

Removal of Fatty Soils from Cotton in Aqueous Detergent Systems¹

W. C. POWE, Whirlpool Corp. Research Laboratories, St. Joseph, Michigan

Abstract

A gravimetric method for studying the factors involved in removing fatty soils from cotton in aqueous detergent systems is described, and comparative data are given for removal of lanolin, lard, sebum, and hydrocarbon soils from cotton. Comparisons are made for a number of surfactants used in detergent formulations and effects of various builders are noted. Effects of some of the parameters of the wash bath such as detergent concentration, water temperature, and wash time are discussed. It is thereby demonstrated that:

1. Maximum fatty soil removal is attained from cotton in 5 min or less at 120F with 0.25% of a good detergent.
2. A group of six representative anionic and non-ionic surfactants vary considerably in their ability to remove sebum from cotton.
3. In general, the relative ability of a detergent system to remove one fatty soil applies to other fatty soils also.
4. The most effective inorganic salts for removing sebum were sodium tripolyphosphate and tetrasodium pyrophosphate.
5. The most effective active-builder combinations tested were built with sodium tripolyphosphate.
6. The improvement in fatty soil removal from cotton produced by building surfactants with inorganic salts was an additive or less than additive effect for the nonionics tested. With the anionics a few synergistic effects were noted. These effects were probably due to the inorganic salts lowering the CMC or increasing the size of the micelle.
7. Emulsification is probably an important mechanism in removing sebum from cotton.

Introduction

PUBLISHED DATA on fat removal from fabrics during the wash process under American home laundering conditions are limited. In a previous study we found that under some washing conditions a large amount of organic material may accumulate on cotton garments. The bulk of this material was unremoved sebum (8).

Deleterious effects of fat accumulation on fabrics are twofold. Redeposition of particulate soil is increased because an oily fiber will adsorb more soil from the wash bath than a clean fiber. The fabric will also tend to yellow on standing because of oxidation and polymerization of unsaturated materials present in the organic soil (7,11).

Wagg and Britt (10) reported that 80% by weight of articles laundered are soiled with sebum. The importance of removing sebum during laundering can be appreciated if it is realized that a man's T-shirt will absorb about 1 gm of sebum in a normal wearing period.

Ehrenkranz (2) studied the removal of C¹⁴ labeled tripalmitin in olive oil from cotton in home washing machines and reported poor removal at 120F and

good removal at 140F. Increasing the temperature to 160F did not increase the soil removal.

Wagg and Britt (10) described a radioactive-tracer technique to determine the removal of individual components from an artificial sebum. Removal of C¹⁴ labeled linoleic acid, stearic acid, tristearin, cholesterol, and octadecane were studied from a number of different type textile fibers. In general, removal of these fatty soils was most difficult from cotton.

Oldenroth (7) published data on build-up of skin fat (sebum) on various fibers including cotton. Skin fat was obtained from dirty undershirts by solvent extraction and swatches were soiled by dipping in a solution of skin fat and allowing them to dry. The swatches were washed, then resoiled. This process was repeated 10 times and the amount of residual fat was determined by extracting the swatches and weighing the residue recovered. Removal was most difficult from cotton.

Walter (12) collected skin fat in a similar manner except that the swatches were soiled and then washed 5 times before determining the residual fat. He also included iron chloride to simulate the iron found in clothes soil and analyzed for residual iron.

This paper is a gravimetric study of some of the factors involved in removing fats from cotton fibers in aqueous detergent systems. Emphasis is on the behavior of sebum because it is the most common and abundant fatty soil encountered in home laundering.

In addition, data are given for lanolin, lard, and petrolatum. Lanolin and petrolatum were studied as representative fatty laundry soils because they are widely used in cosmetic and medicinal preparations. Lard is a representative animal fat found in food stains.

Sebum, the excretion of sebaceous glands in the skin is a complex mixture of hydrocarbons, squalene, wax and cholesteryl esters, triglycerides and the hydrolysis products of triglycerides, diglycerides, monoglycerides, and free fatty acids (5).

Lanolin contains no glyceryl esters. It has a small amount of free fatty acid and the rest is combined as fatty acid esters of aliphatic and triterpene alcohols and cholesterol (13).

