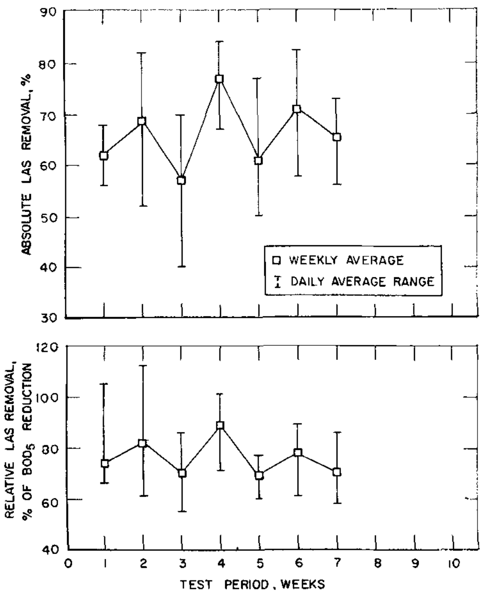

FIG. 4 Removal of a cracked-wax-derived LAS across filter.

data show that this average surfactant removal efficiency is increased by about 5 percentage points when the removals attained by clarification are added to the trickling filter reductions.

When surfactant removal is expressed as per cent of BOD removal, a value of 100% indicates that the surfactant is removed as rapidly as the naturally occurring organics. The lower curve in Figure 3 shows that the relative removal of paraffin-derived LAS was uniform and averaged about 95% of the BOD removal. This field test finding agrees with results from a laboratory-scale study in which an average of about 94% of the BOD removal was obtained (4).

The data obtained during feeding of cracked-wax-derived LAS showed more day-to-day variation as well as a lesser over-all removal of surfactant than did the paraffin-derived material. The average MBAS removal was 68%, with a daily variation of 40 to 85%. The per cent of BOD removal averaged 79.

Rotary-tube trickling filter studies conducted in the laboratory concurrently with the field tests showed relative removals between the paraffin-derived and cracked-wax-derived materials that agreed closely with the results of the full-scale studies. These removals of cracked-wax-derived LAS were significantly higher than that achieved during the prior field test with a similar material (1).

TABLE I

Average Surfactant Removals Across the New Lisbon Trickling Filter

LAS surfactant	Feed range, mg/liter	Average feed concentration, mg/liter[a]	Average surfactant reduction, %	Average BOD reduction, %	Ratio, surfactant removal to BOD removal
Iso-Siv paraffin derived	0–6	4.3	75.5	79.5	0.95
	6–15	9.4	80.0	83.0	0.96
Nondomestic cracked-wax derived	6–15	10.4	64.0	86.5	0.74
	15–20	18.0	73.0	89.0	0.82
	20–25	22.5	67.5	84.0	0.80

[a] Determined as methylene-blue-active surfactant (MBAS).

The filter slimes were periodically tested for adsorbed surfactant using a methanol extraction procedure. The adsorbed surfactant measured during the paraffin-derived LAS and cracked-wax-derived LAS studies were 0.4 and 2.0 mg/g, respectively. These low levels of surfactant associated with the filter solids indicate that the mechanism of removal was bio-oxidation as opposed to adsorption.

In conclusion, these tests have shown that a low-rate trickling filter can remove LAS nearly as readily as it can remove the organic matter in sewage. Highly linear alkylate sources, such as those used for preparing LAS in the United States, are required to achieve the desired removal levels.

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Preparation of Vinyl Esters of Some Chlorinated New Oilseed Crops Fatty Acids

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Abstract

Several mixtures of fatty acids derived from the seed oil of plants being investigated as new crops, have been chlorinated and the chlorinated acids have been converted to the vinyl esters. These products have potential utility as comonomers in vinyl polymerizations.

Introduction

IN THE SEARCH for new oilseed crops, one of the families of plants selected for study has been the *Umbelliferae* (carrots, fennel, parsley, etc.). The seed oils contain 30–76% petroselinic (*cis*-6-octadecenoic) acid, an isomer of oleic acid found (with very few exceptions) only in this family of plants(1).

