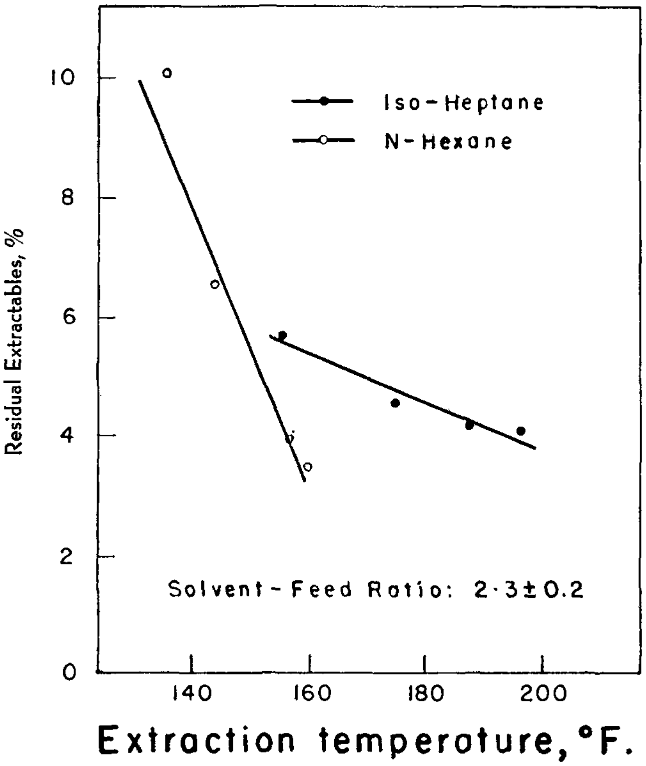

FIG. 6. Effect of temperature on residual extractables, using hexane and iso-heptane as solvents. Extraction time, 25 min. Pilot-plant extraction.

The effect of temperature in 25-min. extraction time on the residual extractables is shown in Figure 6. As would be expected, the amount of oil extracted by both solvents increased with the temperature. Here again hexane appeared to be a somewhat better solvent.

The somewhat better extraction obtained with hexane would have little significance if the two solvents were being compared at the same temperature. However, on the basis of the rate-extraction data, the iso-heptane at 192° F. should be definitely superior to hexane at 157°F. On the other hand, since the rate extraction studies and the pilot plant studies were not carried out under the same extraction conditions, close correlation between the results of the two should not be expected. Based on previous work with other materials, it was expected that the results would show a rough correlation. A possible explanation for the discrepancy is that at 157°F. the agitation caused by boiling hexane might have a beneficial effect. At the solvent-entry end of the extractor vapors from the boiling solvent rising upward with the extracted flakes might condense on them before reaching the dryer and exert an extra washing action. At the feed end vapors passing up into the incoming mass of flakes would condense on the flakes and start dissolving oil.

## Summary and Conclusions

Rate-extractions of corn germ oil by heptane, iso-heptane, and hexane at the same temperature showed the latter two to be better solvents than heptane. Extraction rate increased with the temperature.

Countercurrent extraction in a continuous laboratory pilot plant showed hexane at 157°F. apparently equal to iso-heptane at 192°F. It is suggested that the boiling of the hexane at 157°F. might account for the better extraction.

It can be concluded that hexane is at least as good a solvent for the extraction of corn oil from whole germ as is iso-heptane.

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# Reactions of Unsaturated Fatty Alcohols. I. Preparation and Properties of Some Vinyl Ethers[1]

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ALTHOUGH a polymer of vinyl octadecyl ether was among the first vinyl ether products offered commercially, comparatively little information is available on the preparation, properties, and polymerization of alkyl vinyl ethers having long-chain alkyl groups. Vinyl octadecyl and vinyl oleyl ethers are referred to a number of times in the patent literature, but detailed procedures and descriptions are seldom provided. So far as we have been able to determine, vinyl ethers of polyunsaturated alcohols such as linoleyl and linolenyl alcohols, or of mixed alcohols derived from unsaturated oils like soybean and linseed oils, are not mentioned in the literature. For a general discussion of the chemistry of alkyl vinyl ethers and a review of existing literature Reference 6 should be consulted.

## Preparation of Vinyl Ethers

For laboratory purposes it was desired to synthesize vinyl ethers from the appropriate alcohol and acetylene at atmospheric pressure in order to avoid the hazardous operations and the complexities of technique and apparatus involved in pressure reactions with acetylene (3). Reppe has pointed out (5) that pressure is not required in vinylation of high-boiling alcohols and has described a procedure for the synthesis of vinyl octadecyl ether, using acetylene at atmospheric pressure. This procedure, which is a continuous process intended for industrial use, was not

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considered suitable for laboratory purposes because of the complex equipment required. A study of the reaction of stearyl alcohol with acetylene at atmospheric pressure at various temperatures and with different concentrations of alkaline catalyst was therefore undertaken. The apparatus used is shown in Figure 1. Representative examples of the results obtained are shown graphically in Figure 2.

