Fat-Based Dibasic Acids

R.G. KADESCH, Director, American Technical Service,
15 Mayflower Road, Winchester, MA 01890

ABSTRACT

Aside from "dimer acids" (E.C. Leonard's paper), the best known fat-based dibasic acids consist of eight product types of which only four are commercially important. These are described in detail in this paper: (a.) Azelaic acid produced from oleic acid by either chrome oxidation or ozonolysis of oleic acid also, "brassylic" acid from mixed 55% erucic-containing crambe oil fatty acids. (b.) Sebacic acid from castor oil or possibly dodecanedioic acid from lesquerolic acid by caustic fusion. (c.) C-21 Dibasic acid by Diels Alder reaction between isomerized TOFA and acrylic acid. (d.) C-19 Dibasic acids (carboxystearic acids) from oleic acid by carboxylation. (e.) Mixed C-11/C-12 Dibasic acids by several routes. Both the alkali cleavage and gentle nitric acid oxidations of certain hydroxy fatty acids (e.g., 12-hydroxystearic acid from hydrogenation of ricinoleic acid, etc.) can be used to afford mixed C-11/C-12 dibasic acids. (f.) Dibasic acid mixtures by nitric acid oxidations. Depending upon conditions, both saturated and unsaturated fatty acids are oxidized to a heterogeneous mixture of mono- and dibasic acids by oxidation with nitric acid.

INTRODUCTION

Eight dibasic acids to be discussed here are all aliphatic and all display the normal chemical behavior of aliphatic carboxylic acids. All have acid strength comparable to that of acetic acid. Otherwise they vary considerably. Their physical form varies from crystalline solid to soft waxy solid to viscous liquid. Their configuration may be linear, branched or cyclic. They may be saturated or unsaturated and they may be soluble or insoluble in water. All of the acids, which vary from 8 to 21 carbon atoms, can be distilled, but only at reduced pressure.

All of these acids might be termed "semisynthetic" in that one of their carboxyl groups and the bulk of their structure occurs naturally. The second carboxyl group is introduced into the basic, natural structure by chemical conversion.

In discussing the methods by which these dibasic acids are prepared, emphasis is on the unique derivation of each from a natural fat or oil. For comparison, some other synthetic methods will be mentioned that are unique to the particular dibasic acid. General synthetic methods that are applicable to any dibasic acid will not be covered, such as malonic ester synthesis, hydrolysis of dinitriles, pressure reaction of terminal diols with carbon monoxide, and oxidation of difunctional compounds containing hydroxyl, aldehyde and carboxyl groups.

As a group, because of their difunctionality, these acids are useful in producing various kinds of polymers by condensation polymerization such as polyesters, polyamides, polyurethanes and alkyds. These polymers are used in coatings, molded products, adhesives and fibers. Other important uses shared by some, but not all, of these dibasic acids are diester plasticizers, diester lubricants and surfactants.

SUBERIC ACID C-8

Occurrence

Suberic acid was first obtained by the oxidation of cork and derived its name from this fact. It has also been recovered from plant stems, leaves and wood. It is most readily obtained from a variety of unsaturated fatty acids.

Properties

It exists as long needles or plates which melt at 144 C and sublime at 300 C. It distills at 230 C/15 mm. Only 0.16% dissovles in water at 20 C, but it is quite soluble when hot.

Preparation

Many unsaturated fatty acids are oxidized by dilute nitric acid at high temperature to give a 4-10 carbon atom mixture of linear dibasic acids rich in suberic acid. Typical of the fatty acids that can be used are oleic acid, ricinoleic acid (1) and cottonseed fatty acids. These all have the first double bond at the 9-position so that much of the azelaic acid originally formed is degraded to suberic acid. Procedures for carrying out the oxidation have been patented (2) as have techniques for separating and purifying the mixed acids produced (3).

The above methods produce mixed monobasic acids as a coproduct. This can be neatly avoided by the oxidative cleavage of the double bond in cyclooctene. The resulting ring opening gives suberic acid.

Various oxidizing agents have been used, including nitric acid, chromic acid, potassium permanganate, ozone, and alkaline hydrogen peroxide (4).

The cyclooctene can be obtained either by cyclic tetramerization of acetylene to cyclo-octatetraene followed by partial hydrogenation of by cyclic dimerization of butadiene to 1,5-cyclooctadiene followed by partial hydrogenation.

Commercial Production

It is not available commercially. It was produced commercially for a short time in the 1950s by the oxidation of low grade vegetable fatty acids with hot dilute nitric acid. This was discontinued because of explosion hazards. It was available again for a time in the 1960s from a semi-works plant by the ozonolysis of cyclooctene, obtained from butadiene as described above. Production was discontinued because of high price compared to similar commercially available dibasic acids.

Reactions

It undergoes all of the typical reactions of carboxylic acids. Cyclization to cycloheptanone occurs when heated with iron powder at 320-25 C.

Uses

Various useful polyesters and polyamides have been made but none is commercial.

AZELAIC ACID C-9

Occurrence

Azelaic acid, the common name for nonanedioic acid, $HOOC(CH_2)_7COOH$, is found in rancid oleic acid, rancid butter and many other natural products which contain long chain fatty acids. The origin in these cases is probably unsaturated fatty acid cleavage.

