Characteristics of Laboratory-Processed *Cucurbita foetidissima* Seed Oil

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ABSTRACT

The effects of variations in laboratory processing on the quality of the seed oil of the buffalo gourd, *Cucurbita foetidissima*, were determined. Conditions found most effective were: triple refining at 65 C for 15 min using 16°Be and 20°Be NaOH at 80% of maximum and 20°Be NaOH at the maximum; bleaching at 105 C for 30 min by a mixture of activated bleaching earth (3%) and activated carbon (0.3%); and deodorization with 5% steam at 210 C for 120 min. Processed oil showed these analytical values: carotenoids (3.6 mg/kg), free fatty acids (0.28%), peroxide (0.2 meq/kg), conjugated unsaturated fatty acids (1.59%). Oxidative stability test (AOM) conditions gave peroxide values of 100 in 4.9 hr and 141 in 8 hr. The triglyceride fatty acid composition was 11.9% palmitic, 3.5% stearic, 22.0% oleic and 61.0% linoleic acid.

INTRODUCTION

Curtis (1) first recognized the possible economic value of the seed oil and protein of the buffalo gourd, *Cucurbita foetidissima* HBK, a feral xerophytic cucurbit indigenous to the dry lands of western and southwestern United States and northern Mexico. Ault et al. (2) reported certain physical and chemical characteristics of the oil, and Bolley et al. (3) characterized the oil as a "soft" drying oil with similarities to soybean oil.

Shahani et al. (4) investigated the crude oil of seed harvested from gourds produced one year earlier. The crude oil had a dark color and proved very resistant to bleaching. Processed oil had good stability and did not undergo flavor reversion, but the color at all stages of processing was darker than that of other common edible oils. The abnormal pigmentation was attributed to alteration of color bodies in the seed by weathering of the gourds in the field.

Interest in the buffalo groud as a possible crop for arid areas has been renewed as the cost and availability of water for agricultural use has come under pressure from desertification and urbanization. An interdisciplinary research program at this university has emphasized breeding and utilization of the plant (5). Hybrids have been developed which produce seed of higher quality in greater yield than feral plants. The oil content range is 35-41%, and the properties of the oil and crude commercial vegetable oils have been shown to be similar (6). Preliminary experiments indicated that processing conditions could be selected to produce an oil equivalent in color to commercial vegetable oils.

The purpose of this study was to determine the effects of variations in laboratory processing conditions on levels of substances in buffalo gourd oil which affect its quality as a potential edible oil.

EXPERIMENTAL PROCEDURES

Pepos of *C. foetidissima* were harvested at the University of Arizona Experiment Station at the end of the growing season. They were crushed and dried, and the seed was separated in a Vogel thresher. A composite sample was prepared from open-pollinated seed lots representing genetically diverse germ plasm. It was shown to contain 36.0% crude oil and 32.0% crude protein by proximate analysis.

Seed ground to -10 mesh in a Wiley mill was extracted continuously for 24 hr with hexane in a Lloyd extractor of 1 gal capacity. The crude oil was isolated after filtration of the hexane solution and recovery of the solvent under reduced pressure.

Crude oil samples were subjected to refining, bleaching and deodorization under a variety of conditions. Properties of the crude oil have been reported previously (6). Experiments were performed in laboratory-scale equipment, so data are not reported for refining losses and processing efficiency, which are of practical value only if measured in a Barrow-Agee apparatus (7), or on a pilot-scale basis. The effect of processing variations on oil quality was determined by measuring carotenoids, free fatty acid (FFA), peroxide, conjugated unsaturated acids and oxidative stability. The triglyceride fatty acid profile was determined for a sample processed under conditions found to be most desirable. Means are reported for processing procedures done in duplicate and analytical determinations performed in triplicate.

Refining was done by charging 1,500 g of oil into a 3-necked, round-bottomed flask fitted with a thermometer and stirred magnetically. The oil was heated to 65 C under nitrogen, the required amount of alkali solution was added, and heating was continued for 15 min. The mixture was cooled to 30 C without agitation to aid settlement of foots, which were separated by centrifugation at 3,600 rpm. The oil was washed 3 times with deionized water (20% of oil weight) at 65 C under nitrogen and then centrifuged. The washed sample was dried at 90 C under vacuum for 30 min, cooled to 30 C, and flushed with nitrogen.

