Solvent Winterization of Sunflower Seed Oil[1]

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ABSTRACT

Samples of oil from whole and dehulled sunflower seed were solvent winterized. The solvent mixture, 85% acetone, 15% hexane (v/v), was used at solvent-in-oil concentrations of 20, 40, and 70% by wt and the samples winterized at 0, -5, -10, and -15 ± .01 C for 4 hr. Generally, sunflower oils from whole seed remained free from cloud formation longer on refrigeration when the oils were winterized at lower temperatures and at lower solvent-in-oil concentrations. With oil from the dehulled samples, no winterization condition produced an oil with a predictable clouding time. However, correlations were significant between residual wax content after winterization and clouding time of the oils from whole seed. Oils from dehulled seed were not as highly correlated with wax content as oils from whole seed. This study indicates that crude sunflower seed oil might be winterized with the aid of solvents and that decortication prior to extraction might not be necessary for effective winterization.

INTRODUCTION

Winterization of sunflower seed oil is difficult because of the presence of waxes and mucilagenous materials in the oil. Filtration of the oil is hindered by the high viscosity of the cold oil, the lack of uniformity in crystal formation of the waxes, and the presence of mucilagenous materials which coat the wax crystals and retard filtration (1). The values in the literature for the wax content in the oil vary from .02-.35% (2). It has been reported that the wax content in the oil depends upon the efficiency of decortication, the percentages of waxy material in the pericarp, and the method of obtaining the oil (3).

Numerous methods for dewaxing and winterizing vegetable oils have been reported. Guillaumin and Drouhin (3) described a method of washing crude oil with emulsifying agents which removed waxes and a large percentage of phospholipids. It has been reported (4,5) that cottonseed and peanut oils could be solvent winterized from acetone or an 85/15 acetone-hexane mixture. Mertens, et al., (6) reported that addition of 10% acetone to cottonseed oil improved crystallization of the waxes and reduced the viscosity of the oil. In addition, Volotovskaya, et al., (7) has shown that the addition of small amounts of diatomaceous earth facilitated filtration of cold sunflower seed oil by a factor of 4.

The waxes in sunflower oil are difficult to measure accurately due to their low concentrations. An involved extraction procedure requiring special equipment and long extraction times apparently gives good results (2).

This work was initiated to develop a convenient gas liquid chromatographic (GLC) procedure for the determination of waxes in sunflower seed oil and to investigate the removal of minor components during solvent winterization of crude sunflower seed oil.

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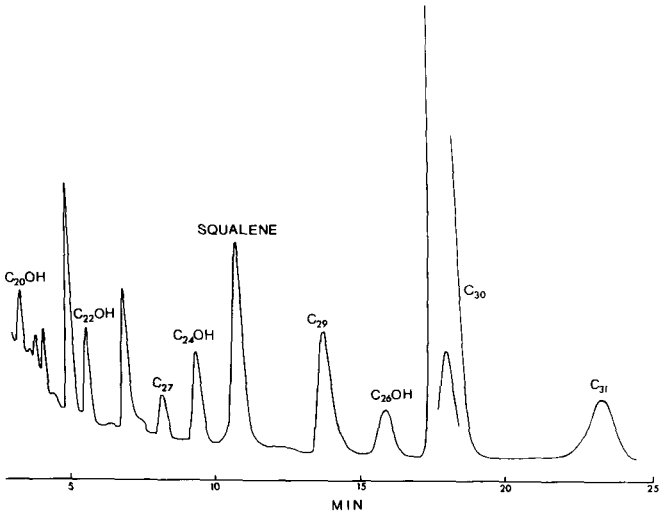

FIG. 1. Gas liquid chromatographic trace of hydrocarbons and N,O-bis(trimethylsilyl)-acetamide derivatives of waxy alcohols in sunflower seed oil.

MATERIALS AND METHODS

Preparation of Samples

Sunflower seed oils were obtained from seed grown in Georgia (whole seed, sample 1; dehulled seed, sample 2); Texas (whole seed, sample 3; dehulled seed, sample 4); and Minnesota (whole seed, sample 5). The seed were ground in a Wiley mill with a 6 mm screen. Dehulled samples were obtained by passing the ground seed through an air classifier. This operation removed at least 80% of the hull from the sample. The ground whole or dehulled samples were extracted for 6 hr with hexane in a Soxhlet extractor with a 10 lb capacity. Solvent was removed from the oils using a Precision Scientific Laboratory concentrator. Suspended particles were removed by filtration through Whatman no. 41 paper under nitrogen pressure with a Frueger stainless steel pressure filter using Hyflo Super Cel as a filter aid.

