Fatty Alcohols

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FATTY ALCOHOLS are a large group of aliphatic alcohols, considered to be fatty because they are derived from natural fats and oils. Fatty alcohols could embrace alcohols of an uneven number of carbon atoms, but the more restrictive definition refers only to alcohols of an even number of carbon atoms. This is because the glycerides found in nature contain acid portions of only even numbered carbon atoms.

Origin

The selection of a fat or oil for the manufacture of fatty alcohols may depend upon several factors, such as price, availability, stability of the market with respect to both price and availability, the type of alcohol or alcohol mixture desired, and the handling characteristics of the fat or oil in the equipment available for the alcohol process.

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There are at least 25 well-known fats and oils which could serve as starting materials. A few of the more common ones are tallow, lard, and coconut, peanut, cottonseed, soybean, linseed, castor, tung, oiticica, and sperm oils. Some are readily recognizable for other well-known uses (1, 2).

Fats and oils are mixed glycerides. Glycerides are esters, which can be hydrolyzed to yield glycerine and a mixture of fatty acids. The fatty acids can then be reduced to fatty alcohols. While these successive steps may illustrate the origin of fatty alcohols, they do not represent the actual processes used in the manufacture of fatty alcohols.

In the mixed glycerides found in nature the fatty acid portions vary over a wide range in carbon chain length. For example, coconut oil contains fatty acid portions having 6 to 18 carbon atoms. There is usually a preponderance of one or two fatty acid portions. The possibilities for variety in R_1COOH, or R_2COOH and R_3COOH are so numerous as to be beyond the scope of this presentation. However it will be well to compare the fatty acid composition of coconut oil and tallow. These differ appreciably in composition and are two of the more important raw materials for the manufacture of fatty alcohols.

The fatty acid portion of some glycerides contain up to 24 carbon atoms in the chain (e.g., peanut oil and lignoceric acid). The glycerides with fatty acid portions C_6 to C_{18} are the most important commercially for the manufacture of fatty alcohols.

Commercial Preparation of Fatty Alcohols

A number of organic reactions can be used to prepare aliphatic alcohols, but the most important commercial methods are hydrogenolysis and sodium reduction. Applied to simple esters, the two methods can be illustrated with the following equations:

Hydrogenolysis

$$RCOOR' + 2H_2 \longrightarrow RCH_2OH + R'OH$$

Sodium Reduction

$$RCOOR' + 4Na + 2R'' \, OH^- \longrightarrow$$
$$RCH_2ONa + R'ONa + 2R''ONa \xrightarrow{+4H_2O}$$
$$RCH_2OH + R'OH + 2R''OH + 4NaOH$$
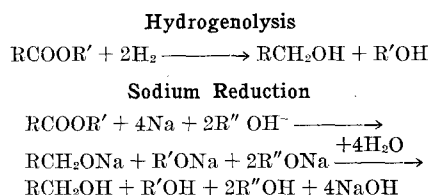
Hydrogenolysis was discovered in 1930 by Adkins and co-workers (2, 5). Since 1930 a number of patents have been issued covering process and catalyst variations. Excellent reviews have appeared in the chemical literature, the latest in 1958 (6). The conditions for catalytic hydrogenation of esters in general are pressure of 3–200 atmospheres at 200–300°C. Above 300°C. the major products can be hydrocarbons instead of alcohols. In Table I it will be observed that unsaturated as well as saturated acids occur as glycerides. Hydrogenolysis processes reduce the carbon-carbon double bond in addition to reducing the ester functional groups to alcohols. The final alcohols are therefore characterized by a low degree of unsaturation, as manifested by low iodine number. For example, commercial lauryl C_{12} alcohols made by this process have iodine numbers less than 0.4.

The conditions selected for hydrogenolysis can lead to a variety of products in addition to saturated alcohols. The carbon-carbon double bond can be left intact to give unsaturated alcohols corresponding to the unsaturated acid portions of the glycerides found in nature. This is achieved with cadmium-copper-zinc chromate catalysts (7). Extremely high temperatures yield hydrocarbons; under some conditions the catalysts will dehydrogenate the alcohols to aldehydes. It is desirable to obtain saturated alcohols by the hydrogenolysis process so conditions are fixed to avoid the other by-products or co-products.

The foregoing has dealt mostly with hydrogenolysis in general as applied to glycerides and simple esters. The complete commercial production of fatty alcohols will now be considered.