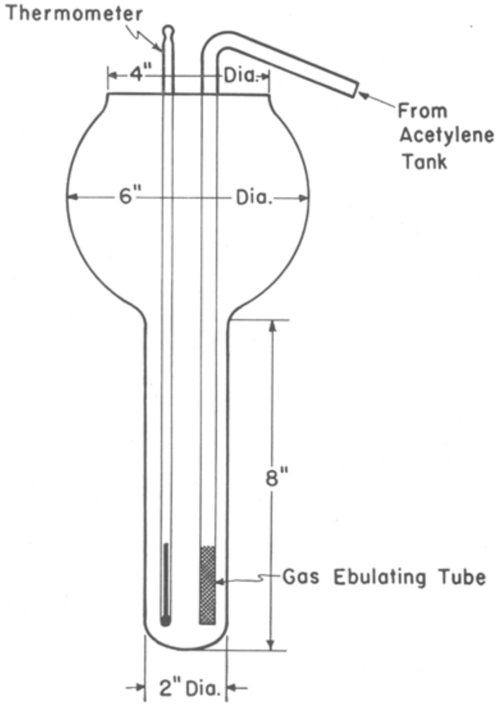

FIG. 1. Vinylation apparatus.

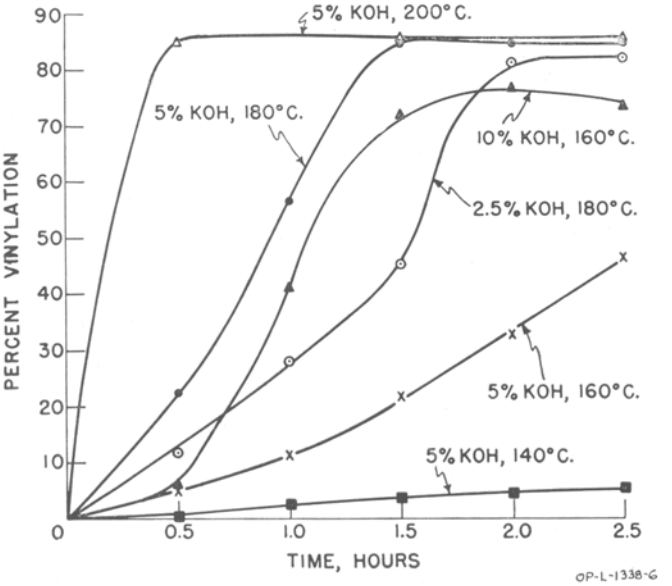

FIG. 2. Effect of catalysts and conditions on vinylation of stearyl alcohol.

On the basis of these results it was concluded that use of 5% of potassium hydroxide as catalyst and a temperature of 180° gave maximum vinylation of 85–88% as determined by direct analysis of the reaction mixture for vinyl groups. The vinyl ethers were isolated in 60–75% yields by direct distillation of the reaction mixture.

The effect of temperature over a range of 140–200° was investigated for the vinylation of stearyl alcohol using a moderate flow of acetylene (12–18 cc./min.) and 5% of potassium hydroxide as catalyst. At 140° vinylation of stearyl alcohol to the vinyl ether proceeded slowly to the extent of 5.2% in 2.5 hrs. At 160° the reaction progressed more rapidly and gave 46% vinylation in 2.5 hrs.

Maximum vinylation (85–88%) was obtained in approximately 1.5 hrs. at 180°. This reaction time varied from 1.25 to 1.75 hrs., depending upon the rate of flow of acetylene used. The optimum rate of flow was not investigated. After maximum vinylation was attained, the reaction mixture foamed excessively and the mixture became viscous and darkened rapidly.

Vinylation of stearyl alcohol at 200 and 220° reached its maximum in 0.5 hr. An additional 2 hrs. of reaction time did not increase the yield of the vinyl ether. During this time the mixture became a black semi-solid mass.

At 160° with 10% of potassium hydroxide as catalyst, 77% vinylation of stearyl alcohol was obtained in 2 hrs. Further vinylation gave a very viscous material with a loss of the vinyl ether group. The use of 2.5% of catalyst at 180° gave a non-viscous oil containing 82.9% stearyl vinyl ether.

Catalysts such as sodium hydroxide and sodium methoxide gave lower vinylation, and isolation of the vinyl ethers in 55–65% yields probably because of the formation of larger amounts of stearic acid (3). The use of zinc stearate as a catalyst resulted in recovery of unreacted starting material.

