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]

N. NICOLAIDES and ROSCOE C. FOSTER JR., Section of Dermatology, Department of Medicine, University of Chicago, Chicago, Illinois

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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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 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 solvent. This was blown off with nitrogen. In this fashion an average of 0.25 g. per day per subject 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.

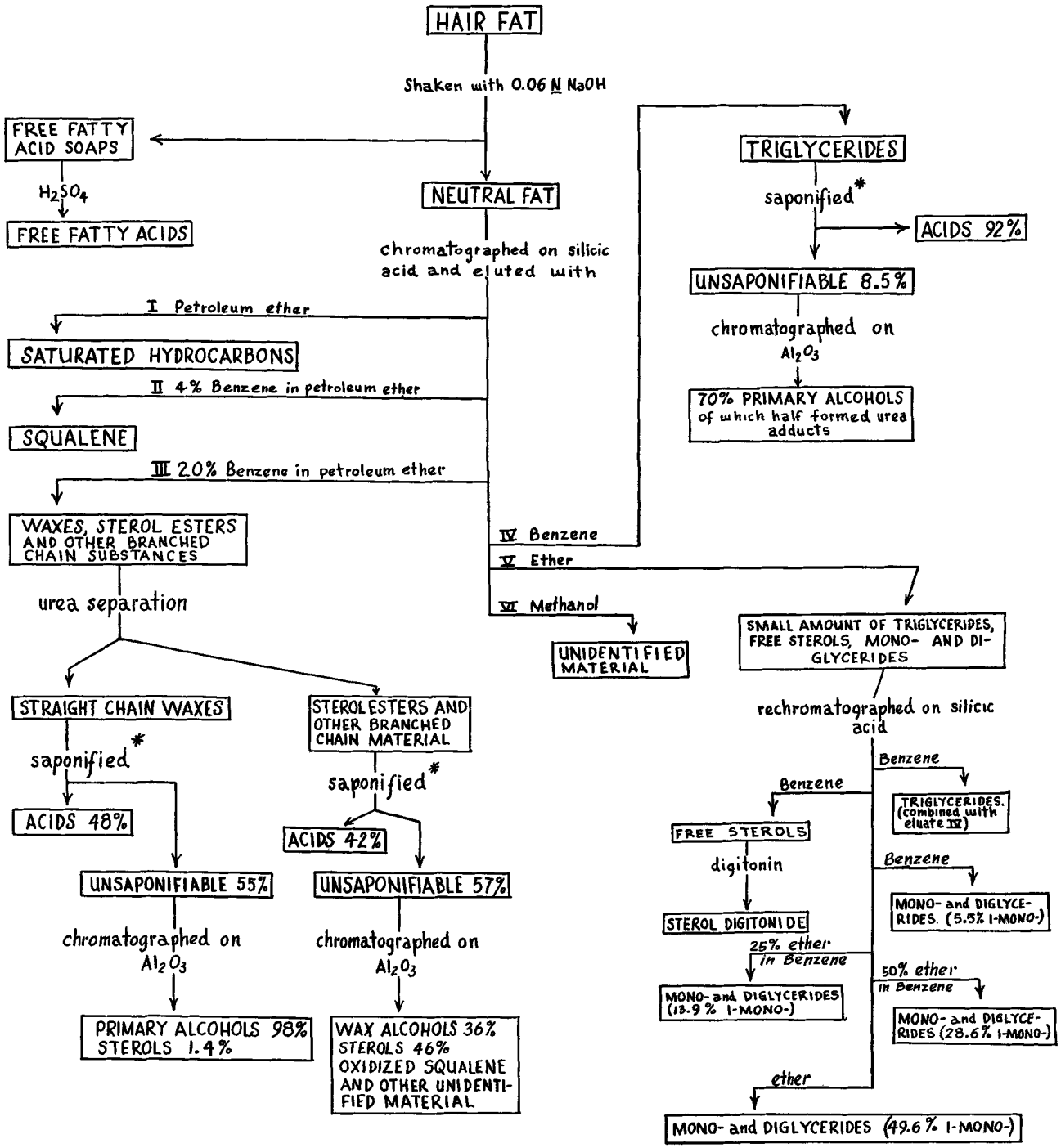
Before chromatographing the neutral fat on silicic