Lard is composed, for the most part, of mixed triglycerides of palmitic, oleic, and stearic acids. Petrolatum is paraffins and olefins blended with mineral oil to reduce the viscosity.

Experimental

Sebum was collected by wearing cotton T-shirts previously solvent extracted with 1:1 v/v chloroform-methanol to remove all sizing and residual plant waxes. Absorbed sebum was extracted from the T-shirts as described above and stored at -10C, under nitrogen, until needed.

The fat solutions were 6.6% w/v in 3:1 benzene-methanol. This concentration was used so that 0.2 ml of solution would contain 13.2 mg of fat, which was 1% of the weight of the swatches used. From studies made on the pickup of sebum by cotton T-shirts in a normal wearing period, we consider a 1% soil level to be a realistic figure for garments in intimate contact with the skin.

¹ Presented at the AOCs meeting in New Orleans, La., 1962.

EFFECT OF TIME ON SEBUM REMOVAL
0.25% BUILT ANIONIC DETERGENT

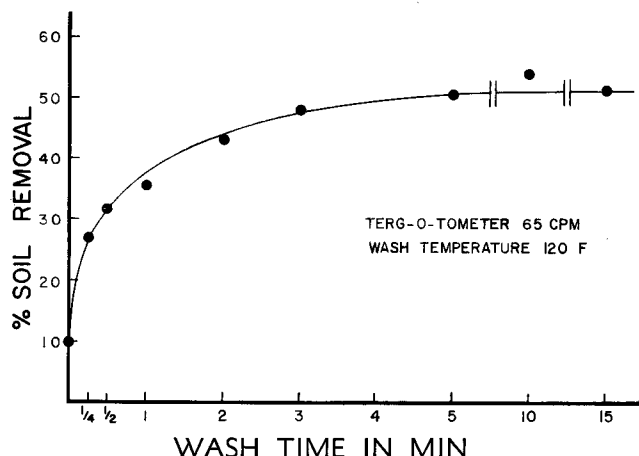


Fig. 1. Removal rate of sebum from cotton.

EFFECT OF AGITATION ON SEBUM REMOVAL
IN THE TERG-O-TOMETER

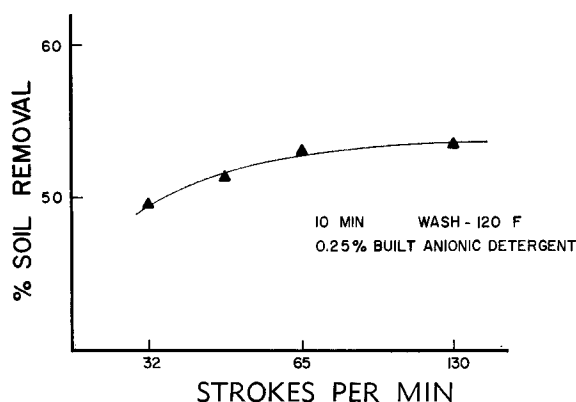


Fig. 2. Effect of agitation on sebum removal from cotton.

Swatches used in these studies were 2" x 2" Indian-head cotton and were pretreated by washing at 160F in 0.25% "Calgon," rinsed in deionized water and dried. The swatches were then soxhlet extracted in 1:1 v/v chloroform-methanol for 24 hr, dried and re-extracted with chloroform for an additional 24 hr to remove residual organic material. Swatches were then air dried and were ready for soiling.

The swatches were placed over the open end of a 50 ml beaker and 0.2 ml of fat solution was applied from a micropipet by touching the pipet to the center of the swatch and allowing the pipet to drain slowly. This application made a soiled ring almost the diameter of the swatch. The soiled swatches were then dried under an infrared lamp for about 1 min. Soiled swatches were placed in a desiccator over a saturated solution of magnesium acetate for at least an hour in a RH of 65%. Freshly soiled swatches were used each day, but the author was unable to detect aging effects in swatches up to a week old.

Soil removal tests were run in the Launder-Ometer or Terg-O-Tometer. For each test, ten 2" x 2" swatches were washed in 300 ml of detergent solution. Tests were run at least in duplicate. Ten steel balls were included in each pint Launder-Ometer jar for agitation, although variation in the number of balls from 0-40 showed no significant difference in soil removal.