Vinylation of 1,12-octadecandiol prepared by catalytic reduction of ricinoleyl alcohol (Adol 40)[4] gave 1,12-octadecandiol divinyl ether. 12-Hydroxystearyl vinyl ether was obtained from 1,12-octadecandiol by stopping the reaction when 90–95% monovinylation had occurred as determined by iodometric analysis.

Catalytic reduction of 12-hydroxystearyl vinyl ether gave the corresponding ethyl ether. Vinylation of this product gave 12-vinyloxystearyl ethyl ether. The position of the vinyl ether group in these products was determined by oxidizing the ethyl hydroxyoctadecyl ether with chromic acid (2). The isolation of a keto ethyl ether demonstrated that the compound oxidized was 12-hydroxy stearyl ethyl ether.

Attempts to prepare the vinyl ether of ricinoleyl alcohol resulted in rapid polymerization. Methyl 12-hydroxystearate gave a solid mass containing less than 1% vinyl ether.

Vinylation of *n*-octyl, oleyl, elaidyl, and *t,t*,9,11-octadecadienyl alcohol at 180° gave the corresponding vinyl ether in 55–65% yields.

The reactions discussed show that acetylene at atmospheric pressure in the presence of an alkaline catalyst may be used to vinylate primary or secondary alcohols having a boiling point greater than 190° (*n*-octanol, b.p. 195°) and not containing an alkali sensitive group (such as an ester).

## Polymerization

Polymerization of stearyl vinyl ether, using various ionic catalysts such as aluminum chloride, stannic

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[4] The mention in this article of commercial products or equipment under names of their manufacturers does not constitute endorsement by the U. S. Department of Agriculture of such firms or products.

TABLE I

Vinyl Ether Polymers

| | Catalyst | Color | M. wt. | Rx time | I. V. | m. p. |
|---|---|---|---|---|---|---|
| | | | *g.* | *hrs.* | | °C. |
| Stearyl vinyl ether | $AlCl_3$ | Orange-brown | 670 | 3 | — | 45–46.5 |
| | $AlCl_3$[a] | Dark brown | 1,450 | 3.5 | — | 48–49 |
| | $SnCl_4$ | Orange | 1,150 | 5.5 | — | 44–45 |
| | $SnCl_2$ | Pale yellow | 2,170 | 48 | — | 48–49 |
| | $ZnCl_2$ | Orange-brown | 2,026 | 70 | — | 46–47 |
| | $BF_3$[b] | White | 1,880 | 3 | — | — |
| | $FeCl_3 \cdot 6H_2O$ | Chalk-white wax | 4,915 | 2 | — | 49° |
| Oleyl vinyl ether | $AlCl_3$ | Yellow oil | 590 | 4 | 83.8 | [c] |
| | $SnCl_2$ | Dark red | 830 | 4 | 90.5 | [c] |
| | $BF_3$ | Water white | 1,360 | 18 | 82.0 | [c] |
| Soybean vinyl ether | $SnCl_4$ | Golden yellow | 1,490 | 48 | 99.5 | [c] |
| | $BF_3$ | Water white | 1,070 | 1 | 93.6 | [c] |
| | $BF_3$[d] | Water white | 2,600 | 1 | 80.0 | [c] |
| Linseed vinyl ether | $SnCl_2$ | Red brown | 1,636 | 48 | 123.0 | [c] |
| | $FeCl_3 \cdot 6H_2O$ | Water white | 1,230 | 2 | 88.0 | [c] |

[a] 0.150 g. of catalyst added every 45 min.

[b] All $BF_3$ polymers prepared at room temperatures.

[c] Liquid polymer obtained.

[d] Prepared without benzene as solvent.

chloride, stannous chloride, zinc chloride, ferric chloride hexahydrate (7), and boron trifluoride, gave polymers with low molecular weights (see Table I). Ferric chloride hexahydrate gave a chalk-white, waxy solid having a molecular weight of 4,915. The color of the other polymers varied from light yellow to dark red, and molecular weights ranged from 600 to 2,500.

The unsaturated vinyl ethers, when polymerized with boron trifluoride, gave viscous colorless liquids. These polymers were found to give hard, dry films at 150° with cobalt naphthenate present as a drier.

## Infrared Absorption

Infrared absorption spectra were used to follow fractionations and confirm reactions as well as to estimate purity. All spectra were obtained on a Perkin-Elmer Model 21 recording double-beam infrared spectrophotometer with a rock salt prism. Most samples were studied both in solution in carbon disulfide in a 0.5-cm. cell and as pure liquid in a 0.0025-cm. cell. Some high melting compounds were studied only in solution, and some very viscous materials were examined only as smears on silver chloride.