Solvent winterization was conducted with reagent grade acetone and hexane, 85/15 volume %; solvent in oil concentrations was 20, 40, and 70 ± .5% by wt. Winterization was done in a Lauda K4/RD circulating cold bath at 0, -5, -10, and -15 ± .01 C. In a typical run, enough oil-solvent mixture of each concentration was added to a 250 ml centrifuge bottle to provide ca. 40 g oil after evaporation of the solvent. The capped bottles were placed in the cold bath at the desired temperature for 4 hr. After centrifuging at 9000 x g for 20 min in a refrigerated centrifuge maintained at the respective winterization temperatures, the oil-solvent supernatent was decanted and evaporated under vacuum.

Measurement of Clouding Time

Treated samples were evaluated for cloud formation by preparing the oils according to the AOCS methods for cold test (8) followed by refrigeration at 2 C for 7 days. Samples were evaluated visually daily for clarity, and the days required for the oil to become cloudy were recorded.

Determination of Hydrocarbons, Sterols, and Waxes

Oil samples were saponified by a modification of an AOAC procedure for unsaponifiable material (9). Initially ca. 1 mg n-triacontane (internal standard) and 2.5 g oil were weighed accurately in a 250 ml Erlenmeyer flask with a 24/40 fitting. To the flask was added 25 ml 95% ethanol and 1.5 ml 60% aqueous KOH. The flask was fitted with an

air condenser and heated on a steam bath for 1 hr. While still warm, the mixture was transferred to a 250 ml separatory funnel with 50 ml water, extracted with 3 x 50 ml diethyl ether, and the combined ether extracts washed with 4 x 20 ml water. The ether was evaporated under vacuum and traces of water were azeotroped with benzene and acetone. After evaporation ca. 0.5 ml benzene was added to the samples.

GLC analysis was conducted on a Tracor MT220 GLC equipped with an Infotronics model CRS-101 digital integrator. A 6 ft x 1/4 in. glass column packed with 3% OV-1 on 100-120 mesh Chromosorb W H-P was used for all analyses. Sterols and methyl sterols were analyzed at a column temperature of 260 C.

The remainder of the sample was silylated with 50 μliter N,O-bis(trimethylsilyl)-acetamide (BSA). Hydrocarbons and the silyl ethers of the waxy alcohols were analyzed at a column temperature of 240 C. BSA derivatives were used, since the retention times for the parent alcohols, acetates, and trifluoroacetates were identical. The acetate and alcohol peaks were masked by hydrocarbons, and the longer retention times of the BSA derivatives made the analysis possible. Figure 1 shows a typical GLC trace of the hydrocarbons and BSA derivatives of the waxy alcohols. The four alcohols measured, C-20, -22, -24, and -26, represent between 70-75% of the total straight chain alcohols in the waxes (10,11), and the distribution of these alcohols should reflect the behavior of the waxes on winterization. The wax content was calculated on the assumption that the alcohols represent 55% of the mol wt of the waxy ester. The hydrocarbons C-27, -29, and -31 represent between 69-75% of the straight chain hydrocarbons in the oil (12,13). Squalene also was included in the percent hydrocarbons. Linear regression analysis was carried out using a programable electronic calculator (model 720B, Wang Laboratories, Tewksburg, Mass.) equipped with an output writer (model 701A). Only those samples with clouding times of 7 days or less were used in the regression analysis. Randon samples were analyzed in triplicate, and the standard deviation for wax content in the samples was .001%.

TABLE I

Initial Content of Hydrocarbons, Sterols, and Waxes in Sunflower Oils

Components, %	Oil samples[a] 1	2	3	4	5
Hydrocarbons	.025	.030	.030	.029	.031
Sterols	.542	.552	.548	.547	.584
Waxes	.034	.008	.044	.015	.032

[a]1 = Georgia, whole seed; 2 = Georgia, dehulled seed; 3 = Texas, whole seed; 4 = Texas, dehulled seed; and 5 = Minnesota, whole seed.

RESULTS AND DISCUSSION

Table I shows the percentage of hydrocarbons, sterols, and waxes present in the different oil samples prior to winterization. Except for wax content, composition differed little between whole and dehulled samples. It has been reported that upon extraction ca. 83% of the wax which appears in the oil comes from the hull (3). If ca. 80% of the hulls were removed, wax content of the dehulled sample could be calculated from the wax content of the whole seed oil. Calculated on this basis, dehulled oil should contain between .011-.015% wax, which agrees with the experimental range of .008-.015%.