Refining experiments involved 1, 2 or 3 treatments with NaOH solutions of different concentrations (7). With double and triple refining, the second and third treatments were applied after foots separation and prior to washing.

Bleaching was done with commercial activated bleaching earth (Superfiltrol 105, Filtrol Corp.), natural bleaching earth (Official, Am. Oil Chem. Soc.) and activated carbon ("Nuchar" C-190N, Matheson Coleman & Bell), individually or in combinations. The appropriate amount of bleaching material, indicated in the tables of data, was added to 500 g of oil at 25 C, pressure was reduced to 5 mm Hg, and agitation was provided by a magnetic stirring bar. The temperature was raised to 110 C, maintained for 30 min, decreased to 30 C, and the vacuum broken with nitrogen. Celite filter aid (0.5%, w/w) was added, and the sample was filtered with suction through a Whatman No. 42 paper.

Deodorization was done in an apparatus consisting of a 500-mL 3-necked round-bottomed flask fitted with a thermometer, a microburet, and a Claisen head connected through condensing traps to a vacuum pump. The thermometer and microburet extended to the bottom of the flask. Bleached oil (100 g) was placed in the flask, and the pressure in the system was reduced to 5-8 mm Hg while the oil was agitated by a magnetic stirring bar and heated to the desired temperature. Water delivered from the microburet into the oil vaporized instantly, sweeping volatile

substances from the oil into the condensing system. When deodorization was completed, the water remaining in the buret was discarded, the buret was filled with 1% aqueous citric acid, and the proper volume was delivered into the oil during cooling. When the oil had cooled to 30 C, the vacuum was broken with nitrogen.

Carotenoid content was measured spectrophotometrically using 1-cm matched silica cells. Oil samples were dissolved in cyclohexane (2.5%, w/v) and the spectra recorded in the range 350-550 mμ. For the quantitative determination of total carotenoids, the absorbance was read at 417 mμ (8).

FFA (as percentage of total fatty acid composition), peroxide, and the active oxygen stability determinations were done by methods described in the AOCS Official and Tentative Methods (7).

Conjugated dienoic acid content was determined by ultraviolet (UV) spectrophotometry in the region 200-260 mμ using a cyclohexane solution (0.05%, w/v); the same solution was used to detect conjugated trienoic and tetraenoic acids in the region 230-310 mμ (9).

Oil samples were prepared for gas liquid chromatography (GLC) by transesterification with acidic methanol (10). The methyl esters were purified by column chromatography on Silica Gel G. Methyl esters were separated on a Beckman GC-5 chromatograph under the following conditions: 6 ft × 1/8 in. stainless steel column packed with 5% Silar SCP on Chromsorb W (100-120 mesh); isothermal operation at 170 C; injector 200 C; detector 200 C; nitrogen carrier gas 20 mL/min.

RESULTS AND DISCUSSION

Refining

The effects of variations in single-, double- and triple-refining on oil properties before bleaching and deodorization are presented in Table I. Carotenoids and FFA were decreased during refining, and the decreases were directly proportional to the number of treatments. Refining had little influence on the total level of conjugated fatty acids, but a shift in the relative amounts of dienoic and trienoic species was noticeable. These effects have been observed not only during refining of edible oils but also during other unit operations to which these oils are subjected (11-15). The change is apparently due not only to interconversion of trienoic and dienoic species, but also to formation of hydroperoxides which are subsequently destroyed during bleaching (15). The increase in peroxide value (PV) which was noted in this work has been observed previously during refining (13).

The effects of refining variations on properties of bleached oil were determined by using a sequence of refining variations followed by bleaching with 2% Superfiltrol 105 + 0.2% activated carbon at 105 C for 30 min in all cases. Data are shown in Table II.

Carotenoids were decreased during bleaching in proportion to their concentration in the refined oils, indicating that the adsorption capacity of the bleaching earth was independent of the refining process used. The concentrations of pigment in the oil samples treated by variations in triple-refining were nearly the same (3.7 and 5.9 mg/kg).

Differences between samples refined in 3 steps were probably due to an increase in decomposition of pigments as a result of multiple refining. The modified pigments were then more susceptible to adsorption by the bleaching earth (11). Because the levels of carotenoids found in the resulting deodorized oils (Table III) were similar to the levels in the bleached oils, this conclusion appears substantiated.