Quantitative data were taken from solution spectra in the form of "differential absorptions." They were measured from a tangent to the transmission peaks on each side of the band in question. Any absorption at the transmission peaks due to the sample was ignored so that a measurement was less than the true absorption by this amount (which is small). Units for partial absorption coefficients were moles/liter for concentration, cm. for length, and base 10 logarithms for the ratio of light. Table II presents the data for all compounds measured. The main bands are listed in columns by number with the measured frequency given in $cm.^{-1}$. The absorption coefficients, when measured, are given in parentheses below the band frequency.

*Alcohols.* The spectra of these compounds were typical of alcohols. In solution, a medium band, due to "OH" unassociated, was found at 3620 $cm.^{-1}$ (Band I of Table II). In the pure liquid a strong band (II) due to OH associated or bonded was found at 3340 $cm.^{-1}$. Partial molecular absorption coefficients for Band I obtained on the three primary alcohols which permitted the measurements agreed very well, but the coefficient for 1,12-octadecandiol, which was expected to be twice that for the monohydric alcohols, was only 20% higher. This result is unexplainable at present. The spectra of these alcohols differ in the 900 $cm.^{-1}$ to 1000 $cm.^{-1}$ region (Bands XII, XIII, XIV, and XV) because of geometric isomerism.

The commercial sample of soybean alcohol (Unadol 40) (I.V., 116.5) contained small amounts (*ca.* 5%) of *trans,trans* conjugation (985 $cm.^{-1}$) and *cis,trans* conjugation (*ca.* 20%) (980 $cm.^{-1}$ and 945 $cm.^{-1}$), giving a total diene of 25%, whereas a sample of soybean alcohol (I.V., 143), prepared in this laboratory, contained less than 1% total diene conjugation. The commercial sample of linseed alcohol (Unadol 90) contained about the same amounts of *trans,trans* and *cis,trans* conjugation as did the commercial soybean alcohol.

*Vinyl Ethers.* The vinyl ethers gave typical spectra. Hydroxyl bands (I or II of Table II) at 3620 $cm.^{-1}$ or 3340 $cm.^{-1}$ were absent. A strong band (V) due to "C=C" stretching in the vinyl group appeared at 1620 $cm.^{-1}$. A strong band (IX) at 1200 $cm.^{-1}$ was found which is attributable to "C—O—C" deforming in the vinyl ether. The four long chain mono-ethers had absorption coefficients of 289, 278, 322, and 323 (average, 303). The coefficient for the divinyl ether was 606, or exactly twice the average value for the mono-ethers. A medium band (XIV) at 965 $cm.^{-1}$ and a weak band (XV) at 945 $cm.^{-1}$ due to "CH" out-of-plane deforming in the vinyl group, were found. A strong band (XVI) at 810 $cm.^{-1}$ was found that was not present in the alcohols or ethyl ethers. A structural assignment is not made for this band; however it appears to be characteristic of the vinyl group.

The vinyl ether of soybean alcohols (laboratory prepared) contained 44% diene conjugation. This conjugation would be expected as the alkaline catalyst should isomerize the main polyunsaturated component (linoleyl alcohol) to the *cis,trans* conjugated configuration. However infrared analysis indicated the presence of 34% of *trans,trans* conjugated isomers.

Since the presence of *trans,trans* isomers was unexpected, the following experiment was performed. A quantity of soybean alcohol containing about 10% *cis,trans* conjugation was divided into two samples. One sample was mixed with 5% of potassium hydroxide, and acetylene was passed into the mixture at

TABLE II

Infrared Data on Alcohols and Ethers. Principal Bands, Relative Intensities, and Some Molecular Absorption Coefficients

| Compounds | Band No., Measured Frequency (cm.$^{-1}$) and Absorption Coefficient[a] (liter mol.$^{-1}$, cm.$^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | I 3620[b] | II 3340 | III 2910 | IV 1650 | V 1610 | VI 1470 | VII 1380 | VIII 1320 | IX 1200 |
| *n*-Octyl alcohol | —[c] | 3340s | 2910s | — | — | 1470s | 1380m | — | — |
| Stearyl alcohol | 3620m(23.9) | — | 2910s | X[d] | X | X | X | X | — |
| Oleyl alcohol | 3620m(23.9) | 3340s | 2890s | 1660w | — | 1460s | 1380m | — | — |
| Elaidyl alcohol | 3620m(22.6) | — | 2890s | X | X | X | X | X | — |
| *t,t*-9,11-Octadecadienyl alcohol | 3620m | — | 2920s | X | X | X | X | X | — |
| 1,12-Octadecandiol | 3620s (27.7) | — | 2960s | X | X | X | X | X | — |
| *n*-Butyl vinyl ether | — | — | 2930s | 1630w | 1610s | 1470m | 1380m | 1320s | 1200s |
| *n*-Octyl vinyl ether | — | — | 2900s | 1640m | 1610s | 1470s | 1380m | 1320s | 1200s |
| Stearyl vinyl ether | — | — | X | X | X | X | X | 1320m | 1200s(289) |
| Oleyl vinyl ether | — | — | 2930s | 1650m | 1620s | 1470s | 1380m | 1320s | 1205s(278) |
| Elaidyl vinyl ether | — | — | 2930s | 1650w | 1620s | 1470s | 1380m | 1320s | 1205a(322) |
| *t,t,*-9,11-Octadecadienyl vinyl ether | — | — | 2920s | 1650m | 1620s | 1470s | 1380m | 1320s | 1206s(323) |
| 1,12-Octadecandiol divinyl ether | — | — | 2910s | m | s | 1470s | 1370m | 1320s | 1198s(606) |
| Stearyl ethyl ether | — | — | X | X | X | X | X | — | — |