TABLE I

The Analysis of Adult Human Hair Fat

Substance	Fat obtained by		
	Scalp soaks		Pooled cut hair extracts
	(male) 11.71 g.	(female) 9.19 g.	(male) 7.75 g.
	%	%	%
1. Free fatty acids	30.7	23.2	56.1
2. Total neutral fat	67.6	74.8	41.6
3. Saturated hydrocarbons	0.55	0.55	3.7
4. Squalene	10.9	7.6	6.8
5. Total straight and branched chain material [a]	22.6	22.9	12.3
6. Straight chain waxes	16.6	12.2 [b]	8.0
7. Branched chain matter [c]	5.1	5.8	3.7
8. Sterol esters [d]	2.37	2.50	2.33
9. Triglycerides [e]	19.5	26.6	5.5
10. Free sterols	1.40	1.40	5.24
11. Total di- and mono-glycerides [f]	7.7	10.0	2.9
12. 1-monoglycerides	.....	1.5	.....
13. Unidentified matter [g]	8.6	13.9	7.1
Ratio of free to esterified sterols	0.97	0.93	0.44

[a] Eluate III, see text.
[b] Some losses were incurred because of excessive handling. See text.
[c] Includes sterol esters, other esters, and oxidized squalene. See text. the rechromatograph of eluate V. See text.
[d] Computed from the yield of free and esterified sterols plus the N.E. of the mixed acids found for the branched chain matter.
[e] Eluate IV exclusive of the wax alcohol unsaponifiable matter computed as wax ester.
[f] Eluate V rechromatographed, excludes unsaponifiables.
[g] Item 2 minus (items 3+4+6+8+9+10+11).



* THE PERCENTAGE OF ACIDS AND UNSAPONIFIABLES REPORTED ARE BASED SOLELY ON WEIGHTS RECOVERED AND DO NOT INCLUDE INCREASES DUE TO THE ELEMENTS OF WATER.

FIG. 1. Schematic Summary of Separations.

acid by the adsorption technique, the method was first worked out on a synthetic mixture of substances having the same total weight and approximate composition as that suspected of the human fat, and in this way a tentative identification of the fractions could be made. The synthetic neutral fat, 8.50 g., had the following composition, computed on the basis that this neutral portion was 70% of a "total" fat, the remainder being free fatty acids: 0.96% saturated hydrocarbons, 15.6% squalene, 12.4% octadecyl stearate, 4.94% cholesteryl palmitate, 34.2% tripalmitin, and 2.36% free cholesterol. The adsorbent was a mixture of 312 g. of silicic acid (Mallinckrodt, 100 mesh, prepared for chromatography by the method of Ramsay and Patterson), 156 g. Celite (Johns-Manville, No. 545), and 28 g. zinc silicate phosphor (Du Pont, No. 609) and formed a column 79 cm. long and 4.1 cm. in diameter. The phosphor made the adsorbed bands somewhat more visible when viewed under ultraviolet light, but this was not found to be too useful as the bands smeared out towards the bottom of the column. The course of the chromatogram was followed mainly by the amount and character of the eluate when a large number of small fractions was taken. A new solvent was used when a negligible amount of fat was eluted for a given volume of solvent.

The synthetic fat mixture could thus be separated into the following eluates: I. saturated hydrocarbons eluted with petroleum ether; II. squalene eluted with 4% benzene in petroleum ether; III. cholesteryl palmitate plus octadecyl stearate eluted with 20% benzene in petroleum ether (The early fractions of this eluate were negative to the Liebermann-Burchard test, thus showing a partial separation of the octadecyl stearate from the cholesteryl palmitate.); IV. tripalmitin in 90% yield (no free cholesterol present) eluted with benzene; and V. the remaining tripalmitin with free cholesterol eluted with absolute ether.