FFA increased during bleaching, particularly in the oils subjected to double- or triple-refining, but only a slight increase occurred in oils refined with 16°Be NaOH in a single step. Bleaching is considered to have little effect on the acidity of oils, but the activated bleaching earth used could have been partially responsible. It has been reported that activated bleaching earths may decompose soaps that adsorb the sodium ions and leave FFA (16). The action may have been enhanced by the multiple-refining processes with their stressful effect on triglycerides.

The bleached oils showed no significant changes in conjugated fatty acid levels in comparison to the levels found in the refined oils. PV were lower than corresponding refined samples. Peroxides, already present before refining of the oils, or formed during that step by oxidation reactions (13), are known to be extensively destroyed during the bleaching process (15).

TABLE I

Effects of Refining Variations on *C. foetidissima* Oil and Characteristics of Refined Oils

Refining methods	Carotenoids (mg/kg oil)	Free fatty acids (%)	Peroxide value (meq/kg oil)	Conjugated fatty acids	
				Dienoic (%)	Trienoic (%)
Crude oil	96.7	1.81	5.4	1.54	0.75
Single-refining processes					
12°Be NAOH (phosphoric acid pretreatment)[a]	77.4	0.18	16.8	1.52	0.00
14°Be NaOH + 0.5% NaOH excess	71.6	0.10	20.6	1.47	0.00
16°Be NaOH	58.9	0.05	8.2	2.13	0.00
20°Be NaOH	54.5	0.06	8.5	1.20	0.00
Double-refining processes					
66.7% max. 12°Be NaOH; max. 12°Be NaOH	56.8	0.09	42.0	1.59	0.62
50.0% max. 16°Be NaOH; 66.7% max. 16°Be NaOH	39.0	0.21	2.9	1.06	0.76
Triple-refining processes					
80% max. 12°Be NaOH; 80% max. 16°Be NaOH; max. 16°Be NaOH	32.4	0.06	7.5	1.16	0.00
80% max. 16°Be NaOH; 80% max. 20°Be NaOH; max. 20°Be NaOH	33.1	0.08	20.3	1.58	0.69

[a]Crude oil pretreated with 0.2% phosphoric acid and degummed with 2% deionized water.

TABLE II

Effects of Refining Variations on *C. foetidissima* Oil and Characteristics of Bleached Oils[a]

Refining methods	Carotenoids (mg/kg oil)	Free fatty acids (%)	Peroxide value (meq/kg oil)	Conjugated fatty acids	
				Dienoic (%)	Trienoic (%)
Single-refining processes					
12°Be NAOH (phosphoric acid pretreatment)[b]	8.9	2.21	5.3	0.84	0.71
14°Be NaOH + 0.5% NaOH excess	8.9	0.17	12.1	2.68	0.49
16°Be NaOH	8.0	0.07	6.0	0.64	0.85
20°Be NaOH	9.1	0.07	3.1	0.58	0.80
Double-refining processes					
66.7% max. 12°Be NaOH; max. 12°Be NaOH	10.0	0.13	4.2	1.06	0.42
50.0% max. 16°Be NaOH; 66.7% max. 16°Be NaOH	6.1	1.09	4.2	1.64	0.57
Triple-refining processes					
80% max. 12°Be NaOH; 80% max. 16°Be NaOH; max. 16°Be NaOH	5.9	0.15	3.8	0.71	0.34
80% max. 16°Be NaOH; 80% max. 20°Be NaOH; max. 20°Be NaOH	3.7	0.18	5.8	0.85	0.51

[a]Bleached at 105 C for 30 min using 2% Superfiltrol 105 + 0.2% activated carbon.
[b]Crude oil pretreated with 0.2% phosphoric acid and degummed with 2% deionized water.

The effects of refining variations on properties of deodorized oil were determined by a processing sequence consisting of refining variations, bleaching with 2% Superfiltrol 105 + 0.2% activated carbon at 105 C for 30 min, and deodorization with 5% steam at 210 C for 120 min. Data are given in Table III.

Deodorized oils which received single-step refining had dark color and elevated FFA. Oils refined in a single step with 14, 16, or 20°Be NaOH showed poor stability properties, as indicated by PV of 237-253 after 8 hr of aeration; about 4 hr were required to reach a value of 100. However, if crude oil was pretreated with 0.2% phosphoric acid, degummed with 2% water and refined with 12°Be NaOH, it gave deodorized oil which showed better stability toward oxidation with PV of 161 after 8 hr of aeration and 100 after 7 hr. PV of the deodorized oil was zero, which differed greatly from values for the other deodorized oils. Phosphoric acid pretreatment of oils is known to favor final quality characteristics, especially oxidative and flavor stability (17-19). Prooxidant metals are inactivated by this pretreatment, minimizing oxidation and related processing difficulties (20-22).

