Deacidification of Sulfur Olive Oil. I. Single-Stage Liquid-Liquid Extraction of Miscella with Ethyl Alcohol

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In this study, a systematic and detailed investigation on liquid-liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions was performed. Optimal extraction conditions for recovery of free fatty acids (FFA) with a minor loss of neutral oil were determined in bench-scale single-stage extractions. It was concluded that, to ensure deacidification with a low triglycerides loss, it is appropriate to extract the miscella with 30% or more dilute ethanol solutions. It was also noted that under these circumstances the free fatty acid percentage extracted is not affected by increases in contents of FFA and partial glycerides of sulfur olive oil, and the solvent must be saturated with hexane before extraction. Changing the oil:hexane ratio in miscella from 1:2 to 2:1 by weight did not have any significant effect on extraction results.

KEY WORDS: Deacidification, fatty acids, liquid-liquid extraction, refining, sulfur olive oil.

Sulfur olive oil is a valuable and important industrial by-product obtained from olive press cakes by solvent extraction. Even though it originates from the same fruit of olive tree (*Olea europaea* L.), sulfur olive oil differs appreciably, especially in impurities, compared to pressed oil. This is due mainly to rapid enzymatic hydrolysis and oxidation of oil in press cakes while stored for extraction. As a result of this unavoidable change, sulfur olive oil contains a relatively high proportion of free fatty acids (FFA), partial glycerides and some oxidation products (1,2).

Sulfur olive oil may be considered as a potential source of free fatty acids already in a free state. For this reason, this study includes a close investigation of deacidification of sulfur olive oil with minor refining loss, and also recovery of its component free fatty acids as valuable by-products.

Deacidification of high acidity oils can be accomplished either by miscella refining or by physical refining instead of conventional alkali neutralization processes, since these latter methods normally cannot be applied to oils containing more then 8–10% free acids (3,4). Another deacidification method for high acidity oils is liquid-liquid extraction based on different solubilities of fatty acids and triglycerides in various organic solvents. This method, conducted at normal temperature and atmospheric pressure, may be considered an alternative process to physical refining which consumes much more energy. In both processes, the fatty acids are recovered in a free state instead of as sodium soaps as in miscella refining.

Deacidification of oil by solvent extraction has been examined by several investigators, and ethanol, methanol and acetone have been emphasized as solvents for extraction of free fatty acids (4–7). Although solubilities of fatty acids and neutral triglycerides are individually different in these solvents, it has not been possible to obtain a complete separation, because the low solubility of the triglycerides is increased in direct proportion to their free fatty acids contents. Extraction of free fatty acids from a solution of oil in hexane (miscella) also has been investigated. Thomopoulos (8) examined deacidification of olive oil with high acidity in miscella and found that the most suitable solvent was 96% ethanol, but observed that it was necessary to slightly hydrate the solvent to diminish loss of neutral oil.

In our study, a systematic and detailed investigation of liquid-liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions has been performed, and optimal extraction conditions for recovery of free fatty acids with minor loss of neutral oil were determined in bench-scale single-stage extractions.

MATERIALS AND METHODS

Sulfur olive oil samples used for this investigation were obtained from a local oil extraction plant in the southern Marmara Sea region of Turkey.

Artificially prepared mixtures of olive oil and oleic acid (E. Merck AG, Darmstadt, Germany) were used for determination of partition of free fatty acids and neutral oil in respective phases of extraction. Free fatty acids contents of these mixtures ranged from 5 to 50% by weight.

The effect of mono- and diglycerides on partition of the constituents between phases was determined by using artificial mixtures of olive oil, oleic acid and technical diolein (Fluka AG, Buchs, Switzerland). These mixtures had fixed contents of free fatty acids but varying percentages of mono- and diglycerides. Technical diolein used for this purpose has been examined by thin-layer chromatography (TLC) and its main constituents were determined as mono-, di-, and triglycerides. The respective hydroxyl values of these artificial mixtures were 13.2, 22.4, and 27.0 (9).

Chemically pure grade hexane (Merck) and 95.6% ethanol were used for preparation of respective miscella based on oil:hexane ratio by weight. The strength of the alcohol-water extraction solvent was diluted with distilled water in accordance with the experimental plan.

Single-stage liquid-liquid extractions were performed in separatory funnels at selected solvent:miscella ratios by volume. The funnels were hand-shaken each time for five minutes and then left still for 15–30 min for the phases to separate at room temperature (19–22°C).