Each of the three human neutral fat samples was then chromatographed, using the same column, adsorbents, and solvents. Eluates corresponding to I, II, III, IV, and V were taken as well as VI, a methanol eluate following V. Nothing further was done with eluates I and II.

Eluate III was separated into a straight and branched chain portion by urea adduct formation as previously described (5). There appeared a faint, but definite Liebermann-Burchard test on the "straight chain" portion even after the latter was subjected to repeated adduct formation. An improvement in the separation was effected by first dissolving the mixture to be adducted in enough petroleum ether so that after urea saturated in methanol was added to this, there still remained a petroleum ether phase, *e.g.*, 1 g. of fat dissolved in 30 ml. petroleum ether and 45 ml. urea saturated in methanol added to this. Practically all the fat then either was adducted with urea and precipitated or else remained in the petroleum ether phase; less than 1% remained in the methanol phase. Even with this technique however sterol esters to the extent of a maximum of 0.6% of the weight of the straight chain waxes co-precipitated (see below). The straight chain waxes were recovered from the adduct by decomposing the latter with approximately 0.05 N HCl, taking up the released fat with petroleum ether, then washing with water, and blowing off the solvent with nitrogen. The straight chain material, "wax esters," was a white, waxy semi-solid substance. The non-adducting material in the petroleum ether phase, "branched chain esters," was washed with water to remove any urea, and the solvent was blown off with nitrogen. This fraction, which contained the sterol esters and other material, was a brownish, somewhat viscous oil from which a solid, too small in amount to work up, was precipitated. The total recovery of straight and branched chain material for the improved procedure was of the order of 95%, except for the fat sample from females where some losses were incurred in developing the procedure.

Eluate IV consisted of more than 90% triglycerides (see below). No further purification was attempted. Eluate V contained a small amount of triglycerides, free cholesterol, and di- and mono-glycerides. These were separated in this order by rechromatographing on silicic acid. The conditions for this chromatogram were the same as those used for the total neutral fat except that the column, although the same length, was much smaller in diameter. Separation of the triglycerides from free cholesterol was done by eluting with a large volume of benzene. With it the triglycerides, the free cholesterol, and the first fraction of mixed di- and mono-glycerides were eluted with little overlapping of the three fractions. Three more fractions of mixed di- and mono-glycerides were then taken with eluents varying from 25% ethyl ether in benzene to pure ether. The latter fractions of this mixture were richer in 1-monoglycerides as discussed below. The free cholesterol was further purified and quantitatively determined by precipitation with digitonin in the usual manner.

Eluate VI was a yellow viscous material constituting about 0.4% of the total fat. Nothing further was done with it. The total recovery for all six eluates was 96.5 to 98% of the neutral fat.

Characterization of the Various Ester Fractions. The general procedure for identifying and characterizing the different ester fractions was to saponify an aliquot of each, take neutralization equivalents and iodine values of the acids released, chromatograph the unsaponifiable matter, and further characterize the alcohols by infrared spectra. Molecular weights and infrared spectra were also taken of the esters. Periodic acid oxidation was performed on the mixed mono- and di-glyceride fractions to determine the presence of 1-monoglycerides.

The saponifications were performed with 10% KOH in 95% alcohol, using a 10-fold excess of base. The reaction mixture was refluxed for 2 hrs. under a nitrogen atmosphere, after which the mixture was diluted with water. The unsaponifiable matter was separated from the fatty acid salts with petroleum ether, and the acids were recovered by the double extraction procedure in much the same manner used to separate the free acids of the fat from the neutral fraction.