Deodorized oil quality was highest when triple-refining was used. Conjugated fatty acid levels showed little variation and were not different from levels found in the bleached oils. PV, although still elevated for a deodorized

TABLE III

Effects of Refining Variations on *C. foetidissima* Oil and Characteristics of Deodorized Oils[a]

Refining methods	Carotenoids (mg/kg oil)	Free fatty acids (%)	Peroxide value (meq/kg oil)	Conjugated fatty acids		Stability (AOM)	
				Dienoic (%)	Trienoic (%)	PV[c] after 8 hr	hr to PV = 106
Single-refining processes							
12°Be NaOH (phosphoric acid pretreatment)[b]	6.1	0.38	0.0	1.59	0.36	160.5	6.6
14°Be NaOH + 0.5% NaOH excess	6.7	0.29	1.6	1.47	0.37	245.7	3.5
16°Be NaOH	8.4	0.12	3.9	1.00	0.55	252.8	3.8
20°Be NaOH	9.5	0.16	3.2	0.89	0.43	236.8	3.8
Double-refining processes							
66.7% max. 12°Be NaOH; max. 12°Be NaOH	12.0	0.18	1.2	1.08	0.82	189.5	4.3
50.0% max. 16°Be NaOH; 66.7% max. 16°Be NaOH	10.0	0.19	1.0	1.64	0.65	256.2	5.3
Triple-refining processes							
80% max. 12°Be NaOH; 80% max. 16°Be NaOH; max. 16°Be NaOH	6.0	0.13	4.2	0.91	0.41	155.6	4.3
80% max. 16°Be NaOH; 80% max. 20°Be NaOH; max. 20°Be NaOH	3.6	0.28	0.2	1.11	0.48	140.6	4.9

[a]Bleached at 105 C for 30 min using 2% Superfiltrol 105 + 0.2% activated carbon. Deodorized with 5% steam at 210 C for 120 min; 0.01% citric acid added during cooling.
[b]Crude oil pretreated with 0.2% phosphoric acid and degummed with 2% deionized water.
[c]PV = peroxide value.

TABLE IV

Effects of Bleaching Variations on Refined *C. foetidissima* Oils[a] and Characteristics of Bleached Oils

Bleaching treatments	Carotenoids (mg/kg oil)	Free fatty acids (%)	Peroxide value (meq/kg oil)	Conjugated fatty acids	
				Dienoic (%)	Trienoic (%)
1% Superfiltrol 105	21.2	0.13	19.3	1.14	0.29
2% Superfiltrol 105	10.5	0.19	7.1	1.39	0.63
Superfiltrol 105 + 0.2% act. carbon	3.7	0.18	5.8	0.85	0.51
3% Superfiltrol 105	5.0	0.24	3.5	0.81	0.50
3% Superfiltrol 105 + 0.3% act. carbon	5.3	0.45	7.8	1.10	1.01
3% Natural blch. earth	13.8	0.10	2.5	0.97	0.78
3% Natural blch. earth + 0.2% act. carbon	48.2	0.09	3.8	0.99	0.71
4.67% Natural blch. earth	10.9	0.14	0.9	0.65	0.62
1% Act. carbon	5.9	0.03	0.9	1.12	0.00

[a]Triple-refined with 80% max. 16°Be NaOH, 80% max. 20°Be NaOH, and max. 20°Be NaOH; each step at 65 C for 15 min.

oil, were usually reduced from the values found in the bleached samples.

A triple-refining process is recommended for purification of *C. foetidissima* oil. The first step would use 80% of the maximal amount of 16°Be NaOH solution required to neutralize the fatty acid content of the crude oil. This treatment should be followed by a second step using 80% of the maximal required amount of a 20°Be NaOH solution and a third step using the maximal amount of this alkali solution.

Bleaching

The effects of variations in bleaching conditions on quality of bleached oil were determined with refined oil prepared by a triple-refining process using 16°Be and 20°Be NaOH solutions. The refined oil was bleached with natural or activated bleaching earths or activated carbon used individually and in combinations. Conditions used and product properties are shown in Table IV.

