Deacidification of Sulfur Olive Oil. II. Multi-Stage Liquid-Liquid Extraction of Miscella with Ethyl Alcohol

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In this study, laboratory-scale multi-stage cross- and counter-current extractions of sulfur olive oil miscella with 70 and 80% ethanol saturated with hexane were investigated. For cross-current extraction, the extraction factor for free fatty acids was constant in each extraction stage. Therefore, the extraction factors determined in single-stage extractions were used to calculate the extracted free fatty acid percentages for cross-current and counter-current multi-stage extractions and results were in close agreement with the experimental data. It was possible to determine the amount of solvent and the number of stages required for counter-current extraction to remove the desired amount of free fatty acids from a given sulfur olive oil with 70 or 80% ethanol. Comparison of the results for these two solvents showed that 80% ethanol was more suitable.

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 cake by solvent extraction. It contains a relatively high proportion of free fatty acids, partial glycerides and some oxidation products as the result of rapid enzymatic hydrolysis and oxidation of oil in press cake during storage for later extraction.

Deacidification of high-acid oil can be accomplished by liquid-liquid extraction, because the solubilities of fatty acids and triglycerides in various organic solvents are different. In a previous paper (1), liquid-liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions was investigated, and optimal extraction conditions for deacidification of sulfur olive oil with minor loss of neutral oil were determined in bench-scale single-stage extractions. To ensure deacidification with a low triglyceride loss, it was appropriate to extract the miscella with 70 or 80% ethanol solution. Extracted free fatty acid percentage was 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 miscellas from 1:2 to 2:1 by weight did not have any significant effect on extraction results.

In this part of the study, laboratory-scale multi-stage cross- and counter-current extractions of sulfur olive oil miscella with 70 and 80% ethanol were performed at optimal extraction conditions (1). It was possible to determine the amounts of the solvents and the number of stages for counter-current extraction to obtain prerefined oil and fatty acids from a given sulfur olive oil.

MATERIALS AND METHODS

Materials. Sulfur olive oil used in this study was obtained from a local oil extraction plant in the Southern Marmara Sea region of Turkey. Artificial miscellas of sulfur olive oil and hexane (E. Merck, Darmstadt, Germany) were prepared based on oil/hexane weight ratios. For extraction, 70 and 80% aqueous ethanol saturated with hexane were used at selected solvent/miscella volume ratios.

Cross-current multistage extraction. Laboratory-scale cross-current multi-stage extraction was carried out in separatory funnels at room temperature. In these experiments, after separating alcoholic phases obtained in the first stage, the same volume of fresh solvent was added to the raffinate left in the funnel. These operations were repeated until the last stage of extraction.

Counter-current extraction. For laboratory-scale counter-current extraction, the "Batch Simulation of Continuous Processes" was used (2,3). This procedure was carried out with separatory funnels according to the plan shown in Figure 1. The upper part of this Figure shows the extraction pattern that was followed for batch simulation of the five-stage continuous countercurrent extraction process shown at the bottom. Each of the circles

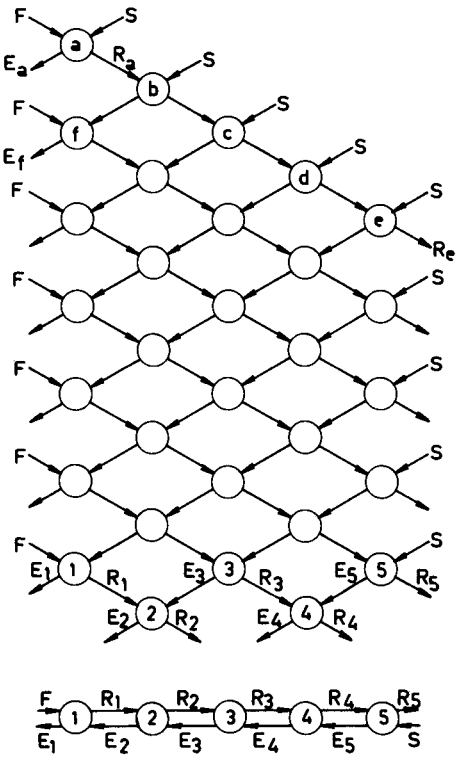

FIG. 1. Batch simulation of five-stage continuous countercurrent extraction.