The bottom alcoholic phases (extract phases) were

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first examined by TLC using Silica gel G coated plates and hexane/diethyl ether/acetic acid (70:30:1.5, v/v/v) as the solvent system (10). The free fatty acid contents of these phases were then determined by alkali titration.

After evaporating solvents from the raffinate phases, the residual oil in these phases and free acid contents of these oils were determined (9).

The extracted free fatty acid percentage (EFFA %) and extracted neutral oil percentage (ENO %) were calculated for each extraction experiment by the following definitions:

$$\text{EFFA \%} = \frac{\text{amount of free acid in extract phase}}{\text{amount of free acid in miscella}} \times 100$$

$$\text{ENO \%} = \frac{\text{amount of neutral oil in extract phase}}{\text{amount of neutral oil in miscella}} \times 100$$

RESULTS AND DISCUSSION

Figure 1 shows relationships of EFFA % to free fatty acid contents of olive oil-oleic acid (hexane) miscellas extracted with various aqueous ethanol solutions. The oil:hexane ratio in miscellas was 1:1 (w/w), and the solvent:miscella ratio was 1:1 (v/v).

EFFA % increased as free fatty acid content of the oils increased for 95.6, 90 and 85% ethanol solutions. But, the same values decreased slightly for extractions with 80% and more dilute solutions.

It wasn't possible to extract miscellas of oils with free acid contents of 40% or more with 95.6% ethanol because only one phase was obtained in these circumstances.

Figure 2 shows relationships of ENO % to free acid contents of the oils for the experiments described above. For extractions with 95.6, 90 and 85% ethanol solutions, ENO % increased as the acid content increased. Examination of these extract phases by TLC showed that they contained an appreciable amount of triglycerides besides the free fatty acids. For extractions with 80, 76.8 and 70% ethanol, ENO % was almost constant as FFA increased from 5% to 50%. The chromatogram obtained from TLC examination showed that only a minor amount of triglycerides was present in these phases.

The selectivity diagram for the systems oleic acid-olive oil-hexane-aqueous ethanol solution according to these extractions is presented in Figure 3.

The miscellas (oil:hexane, 1:1, w/w) of the three oils with 25% FFA but different partial glycerides con-

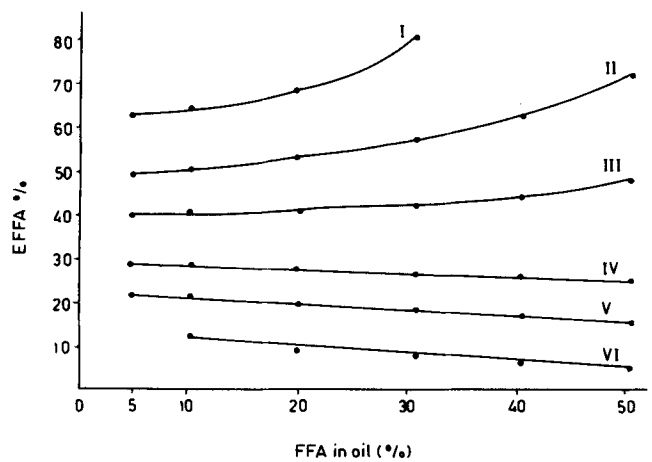

FIG. 1. Relationships of EFFA % to free fatty acid contents of olive oil-oleic acid mixtures: I, 95.6% ethanol; II, 90% ethanol; III, 85% ethanol; IV, 80% ethanol; V, 76.8% ethanol; VI, 70% ethanol.

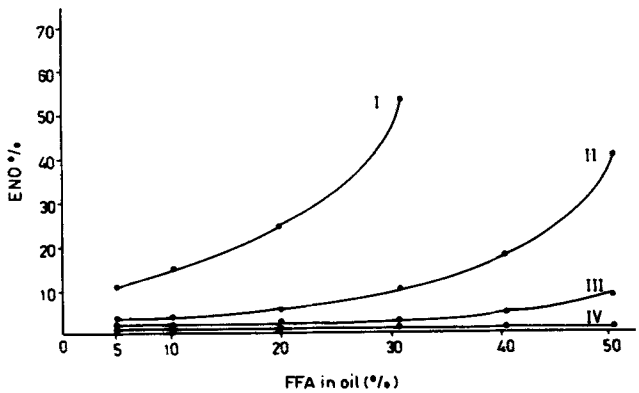

FIG. 2. Relationships of ENO % to free fatty acid contents of olive oil-oleic acid mixtures: I, 95.6% ethanol; II, 90% ethanol; III, 85% ethanol; IV, 80% ethanol.