A mixture of 2% Superfiltrol 105 + 0.2% activated carbon decreased carotenoids most effectively (from 33.1 to 3.7 mg/kg oil). Natural bleaching earth alone and in combination with activated carbon was very effective in maintaining a low level of FFA, but activated carbon used alone was the superior agent in this respect (from 0.08 to 0.03%). Total conjugated fatty acids was reduced from 2.3% in the refined oil to about 1.4% in some of the bleached oil samples.

The effects of bleaching variations on deodorized oil were determined by deodorizing all bleached samples with 5% steam at 210 C for 120 min. Properties of the deodorized oils are given in Table V.

The oil sample bleached with 3% natural bleaching earth + 0.3% activated carbon produced a deodorized oil with better stability properties. Its PV were 114 after 8 hr aeration and 100 after 5.6 hr. However, this sample was dark in color and had a carotenoid level of 13 mg/kg oil and a PV of 3 meq/kg oil.

The sample of oil bleached with 2% Superfiltrol 105 + 0.2% activated carbon showed similar stability, as indicated by PV of 141 after 8 hr aeration and 100 after 5 hr. This sample also had the lowest carotenoid value (3.6 mg/kg). Thus, treatment of *C. foetidissima* oil with 2% Superfiltrol 105 or comparable commercial activated bleaching earth, in combination with 0.2% of activated carbon, can produce a bleached oil with better chemical properties and oxidative stability than oils produced by other bleaching treatments.

TABLE V

Effects of Bleaching Variations on Refined *C. foetidissima* Oils[a] and Characteristics of Deodorized Oils[b]

Bleaching treatments[c]	Carotenoids (mg/kg oil)	Free fatty acids (%)	Peroxide value (meq/kg oil)	Conjugated fatty acids		Stability (AOM)	
				Dienoic (%)	Trienoic (%)	PV[d] after 8 hr	hr to PV = 100
1% Superfiltrol 105	21.2	0.27	15.6	1.32	0.28	309.8	2.3
2% Superfiltrol 105	11.5	0.28	0.4	1.30	0.41	300.2	3.1
2% Superfiltrol 105 + 0.2% act. carbon	3.6	0.28	0.2	1.11	0.48	140.6	4.9
3% Superfiltrol 105	7.4	0.28	1.0	1.22	0.49	301.8	3.1
3% Superfiltrol 105 + 0.3% act. carbon	6.2	0.11	2.5	1.07	0.38	236.5	6.5
3% Natural blch. earth[d]	15.2	0.14	1.7	1.29	0.62	221.8	4.1
3% Natural blch. earth + 0.2% act. carbon	13.0	0.11	3.0	0.81	0.55	113.8	5.6
4.67% Natural blch. earth	9.5	0.12	2.3	0.85	0.69	236.7	4.4
1% Act. carbon	6.4	0.06	4.6	1.59	0.00	214.0	5.6

[a]Triple-refined with 80% max. 16°Be NaOH, 80% max. 20°Be NaOH and max 20°Be NaOH; each step at 65 C for 15 min.
[b]Deodorized with 5% steam at 210 C for 120 min; 0.01% citric acid added during cooling.
[c]Bleaching treatments were done at 105 C for 30 min.
[d]PV = peroxide value.

TABLE VI

Effects of Deodorization Variations on Bleached *C. foetidissima* Oils[a] and Characteristics of Deodorized Oils

Deodorization conditions					Conjugated fatty acids		Stability (AOM)	
Temp. (C)	Time (min)	Carotenoids (mg/kg oil)	Free fatty acid (%)	Peroxide value (meq/kg oil)	Dienoic (%)	Trienoic (%)	PV[b] after 8 hr	hr to PV = 100
210	30	3.8	0.22	0.0	1.21	0.46	218.7	4.1
210	60	3.0	0.30	1.3	1.15	0.43	204.3	4.1
210	120	3.6	0.28	0.2	1.11	0.48	140.6	4.9
210	180	3.1	0.35	0.5	1.10	0.48	236.8	4.5
260	30	3.1	0.09	2.6	1.29	0.39	186.5	3.2
260	60	2.9	0.10	2.5	1.14	0.46	297.8	2.9
260	120	4.4	0.84	1.6	2.70	0.09	137.0	5.1
180	260	3.0	0.51	1.3	2.46	0.15	214.8	5.2

[a]Triple-refined with 80% max. 16°Be NaOH, 80% max. 20°Be NaOH and max. 20°Be NaOH; each step at 65 C for 15 min. Bleached at 105 C for 30 min using 2% Superfiltrol 105 + 0.2% activated carbon.
[b]PV = peroxide value.