Wash conditions unless otherwise indicated were: Launder-Ometer, 10 min wash at 120F. All detergent solutions were made with distilled water. The surfactants were essentially 100% active and the builders were commercial products

After washing, the swatches were rinsed thoroughly in deionized water to remove residual detergent. The rinsing process did not remove additional soil. Swatches were dried for 25 min in a forced air oven at 60C and then placed in a soxhlet extractor without a thimble. The reservoir was a tared 250 ml flat bottomed boiling flask.

Swatches were extracted overnight in 1:1 v/v chloroform-methanol. Solvent was evaporated from the flask with a rotary evaporator under vacuum, then placed in a vacuum oven for 1 hr at 60C, 30 psi; allowed to cool and weighed to the nearest 0.1 mg.

Soil removal was calculated from the amount of soil applied to the swatches and the amount recovered from the swatches by extraction. The standard

error for this method is about $\pm 2.0\%$ from the same batch of soil.

Data and Discussion

This method has some limitations because it cannot be used under all conditions without modification. Since the method is gravimetric, it is necessary that all finishing materials be removed from a fabric before it is soiled. Checks must be made that detergents are not adsorbing on the swatches in weighable amounts. If hard water is used, some modification in extraction procedure must be made to separate the original soil from insoluble soaps formed with the free fatty acids in the soil and detergent-calcium or -magnesium complexes.

Enough soil solution should be made so that a complete series of evaluations can be run from the same batch. The soil removal level changes slightly each time a new quantity of soil solution is prepared. However, relative removal values remain the same. Aliquots of the soil solution should be taken at frequent intervals to determine that the soil concentration has not changed. When new soil is prepared, the soil removal characteristics should be checked by determining soil removal with water and with some standard surfactant such as sodium lauryl sulfate (NaLS).

EFFECT OF TEMPERATURE ON FAT REMOVAL
0.25% BUILT ANIONIC DETERGENT

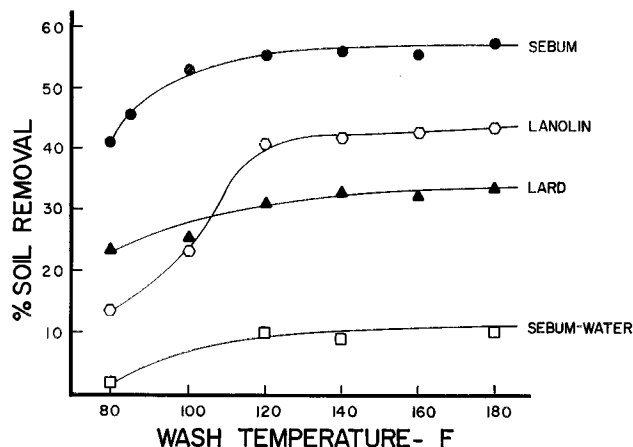


Fig. 3. Effect of wash temperature on removal of sebum, lanolin and lard from cotton.

EFFECT OF TEMPERATURE ON REMOVAL OF
VARIOUS HYDROCARBONS
0.25% BUILT ANIONIC DETERGENT

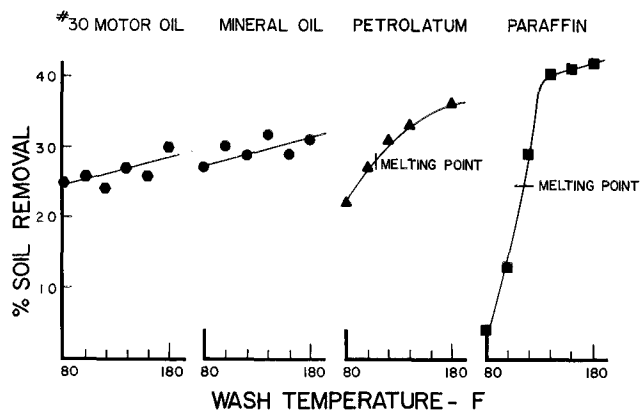


FIG. 4. Effect of melting point on removal of hydrocarbon soils from cotton.

Figure 1 is the removal rate of sebum from cotton in the Terg-O-Tometer at 120F with a 0.25% heavy-duty anionic detergent. About 50% of the sebum is removed in 5 min and no further significant removal occurs within 15 min. Wagg and Britt reported greatest removal of fats from cotton early in the wash (10).