| Compounds | X 1130 | XI 1080 | XII 988 | XIII 981 | XIV 965 | XV 945 | XVI 810 | XVII 720 |
|---|---|---|---|---|---|---|---|---|
| *n*-Octyl alcohol | 1120m | 1060s | 990w | — | 957w | — | — | 725s |
| Stearyl alcohol | X | X | — | — | — | — | X | X |
| Oleyl alcohol | 1130w | 1060s | — | — | — | — | — | 720s |
| Elaidyl alcohol | X | X | — | — | 965s (124) | — | X | X |
| *t,t*-9,11-Octadecadienyl alcohol | X | X | 985s(356) | — | — | — | X | X |
| 1,12-Octadecandiol | X | X | — | — | — | — | X | X |
| *n*-Butyl vinyl ether | 1130m | 1080m | — | — | 962m | 945w | 810s | 700w |
| *n*-Octyl vinyl ether | 1135m | 1080s | — | — | 964m | 944w | 810s | 721m |
| Stearyl vinyl ether | X | X | — | — | 962m(60.7) | 942w(16) | 808s(143) | X |
| Oleyl vinyl ether | — | — | — | — | 963m(60.3) | 945m(17.7) | 809s(152) | 720m |
| Elaidyl vinyl ether | — | 1080m | — | — | 966s (159) | 944w(11.6) | 809s(183) | 720m |
| *t,t,*-9,11-Octadecadienyl vinyl ether | — | 1080m | 988s(245) | — | 964m(72) | 948w(38) | 810s(164) | 722m |
| 1,12-Octadecandiol divinyl ether | 1130w | 1080m | — | 981w | 964m(116) | 946m(86) | 809s(247) | 721m |
| Stearyl ethyl ether | 1115s | X | — | — | — | — | — | X |

[a] Absorption coefficients are given in parentheses.
[b] OH stretching, unassociated. This band appears only in the spectrum of a dilute solution.
[c] "—" indicates the absence of a band.
[d] "X" indicates that the material was examined only in solution; solvent absorption masked the region.

180°C. for 45 min. The second sample was treated in the same way except that oxygen-free nitrogen was used in place of acetylene. Absorption at 985 cm.$^{-1}$ was greatly enhanced in both samples. In the second sample, 30.3% of *cis,trans* conjugated product and 20.5% of *trans,trans* conjugated product were observed. This experiment indicates that the *trans,trans* conjugated isomer can be formed directly by alkali isomerization under these conditions.

Vinylation of the *trans,trans*-9,11-octadecadienyl alcohol gave a product having a lower molecular coefficient at 988 cm.$^{-1}$ (Band XII) and a higher molecular coefficient at 948 cm.$^{-1}$ (Band XV) than the original alcohol. While these differences cannot be wholly explained on a quantitative basis, it is evident that some of the *trans,trans* conjugated system was isomerized to the *cis,trans* configuration during vinylation. The results indicate that an equilibrium may exist under these conditions in which *trans,trans* and *cis,trans* conjugated isomers are present in a ratio of 3:1.

*Ethyl Ethers.* Catalytic reduction of stearyl vinyl ether to stearyl ethyl ether resulted in typical changes in the infrared absorption. The "CH" bands of the vinyl group at 965 cm.$^{-1}$ and 945 cm.$^{-1}$ (Band XIV and XV) disappeared. The "C—O—C" deformation band (IX) at 1200 cm.$^{-1}$, characteristic of vinyl ethers, shifted to 1115 cm.$^{-1}$ (Band X), characteristic of alkyl ethers. The molecular absorption coefficient for stearyl ethyl ether was 299, a value nearly equal to the average value (303) for the vinyl ethers. Infrared absorption spectra of other ethyl ethers listed in Table IV differed similarly from those of the related vinyl ethers.

