is probable that the nutrition of cotton nectar feeding insects is significantly influenced by this array of amino acids. It is also possible that some of the less common acids may act as phagostimulants.

Unfortunately, the dietary requirements and preferences of adult cotton insects are, at best, imperfectly known. The fact that cotton nectar is a relatively rich source of amino acids should stimulate investigations in this direction. Such knowledge should have basic importance in the realm of biological control of these insects.

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Analysis of Fatty Acid Esters in Processed Raisins by Gas Chromatography

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An analysis procedure for the determination of the fatty acid ester residue on processed raisins was developed. Gas chromatographic analysis of the dipping oils which were used to increase the drying rate of grapes showed the presence of two or more of the following fatty acid esters: oleate, stearate, palmitate, and linoleate, with oleate accounting for the largest percentage. The esters were removed from the raisins by extraction with chloroform and the hexane-soluble fraction which contained the esters was analyzed by gas chromatography. Grapes dipped in 0.5–6.0% water emulsions of a commercial Australian ethyl ester dipping oil produced residues on the processed raisins of 41–397 ppm of total fatty acid esters, as measured by gas chromatography.

Fatty acid esters have been used for many years in Australia and the Middle East to reduce the drying time of grapes. This shorter drying time is caused by the interaction of esters in the dip with the waxy surface of the grapes to increase the rate of water loss during drying (Grncarevic, 1963). In contrast, most California raisin grapes are sun dried without the use of a drying aid, which results in a raisin with a blue-black color, darker than that of Australian raisins. Because of the long drying time required, sun-dried California raisins are very susceptible to rain damage.

Ponting and McBean (1970) at this laboratory determined the effect on the drying rate of dipping waxy skin fruits in water emulsions of ethyl esters of fatty acids in the C_{10}–C_{18} range. Other pretreatment processes were also studied but it was found that dipping waxy skin fruit in an emulsion of ethyl oleate was the most effective and convenient. This work has continued with expanded field studies by Petrucci *et al.* (1973), at California State University at Fresno. These studies have included on-the-vine dried and tunnel dehydrated raisins using methyl and ethyl fatty acid ester mixtures of plant and animal origin, to reduce drying time and produce a lighter colored raisin without the use of sulfur dioxide. Taste threshold determinations have indicated that there is a wide variation in the thresholds for the fatty acid esters mixtures used (Guadagni, 1972). This work indicated a need for a method of determining the quantity of esters left on raisins after processing, in order to adjust the concentration of esters in the emulsion for optimum drying time without exceeding the taste threshold. This paper describes a procedure for analysis of fatty acid esters on processed raisins.

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EXPERIMENTAL SECTION

The grapes used in these experiments were machine harvested Thompson seedless from the Fresno area. For de-

Table I. Per Cent Composition of Fatty Acid Ester Mixtures from Different Sources

	Methyl ester dipping oils		Ethyl ester dipping oils	
	A	B	A	B
Oleate	65.7	54.3	29.1	86.6
Stearate	1.1	23.7	12.1	
Palmitate	4.6	3.1	12.6	3.3
Linoleate	12.5	9.7		
Others[a]	16.1	9.2	46.2	10.1

[a] By subtraction. Precision: each value in the table is a mean of duplicates; standard deviation between duplicates (13 degrees of freedom) = 0.97%; 95% confidence interval (mean of duplicates) = ±1.5%.

Table II. Means of Duplicate Analyses of Processed Raisins

% dipping oil in emulsion	Esters present, ppm				
	Ethyl oleate	Ethyl stearate	Ethyl palmitate	Methyl oleate	Total esters
0.0	14	4	2	4	24
0.5	21	7	5	8	41
1.0	40	13	6	6	65
2.0	77	30	16	19	142
4.0	133	58	31	29	251
6.0	212	90	52	43	397
s^a	4.0	3.2	3.2	3.0	4.2
CI($\bar{x}$)[b]	±6.8	±5.5	±5.5	±5.2	±7.2
CI(b)[c]	(31.3, 35.0)	(13.7, 15.6)	(7.4, 9.3)	(5.6, 7.6)	(59.6, 65.9)

