarate, was added. The combined mixture was reduced to less than 10 ml in a vacuum rotary evaporator and placed in a 10 ml volumetric flask containing a small amount of anhydrous sodium sulfate.

Raisin samples were prepared for analysis of the surface esters by placing the weighed sample (ca. 15 g) into a 250 ml Erlenmeyer flask. Approximately 200 ml of dichloromethane was added along with a known amount of methyl margarate internal standard, and the sample was stirred for 5 min. The dichloromethane was decanted and the sample extracted with an additional 100 ml of dichloromethane. The extracts were combined, and residual moisture was removed with anhydrous sodium sulfate and taken to dryness in a vacuum rotary evaporator. To the residue in the flask, 200 ml of distilled Skellysolve B was added and the mixture was heated to boiling in a 100 C water bath and then decanted. The extract was cooled until it could be reduced to less than 10 ml in a vacuum rotary evaporator and transferred to a volumetric flask containing a small amount of anhydrous sodium sulfate.

Quantitative analysis of the esters was accomplished by the gas chromatographic method described by Stafford et al. (6) except that Alltech AT-1000 was used as the stationary phase on the column packing.

RESULTS AND DISCUSSION

The data in Table I show that 67% of the methyl esters of fatty acids applied to the surface of the grapes were lost in 3 hr by vapor distillation. To determine whether significant amounts of esters were lost by hydrolysis during drying, the extracts from dried raisins and trapped condensate obtained in these experiments were esterified with BF_3 methanol. Analysis of the esterified extracts and condensate showed that no significant hydrolysis of the esters had occurred.

The effect of loss of esters on the drying rate of raisins is seen in Figure 2. During the first 3 hr of drying, the rate of water loss from ester-treated grapes was much greater than that of the controls. This rate of water loss slows after 50% of the esters are lost and, as might be expected, equals the rate for controls after 95% of the esters are lost.

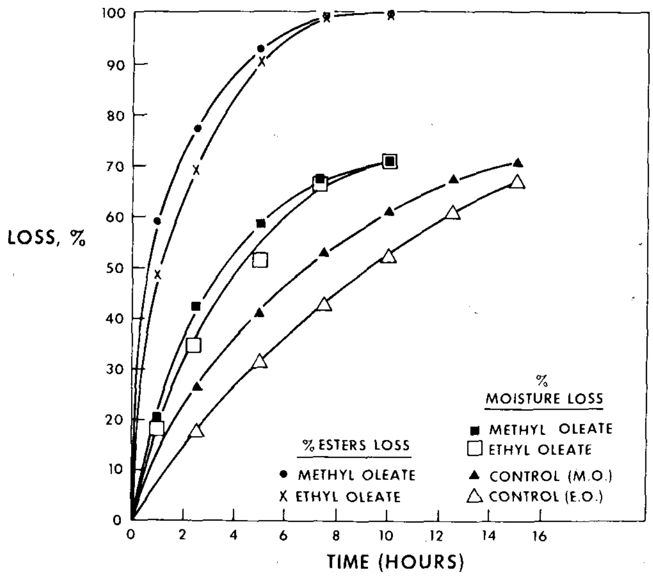

FIG. 2. Loss of moisture and esters during drying of raisins at 71 C.

Table II shows that ester loss is not solely a result of forced air dehydration. These raisins were dried in the laboratory by placing a weighed sample on a perforated metal screen tray and allowing them to dry at ambient temperature averaging ca. 20 C and without forced air circulation. The results indicate that a similar loss of esters should occur during sun drying in the vineyard. Analysis of samples of dried-on-the-vine (DOV) and sprayed-on-the trays (SOT) sun-dried raisins from the California State University—Fresno, has shown similar loss of esters during drying. Low fatty acid ester residues have been found on DOV and SOT raisins from California State University—Fresno, averaging 20-30 ppm.

The effect of replacing esters lost from the surface of raisins during dehydration at 43 C on drying rate is shown in Figure 3. The effect of loss of esters on drying rate is similar to that shown in Figure 2 even though the drying temperature is 28 C less. Re-dipping the grapes dramatically increases the drying rate showing that the concentration of esters on the surface of the grape skin is the most important factor affecting the drying rate during the dehydration of raisins. It had been thought, previously, that the slower drying rate during the later stages of drying was caused by a slowed moisture movement within the raisins as the sugar

TABLE II

Loss of Esters from Grapes at Ambient Drying Temperature (20 C)

Time (days)	Weight grapes (grams)	Weight ester (milligrams)	(PPM)	Esters lost (%)	Moisture lost (%)
Methyl Esters					
0	52.1	11.3	217.0	—	—
15	14.6	3.2	217.8	71.9	71.9
Ethyl Esters					
0	50.0	10.9	218.0		
18	15.1	2.86	177.9	73.8	69.8

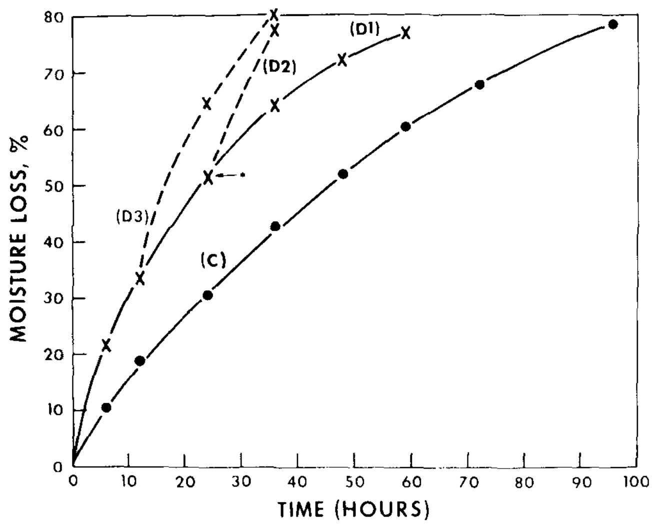

FIG. 3. Effect of multiple dips on drying rate of raisins at 43 C (C) control, (D1) one dip, (D2) two dips, (D3) three dips. *At 24 hr 95% of the esters were lost.

concentration increased and the cellular structure was disrupted. These experiments indicate that the re-application of esters to the surface of the grapes during the later drying stages replaces esters lost during drying and will maintain the accelerated drying rate throughout the drying process. This will result in significantly reduced drying times for sun-dried and forced-air dehydrated raisins.

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[Received August 10, 1979]