*Vinyl Ether Polymers.* All the bands due to vinyl groups were absent in the polymers, but those due to geometric isomerism remained apparently unchanged. The "C—O—C" band shifted from 1200 cm.$^{-1}$ to 1090 cm.$^{-1}$ characteristic of alkyl ether linkages. This indicates that polymerization involved only the vinyl groups.

## Methods of Analysis

Although several methods of analysis for the vinyl group in vinyl ethers have been reported (8), only a few procedures are adapted for the vinyl ethers of long-chain fatty alcohols. These methods often give inconsistent results due to insolubility of a specific sample. We have modified the iodometric procedure of Siggia and Edsburg (9) and the hydroxylamine hydrochloride procedure of Bryant and Smith (1). Both modified procedures were found to work well for *n*-octyl, stearyl, and the various unsaturated $C_{18}$ vinyl ethers studied. An infrared method of analysis for vinyl groups was also developed that is based on oleyl vinyl ether as a standard. A comparison of the three methods of analysis is given in Table III.

TABLE III

Comparison of Methods of Analysis for Vinyl Groups in Two Different Samples of Stearyl Vinyl Ether

| Sample no. | Vinyl groups (%) by method stated | | |
|---|---|---|---|
| | Iodometric | Hydroxylamine | Infrared |
| 1 | 94.0<br>93.6<br>93.6 | 94.1<br>94.2<br>— | 90.2<br>—<br>— |
| 2 | 93.1<br>91.7 | 90.2<br>91.2 | 90.4<br>— |

*Iodometric Method.* This method is rapid and gives results within 1% of those obtained by the hydroxylamine hydrochloride procedure. Ethanol is used as solvent to insure complete solubility of the sample of long-chain vinyl ether. Acetic acid is added to keep the solution in the proper pH range, thus avoiding such side reactions as the iodoform reaction.

TABLE IV

Properties and Analyses of Products

| Compound | m.p. | b.p. | $n_D^{30}$ | Analysis |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Calculated |  | Found |  |
|  |  |  |  | C | H | C | H |
|  | °*C.* | °*C./mm.Hg.* |  | % | % | % | % |
| Methyl *t,t*-9,11-octadecadienoate | — | 164-5/0.6 | 1.4692 | 77.49 | 11.64 | 76.98 | 11.48 |
| *t,t*-9,11-Octadecadienyl alcohol | 42.4-42.7[a] | — | — | 81.25 | 12.78 | 80.87 | 12.64 |
| 1,12-Octadecandiol | 78.5-79.5[b] | — |  | Calculated OH, 11.85; Found, 11.81 |  |  |  |
| *n*-Octyl vinyl ether | — | 187 | 1.4427 | 76.86 | 12.90 | 76.98 | 12.86 |
| Stearyl vinyl ether | 31 | 164/0.4 | 1.4451 | 81.00 | 13.59 | 81.16 | 13.50 |
| Oleyl vinyl ether | — | 165/1.25 | 1.4529 | 81.56 | 13.00 | 81.52 | 12.87 |
| Elaidyl vinyl ether | — | 135-8/0.25 | 1.4530 | 81.56 | 13.00 | 81.52 | 12.98 |
| Soybean vinyl ether | — | 146-56/0.2 | 1.4642 | — | — | — | — |
| Linseed vinyl ether | — | 136-56/0.15 | 1.4701 | — | — | — | — |
| 9,11-Octadecadienyl vinyl ether | — | 160-2/0.6 | 1.4736 | 82.21 | 12.34 | 81.59 | 12.31 |
| 12-Hydroxystearyl vinyl ether | 50.5-51.5[c] | 135-80/2.0 | — | 76.99 | 12.81 | 76.78 | 12.76 |
| 1,12-Octadecandiol divinyl ether | — | 166/0.35 | 1.4524 | 78.10 | 12.42 | 78.14 | 12.31 |
| 12-Vinyloxystearyl ethyl ether | — | 182/1.0 | 1.4459 | 77.58 | 13.02 | 77.69 | 12.97 |
| Stearyl ethyl ether | 29.0-30.0 | 134-5/0.15 | — | 80.46 | 14.14 | 80.48 | 14.08 |
| 12-Hydroxystearyl ethyl ether | 45.0-45.5[d] | — | — | 76.25 | 13.34 | 76.45 | 13.33 |
| 12-Ketostearyl ethyl ether | 36.5-37.5[c] | — | — | 76.86 | 12.90 | 76.72 | 12.88 |
| 1,12-Octadecandiol diethyl ether | −13 | 178-80/0.2 | 1.4396 | 77.12 | 13.53 | 77.09 | 13.51 |

[a] Crystallized from methanol.
[b] From petroleum ether (b.p. 80-98°).
[c] From *n*-hexane.
[d] From petroleum ether (b.p. 30-60°).