Figure 2 demonstrates the effect of agitation on the removal of sebum from cotton. Maximum removal of sebum occurs at about 65 cpm and doubling this rate does not significantly increase removal.

Figure 3 shows the effect of wash temperature on removal of lanolin, lard, and sebum. Sebum is easiest to remove and lard the most difficult; lanolin is intermediate. There are several factors inherent in fatty soils that will affect removal. The size and shape of the molecules, polarity of the material, and melting point are all important. Certainly a fat must be somewhere near its melting point before maximum removal can be expected in an aqueous detergent system. Sebum melts at about 86F, lanolin at about 95F, and lard near 98F. Fatty soil removal was not significantly increased by wash temperatures above 120F.

Figure 4 illustrates the effect of melting point on soil removal for a number of hydrocarbon soils. Number 30 motor oil and mineral oil which are liquids at

80 F show only slightly improved removal with increase in temperature. Petrolatum, which is a semi-solid at 80F shows a definite temperature effect and a medium paraffin that melts at 118F shows a marked increase in removal above its melting point.

Figure 5 shows the effect of detergent concentration on removal of sebum, lanolin, and lard from cotton with a built heavy-duty anionic detergent at 120F. Removal curves rise rapidly for all 3 soils until about 0.1% detergent concentration is reached, then start to level off. There was very little advantage in adding over 0.25% detergent for these oils.

Figure 6 is a comparison of the effectiveness of some common unbuilt anionic and nonionic detergents in removing sebum at various concentrations. There is a significant difference in the abilities of various surfactants to remove sebum from cotton. The relative effectiveness of a surfactant at a low concentration is not necessarily the same at a higher concentration. The poorer detergents for sebum reach a plateau at about 0.2% and doubling the amount doesn't increase the removal of soil. At 0.1% concentration and above, lauryl sulfate and nonylphenol + 10EO were the most effective anionic and nonionic surfactants tested for removing sebum from cotton.

These data support the findings of others (4,6) obtained by studying fat removal from hard surfaces that soil removal often starts near the critical micelle concentration (CMC) of the detergent solution but that maximum soil removal is usually at many times the CMC.

Table I is a comparison of the abilities of various common inorganic builders to remove sebum from cotton at 120F. Tetrasodium pyrophosphate and sodium tripolyphosphate remove almost as much sebum as heavy-duty anionic detergent. Sodium orthophosphate and sodium metasilicate are less effective. Sodium carbonate, sodium "hexametaphosphate," and sodium tetraborate are relatively poor and sodium sulfate is not much better than water. The effectiveness of sodium tripolyphosphate and tetrasodium pyrophosphate on removal of tristearin from glass has been reported (1).

Table II is removal of sebum from cotton by various surfactant-builder combinations. The builders are those most commonly found in any quantity in heavy-duty powder detergents. The amount of surfactant

EFFECT OF DETERGENT CONCENTRATION ON
FAT REMOVAL

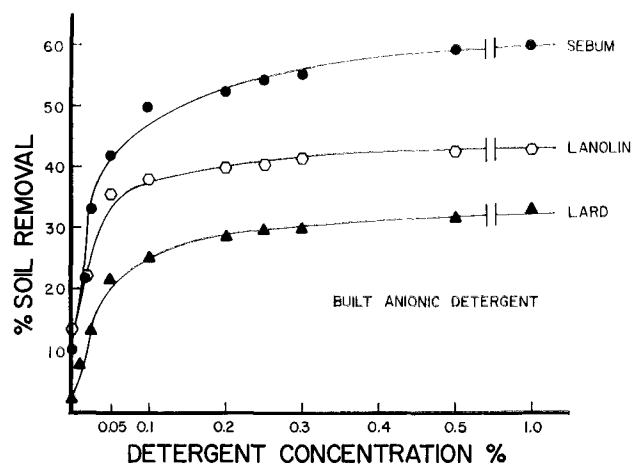


FIG. 5. Effect of detergent concentration removal of sebum, lanolin and lard from cotton at 120F.