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represents a batch shake-out. The procedure consisted of repeated injections of feed material and solvent into a series of batch extractions, plus withdrawal of extract and raffinate phases. The overall result was actually continuous, not batch, because feed and solvent were introduced intermittently. After a number of cycles of feed and solvent introductions, extraction, and product removal, the systems approached steady-state and the liquids in funnels should resemble the streams that would exist in true counter-current continuous extraction.

Analyses. The free fatty acid contents of the extract phases obtained separately were determined by alkali titration. After evaporating the solvent from the raffinate phase, the residual oil in this phase and free fatty acid content of this oil were determined.

The extracted free fatty acid percentage (EFFA %) and the extracted neutral oil percentage (ENO %) were calculated by using the following equations:

$$\text{EFFA \%} = \frac{\text{Amount of free acid in extract phase}}{\text{Amount of free acid in miscella}} \times 100 \quad [1]$$

$$\text{ENO \%} = \frac{\text{Amount of neutral oil in extract phase}}{\text{Amount of neutral oil in miscella}} \times 100 \quad [2]$$

RESULTS AND DISCUSSION

Table 1 shows the results obtained from multi-stage cross-current extractions of sulfur olive oil (FFA % = 36.8) miscella with 70% ethanol saturated with hexane. The oil/hexane ratio in miscella was 1:1 by weight and the solvent/miscella ratio was 8:1 volume for each stage.

As can be seen in Table 1, EFFA % were nearly the same in each stage. Therefore, the extraction factor of free fatty acids (E_{FFA}) was constant in each stage, because this factor was calculated according to (4):

$$E = \frac{\text{Quantity of the component in the extract phase}}{\text{Quantity of the component in the raffinate phase}} \quad [3]$$

We can also describe the extraction factor of free fatty acids as a function of EFFA %:

$$E_{FFA} = \text{EFFA \%}/100 - \text{EFFA \%} \quad [4]$$

TABLE 1

Multi-Stage Cross-Current Extraction of Sulfur Olive Oil Miscella with 70% Ethanol

Number of stages	For all stages		For each stage	
	EFFA %	ENO %	EFFA %	E_{FFA}
1	44.12	2.22	44.12	0.79
2	69.87	3.14	45.46	0.83
3	84.02	4.20	46.50	0.87
4	90.81	4.98	46.18	0.86
5	94.36	6.84	46.07	0.85
6	96.62	7.67	43.17	0.76

When EFFA % is the same in each stage, E_{FFA} will be constant in each stage.

In the previous paper (1), we concluded that EFFA % was not affected by increases in FFAs and partial glycerides contents of sulfur olive oil for 70 and 80% ethanol. This means that extraction factors of free fatty acids are practically constant for all sulfur olive oil samples.

When the extraction factor is constant, it is possible to calculate the percentage of extracted component (ψ) and of non-extracted component (ϕ) for multi-stage extractions by means of the following equations (4). For cross-current extraction,

$$\phi = 100/(E+1)^n \quad [5]$$

$$\psi = 100 - \phi \quad [6]$$

For countercurrent extraction,

$$\phi = 100\ (E-1)/(E^{n+1}-1) \quad [7]$$

$$\psi = 100 - \phi \quad [8]$$

where n = number of stages.