The animal and vegetable oils consist mainly of one type of triglyceride molecule containing different fatty acids, such as palmitic, stearic, and oleic. In addition, fats and oils contain a varying amount of free fatty acid, sterols, aromatic alcohols, etc. Some of these impurities are removed in the refining process. Hydrogenolysis is usually applied to refined fats and oils.

TABLE I
Average Fatty Acid Composition of Coconut Oil and Tallow

	Av. composition, % of total acid content	
	Coconut oil	Tallow
Saturated acids		
Caproic	0.2	......
Caprylic	8.0	......
Capric	7.0	......
Lauric	48.0	......
Myristic	17.5	3.0
Palmitic	8.8	29.0
Stearic	2.0	18.5
Unsaturated acids		
Oleic	18.5	46.5
Linoleic	0.7	3.0

In direct hydrogenolysis, glycerine, which would otherwise be recovered, is reduced progressively to mixtures of propylene glycol and 2-propanol (6). This is a valuable by-product. In processes where it is desirable to save the glycerine, the first step involves "glyceride-splitting," or "fat-splitting," in the more general sense. This can be accomplished by hydrolysis to glycerine and fatty acids, by saponification to glycerine and soaps, or by alcoholysis to glycerine and esters. Before hydrogenolysis the acids and methyl esters can be separated by fractional distillation, or they may be hydrogenated first. The resulting fatty alcohols are then separated from water or methanol and fractionally distilled under reduced pressure.

The nonalcohol impurities sometimes found in commercial fatty alcohols are ester, hydrocarbon, water, and aldehyde. In most products these are usually present in only very small concentration, if at all.

The methyl esters obtained in the fat-splitting step are of interest in themselves. They are supplied commercially and may be used for hydrogenolysis to fatty alcohols. The methyl ester of lauric acid is used in the manufacture of lauric diethanolamide, which in turn is of interest in synthetic detergents (8).
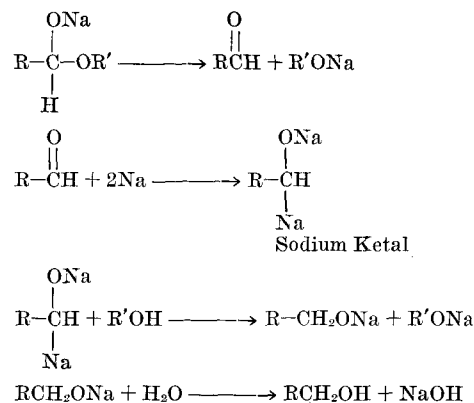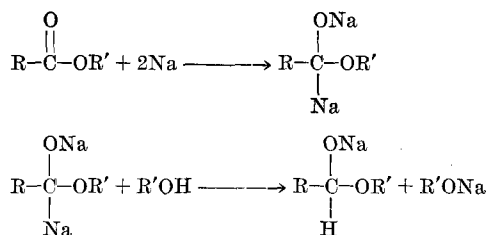
Fatty alcohols obtained by the hydrogenolysis process can be essentially pure, if fractionally distilled under careful conditions. There are some rather fine cuts available commercially.

The hydrogenolysis process can be easily adjusted to give individual alcohols of high purity. The economics of a process so adjusted then depends upon what can be done to utilize the remaining alcohols. For example, from coconut oil can be manufactured 97–98% purity lauryl alcohol C_{12}. This is economically feasible however, only if the other alcohols (hexyl, octyl, myristyl, cetyl, and stearyl) can be utilized in some way.

Sodium Reduction

The sodium reduction method has also been reviewed in the chemical literature (6). The over-all reaction is the reduction of the fatty acid portion of glycerides to alcohols and the oxidation of sodium to sodium ion. However the practice is first to split the glyceride to permit clean separation of the glycerine. This is done by transesterification with methyl-isobutyl carbinol (MIBC), which is also used as the reducing alcohol R"OH.