Another plant which is being studied as a new oilseed crop is *Limnanthes douglasii*. The fatty acids

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obtained from its seed oil are primarily unsaturated and of greater chain length than 18 carbons (2–4). The predominant component is *cis*-5-eicosenoic acid, with substantial amounts of *cis*-5- and *cis*-13-docosenoic acid, and *cis,cis*-5,13-docosadienoic acid.

In the course of utilization studies on petroselinic acid and the *Limnanthes* fatty acids, the vinyl esters have been prepared from certain fractions of acids after saturation of the double bonds by the addition of chlorine. Chlorinated long chain fatty acids and their methyl esters have found utility as plasticizers for polyvinyl chloride and other plastics (5–8). The use of the vinyl esters in the present work will allow incorporation of the chlorinated derivatives in the polymer as a comonomer, which may give improved properties.

The vinyl esters described here include esters of the following acids after chlorination: 1) *Limnanthes* mixed fatty acids; 2) a fraction of *Limnanthes* acids containing approximately 96% 5-eicosenoic acid, this sample derived by fractional distillation of the methyl esters of the mixed acids after removal of the C-22 dienoic acid as is being described (9); 3) a higher boiling fraction of *Limnanthes* fatty acids which contained 92% of C-22 monoenoic acids; and 4) a sample of C-18 monoenoic acids from *Petroselinum sativum* (parsley) seed oil, derived by fractional distillation of the methyl esters. This oil would be expected to be similar to that for which analyses have been reported (10,11), and in which the C-18 monoenoic acids were approximately 83% petroselinic acid and the remainder oleic acid.

Experimental

Materials

Limnanthes douglasii oil was obtained by hexane extractions of the ground seed. The oil was converted to the methyl esters by alcoholysis with methanol employing sodium methoxide as catalyst. The per cent composition of the methyl esters, as determined by GLC, was: 16:0, 0.4; 16:1, 0.2; 18:0, 0.2; 18:1, 1.9; 18:2, 0.8; 20:0, 0.6; 20:1, 63; 20:2, 0.6; unknown, 0.2; 22:1, 20; 22:2, 11; unknown, 0.4; unknown, 0.7. A sample of these mixed esters was freed of most of the C_{22} dienoate by fractional crystallization from acetone, as is being described (9), and the remaining esters fractionally distilled as follows to give the fractions of methyl 5-eicosenoate and mixed methyl docosenoates used in this work. The esters were fractionated through a Todd Precise Fractionation Assembly using the 12-mm column packed with glass helices. A fraction was taken at 179–182C/1 mm, n_D^{25} 1.4520, and used to prepare the vinyl 5,6-dichloroeicosanoate reported in this paper. Gas-liquid chromatography (GLC) analysis of this sample showed it to contain 96% methyl 5-eicosenoate, 2% mixed (5- and 13-isomers) methyl docosenoates, and small amounts of other esters. After removal of most of the methyl 5-eicosenoate through the Todd column, the residue was distilled through a Claisen head to give a fraction at 155–160C/85–100 μ, n_D^{25} 1.4541, which was used to prepare the vinyl dichlorodocosanoate reported in this paper. GLC analysis of this fraction indicated it to be composed of: 20:1, 3; 22:1, 92; and 22:2, 5%.

Parsley seed oil was obtained by hexane extraction of the ground seed. The oil was converted to the methyl esters by alcoholysis with methanol employing sodium methoxide as catalyst. The esters were fractionally distilled through a Podbielniak 4-ft Heli-Grid packed column. The sample of material used in this work had bp 148C/0.5 mm, n_D^{25} 1.4510, and gave, on GLC analysis, a single peak at the point expected for methyl petroselinate or methyl oleate.

Preparation of Vinyl 5,6-dichloroeicosanoate

Methyl 5-eicosenoate (150 g, 0.462 mole) was dissolved in 450 ml of 95% ethanol and heated in a water bath to reflux. A solution of 50 g of KOH in 50 ml of water was added through a dropping funnel over a 5-min period. The solution was allowed to reflux for 25 min longer, then removed from the bath. The soap was treated with concentrated HCl and the acid extracted with petroleum ether washings. The ether solution was dried, then removed below 60C with water aspirator vacuum, then pump vacuum. The residue weighed 140.8 g (98% yield) and was a soft semisolid a room temperature, n_D^{25} 1.4599.