Deodorization

To determine the influence of variables in the deodorization process on the quality of processed oil, a bleached oil was used which had received triple-refining with 16°Be and 20°Be NaOH solutions and bleaching with 2% Superfiltrol 105 + 0.2% activated carbon. The influence of temperature and time was determined with 210 and 260 C for periods ranging from 30 to 180 min. Data are presented in Table VI.

Minor decreases occurred in carotenoid levels, and PV were lower in all products than in bleached oil.

FFA levels generally increased slightly during deodorization, and there was some shift of trienoic to dienoic fatty acids which was favored by higher temperature and longer time.

The duration of the deodorization process influenced oxidative stability of the oil products. The best results were obtained when oils were processed for 120 min; the PV for oils deodorized at 210 and 260 C for that time were only 141 and 137, respectively, after 8 hr.

The deodorization temperature appeared to have only minor influence on oil properties. When 210 and 260 C were compared for specific times, the stability of the oils was generally similar; other characteristics were slightly different and generally favorable to deodorization done at 210 C.

Except for the addition of the chelating agent citric acid during the cooling stage of deodorization, no antioxidant was added to any of the obtained deodorized oils. The addition of antioxidants such as butylated hydroxytoluene or butylated hydroxyanisole, normally used in edible fats and oils, would be expected to improve the oxidative stability of *C. foetidissima* oil.

On the basis of this laboratory study, the conditions recommended for processing of *C. foetidissima* oil are: (a) triple-refining with 16° and 20°Be NaOH at 80% of the maximum and 20°Be NaOH at 100% of the maximal amount to neutralize the FFA content; (b) bleaching by a combination of Superfiltrol 105 (2%), or a comparable commercial activated bleaching earth, and activated carbon (0.2%) at 105 C for 30 min; (c) deodorizing with 5% steam at 210 C for 120 min.

The visible spectra of *C. foetidissima* oil after specific recommended steps of processing are presented in Figure 1. The spectra show the progressive disappearance of carotenoid pigments until a very low level in the deodorized sample, comparable to that found in other processed commercial edible oils, is reached. UV spectra of the same samples are shown in Figure 2 and indicate the levels of dienoic and trienoic conjugated fatty acids and the occur-

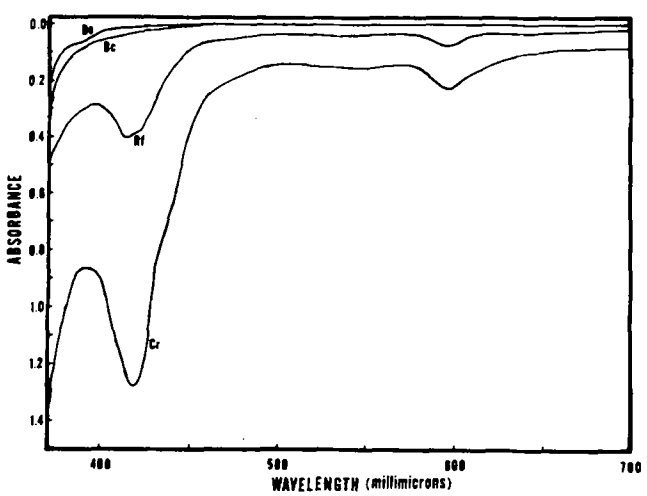

FIG. 1. Visible spectra of *C. foetidissima* oil indicating carotenoids content at different stages of processing: Cr = crude oil, 25.55 g/L; Rf = refined oil, 25.50 g/L; Bc = bleached oil, 25.48 g/L; Do = deodorized oil, 25.50 g/L.