REMOVAL OF SEBUM WITH UNBUILT DETERGENTS
TERG-O-TOMETER-120 F

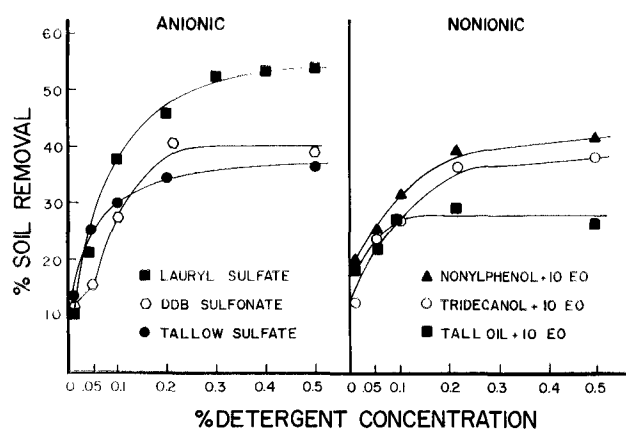


FIG. 6. Comparison of sebum removal from cotton by some unbuilt surfactants at various concentrations.

TABLE I
Efficiency of Builders in Removing Sebum from Cotton at 120F in the Launder-Ometer

0.25% Detergent concentration ^a	Per cent soil removal			
	"Active"	Na ₅ P ₃ O ₁₀	Na ₂ CO ₃	Na ₂ SO ₄
Built heavy duty anionic detergent.....	53			
Sodium pyrophosphate.....	47			
Sodium tripolyphosphate.....	46			
Trisodium orthophosphate.....	41			
Sodium metasilicate.....	41			
Sodium carbonate.....	36			
Sodium tetraborate.....	33			
Sodium "hexametaphosphate".....	32			
Sodium sulfate.....	19			
Water.....	10			

^a Builders are on anhydrous basis.

used in these formulations is in the general range used for heavy duty laundry detergents.

None of the "actives" at 0.04% removed more than one-half as much sebum from cotton as a well built anionic detergent. Tripolyphosphate, alone, removed about 90% as much sebum as the built detergent. The best removal for all the surfactants studied was in combination with sodium tripolyphosphate. Sodium carbonate surfactant combinations were intermediate. Sodium sulfate combinations were poorest but still better than the unbuilt "actives."

Table III is a similar study on the removal of lanolin from cotton. Effectiveness of the unbuilt "actives" was of the same order as for the removal of sebum. However, the difference in the detergency of the builders for lanolin is much less. The differences between sodium tripolyphosphate and sodium sulfate are very small. Similarly, the building effects on the "actives" was much less than for sebum. In fact the detergency of sodium tallow sulfate was not improved by building.

Table IV is a similar comparison for lard. The unbuilt "actives" are rated in the same order as for lanolin and sebum. Removal of lard from cotton by builders is low.

Table V is a study on the removal of petrolatum from cotton. The responses are very similar to those observed with lard.

The improved detergency for fats produced by building the surfactants with inorganic salts was, within the limits of experimental error, an additive or less than additive effect for all the nonionics tested. For the anionic surfactants no synergistic active-builder effects were observed with lanolin or petrolatum.

A synergistic effect was produced for removal of sebum by NaLS and sodium dodecylbenzene sulfonate (NaDDBS) by building with sodium sulfate. However, the soil removal was still less than when those two "actives" were built with sodium tripolyphosphate or sodium carbonate. The effect of sodium sulfate on tallow sulfate (NaTS) was less than additive.

TABLE II
Effect of Surfactant-Builder Combinations on Removal of Sebum from Cotton

Surfactant	Per cent removal			
	"Active"	Na ₅ P ₃ O ₁₀	Na ₂ CO ₃	Na ₂ SO ₄
	0.04%	0.21%	0.21%	0.21%
Nonionic				
Nonylphenol + 10EO.....	24	52	51	35
Tridecanol + 10EO.....	21	51	48	35
Tall oil + 10EO.....	15	49	47	28
Anionic				
Sodium tallow sulfate.....	26	54	51	31
Sodium lauryl sulfate.....	19	53	49	43
Sodium dodecylbenzene sulfonate.....	12	53	48	40
Water.....		47	36	19

Water—10% removal.
0.25% Built anionic detergent—53% removal.