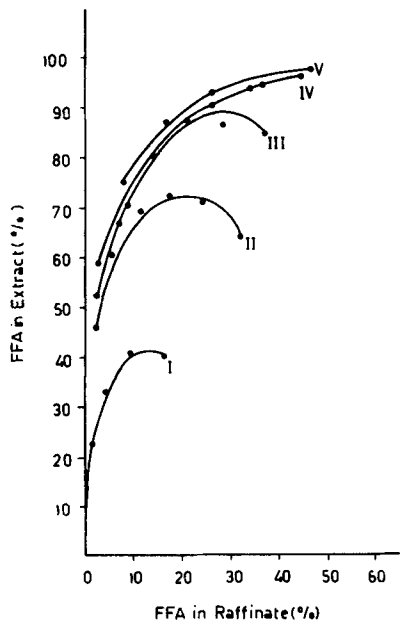

FIG. 3. Selectivity diagram for the systems olive oil-oleic acid-hexane-aqueous ethanol solutions: I, 95.6% ethanol; II, 90% ethanol; III, 85% ethanol; IV, 80% ethanol; V, 76.8% ethanol.

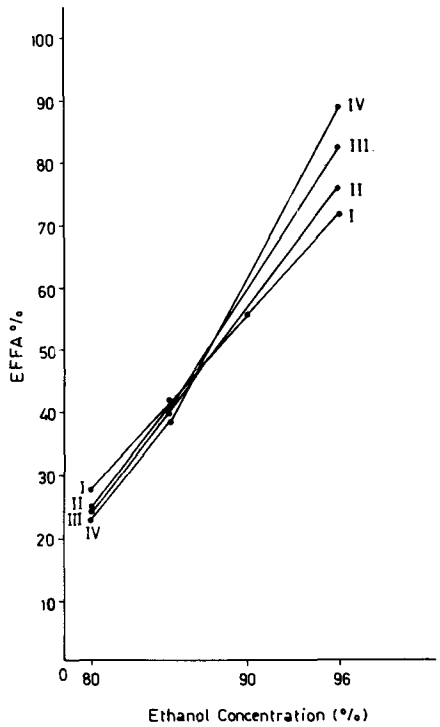

FIG. 4. Relationships of EFFA % to ethanol concentration for olive oil-oleic acid mixtures with different amounts of partial glycerides: I, the mixture containing no partial glycerides; II, the mixture containing partial glycerides (HV = 13.2); III, the mixture containing partial glycerides (HV = 22.4); and IV, the mixture containing partial glycerides (HV = 27.0).

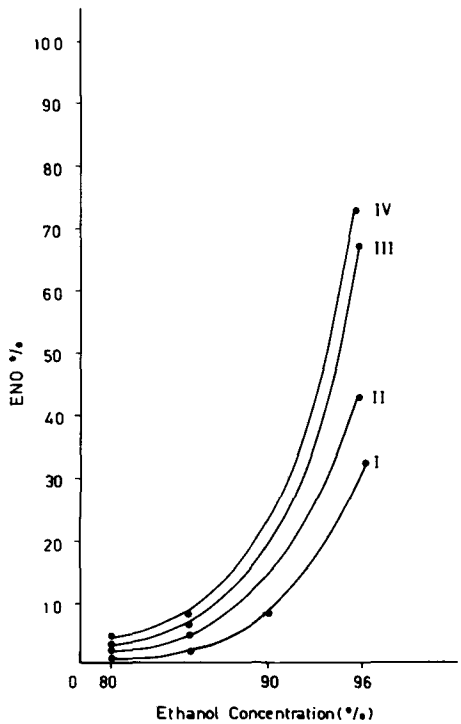

FIG. 5. Relationships of ENO % to ethanol concentration for olive oil-oleic acid mixtures with different amounts of partial glycerides: I, the mixture containing no partial glycerides; II, the mixture containing partial glycerides (HV = 13.2); III, the mixture containing partial glycerides (HV = 22.4); IV, the mixture containing partial glycerides (HV = 27.0).

tents were extracted with 95.6, 85 and 80% ethanol solutions using 1:1, v/v, solvent:miscella ratios, and the results were compared with those of olive oil-oleic acid mixtures with the same FFA. Figure 4 shows that as the partial glycerides content of the oil increased EFFA % increased for 95.6% ethanol. This means that the partial glycerides increased solubility of fatty acids in 95.6% ethanol. But, for extractions with 85 and 80% ethanol solutions, EFFA % decreased slightly as partial glycerides in the oil increased. This means that the partial glycerides decreased solubility of fatty acids in these solvents.