Some unsaponifiable matter was obtained from every ester saponification including the triglycerides. These unsaponifiable fractions were chromatographed on alumina, Brochmann Grade II, as previously described (9). Eluting solvents were 10% ether in petroleum ether (which eluted one of the oxidized squalene products), 25% ether in petroleum ether (which eluted the wax alcohols), and 100% ether (which eluted the sterols).

Neutralization equivalents were determined on all the different acid specimens by titrating a 50% alcoholic solution of the acid with 0.02 N NaOH, using metacresol purple as indicator. Two or more titrations were made for each specimen so that the maximum deviation of the values reported was ±2.0% and the average deviation ±0.5%.

The iodine values were determined by the method of Benham and Klee (1), with maximum deviation for duplicate titrations being ±1.0% and the average deviation ±0.25%.

Infrared spectra (Perkin and Elmer, Model 21, Spectrophotometer) were taken of the various esters and alcohols both as the solid films and as a 10% solution (by weight) in CCl_4 and/or $CHCl_3$, and these were compared with spectra of known substances.

Molecular weights were performed by the Rast method, with cyclopentadecanone as the solvent. The method gave an error of approximately 6% of the molecular weight with known similar esters.

Besides the elution of each type of ester in the silicic acid chromatogram of neutral fat at a point comparable with the chromatogram of known materials, the following evidence is presented for the identification of each type of ester:

1. *Triglycerides.* The infrared spectrum of eluate IV was practically identical to that of pure tristearin. In addition to the two characteristic vibrations of the ester group, C = O stretching vibration at 1735 cm.$^{-1}$ and C — O stretching at 1168 cm.$^{-1}$, there was present a vibration at 1120 cm.$^{-1}$, indicating the secondary C — O bond of glycerol. The molecular weight was 846 ± 51. The theoretical molecular weight of a triglyceride having the neutralization equivalent of the acids derived from this material (N.E. = 262) is 824. Saponification gave 92% of the acids theoretically required, and the unsaponifiable matter recovered was 8.5% of the starting weight of triglycerides. Infrared spectra of the chromatographed fractions of the unsaponifiable matter (on alumina) showed that a maximum of 70% of it was primary alcohols. Half of these alcohols could be adducted with urea. These alcohols could have been present in the original material as free alcohols (since it is our experience that the wax alcohols, too, are eluted from silicic acid with benzene), or as esters, or as a mixture of free and esterified alcohols. If all the wax alcohols which could be adducted with urea were as free alcohols in the original fat, we would have, as a maximum, 0.7% free wax alcohols in the total fat. If all the primary alcoholic material were esterified in the original fat, then, on saponification of our triglyceride fraction, acids released from these esters would contaminate the acids of the triglyceride. If we assume a molecular weight of 260 for these contaminating acids, we would get, as a maximum contamination of the acids isolated from the triglycerides, 3% of their weight derived from acids of the waxes and 3% from acids of unknown origin.

In unpublished work done with Hans Ernst the aqueous phase from the saponification of hair fat (obtained from scalp soaks) was investigated for other 1,2-diols than glycerol. Analysis for glycerol by a) oxidation of the neutralized aqueous phase with HIO_4 and titrating of the released formic acid with standard base, and b) titrating of the consumed HIO_4 iodometrically gave identical results. This shows that no other 1,2-diols but glycerol are present (4).

2. *Mono- and di-Glycerides.* The last four fractions from the rechromatographed eluate V were examined for di- and 1-mono-glycerides. No attempt was made to analyze for 2-monoglycerides. An infrared spectrum of the first of these could nearly be superimposed on that of pure 1,3-distearin. Besides the vibrations characteristic of esters, namely, those at 1735 cm.$^{-1}$ and 1168 cm.$^{-1}$ and besides the vibration at 1120 cm.$^{-1}$ of the secondary C — O group of glycerol, this substance showed the presence of a free OH group by virtue of its absorption at 3500 cm.$^{-1}$.