TABLE III
Effect of Surfactant-Builder Combinations on Removal of Lanolin from Cotton

Surfactant	Per cent removal			
	"Active"	Na ₅ P ₃ O ₁₀	Na ₂ CO ₃	Na ₂ SO ₄
	0.04%	0.21%	0.21%	0.21%
Nonionic				
Nonylphenol + 10EO.....	31	37	36	35
Tridecanol + 10EO.....	24	34	32	29
Tall oil + 10EO.....	16	30	26	25
Anionic				
Sodium tallow sulfate.....	38	38	37	35
Sodium lauryl sulfate.....	24	39	39	39
Sodium dodecylbenzene sulfonate.....	15	32	32	31
Water.....		19	17	16

Water—14% removal.
0.25% Built anionic detergent—37% removal

A synergistic effect for lard removal was noted with NaLS and NaDDBS with all three builders. However, the soil removal level for NaDDBS was very low even when built with sodium tripolyphosphate. The effect of the builders on NaTS was additive or less.

The synergistic effects noted for NaLS and NaDDBS are probably due to the salts reducing the CMC of the wash solution, or increasing the size of the micelle (3).

TABLE IV
Effect of Surfactant-Builder Combinations on Removal of Lard from Cotton

Surfactant	Per cent removal			
	"Active"	Na ₅ P ₃ O ₁₀	Na ₂ CO ₃	Na ₂ SO ₄
	0.04%	0.21%	0.21%	0.21%
Nonionic				
Nonylphenol + 10EO.....	24	31	30	27
Tridecanol + 10EO.....	22	29	25	24
Tall oil + 10EO.....	12	19	17	15
Anionic				
Sodium tallow sulfate.....	22	27	23	24
Sodium lauryl sulfate.....	7	25	22	21
Sodium dodecylbenzene sulfonate.....	3	10	10	11
Water.....		5	3	0

Water—0% removal.
0.25% Built anionic detergent—30% removal.

Both NaLS and NaDDBS have a high CMC. NaTS, which was not synergistically improved by building has a lower CMC and the nonionics tested have a very low CMC.

It was previously mentioned that sebum and lanolin were the easiest fatty soils tested to remove. Both of these materials form emulsions with water with relative ease. Sebum on the skin surface is usually an oil in water emulsion but if conditions are right it will spontaneously form a water in oil emulsion (9). The low melting point of sebum is also important but the presence of known emulsifying agents, monoglycerides, and wax esters in sebum, are suggestive that emulsification is an important mechanism in sebum removal.

TABLE V
Effect of Surfactant-Builder Combinations on Removal of Petrolatum from Cotton

Surfactant	Per cent removal			
	"Active"	Na ₅ P ₃ O ₁₀	Na ₂ CO ₃	Na ₂ SO ₄
	0.04%	0.21%	0.21%	0.21%
Nonionic				
Nonylphenol + 10EO.....	22	25	25	25
Tridecanol + 10EO.....	18	21	21	21
Tall oil + 10EO.....	13	20	20	19
Anionic				
Sodium tallow sulfate.....	22	23	22	23
Sodium lauryl sulfate.....	10	12	12	12
Sodium dodecylbenzene sulfonate.....	6	11	11	12
Water.....		4	3	4

Water—2% removal.
0.25% Built anionic detergent—28% removal.

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Three New Oilseeds Rich in *cis*-11-Eicosenoic Acid¹

K. L. MIKOLAJCZAK, C. R. SMITH, JR., and I. A. WOLFF, Northern Regional Research Laboratory,² Peoria, Illinois

Abstract

Marshallia caespitosa Nutt. seed oil (family Compositae) contains 44% *cis*-11-eicosenoic acid, and is the first oil from the Compositae found to contain a high proportion of C₂₀-monoenoic acid. Seed oils of *Alyssum maritimum* (L.) Lam. and of *Selenia grandis* Martin (family Cruciferae) contain 42 and 58% of the same acid, respectively.

The C₂₀ acids from all three oils were obtained in nearly pure form by fractional distillation of the mixed methyl esters by means of a spinning band column. Permanganate-periodate oxidation of the purified methyl esters yielded predominantly nonanoic and undecanedioic acids.

Introduction

MARSHALLIA CAESPITOSA is a tufted perennial herb, with a flowering scape about 1 ft high, found from Missouri to Texas (1). A member of the Compositae, it is occasionally used for outdoor decorative plantings. *Selenia grandis* is a winter annual native to Texas and is not known in cultivation. *Alyssum maritimum* (sweet alyssum), or according to some authors, *Lobularia maritima* (L.) Desv., is a common low-spreading perennial of the Cruciferae grown as an annual in many rock gardens (1).