The 5-eicosenoic acid (140 g, 0.444 mole) was transferred to a 3-necked rb flask with 400 ml of CCl_4. The flask was equipped wtih a magnetic stirring bar, a thermometer, a gas inlet tube, and a gas outlet tube directed up a hood. The flask was immersed in an acetone-ice bath and covered with aluminum foil to exclude light. As the solution was stirred the temperature was allowed to drop to ca. 0C. Chlorine gas was then bubbled through the solution at such a rate that the solution temperature did not rise above 20C. Completion of the chlorination was observed after 60 min when the greenish-yellow color of chlorine persisted and when the reaction temperature began to drop rather than rise as the chlorine was added. Excess chlorine was removed by bubbling nitrogen through the solution as it began to warm to room temperature. The solvent was removed on a rotary evaporator below 50C with aspirator vacuum. The residue was a white waxy solid weighing 174 g. This is crude 5,6-dichloroeicosanoic acid. A sample of this crude acid was recrystallized twice from acetone. The recrystallized acid melted at 58.2–60.2C.

Anal. Calcd. for $C_{20}H_{38}Cl_2O_2$: C, 62.98; H, 10.04; Cl, 18.59; eq wt, 381.4. Found: C, 63.12; H, 9.92; Cl, 18.65; eq wt (by titration), 378.0.

A sample of 97 g (0.254 mole) of crude dichloroeicosanoic acid (mp 51–53.5C) was converted to the vinyl ester by treatment with vinyl acetate in the presence of mercuric sulfate catalyst according to the procedure of Lewis and Hedrick (12) with slight modification. The vinylation was allowed to proceed for 88 hr under a nitrogen atmosphere with stirring. The reaction flask was covered with aluminum foil to exclude light. Excess vinyl acetate was removed on a rotary evaporator below 40C with aspirator vacuum, then pump vacuum. The crude vinyl ester was transferred to a separatory funnel with a 50/50 mixture of petroleum ether and diethyl ether. This was washed with 0.5% H_2SO_4 once, then with distilled water twice. These washings were discarded. The ether solution was washed 3 times with 25% alcohol in 0.5 N KOH, then with water to neutrality. The ether solution was dried over Na_2SO_4 and the ether removed below 40C on a rotary evaporator under vacuum. The residue was an orange-colored oil weighing 63.7 g. The alkaline and water washings were acidified and the acids extracted with ether to yield 34 g of recovered material, which proved to be mainly vinyl ester. The ester (23.3 g) was separated from the acids by elution through an alumina column (100 g of alumina packed by gravity to a height of 45 cm in a column of 1.9 cm diam) with diethyl ether. The total yield of 97 g of vinyl 5,6-dichloroeicosanoate represents 93% of the theory. It had n_D^{25} 1.4720.

Anal. Calcd. for $C_{22}H_{40}Cl_2O_2$: C, 64.85; H, 9.90; Cl, 17.40. Found: C, 64.82; H, 9.84; Cl, 17.56.

Preparation of Vinyl Dichlorodocosanoate

Methyl docosenoate (110 g, 0.312 mole) was saponified as described for the eicosenoate to yield 103 g (97%) of the mixed docosenoic acids, n_D^{25} 1.4611. This material was chlorinated, yielding 126 g of mixed chlorinated acids. A sample of 121 g of this waxy material was converted to the vinyl ester as described for dichloroeicosanoic acid and the product washed free of unreacted acid with alkali. A yield of 99.2 g (77%) of vinyl ester was obtained, which had n_D^{25} 1.4738 and analyzed 17.59% chlorine (calcd. for $C_{24}H_{44}Cl_2O_2$: Cl, 16.29). The impurity of the starting ester prevented the obtaining of analytically pure vinyl dichlorodocosanoate. The material washed out with alkali amounted to 24 g and, judging from the IR spectrum, contained considerable vinyl ester, but was not further investigated.