TABLE 2

Experimental and Calculated Values of EFFA % and ENO %

Number of stages	EFFA %		ENO %	
	Experimental	Calculated	Experimental	Calculated
1	44.12	44.12	2.22	2.22
2	69.87	69.79	3.14	4.45
3	84.02	82.56	4.20	6.59
4	90.81	90.26	4.98	8.70
5	94.36	94.56	6.84	10.75
6	96.62	96.96	7.67	12.75

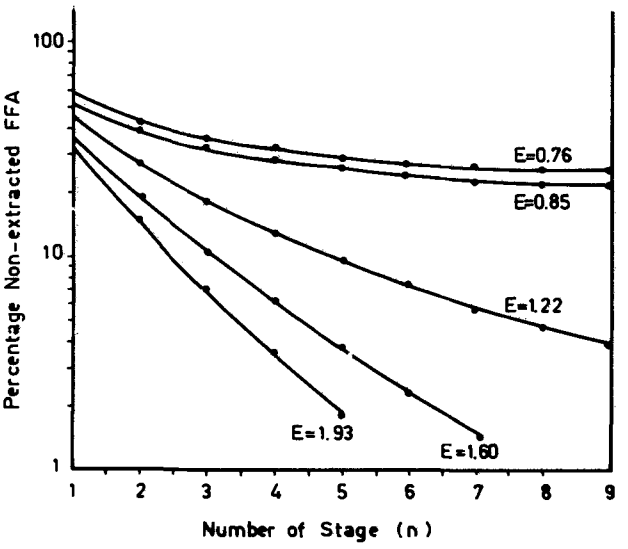

FIG. 2. Relationships between the number of stages (n) and the percentage of nonextracted FFA (ϕ) for counter-current extractions at various E values.

If we experimentally determine the extraction factor of free fatty acids in a single-stage extraction, then we can calculate EFFA % for all of the stages of multi-stage cross- and counter-current extractions. We can also calculate ENO %, if the extraction factor of neutral oil is constant in each stage. But in the previous paper (1), we concluded that ENO % was affected by increasing partial glyceride contents of sulfur olive oil. This means that the extraction factor of neutral oil was not constant in each stage and for all sulfur oil samples.

Table 2 shows experimental and calculated values of EFFA % and ENO % for cross-current extraction of sulfur olive oil miscella with 70% ethanol described above. As can be seen, the experimental and calculated values of EFFA % were close to each other, but the values of ENO % were different.

Even though it was possible to predict the amount of fatty acids that would be extracted from a given sulfur olive oil under various extraction conditions, it was not possible to predict the amount of neutral oil by applying Equations [6] and [8]. However, with ENO % generally being small compared with EFFA %, it was possible to calculate the amounts and compositions of the raffinate and the extract that would be obtained from a sulfur olive oil of given composition. In fact, results calculated in this way were in agreement with the experimental data in both

TABLE 3

Four Stages of Cross-Current Extraction of Sulfur Olive Oil Miscella with 70% Ethanol[a]

			Amount (%)		FFA %	
	EFFA %	ENO %	Raffinate	Total extract	Raffinate	Total extract
Experimental	89.86	6.03	63.12	36.88	5.91	89.7
Calculated	89.58	9.76	60.87	39.13	6.30	84.3

[a]Oil/hexane, 2:1, w/w; solvent/miscella, 8:1 v/v, in each state; E_{FFA}, 0.76; and E_{NO}, 0.026; as determined from single-stage extraction.

TABLE 4

Five Stages of Cross-Current Extraction of Sulfur Olive Oil Miscella with 80% Ethanol[a]

			Amount (%)		FFA (%)	
	EFFA %	ENO %	Raffinate	Total extract	Raffinate	Total extract
Experimental	97.39	14.13	55.23	47.77	1.74	80.00
Calculated	98.15	20.15	50.94	49.06	1.34	73.50

[a]Oil/hexane, 1.5:1, w/w; solvent/miscella, 4:1, v/v, in each stage; E_{FFA}, 1.22; and E_{NO}, 0.047; as determined from single-stage extraction.

TABLE 5

Five Stages of Counter-Current Extraction of Sulfur Olive Oil Miscella with 70% Ethanol[a]

			Amount (%)		FFA (%)	
	EFFA %	ENO %	Raffinate	Extract	Raffinate	Extract
Experimental	68.10	3.81	72.53	27.47	16.2	91.2
Calculated	70.27	2.60	72.50	27.50	15.1	94.0

[a]Oil/hexane, 2:1, w/w; solvent/miscella, 8:1, v/v; E_{FFA}, 0.76; and E_{NO}, 0.026.