Seed of the first two species were collected from the wild by Department botanists; the *Alyssum* seed was purchased from a commercial seed company which deals in specialty plant materials not widely available. Seeds were stored at 40F from time of receipt at the laboratory until ground for oil extraction.

The first plant material reported to contain *cis*-11-eicosenoic acid was the liquid wax extracted from *Simmondsia chinensis* (Link) Schneider (jojoba) seed (5). Since then a number of workers have isolated and characterized this C₂₀-monoenoic acid from various Cruciferae seed oils (2,7-9,12). The acid has also been found in some fish oils (9) and in certain seed oils of Sapindaceae (4) and of Ranunculaceae (3); one of the former (*Cardiospermum halicacabum* L.) contains 42%.

The presence of 43.9% *cis*-11-eicosenoic acid in the seed oil of a composite, *Marshallia caespitosa*, is reported here. The acid has not previously been known to occur in seed oils of this family in quantities greater than about 1-2%. In addition, the structure of the C₂₀-monoenoic acids, reported earlier in *Alyssum* (41.8%) and *Selenia* (58.5%) seed oils (10), also has been proved to be *cis*-11-eicosenoic acid. These three new oils are among the richest sources known for this acid.

Experimental

Oil Extraction. Oil was obtained from ground seeds of the three species by soxhlet extraction with petroleum ether (bp 30-60C). The solvent was removed in a rotary evaporator. Yield of oil was 22.8% for *Marshallia*, 31.3% for *Alyssum*, and 18.3% for *Selenia*.

Preparation of Methyl Esters. *Marshallia* seed oil (8.90 g) was saponified by refluxing with 1 N ethanolic potassium hydroxide under nitrogen for 1½ hr. The saponification mixture was extracted with ethyl ether, acidified, and re-extracted with ethyl ether; a yield of 0.48 g of unsaponifiable material and 7.70 g of fatty acid was obtained. The unsaponifiables were removed from this oil because it was very dark colored. The fatty acids (6.8 g) were esterified by refluxing 2 hr with 1% sulfuric acid in methanol; 6.4 g of methyl esters were obtained.

Methyl esters of *Alyssum* and *Selenia* oil were prepared by transesterification with 1% sulfuric acid in methanol. The yield of *Alyssum* esters was 99.5% and of *Selenia* esters, 94.6%.

Spinning Band Column Distillation. The mixed methyl esters of each of the three seed oils were fractionally distilled through a Nester and Faust spinning band column. Pure methyl erucate (C₂₂-monoene) was used as a chaser in the pot for the distillation of *Marshallia* and *Alyssum* esters because of the small amount of material available. Recovery of seed oil methyl esters in the distillate was quantitative. A chaser was not used in the distillation of *Selenia* esters; therefore the recovery of esters in the distillate was only 74% of the charge weight.

Distillation conditions and the weights of collected fractions are shown in Table I. The vacuum in the apparatus was released each time a fraction was removed from the collector. The column was operated at total reflux for some time before each collection. The head temperatures given in Table I were obtained at total reflux and at the end of the collection.

Gas liquid chromatographic (GLC) analysis of selected fractions indicated that fractions 9, 10, and 11 of *Marshallia*; 8, 9, and 10 of *Alyssum*; and 2, 3, and 4 of *Selenia* could be combined and used for identification of the C₂₀-monoene. The GLC analyses of the original oil (methyl esters) and the combined distillate fractions are shown in Table II. Infrared spectra (liquid film on sodium chloride plates) of the combined fractions indicated no *trans* C=C (10.34 μ) absorption in any of the three samples.

Identification of the C₂₀-Monoene. *Marshallia caespitosa*. A 0.13-g portion of combined fractions 9, 10, and 11 was saponified by the usual procedure giving 0.12 g of a viscous colorless liquid. Infrared analysis showed no *trans* C=C absorption. After three recryst-

¹ Presented at the AOCs meeting, Toronto, Canada, 1962.

² A laboratory of the Utiliz. Res. & Dev. Div., ARS, U.S.D.A.