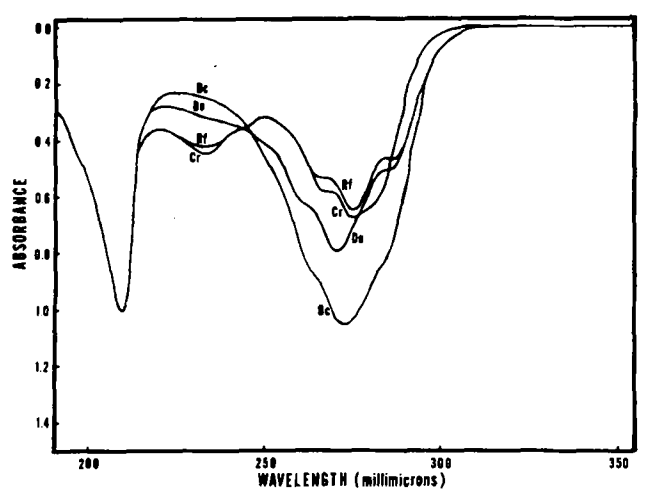

FIG. 2. Ultraviolet spectra of *C. foetidissima* oil indicating conjugated fatty acids content at different stages of processing: Cr = crude oil, 256 mg/L; Rf = refined oil, 255 mg/L; Bc = bleached oil 255 mg/L; Do = deodorized oil, 255 mg/L.

rence of the shifting effect during processing.

GLC of the fatty acid methyl esters derived from an oil obtained by the recommended processing conditions showed the following fatty acid composition for major components: palmitic, 11.9%; stearic, 3.5%; oleic, 22.0%; and linoleic, 61.0%.

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The Effect of Glycols on the Hydrophile-Lipophile Balance and the Micelle Formation of Nonionic Surfactants

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ABSTRACT

The empirical hydrophile-liophile balance (HLB) value of nonionic surfactants is an important parameter used to predict performance as, e.g., emulsifiers, solubilizers and wetting agents. However, the HLB value is based on an original molecular structure and does not take into account all the factors affecting the performance of nonionics, such as presence of additives, type of solvent, temperature, degree of hydration, structural modifications of the surfactant molecule and decomposition of surfactants. On a performance basis, where these factors come into play, a given nonionic surfactant may exhibit a multiplicity of apparent HLB values. Accordingly, we recently introduced the term "effective HLB value" which is a performance value which incorporates into the HLB the parameters listed above. The HLB value thus becomes a variable depending on the physical and chemical conditions at the time of the measurement. In this work, we investigated the effect of adding glycols and diglycols on the HLB using 3 different methods: cloud point, phenol index and critical micelle concentration (cmc). We found that this type of additive increases the cloud point, phenol index, cmc and the "effective HLB" of a polyoxyethylated nonionic surfactant. The effectiveness of the glycols in causing these increases was in the following order; dipropylene glycol > 1,4-butanediol > 1,2-propanediol > diethylene glycol > ethylene glycol. The solvent effect of glycols and diglycols on the hydrophobic and hydrophilic portions of the surfactant molecule are discussed. On the hydrocarbon part of the surfactant molecule, the solvents cause a weakening of the hydrophobic bond and an increase in the cmc. On the polyoxyethylene part of the molecule, the solvent may cause either an increase or a decrease in the cmc. The effect on the hydrophilic portion is related to hydrogen bonding exhibited by the additives. The results obtained again suggest that the effective HLB value, which is a measure of the HLB under operative conditions, may be of greater practical significance than calculated HLB.

INTRODUCTION

Glycols and diglycols are often used in combination with surfactants in pharmaceutical, cosmetic and pesticide formulations. Therefore, an investigation of the effect of these solvents on the physical properties of surfactant solutions is highly desirable.

The hydrophile-lipophile balance (HLB) value of nonionic surfactants not only is used to predict performance as emulsifiers, solubilizers and wetting agents, but also may be used to predict micellization. The micellization of surfactants in an aqueous solution is regulated by the balance between 2 opposing forces: the cohesive force between the hydrophobic groups (which favors micelle formation) and the attractive forces between the hydrophilic group and water molecules (which aids in keeping the nonionic surfactants in solution). Thus, because HLB is a measure of the balance between hydration and cohesion, it also may be used to predict the formation of micelles.

An HLB value of a nonionic surfactant is not a constant but is affected by factors such as additives (1-3), temperature (4,5) and structural modification of the surfactant molecule (6). Therefore, we refer to an "effective HLB value" which is an observed HLB equivalent to a reference surfactant, devoid of additives, having the same physical properties as the one under investigation (7). To estimate the degree and direction of the HLB change (reference HLB to effective HLB) we determined the critical micelle concentration (cmc), phenol index and cloud point of the surfactant measured in the absence and presence of a given