Fifty milliliters of aqueous iodine-potassium iodide solution (12.7 g. of iodine and 15 g. of potassium iodide per liter) are added to a glass-stoppered flask containing a solution of approximately 0.001 mole of sample dissolved in 50 ml. of 95% ethanol containing 5 drops of glacial acetic acid. The flask is swirled for 5 min. and immediately titrated with 0.1 N sodium thiosulfate solution. A blank determination is made simultaneously. Results are calculated from the following equation:

$$\%\ \text{vinyl ether} = \frac{(\text{ml. for blank} - \text{ml. for sample})\ \text{x}\ (\text{N of Na}_2\text{S}_2\text{O}_3)\ \text{x}\ (\text{M.W. ether})\ \text{x}\ 100}{(\text{wt. of sample})\ \text{x}\ 2{,}000}$$

*Hydroxylamine Hydrochloride Method.* The sample (0.001 mole) is added to 50 ml. of methanol and 5 ml. of IM aqueous hydroxylamine hydrochloride solution (freshly prepared). The sample and a blank are refluxed for 1 hr. and then cooled rapidly to room temperature. Fifty milliliters of water are added to each flask. The sample is then titrated with 0.1 N sodium hydroxide solution to the pH of the blank. Results are calculated from the following equation:

$$\%\ \text{vinyl ether} = \frac{(\text{ml. NaOH for sample})\ \text{x}\ (\text{N of NaOH})\ \text{x}\ (\text{M.W. ether})\ \text{x}\ 100}{(\text{wt. of sample})\ \text{x}\ 1{,}000}$$

*Infrared Method.* The samples were dissolved in carbon disulfide and the absorption of the band at 1200 cm.$^{-1}$ (Band IX, Table II) was determined. With oleyl vinyl ether as a reference compound, the percentage of vinyl ether is calculated from the following equation:

$$\%\ \text{vinyl ether} = \frac{(\text{A})\ \text{x}\ (\text{M.W. ether})\ \text{x}\ 100}{(327)\ \text{x}\ (\text{L})\ \text{x}\ (\text{C})}$$

where A is the absorptivity at 1200 cm.$^{-1}$.
L is the path length in cm.
C is the concentration in g./l.
327 is the molecular absorption coefficient maximum at 1200 cm.$^{-1}$ in l./cm. g. units for oleyl vinyl ether.

## Experimental

Properties and analyses of products prepared are listed in Table IV.

*Materials.* *n*-Octyl alcohol (yellow label), stearyl alcohol (m.p. 57.5–58.0°) (white label), and *n*-butyl vinyl ether (yellow label) were obtained from Eastman Kodak Company. *n*-Butyl vinyl ether was distilled from sodium, then fractionated using a Podbielniak column. A fraction b.p. 91.8–92.0° was retained.

Oleyl alcohol and soybean alcohols were prepared by reduction of the methyl esters with sodium in absolute alcohol. The oleyl alcohol (b.p. 153–155°/0.5 mm.; $n_D^{30}$, 1.4459) showed a small amount of *trans* material in the infrared spectrum. The soybean alcohols (b.p. 153–163°/0.45 mm.; $n_D^{30}$, 1.4682) appeared to be free of any *trans* material and contained 0.44% diene and no triene conjugation. Both alcohols were contaminated by a small amount of fatty acid, as evidenced by a weak band at 1710 cm.$^{-1}$.

Elaidyl alcohol (m.p. 34–35°) was furnished by the Eastern Utilization Research Branch. This material had a partial molecular coefficient of 124 for the band at 965 cm.$^{-1}$ (absorption due to *trans* configuration).

Ricinoleyl alcohol (Adol 40), soybean fatty alcohols (Unadol 40), and linseed fatty alcohols (Unadol 90) were obtained from the Archer-Daniels-Midland Company. These materials were distilled before use. A small fore-run and residue were discarded.

1,12-Octadecandiol was prepared by catalytic hydrogenation of ricinoleyl alcohol. The absorption coefficient of this compound at 3620 cm.$^{-1}$ was 27.7, whereas one of the order of 46 was expected. Nevertheless the preparation appeared to be pure because its divinyl ether gave the expected absorption coefficient (606). The low value is unexplainable at present.

*General Vinylation Procedure.* All vinylation reactions were carried out in a large test tube having a flared top to accommodate foaming. This test tube was constructed from a 2-liter, long-necked, Florence flask by removing the bottom and sealing the neck (see Figure 1).