The mechanism of the reaction has been studied by Hansley (9), who pointed out that the reduction proceeds through the soluble sodium ester ketals. In the equations representing the mechanism of the reaction it is interesting to note that the generation of hydrogen by reaction of alcohol with sodium and the subsequent reaction of hydrogen with the glyceride to reduce it is not a part of the mechanism.

$$R{-}\underset{\underset{Na}{|}}{\overset{\overset{O}{\|}}{C}}{-}OR' + 2Na \longrightarrow R{-}\underset{\underset{Na}{|}}{\overset{\overset{ONa}{|}}{C}}{-}OR'$$

$$R{-}\underset{\underset{Na}{|}}{\overset{\overset{ONa}{|}}{C}}{-}OR' + R'OH \longrightarrow R{-}\underset{\underset{H}{|}}{\overset{\overset{ONa}{|}}{C}}{-}OR' + R'ONa$$

$$R{-}\underset{\underset{H}{|}}{\overset{\overset{ONa}{|}}{C}}{-}OR' \longrightarrow RCH + R'ONa$$

$$R{-}\overset{\overset{O}{\|}}{C}H + 2Na \longrightarrow R{-}\underset{\underset{Na}{|}}{\overset{\overset{ONa}{|}}{C}}H$$
Sodium Ketal

$$R{-}\underset{\underset{Na}{|}}{\overset{\overset{ONa}{|}}{C}}H + R'OH \longrightarrow R{-}CH_2ONa + R'ONa$$

$$RCH_2ONa + H_2O \longrightarrow RCH_2OH + NaOH$$

The sodium reduction process does not reduce carbon-carbon double bonds. Consequently if one starts with glycerides containing unsaturated fatty acid portions, unsaturated alcohols are obtained. The iodine number of these alcohols is therefore correspondingly higher than with alcohols made by hydrogenolysis.

Physical Properties

The higher fatty alcohols vary from mobile liquids to solids. Some of the physical properties of pure individual alcohols obtainable from a mixture of coconut oil and tallow by hydrogenolysis are listed in Table II. Differences between saturated alcohols of even number and odd number of carbon atoms are of interest. When the melting points are plotted against the number of carbon atoms, the lower members show an appreciable alternation; for the higher homologs the alternation becomes negligible. The dividing line is at lauryl C_{12} for the homologs above C_{12} apparently fall on a continuous curve. The melting points of unsaturated alcohols are lower than the saturated counterparts. For example, oleyl C_{18} is a liquid at room temperature, compared to stearyl C_{18} melting at 59°C.

Commercial fatty alcohols are generally supplied as mixtures. For example, lauryl alcohol is actually a mixture of three to five components. This apparently gives the desired combination of physical properties to the end-use products. However there is increasing interest in commercial lauryl alcohols with fewer components.

Hydroxyl number is important in determining the average molecular weight of alcohol mixtures. This is useful for determining the stoichiometric quantities of reactants for some reactions, such as the addition of chlorosulfonic acid to lauryl alcohol as a step in the synthesis of sodium lauryl sulfate. Hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g. of the alcohol. Probably the method most generally used is that of Verley and Bolsing, which is based on the acetylation of the alcohols with acetic anhydride.

TABLE II
Physical Properties of Fatty Alcohols

Alcohol	Boiling point 760 mm. B.p., °C.	Melting point, °C.	Molecular weight
n-Hexyl C₆	157.2	−51.6	102.17
n-Octyl C₈	195.0	−16.3	130.23
n-Decyl C₁₀	231.0	− 6.0	158.28
Lauryl C₁₂	255.0	22.6	186.33
Myristyl C₁₄	263.2	37.62	214.38
Cetyl C₁₆	344.0	49.3	242.44
Stearyl C₁₈	210.5/15 mm.	59.0	270.99

Other physical properties are no less important: the ester value which is a measure of unreduced esters, the iodine number which measures unsaturation, and the acid number which gives an indication of the amount of free carboxyl groups of fatty acids present. Specific gravity, refractive index, viscosity, and latent heat are useful for identification, engineering data, and so on.

Reactions

The higher fatty alcohols undergo chemical reactions which are typical of monohydric aliphatic types. The most important commercially are sulfation, halogenation, and ethoxylation. These and other reactions are summarized below:

Reactions of RCH_2OH

1. Oleum or Chlorosulfonic acid or ———→ RCH_2OSO_3Na Sulfur trioxide
2. HCl ———→ RCH_2Cl
3. $\overset{O}{\overset{/\backslash}{CH_2CH_2}}$ ———→ $RCH_2(OCH_2CH_2)_nOH$
4. $R'COOH^-$ ———→ $RCH_2O-\overset{\overset{O}{||}}{\underset{\underset{H}{|}}{C}}-R'$ (or anhydrides)
5. Dehydration ———→ $R\overset{\underset{H}{|}}{C}=CH_2$
6. Oxidation ———→ $R\overset{\underset{H}{|}}{C}=O$
7. $R'-\overset{\overset{O}{||}}{C}-OR''$ ———→ $R'-\overset{\overset{O}{||}}{C}-OCH_2R + R''OH$
8. $HONO_2 \xrightarrow{H_2SO_4} RCH_2ONO_2$
9. $POCl_3 \xrightarrow{pyridine} PO(OCH_2R)_3$
10. $HC \equiv CH$ ———→ $RCH_2O-\overset{\underset{H}{|}}{CH}=CH_2$
11. $R'-O-\overset{\underset{H}{|}}{C}=CH_2$ ———→ $RCH_2OCH=CH_2 + R'OH$