Each of the four fractions was then analyzed for 1-monoglycerides by periodic acid oxidation according to the method of Pohle *et al.* (13). The method was tested with pure glycerol. The four fractions gave respectively 5.5, 13.9, 28.6, and 49.6% 1-monoglycerides, making the total content 15% for the entire mixed glyceride eluate.

The molecular weight of the second of these fractions was 563 ± 34, which is within range of experimental error, and 500 ± 30 for the third fraction. The latter is somewhat low, but other lower molecular weight substances, *e.g.*, 2-monoglycerides probably present, and unsaponifiable matter known to be present, could account for this. Saponification of an aliquot of the entire eluate V before rechromatography gave 11.1% unsaponifiables and 92% of the acids expected. Chromatography of the unsaponifiables on alumina yielded 45% sterols (presumably free cholesterol) and some oils which had the odor of oxidized squalene. At worst, it is estimated that the acids isolated from the mixed glycerides could be contaminated with acids from other esters to the extent of 5%. It is quite conceivable that this entire fraction was an artifact arising from chemical manipulations, *e.g.*, by hydrolysis of the triglycerides from the base used in separating the free fatty acids from the neutral fat, and/or by hydrolysis on the silicic acid column. To rule out these possibilities a portion of the triglycerides of eluate IV was worked up again as if it were whole hair fat, *i.e.*, shaken with base and chromatographed on silicic acid. All materials were used in proportionally smaller quantities. Some tailing of material to the extent of 2.7% of the triglycerides did occur in that portion of the chromatogram corresponding to the mixed mono- and diglycerides. For the fat sample from females this means that, since 26.6% was triglyceride, a maximum of only 0.72% of the total fat could be partially hydrolyzed glycerides arising from chemical manipulation. But this sample yielded partially hydrolyzed glycerides to the extent of 10% of its weight. Thus nearly all of this fraction must have come from natural sources. Its maximum contamination due to chemical manipulations was 7.2%.

Our findings of such a large fraction of mono- and diglycerides in the surface fat from the scalp are at variance with the results reported by MacKenna, Wheatley, and Wormall in their important work on the analysis of surface fat from the forearm (7). On the basis of the determination of the acetyl number of the total fat they report that the glycerides present are almost certainly triglycerides. Such a discrepancy might conceivably arise from the fact that conditions on the forearm are not the same as those on the scalp.

3. *Waxes.* The infrared spectrum for the straight chain fraction of eluate III was that for a typical long chain ester; strong peaks were observed at 1730 cm.$^{-1}$ and 1170^{-1}. There was also a weak absorption at 720 cm.$^{-1}$, indicating the presence of four or more CH_2 groups in a chain. The wax alcohols recovered after saponification and chromatography gave a strong absorption at 1060 cm.$^{-1}$ characteristic of primary alcohols. The molecular weight of the waxes was 562 ± 34, which is within the error of that required of acids of N.E. 255 and alcohols of molecular weight 300 (5). Saponification gave theoretical recoveries of acid and alcohol. Chromatography of the alcohols on alumina gave 98% wax alcohols and 1.4% sterols. Thus the acids from the waxes are estimated to be contaminated with 1% acids from sterols.

4. *Branched Chain Esters.* This complex mixture from the urea separation contained the sterol esters. An aliquot was saponified to yield 57.4% unsaponifiables and 42.2% acids. The chromatogram of the unsaponifiable on alumina showed 36% wax alcohol and 46% sterol, and, although the remainder was unidentified, it had a strong odor of oxidized squalene. The wax alcohols from this chromatogram gave the same infrared spectrum as did the main bulk of alcohols from the waxes. The spectrum included a strong absorption peak at 720 cm.$^{-1}$, indicating many CH_2 groups in a chain. Thus the possibility exists that these alcohols were present because of incomplete removal of all of the straight chain waxes. This would then mean that the acids from the saponification of these branched chain esters are as much derived from sterols as they are from waxes. The further probability exists that lesser amounts of acids from unknown esters are also present.