TABLE 6

Five Stages of Counter-Current Extraction of Sulfur Olive Oil Miscella with 80% Ethanol[a]

			Amount (%)		FFA (%)	
	EFFA %	ENO %	Raffinate	Extract	Raffinate	Extract
Experimental	93.46	8.60	60.17	39.83	4.00	86.4
Calculated	90.42	4.71	63.83	36.25	5.53	91.89

[a]Oil/hexane, 1.5:1, w/w; solvent/miscella, 4:1, v/v; E_{FFA}, 1.22; and E_{NO}, 0.047.

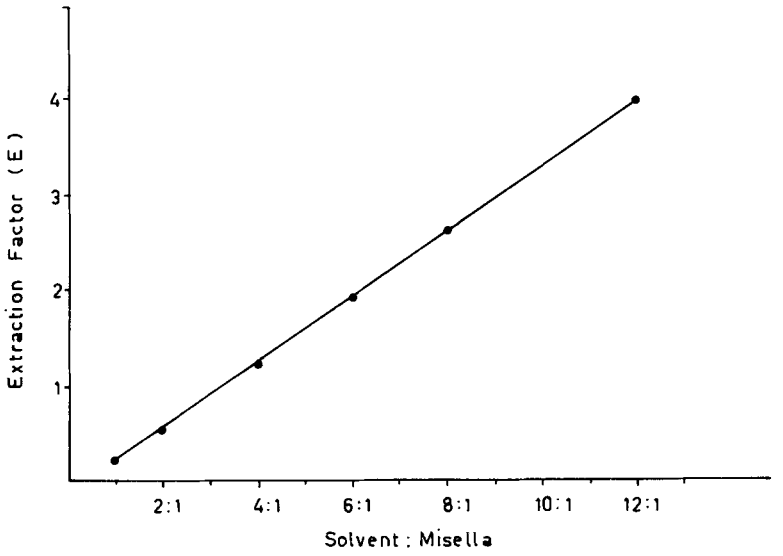

FIG. 3. Relationships between E_{FFA} and solvent/miscella ratio (v/v).

multi-stage cross- and counter-current extractions.

Table 3 shows results obtained from four stages of cross-current extraction of miscella with 70% ethanol, and Table 4 shows results from five stages of cross-current extraction of miscella with 80% ethanol. The results obtained from five stages of counter-current extraction of miscella with 70 and 80% ethanol are shown in Tables 5 and 6.

In Figure 2, the relationships of number of stages to percentage of nonextracted fatty acids (ϕ), calculated according to Equation [7], are presented. Using this graph, it was possible to determine the number of stages, amount of solvent, and the concentration of ethanol solution required to remove the desired amount of FFA.

If 70% ethanol is used at a solvent/miscella ratio of 8:1, E_{FFA} would be 0.76 (for oil/hexane, 2:1), and it would be possible to extract approximately 75% of the free fatty acids in nine stages. If 80% ethanol is used at a solvent/miscella ratio of 4:1, E_{FFA} would be 1.22 (for oil/hexane, 1.5:1) and EFFA % would be 96% in the same number of stages.

Relationships of E_{FFA} with solvent/miscella ratios for 80% ethanol saturated with hexane are shown in Figure 3. The values of E_{FFA} in this graph were calculated by using EFFA % values determined experimentally in the previous paper (1).

It was possible to determine the amount of solvent from these two graphs. For example, when solvent/miscella ratio was 3:1 (E_{FFA} = 0.85), it was possible to extract 70% of the total free fatty acid content in five stages; and when the solvent/miscella ratio was 5:1 (E_{FFA} = 1.60), EFFA % was 96.5% with five stages.

It has been shown that the removal of free fatty acids from the high-acid sulfur olive oil could be performed with low neutral oil loss by counter-current extraction of sulfur oil miscella with 80% ethanol. The refining factor (R) was 39.83/36.8 = 1.08 (experimental results in Table 6) and prerefined oil and technical grade fatty acids were obtained.

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