[a] Standard deviation between duplicates (6 degrees of freedom). [b] 95% confidence interval on a mean of duplicates. [c] 95% confidence interval of the slope (parts per million of ester/per cent concentration of oil) based on linear regression analysis.

hydration the fruit was dipped as individual berries in 0.5–6.0% emulsions of dipping oil and dried using a two-tunnel dehydration schedule. The process for making on-the-vine dried raisins was as follows. When the fruit reached 20–23° balling the canes were cut and an emulsion of 2% commercial Australian ethyl ester dipping oil and 2% potassium carbonate was applied by spraying. Five days later the procedure was repeated with an emulsion of 1% dipping oil and 1% potassium carbonate. When the fruit reached approximately 16% moisture it was mechanically harvested.

The samples were prepared for analysis of the fatty acid esters by weighing 50 g of the raisins into a 250-ml erlenmeyer flask. Approximately 200 ml of chloroform was added along with a weighed amount of internal standard ester and the sample was stirred for 5 min. The chloroform was decanted and the extraction procedure was repeated. The raisins were then blended in a blender with 300 ml of chloroform for 3–5 min and all extracts were combined. The combined extracts were taken to dryness in a rotary vacuum evaporator.

To the residue in the flask, 300 ml of distilled hexane was added and the mixture was heated to boiling in a water bath. The hexane was allowed to cool until it could be reduced to less than 50 ml in a rotary vacuum evaporator. The hexane solution was decanted into a 50-ml centrifuge tube and centrifuged to settle out suspended material. The hexane fraction was then decanted into a flask and reduced to less than 10 ml in a rotary vacuum evaporator. The fraction was transferred to a 10-ml volumetric flask and made up to volume with hexane.

ANALYSIS

Gas Chromatography. Qualitative analysis of the major fatty acid esters present and quantitative determination of the amount present in processed raisins were accomplished by gas chromatography. The column was a 6 ft × ⅛ in. i.d. stainless steel column with 10% FFAP on Chromosorb W, acid-washed DMCS. A flame ionization detector was used and the Micro-Tech gc 2000 R was operated isothermally at 160–170° depending on the ester mixture. Helium flow at the detector was 30 ml/min, and the detector and inlet were operated at 250°. Depending on the concentration of esters present in the sample 0.2–0.8 μl of the hexane solution was injected onto the column.

Identification of the fatty acid esters present in the dipping oils was accomplished by adding known esters and comparing the chromatogram to a chromatogram without the added ester. Synthetic mixtures were also made up and compared with the unknown mixture under identical gas chromatograph conditions. Methyl and ethyl palmitate were used as internal standards for the quantitative analysis of ethyl and methyl esters, respectively. Using these standards and the fatty acid esters to be measured, curves were made of the component/standard area ratio *vs.* the component/standard weight for each ester (McNair and Bonilli, 1966).

RESULTS AND DISCUSSION

Analysis. The compositions of representative samples of four fatty acid ester mixtures are shown in Table I along with precision estimates of the analysis. The percentages listed under "others" are mainly mono- and diglycerides and minor esters not measured except for the ethyl ester dipping oil A, which contains approximately 30% anionic emulsifier.

Gc analyses of raisins, sun dried without the use of a dipping oil, showed small amounts of various naturally occurring compounds with retention times similar to those of methyl and ethyl fatty acid esters. In order to establish the necessary blank values for these compounds the areas under their peaks were measured and reported as fatty acid esters with similar retention times. Extraction of the fatty acid esters on processed raisins appeared complete, since no additional esters were found in raisins which had been previously extracted. Recovery of added esters was 97%.

The results of duplicate analyses on the raisins processed in water emulsions of ethyl ester mixture A are shown in Table II. The quantity of individual or total esters added to the processed raisins by the dipping procedure is obtained by subtracting the appropriate blank value shown in Table II, line 1. Precision estimates on the analysis are also presented in Table II. The presence of a methyl ester on these raisins was due to the prior use of the dipping equipment in treating grapes with methyl esters. On-the-vine dried samples contained 108 ppm of added ethyl esters.

The treatment of grapes with fatty acid esters in the United States is still in the experimental stage and the ester mixtures applied in these experiments have not yet been approved for this use.

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