Odor Evaluation of Fatty Methyl Esters Purified as Urea Adducts

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Abstract

Volatile oxidative cleavage products which are present in distilled fatty methyl esters make them unsuitable starting-materials for odor evaluation studies. Sensory evaluation of treated and untreated esters shows that crystallization with urea removes undesirable odor constituents which result from autoxidation, metal-catalyzed oxidation, light exposure, and distillation. The method is simple and by clathrate formation gives, in high yields, pure fatty esters, the fatty acid composition of which appears unaltered from the original material.

Introduction

LABORATORY STUDIES on odor precursors required samples of methyl linolenate, soybean, and cottonseed methyl esters initially free of odors. Conventional procedures, such as distillation under high vacuum, water-washing, steam deodorization, and filtration through carbon, only remove odors partially.

Urea-inclusion compounds have proved a valuable tool for fractionation or enrichment of a variety of complex mixtures (1–3,5,8–10). Necessary structural requirements for formation of urea-inclusion compounds (4) are an unbranched chain containing at least 4–6 carbon atoms.

Privett and Blank (7) improved oxidative stability of unsaturated esters by using a sequential purification technique that included crystallization from urea and, finally, high-vacuum distillation. In the experience of this laboratory, the most careful distillation of unsaturated methyl esters, even when all possible precautions are taken to avoid contact with air, still yields products that retain enough odor to render them useless for odor precursor studies. Since fatty esters fulfill the structural requirements, they can serve as psychometric standards after urea crystallization. A single urea crystallization was satisfactory for removing odor constituents from fatty methyl esters except for the most highly oxidized samples. The method gives high yields of pure esters, the fatty ester composition of which is unaltered from the original material. These are suitable substrates for basic odor studies. The initial concentration of odorous compounds is too small to be measured directly by gas chromatographic means; therefore this sensory work may be the first to show that volatile oxidative cleavage products are easily removed from fatty esters by urea treatment.

Experimental Section

A routine method is given for the daily preparation of samples required by a 10–20 member panel to test odors. Two grams of freshly distilled esters are added to a 250-ml flask containing absolute methanol (120 ml) saturated with urea. This flask is warmed on a steam bath long enough to bring the reactants into solution and then is allowed to cool at room temperature for several hours. Cooling the solution overnight in a refrigerator at 0C completely crystallizes the ester as the adduct. The crystals are recovered by vacuum filtration and are washed several times with 10-ml volumes of methanol-saturated urea solution which have been chilled to 0C. Purified esters are liberated from their adduct shell by adding 30 ml of distilled water and centrifuging at 1,000 rpm for 10 min. The esters are recovered with a medicine dropper and are stored under a nitrogen atmosphere if they are not to be used immediately.

Table I shows the yields and composition of distilled soybean and cottonseed esters before and after urea-adduct treatment. Fatty ester compositions were determined by gas-liquid chromatography on a 4-ft×¼-in. 25% DEGS column, operated isothermally at 200C. Only slight differences were detected between the fractionated and unfractionated samples. Samples were evaluated for odor by a trained taste panel composed of 18 members. Five drops of ester were placed on a ¾×3-in. strip of filter paper that was folded in the middle and inserted into a small glass jar as an inverted "V." The jars, about the size of 100-ml beakers, were sealed with tight-fitting polyethylene caps. Samples were warmed to 55C before sensory evaluation.

Two 30-g lots of distilled soybean methyl esters were oxidized by aeration at 100C. No oxidation catalyst was added to one sample whereas 333 ppm of cupric ion (as copper sulfate) were added to the other. The sample without catalyst reached a peroxide value of 174 meq/kg in 4 hr whereas the sample with catalyst required only one hour to reach a similar peroxide value.

Thirty grams of distilled soybean methyl esters were exposed to fluorescent light for 3.5 hr in the apparatus described by Moser et al. (6). Urea adducts of autoxidized and light-exposed esters were prepared as described for distilled esters.

