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°C (0.6 mm.): ν max 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°C; maximum E°, EM, = 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°C. Water was added to quench the reaction at the end of 1 hr. The reaction mixture was then treated as in Method A.

**Summary**

A number of vinyl ethers of C18 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**

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It has long been known that skin surface fat contains sterol esters for in 1910 Salkowskoy isolated and identified cholesteryl palmiate 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_{15} to C_{26}. Of special 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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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-monoglycerides. 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 Podbielniak 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 could be obtained. (For variation of fat yield among individuals and other details on the method, see [2].) Aliquots of some samples from individuals were analyzed for other investigations. The remainder was pooled into two larger samples. One of these, 11.71 g., was collected from 11 white males, ages 22 to 35 years, and the other 9.19 g., from 4 white females, also ages 22 to 35 years.

In the second method of obtaining hair fat, hair was collected from prisoners who shampooed their heads with soap the day before their hair was cut. The cut hair was then put directly into a bottle containing petroleum ether and stored until a large enough sample could be accumulated. The fat was extracted from the hair in the bottle with anhydrous ethyl ether. The solvent was replaced daily with a fresh batch of ether, and the mixture was allowed to stand overnight on a warm oven so that mild refluxing occurred. Each extract was filtered, and the fat was recovered as described above. Extractions were continued until less than 1% of the weight of the total accumulated fat was obtained. In this fashion a sample of 7.75 g. was collected, requiring some 12 batch extractions.

In both methods every attempt was made to avoid contamination with extraneous oils and greases. Better control was obtained in this regard by the first method. Also, because of the completeness of the removal of the surface fat each day by this method, a sample free of oxidation products and more constant in composition could be obtained.

Separation of Free Fatty Acids and the Different Ester Fractions. A schematic summary of the separations performed is given in Figure 1. The free 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...