The catalyst (dissolved in a small amount of methanol) was added slowly to the compound at the desired vinylation temperature, and sufficient time was allowed to volatilize the methanol before passing in tank acetylene at a moderate rate through a gas diffusion tube. At the completion of the reaction (as determined by a vinyl ether analysis) the mixture was cooled, transferred quantitatively to a distilling flask (benzene can be used as a solvent), and rapidly distilled. Fractional distillation of the vinyl ethers, using a 40 x 0.8 cm. Vigreux column, gave the products submitted for analysis (see Table II).

*Methyl t,t-9,11-Octadecadienoate.* A solution of 15 g. of *t,t*-9,11-octadecadienoic acid dissolved in 150 ml. of absolute methanol containing 15 drops of concentrated sulfuric acid was refluxed for 21 hrs. The solution was poured into 300 ml. of water and extracted with three 50-ml. portions of ether. The combined ether extracts were washed with water, 25 ml. of a 50% sodium carbonate solution, and again with water. Removal of the ether followed by distillation of the residue gave 11.2 g. (72%) of product boiling at 164–165° (0.6 mm.): $n_D^{30}$ 1.4692.

*t,t-9,11-Octadecadienyl Alcohol.* A solution of 10.8 g. of methyl *t,t*-9,11-octadecadienoate in 20 ml. of absolute ether was added dropwise to 1.6 g. of lithium aluminum hydride in 100 ml. of ether. The mixture was stirred 4 hrs. before adding excess ethyl acetate to decompose unreacted hydride. Dilute hydrochloric acid was added to dissolve the precipitated salts, and the ether layer was separated. After washing the ether layer with water and removal of the ether, the crude product solidified. Three recrystallizations from methanol gave 7.9 g. (81%) of white crystalline product, m.p. 42.4–42.7°; maximum $E_{1\%}^{1\,cm.} = 1196$.

*Reduction of Vinyl Ethers.* Stearyl ethyl ether, 12-hydroxystearyl ether, and 1,12-octadecanediol diethyl ether were prepared by catalytic hydrogenation (40-lb. gauge pressure) of the corresponding vinyl ether in absolute ethanol using platinum oxide as catalyst.

*Polymerization of the Vinyl Ethers.* (See Table II for properties of some of the vinyl ether polymers.)

A. *General Procedure.* The vinyl ether (15 g.) dissolved in at least 10–15 ml. of absolute benzene was added dropwise to 150 mg. of the catalyst in 10 ml. of absolute benzene. Polymerization reactions involving aluminum chloride were refluxed for 4 hrs.; stannous chloride and zinc chloride reactions were refluxed for 48 hrs. Steam distillation of the benzene solution followed by decantation gave the polymer as a residue. The polymer was purified by trituration with hot methanol to remove monomer and any long-chain alcohol that might be present. Excess methanol was eliminated from the polymer by evaporation *in vacuo.*

B. *Polymerization with Boron Trifluoride.* One drop of 15% boron trifluoride etherate was added to 15 g. of the monomer in 15 ml. of absolute benzene. The temperature was not allowed to rise above 30°. Water was added to quench the reaction at the end of 1 hr. The reaction mixture was then treated as in Method A.

Molecular weights of polymers were determined by measuring boiling point elevation of benzene solutions.

## Summary

A number of vinyl ethers of $C_{18}$ fatty alcohols have been prepared by reaction of the alcohol with acetylene at atmospheric pressure in the presence of a basic catalyst. Infrared spectroscopic data on long-chain fatty alcohols, their vinyl ethers, and related chemical derivatives have been obtained. Methods of analysis of long-chain vinyl ethers for vinyl group have been developed, namely, iodometric, hydroxylamine, and infrared methods.

Preliminary experiments on the polymerization of long-chain vinyl ethers with ionic catalysts were carried out.

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# Esters in Human Hair Fat[1]

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IT HAS LONG BEEN KNOWN that skin surface fat contains sterol esters for in 1910 Salkowsky isolated and identified cholesteryl palmitate from epidermal scales (12). Since then the presence of sterol esters in human hair fat and other skin surface fats has been shown indirectly by digitonin precipitation of sterols before and after saponification. More recently, the presence of glycerol in the aqueous phase after saponification indicated the presence of glycerides (16). From the fact that a very low acetyl value has been reported for the total fat (7), while the unsaponifiable matter contains a sizeable fraction of wax alcohols (5, 6, 7), it could be assumed that the wax alcohols were present originally as esters. (See discussion, p. 408.) However none of the glycerides or wax esters had previously been isolated as such.

Human hair fat also contains a large fraction of free fatty acids (7, 9) which have been analyzed (6, 15). They constitute a normal series of straight chain homologues ranging from $C_5$ to $C_{22}$. Of especial interest is the fact that chains having an *odd* as well as an *even* number of carbon atoms are present, and both groups show unsaturation as well as saturation for some of their members.

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