As can be seen in Figure 5, ENO % increased considerably for 95.6% ethanol as the partial glycerides content increased. For 85 and 80% ethanol, these values also increased, but TLC examination showed (especially for extractions with 80% ethanol) that the extracted neutral oil consisted mainly of mono- and diglycerides, and practically no triglycerides were extracted under these circumstances.

In this part of the study, sulfur olive oil miscellas (oil:hexane, 1:1, w/w) were extracted with 70 and 80% ethanol solutions, with the solvent:miscella ratio changing from 1:1 to 12:1 (v/v). The FFA of the oil was 35.6%.

Figures 6 and 7 show relationships of EFFA % and ENO % to the solvent:miscella ratio. In these experiments, especially for extractions with 80% ethanol, the

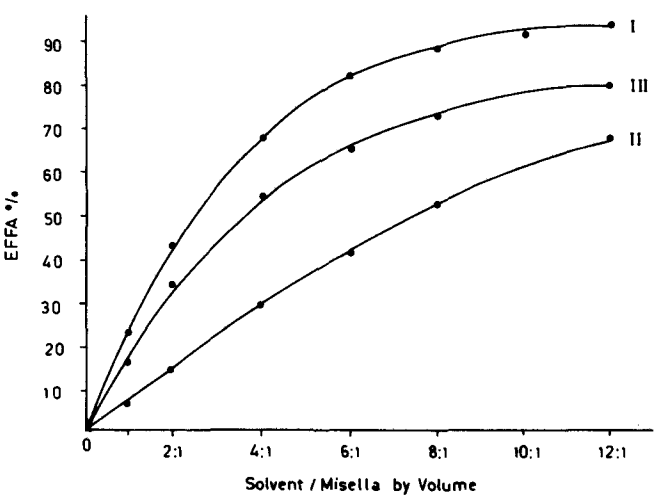

FIG. 6. Relationships of EFFA % to solvent:miscella ratios: I, 80% ethanol; II, 70% ethanol; III, 80% ethanol saturated with hexane.

appearance of the raffinate phase changed as the amount of the solvent increased. When solvent:miscella were 10:1 and 12:1, the alcoholic phase became the upper phase and the oil phase became the bottom phase. This

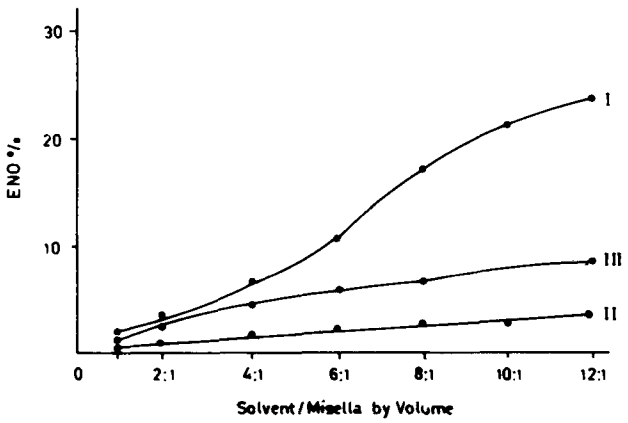

FIG. 7. Relationships of ENO % to solvent:miscella ratios: I, 80% ethanol; II, 70% ethanol; III, 80% ethanol saturated with hexane.

means an appreciable amount of hexane was soluble in the extract phase. The increase in ENO % above the solvent miscella ratio of 6:1 in Figure 7 was greatly affected by mutual solubilities of solvents, and it became difficult to separate the phases as their densities became similar. But these difficulties were overcome when the ethanol solutions were saturated with hexane before extraction. The results obtained with 80% ethanol saturated with hexane are shown in Figures 6 and 7.

Changes in oil:hexane ratio of miscella from 1:2 to 2:1 (w/w) did not have any significant effect on extraction results. Table 1 shows results obtained from extractions of sulfur olive oil miscellas containing 36.8% FFA with 70% ethanol saturated with hexane. The solvent:miscella ratio was 8:1 (v/v).

Based on these experiments, it was concluded that to reduce triglyceride loss during deacidification, extraction of the miscella with 80% or more dilute ethanol is preferred. It was also noted that under these circumstances EFFA % is not affected by increases in FFA and partial glyceride content of the sulfur olive oil, and the solvent must be saturated with hexane before extraction.

TABLE 1

Extraction of Miscellas with Different Compositions by 70% Ethanol Saturated with Hexane

Oil:hexane ratio in miscella (w/w)	EFFA %	ENO %
1:2	45.1	2.18
1:1	44.1	2.22
2:1	43.2	2.54

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