The first three reactions account for most of the commercial usage of fatty alcohols. Sulfation can be achieved in a number of ways, but the most common methods are the reaction of the alcohols with oleum, chlorosulfonic acid, or sulfur trioxide.

The reaction of oleyl alcohol with oleum is reported to give a diol ester, 1,9-octanediol di-sulfate (10). Chlorosulfonic acid is probably the most widely used sulfating reagent, and there are a number of publications describing its use in making sodium lauryl sulfate (11, 12, 13.) With oleum the reaction by-product is water. With chlorosulfonic acid the by-product is hydrogen chloride, which boils off at the low reaction temperatures used for the process (35–50°C.).

A recent publication gives process details for sulfation of lauryl alcohol with sulfur trioxide (14). Sulfur trioxide is recommended for low-salt grade sodium lauryl sulfate.

Of the known methods for making alkyl halides, only those which are based on the reaction of hydrogen halides with fatty alcohols are of practical value. The chlorides receive most attention, and there is a great deal of background information in the chemical literature on their preparation. One of the more interesting developments was the use of zinc chloride to catalyze the reaction and to improve the yields of chloride (15). Lauryl chloride is used as an intermediate for the preparation of quaternary compounds and for dodecyl mercaptan.

The ethoxylation reaction is used to prepare polyethers of lauryl and other higher fatty alcohols.

These have surfactant behavior and are of interest as emulsifiers for a number of applications.

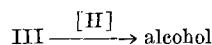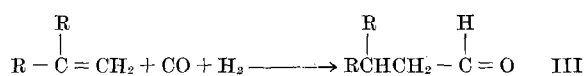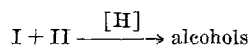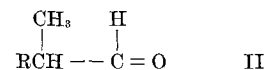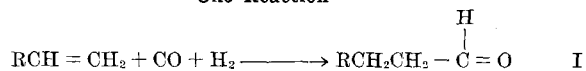### Uses

The following list suggests applications for the alcohols as chemical intermediates:

Cosmetics—additives for cosmetic creams, adsorption bases, and hand lotions
Rubber and plastics—polymerization regulators
Lubricating oils—detergents, viscosity index improvers, and pour-point depressants
Textile—finishing and softening agents
Pharmaceuticals—quaternary ammonium compounds
Surface-active agents—emulsifiers and detergents
Water evaporation control—direct use

Oxo Alcohols

Another method of alcohol synthesis should be mentioned for at least one of the products is of interest in the detergent and rubber fields. The Oxo Process for the synthesis of alcohols is represented by the following equations:

Oxo Reaction

$$RCH=CH_2 + CO + H_2 \longrightarrow RCH_2CH_2-\overset{\overset{H}{|}}{C}=O \qquad I$$

$$RCH--\overset{\overset{CH_3}{|}}{\underset{}{\overset{H}{|}}{C}}=O \qquad II$$

$$I + II \xrightarrow{[H]} alcohols$$

$$R-\overset{\underset{|}{R}}{C}=CH_2 + CO + H_2 \longrightarrow R\overset{\underset{|}{R}}{CH}CH_2-\overset{\overset{H}{|}}{C}=O \qquad III$$

$$III \xrightarrow{[H]} alcohol$$

The mixture of aldehydes can be reduced to alcohols. A branch at the 2-carbon system will give only one aldehyde and one alcohol. If higher olefins are used in the process, higher fatty alcohols in the molecular weight range of those obtained from fats and oils result. One of these is tridecyl alcohol, which is a 13-carbon branched-chain primary alcohol. The sulfate, mercaptan, and ethoxy derivatives of tridecyl alcohol have been prepared and have been of interest in some of the applications mentioned for commercial lauryl alcohols.

The Oxo Process was patented by Otto Roelen in Germany in 1938 (16). The basic U. S. patents were seized by the Alien Property Custodian.

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