Preparation of the Vinyl Ester of Limnanthes douglasii Mixed Chlorinated Fatty Acids

Limnanthes douglasii oil (150 g) was chlorinated as described for eicosenoic acid. The weight of chlorinated oil obtained was 197.5 g. This was refluxed with 50 g KOH in 95% alcohol for 70 min. The unsaponifiables were removed by gently washing the soaps with petroleum ether. The soap solution was acidified and the acids removed with petroleum ether washings. The recovered chlorinated *Limnanthes* acids were solid at room temperature and weighed 153 g This was converted to the vinyl ester using 2.8 moles of vinyl acetate. The unreacted acids (51 g) were removed by alkaline washings (as previously described). No attempt was made to recover more vinyl ester from the washed out material. The yield of vinyl ester was 108 g. It was treated twice with carbon black and Na_2SO_4 to give 96 g of an orange-colored oil having n_D^{25} 1.4735 and analyzing for 17.06% chlorine.

Preparation of Vinyl Dichlorostearate

A sample of 125 g (0.422 mole) of the methyl ester of the C-18 monoenoic acids from parsley seed oil was chlorinated as described for eicosenoic acid, yielding 159.5 g of crude methyl dichlorostearate, n_D^{25} 1.4707. This material (158 g) was saponified with 50 g of KOH by refluxing in 95% alcohol for 50 min. Excess alcohol was removed on a rotary evaporator below 50C. The soaps were taken up in water and any unsaponified material removed by gently washing with a 50:50 mixture of petroleum ether and diethyl ether. The aqueous layer was acidified with HCl and the acids recovered by washing with petroleum ether. The ether solution was washed free of mineral acid, dried over Na_2SO_4 and filtered. The ether was removed below 70C on a rotary evaporator with house vacuum, then pump vacuum. The residue weighed 139 g (91% yield), had mp 39–57C, and analyzed 17.19% chlorine (theory, 20.07).

This crude acid (127 g) was converted to the vinyl ester by the method previously described. The ester was taken up in diethyl ether and washed with 0.5% H_2SO_4 then with water to neutrality. The ether solution (400 ml) was dried over Na_2SO_4 and filtered.

An alumina column, instead of alkaline washings, was used to remove the unreacted acids. A glass column (4.2 cm in diam) was packed by gravity in diethyl ether with 400 g of alumina to a height of 40 cm. The 400 ml of ether solution of crude vinyl ester was eluted through the column and followed with 800 ml of fresh ether. The first 400 ml of eluate waws discarded. The next 900 ml was put on a rotary evaporator below 40C with house vacuum, then pump vacuum. The vinyl dichlorostearate was obtained as an orange-colored oil weighing 91 g (67% yield), n_D^{25} 1.4703.

Anal. Calcd. as $C_{20}H_{36}Cl_2O_2$: C, 63.31; H, 9.57; Cl, 18.69; OH, none. Found: C, 63.44; H, 9.56; Cl, 15.37; OH, 3.66.

Discussion

A problem encountered in this work was that chlorination of the free fatty acids resulted in the formation of a small amount of ester or polyester, as detected by a shoulder at 5.73 μ on the side of the carboxyl absorption band (at 5.82 μ) in the IR spectrum. Reaction of the carboxyl group with the chloronium intermediate on addition of chlorine to a double bond is a known reaction (13). This problem was avoided in the case of the methyl petroselinate sample from parsley seed oil by chlorination of the ester. However, a more serious problem was introduced since a substantial amount of chlorine was removed from the product on saponification, and hydroxyl groups were introduced.

Another problem encountered was the removal of a substantial amount of the vinyl ester along with the unreacted chlorinated fatty acid on alklaline washing of the product after vinylation. The presence of the ester in the recovered "unreacted acid" was clearly discernible from the presence of absorption bands at 6.05 μ, 10.55 μ, and 11.50 μ in the IR spectrum, these bands being characteristic of the vinyl ester grouping. This problem was solved by removal of the acids on an alumina column using diethyl ether as the eluent, as described in the "Experimental" section.

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Analysis of the *Limnanthes* mixed methyl esters and removal of the dienoate by Sara P. Fore.

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