Discussion of Results

Table I gives the analysis of human fat for adult males and for adult females. Comparison of the free fatty acid content with the total glyceride content between samples reveals an interesting inverse relationship. For example, the free fatty acid content is much higher in the case of the pooled cut hair than it is for either of the two samples from scalp soaks. Conversely, the total amount of glycerides is considerably lower for the fat derived from cut hair than

it is for fat from scalp soaks. This same relationship holds when one compares the two samples from scalp soaks with each other, *e.g.*, that sample which has the lower free fatty acid content has the higher glyceride content. (A similar relationship was noted earlier (9) between the free and the total esterified acids of pooled cut hair compared with those of fat from scalp wipings with cotton pledgets.) This inverse relationship, together with the fact that there exists in the fat di- and mono-glycerides, suggests that the free fatty acids and di- and mono-glycerides represent more or less complete stages of hydrolysis of triglycerides.

Table II lists neutralization equivalents and iodine values for various acid and alcohol samples. The constants for the acids of the triglycerides are much more similar to those of the free fatty acids than are those of the other acids. This is in accord with the hypothesis that the free fatty acids are derived from the glycerides by hydrolysis. There is however a significant rise in molecular weight and iodine value in going from the tri- to the di- to the mono-glycerides. The meaning of this is not clear.

TABLE II

Neutralization Equivalents and Iodine Values for Various Acids and Alcohols from Adult Human Hair Fat

	Fat obtained by					
	Scalp soaks				Pooled cut hair extracts	
	(male)		(female)		(male)	
	N.E.	I.V.	N.E.	I.V.	N.E.	I.V.
1. Acids						
Free	261	45.3	266	44.6	261	48.3
From triglycerides	262	43.4	262	44.9	269	53.5
From di- and mono-glycerides (early)[a]	279	52.9	.....	.....	333	.....
From di- and mono-glycerides (later)[a]	282	53.6	320	.....		
From waxes	255	82.8	255	80.1	258	73.4
From branched chain esters[b]	268	78.8	267	75.5	263	56.4
2. Alcohols (wax)	.....	37.2	.....	36.8	.....	34.3

[a] "Early" and "later" refer to first and second half, respectively, of the rechromatograph of eluate V. See text.

[b] Includes 50% sterol esters.

In Table II are more data regarding the general question as to whether there is any preferential esterification of the acids by the different alcoholic groups. The acids from the waxes are of slightly lower molecular weight and are definitely more unsaturated than are those from the triglycerides. Thus some preferential esterification of the acids of the hair fat does occur. The more interesting question as to whether the acids with an odd number of carbon atoms are preferentially esterified is now under investigation.

Some final comments regarding the over-all analysis of human hair fat can also be made. Excluding the differences arising from the relationship between glyceride and free fatty acid content, the analysis of the hair fat of adult males is very similar to that of adult females. The very low value for the saturated hydrocarbon content in the better controlled samples from scalp soakings is consistent with the feeling among workers in this field that these are not endogenous (3, 8, 11, 14). (In unpublished analyses of hair fat where extremely rigid control against contamination was made, the saturated hydrocarbon content dwindled to a mere 0.1%.) Except for the high value for the free sterol content in the analysis of the fat from cut hair (for which we have no explanation), the analysis of this fat is very similar to that computed from earlier data (9). The difference in the over-all analysis of fat derived from cut hair extracts with fat derived from scalp soakings may reflect differences inherent in the manner of collecting samples.

Summary

A study was made of the hair fat composition of human adults with special reference to its ester content. Waxes, triglycerides, and a mixture of mono- and di-glycerides were isolated and charcterized. Indirect evidence is presented that the free acids of hair fat are derived from lipolysis of triglycerides. Some preferential esterification of some kinds of fatty acids as glycerides and others as waxes was observed. No significant differences could be observed in the analysis of the hair fat of adult males compared with that of adult females of the same age group.

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