Results and Discussion

Each freshly distilled methyl linoleate, cottonseed, and soybean methyl ester gave a variety of different odor responses and was unsuitable for sensory evaluation. Table II describes the predominant odor of methyl linolenate, soybean, and cottonseed methyl esters before and after treatment with urea to form

TABLE I

Yield and Composition of Urea-Fractionated Soybean and Cottonseed Oil Methyl Esters

		Fatty Acid Composition[1]						
Ester, treatment	Yield, %	Myr	Pal	Pal-01	St	01	Lo	Ln
Soybean oil, original	......	Trace	10.8	....	4.9	23.2	52.8	8.2
Soybean oil, urea-treated	98.1	Trace	11.1	....	4 4	23.7	53.3	7.5
Cottonseed oil, original	......	0.9	23.0	0.8	2.6	17.6	55.0	....
Cottonseed oil, urea-treated	93.5	0.9	22.9	0.9	2.5	17.8	53.3	....

[1] Average of two determinations. Myr, myristate; Pal, palmitate; Pal-01, palmitoleate; St, stearate; 01, oleate; Lo, linoleate; Ln, linolenate.

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[1] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE II

Odors of Esters Before and After Treatment

Methyl esters	Predominant odor descriptions
Soybean	Heated-stale, grassy-hay, rancid, painty
Soybean, urea-treated	Bland, heated-stale
Cottonseed	Heated-stale, grassy-hay, rancid, beany nutty
Cottonseed, urea-treated	Bland, heated-stale
Linoleate	Rancid, painty, grassy-hay
Linoleate, urea-treated	Bland, heated-stale, beany-nutty
Control[1]	Heated-stale, grassy-hay, paper

[1] Filter paper moistened with either water or a salt solution.

adducts. These samples received no intentional oxidation or light treatment. The cottonseed and soybean methyl esters were distilled under high vacuum and the methyl linolenate was a commercially prepared analytical sample, which was received, sealed, in a glass vial under nitrogen. Control experiments with filter papers without an ester sample, but moistened with distilled water on saline solution, provided characteristic odor responses (Table II). Sensory results indicate that untreated esters are not bland and cannot serve for odor precursor studies.

Table III shows odor evaluation of urea-purified soybean methyl esters, presented to the panel in a triangle test in which two of the samples were identical and untreated. The rancid, grassy responses that predominate in the untreated samples were greatly reduced after urea treatment. When two untreated samples were presented with one urea-purified sample, 16 of the 18 panel members had no difficulty in selecting the identical pair.

These studies indicate that a highly oxidized sample of methyl linolenate (PV 264) may require two successive urea crystallizations before a suitable odor base is achieved. Table IV gives sensory evaluations of two methyl linolenate samples, twice urea-crystallized, which were presented in a triangle test with a control sample that had not received a urea treatment. The correct pair was selected by 12 of 14 panel members. Rancid, painty, and fishy odors were removed by the urea treatment.

In other tests the panel was unable to distinguish between any combination of urea-purified samples of methyl linolenate, cottonseed, or soybean methyl esters. In all triangle tests however they identified any untreated sample when presented with treated ones.

To test the method for removal of odor constituents further, soybean methyl esters were deliberately autoxidized with and without copper catalyst. When distilled esters were presented to the panel in a triangle test, along with a sample autoxidized without catalyst (PV 174), panel members were unable to identify or select the correct pair. This experiment further attests to the unsuitability of distilled soybean methyl esters for odor precursor studies. Triangle tests with any of the urea-purified autoxidized esters and urea-purified unoxidized esters showed that the panel could not distinguish between any combination of the three samples. These results indicate that oxidized esters may be purified with the same ease as the distilled samples and that odor improvements are as marked. Identical tests with samples autoxidized with a copper catalyst showed the same results. Urea-purified, copper-oxidized samples were indistinguishable from urea-purified, unoxidized ones (Table V).

TABLE III

Odor Evaluation of Treated and Untreated Soybean Oil Methyl Esters

Predominant odor responses	[1] Soybean oil untreated			Soybean oil untreated			Soybean oil urea-treated		
	W	M	S	W	M	S	W	M	S
Bland				1			11		
Heated-stale	3	1		2			3	1	
Beany-nutty	3	5	4	2	1		3		
Grassy-hay	4	3	1	4	7		2		
Rancid	3			5	2	1	1		
Fishy	2			1			1		

[1] No. of responses. Untreated samples identical. W, weak; M, moderate; S, strong.

