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 1,4,9,11-Octadecadienoate. A solution of 15 g. of methyl 1,4,9,11-octadecadienoate 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.): nD^20 1.4692.

1,4,9,11-Octadecadienoate. A solution of 10.8 g. of methyl 1,4,9,11-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^cm. = 1196.

Reduction of Vinyl Ethers. Stearyl ethyl ether, 12-hydroxy-stearyl 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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Some preliminary work on the esterified acids (10) showed that this mixture, too, is as complex as is the mixture of free fatty acids. Thus we have here a complex group of alcohols (glycerol, sterols, and an homologous series of wax alcohols) (5, 6) combined with a complex series of acids. The question arises as to whether or not there is any preferential esterification of certain acids by the different alcoholic groups. That indeed such might be the case was suggested by the fact that the total fraction of esterified acids was more unsaturated than was the free acid portion. If one assumes that all the acids are built up by some common pathway, then some preferential esterification (or hydrolysis) must have occurred.

In the present study straight chain waxes, an impure mixture of sterol esters, triglycerides, and hitherto unobserved diglycerides, were isolated from adult male and from adult female hair fat and partially characterized. Evidence is presented for the presence of 1-mono-glycerides. Some preferential esterification of the acids by the different alcoholic groups was also observed.

**Experimental**

**Collecting the Fat Samples.** Human hair fat was obtained by two methods: a) by daily soaking of the scalp of adults in ether, and b) by the ether extraction of pooled cut hair of prisoners. (All solvents in this work were predistilled through a Poddbielnia distilling column to remove traces of non-volatile residue.) In the first method, 24 hrs. prior to soaking the scalp, the subjects were shampooed with tincture of green soap and rinsed with 4 liters of distilled water. Absence of soap in the final 500 ml. of rinse water was shown by the lack of any extractable fatty acids when the solution was acidified. Hair fat was then collected daily by the subject's immersing the crown of his head for 10 seconds in a bowl containing 600 ml. of anhydrous ether. The bowl was made from half of a 12-liter flask and mounted on a stand. The extract was drained from the bowl by means of a stopcock sealed to the bottom. After three such soaks in rapid succession, approximately 90% of the fat was removed as determined by the progressively decreasing amounts of fat obtained in each successive extract. The extract from the three soaks was pooled and filtered; the bulk of the ether was distilled, and the residue was transferred to a small flask with petroleum ether. This was blown off with nitrogen. In this fashion an average of 0.25 g. per day per subject could be obtained. Precipitation of the esters and other neutral contaminants occurred. The final petroleum ether solution of the acids and that of the neutral fat were washed twice with water, and the solvent was blown off with nitrogen. Recoveries of free fatty acids plus neutral fat were approximately 98% of the original sample weight.

**Fatty Acids were separated from the Neutral Fraction by dissolving each sample of fat in petroleum ether and washing successively with 200, 100, 70, and 60 ml. of 0.06 N NaOH in 50% ethanol. The last washing contained a negligible amount of fatty acids. The basic washings were then pooled and counter-washed four times with petroleum ether; and the latter washings were combined with the bulk of the neutral fraction. The aqueous phase was acidified with 6 N sulfuric acid and washed four times with petroleum ether. It was necessary to re-extract the acids with alcoholic base from the petroleum ether solution of acids to remove about 1% of the neutral components which were carried along with the acids. After such a re-extraction the acids gave a negative Liebermann-Burchard test for sterols whereas before the re-extraction this test was faintly positive. Both the final petroleum ether solution of the acids and that of the neutral fat were washed twice with water, and the solvent was blown off with nitrogen. Recoveries of free fatty acids plus total neutral fat were approximately 98% of the original sample weight. Before chromatographing the neutral fat on silicie