Table II shows the amounts of wax remaining in the oil samples after winterization and the refrigeration time necessary for cloud formation. Samples 1, 3, and 5 are oils from whole seed and show a regular pattern involving clouding time, solvent concentration, and winterization temperature. Samples 1 and 3 show increased clouding times as the solvent concentrations and winterization temperatures decrease. Sample 5 differs in that lower temperature and higher solvent concentrations produce longer clouding times. Linear regression analysis of the clouding times and residual wax content after winterization showed highly significant correlations (99%) for samples 1 and 5. Sample 3 showed a correlation significant at the 95% level.

Samples 2 and 4 are the dehulled seed oil samples.

TABLE II

Effect of Solvent Winterization upon Sunflower Oil Wax Content and Refrigeration Time Required for Cloud Formation

Sample[a]	Winterization temperature (C)	Solvent in oil concentration[b] 20% Wax, %	20% Clouding time (days)	40% Wax, %	40% Clouding time (days)	70% Wax, %	70% Clouding time (days)	Correlation[c] coefficient
1	0	.013	4	.018	1	.014	1	−.87**
	−5	.011	7	.009	7	.013	1	
	−10	.008	>7	.008	7	.010	4	
	−15	.010	>7	.010	>7	.008	>7	
2	0	.007	>7	.003	>7	.003	4	−.80*
	−5	.002	6	.003	4	.002	4	
	−10	.004	3	.002	4	.006	3	
	−15	.001	>7	.005	>7	.006	2	
3	0	.008	>7	.008	2	.007	1	−.80*
	−5	.006	>7	.006	4	.008	2	
	−10	.004	>7	.005	7	.005	5	
	−15	.003	>7	.003	>7	.003	6	
4	0	.004	>7	.003	5	.003	>7	−.72
	−5	.003	4	.004	4	.004	>7	
	−10	.003	>7	.002	7	.008	4	
	−15	.006	>7	.002	>7	.005	3	
5	0	.020	2	.018	1	.010	3	−.80**
	−5	.015	2	.011	3	.010	7	
	−10	.011	3	.009	7	.008	7	
	−15	.010	7	.004	>7	.005	>7	

[a]1 = Georgia, whole seed; 2 = Georgia, dehulled seed; 3 = Texas, whole seed; 4 = Texas, dehulled seed; and 5 = Minnesota, whole seed.
[b]Solvent: 85% acetone, 15% hexane by volume.
[c]Correlation between clouding time and residual wax content after winterization. * = Significant at the 95% level and ** = significant at the 99% level.

Clouding times for these samples showed no patterns involving clouding time, solvent concentration, or winterization temperature. The significance of the correlations between clouding time and residual wax content are lower than with the whole seed samples.

Comparison of the pairs of whole and dehulled seed oils suggests that, although the dehulled samples generally have less wax after winterization than the corresponding whole seed samples, they tend to cloud sooner during refrigeration than oils from whole seed. Contents of hydrocarbons and sterols initially showed no change due to dehulling and were not affected by winterization. Sunflower seed oil contains only 3% disaturated triglycerides, which would be solid at room temperature as compared to 11 and 20% for peanut and cottonseed oil, respectively (14). Therefore, the principal factor in cloud formation for sunflower oil is the waxy ester content, as shown by the correlations between clouding time and residual wax content.

The poor winterization of the dehulled samples could be explained by the fact that these samples had not been degummed or refined and thus contained most of the original phospholipids. Bailey (15) reported that lecithin acts as a crystal inhibitor in cottonseed oil. Similarly Rac (1) has shown that the addition of 1% lecithin to an oil containing 1% pure wax reduces wax crystal size on refrigeration from the range of 50-90 μ to 20-30 μ. In sunflower seed oil phosphatidylcholines represent 51% of the phospholipids in the oil (16). Although both whole and dehulled seed oils contain phospholipids, the effect of crystal inhibition appears to be most evident at low wax concentrations. In samples 1 and 5 (Table II), the residual wax content is relatively high, and the clouding times change with a change in winterization conditions. In samples 2 and 4, the wax content is relatively low, and clouding times are irregular, and poor correlations are found for clouding time and wax content. In this study, it generally appeared that, as wax concentration falls below .01%, predicting the effectiveness of winterization conditions became more difficult.

This study indicates that, even though the principal source of waxes is the hull, decortication may not be essential for the production of a high quality, cloud free oil and that other minor chemical constituents may be partially responsible for cloud formation.

ACKNOWLEDGMENT

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