TABLE IV

Sensory Evaluation of Twice-Treated and Untreated Methyl Linolenate

Predominant odor responses	Methyl linoleate 2x urea-purified			Methyl linoleate 2x urea-purified			Methyl linoleate		
	W[1]	M	S	W	M	S	W	M	S
Bland	2			2					
Heated-stale	5			5			1	1	
Beany-nutty	1	1			1			1	
Grassy-hay	3			3			3		
Rancid							2	3	
Fishy							1	1	
Painty							2	1	
Sweet	2	1		2					

[1] See Table III.

The deleterious effect of light on the stability of edible oils is well known (6). Strong, grassy, pungent odors develop in fatty esters exposed to light which are exceedingly difficult to remove. Consequently this type of sample may require two urea crystallizations to achieve a suitable odor base. A few rancid responses appeared in urea-purified, light-exposed soybean methyl esters. Rancid responses also occurred in tests when clean empty beakers, containing no sample, were presented to the panel along with urea-purified esters. Sometimes rancid responses were described in one sample but not in the other of an identical pair. Evidently factors other than the sample presented influence evaluation scores when the sample is odor-free or practically odor-free. In triangle tests the panel was unable to distinguish betwen a sample of light-exposed soybean esters after urea crystallization and a urea-purified control (Table VI).

Some difficulties were encountered in recovering good yields of highly autoxidized, copper-oxidized, and excessively light-exposed soybean methyl esters. Evidently appreciable quantities of hydroperoxides interfer with complete crystallization of the adducts. Yields in the order of 80% were achieved with the copper-autoxidized sample. In these highly oxidized oils the fatty acid composition would not be expected to be identical to the original material. Such results are of no particular consequence to these experiments since they were performed only to demonstrate the utility of the method.

Volatile low-molecular-weight compounds, presumably autoxidatively derived cleavage products, are excluded from the adduct when the esters are occluded

TABLE V

Comparison of Urea-Purified Soybean Methyl Esters and Urea-Purified, Copper-Oxidized Soybean Esters

Predominant odor responses	Soybean esters urea-purified			Copper-oxidized soybean esters 2x purified			Copper-oxidized soybean esters 2x purified		
	W[1]	M	S	W	M	S	W	M	S
Bland	2			6			4		
Heated-stale	8	2		5	2		8	1	
Beany-nutty	1			2	2		2		
Grassy-hay	3	1		1	1		2		
Rancid									
Painty							1		
Ester				1			1		

N= 15
5 thought 2nd and 3rd samples similar.
4 thought 1st and 2nd samples similar.
3 thought 1st and 3rd samples similar.
3 thought all samples similar.

[1] See Table III.

TABLE VI

Comparison of Light-Exposed Soybean Methyl Esters Purified with Urea and Soybean Esters Purified with Urea

Predominant odor responses	Light-exposed soybean esters urea-purified			Soybean ester urea-purified			Light-exposed soybean esters urea-purified		
	W[1]	M	S	W	M	S	W	M	S
Bland	4			1	1		2	1	
Heated-stale	7	1		6	1		8	1	
Beany-nutty	1			1	1		1	1	
Grassy-hay	3			3			3		

$N = 16$
4 thought 1st and 2nd samples similar.
6 thought 1st and 3rd samples similar.
5 thought 2nd and 3rd samples similar.
1 thought all samples similar.
Repeated Tests $N = 14$
3 thought 1st and 2nd samples similar.
5 thought 2nd and 3rd samples similar.
3 thought 1st and 3rd samples similar.
3 thought all samples similar.
$N = 14$
1 thought 1st and 2nd samples similar.
3 thought 1st and 3rd samples similar.
5 thought 2nd and 3rd samples similar.
5 thought all samples similar.

[1] See Table III.

in a urea clathrate. Such treatment provides esters suitable as starting materials for characterization of the type of odor derived from a specific fatty acid structure. The relationship between a specific fatty ester structure and a fat oxidation odor is under investigation.

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