Properties

Azelaic acid crystallizes in flat needles or leaflets which melt at 106.5 C. It distills at 287 C/100 mm and at 225

C/10 mm. At normal pressure it distills partially at above 360 C with partial decomposition to a mixture of products including azelaic anhydride. It is nonvolatile in steam. The solubility in water is only 0.2% at 15 C and 2.2% at 65 C but highly soluble at 100 C.

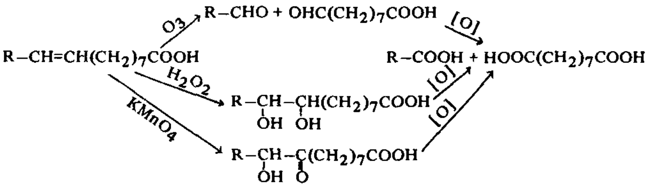
Preparation

The most common and feasible method of preparing azelaic acid in good yield involves the oxidative cleavage of a natural unsaturated fatty acid containing the grouping

$$-CH{=}CH-(CH_2)_7COOH$$

Typical fatty acids used are oleic acid, linoleic acid and ricinoleic acid. Oxidation can be achieved by any of a wide variety of common oxidants including nitric acid, potassium permanganate (5,6), chromic acid and ozone (7). An equivalent amount of a monobasic coproduct is also produced which, in the case of oleic acid, is nonanoic acid, commonly known as pelargonic acid.

The same mixture of monobasic and dibasic acid cleavage products may be obtained from the same initial unsaturated fatty acid by different routes involving various insolatable intermediates.



If ozone is used, the resulting ozonide can be cleaved reductively by palladium-hydrogen, zinc-water or zinc-acetic acid (Ref. 8 reviews these methods as applied to oleic acid) to give the aldehyde mixture which is readily oxidized to the carboxylic acids.

Direct hydroxylation of the double bond gives the corresponding 1,2-glycol. Various hydroxylating agents have been used including performic acid, peracetic acid (9,10), alkaline hydrogen peroxide, hydrogen peroxide-ferrous sulfate (Fenton's reagent), dilute alkaline potassium permanganate (11) and osmium tetroxide. The glycol can then be cleaved by sodium hydroxide fusion or by potassium hydroxide-potassium chlorate at 200-220 C.

A third intermediate is 9(10)-10(9)-ketohydroxystearic acid, obtained by oxidation of oleic acid with neutral aqueous potassium permanganate (12), which can be cleaved by further oxidation.

Commercial Production

Emery Industries, Inc. is the only commercial producer of azelaic acid. Initially they used chromic acid to oxidize oleic acid (13). This method was relatively expensive because the spent chromic acid solutions had to be regenerated in electrolytic cells. Another disadvantage was the presence in the azelaic acid of some lower dibasic acids resulting from degradation.

In the 1950s Emery replaced chromic acid with ozone as the oxidant, the method that they use today in Cincinnati, OH and in the Netherlands. The process (14) involves the initial formation of oleic acid ozonide by continuous countercurrent contact in a vertical column at ca. 40 C between a rising stream of 2% ozone in oxygen and a falling solution of oleic acid in pelargonic acid. The resulting solution of ozonide in pelargonic acid is fed continuously into a pool of previously decomposed ozonide at ca. 100 C. This is done in the presence of a manganous salt while passing through a stream of oxygen so that the aldehyde-acid mixture formed by initial cleavage is converted immediately and completely to acids. The mixed product contains pelargonic acid, azelaic acid, unchanged stearic acid and palmitic acid, and other high boiling byproducts. The pelargonic acid is first removed by distillation. The residue is extracted with hot water and azelaic acid recovered from the extract by evaporation or crystallization.

Reactions

Azelaic acid undergoes the usual reactions of the carboxyl group. When heated above 360 C it undergoes decomposition to caprylic acid and cyclooctanone. Heating with barium oxide and iron gives cyclooctanone. Heating over a dehydrating agent gives linear azelaic polyanhydride.

Uses

The uses for azelaic acid along with use patents have been reviewed (15,16). The commercial applications for azelaic acid fall largely into three areas: (a) diesters and linear polyesters as plasticizers for polyvinyl chloride; (b) diesters as engine lubricants; (c) polymer intermediates in polyamide, polyester and polyurethane coatings, fibers, adhesives and resins.

The most common diester plasticizers are isooctyl and 2-ethyl-hexyl azelate. They confer good low temperature properties, combined with low water extraction, on polyvinyl chloride making them especially suitable for applications such as rain wear and garden hose. The linear polyesters are used with polyvinyl chloride also and are derived from azelaic acid, adipic acid (to lower cost), propylene glycol and pelargonic acid. They are used where very low volatility and migration are required.

Dioctyl azelate, didecyl azelate and ditridecyl azelate are all outstanding lubricants for piston and turbine engines. They were used originally in jet aircraft where properties superior to conventional hydrocarbon lubricants were required, such as high temperature stability and relatively low viscosity at low temperature.

Azelaic acid has found its way into a variety of specialty polymer applications. It increases the flexibility of unsaturated polyesters. Azelaic acid is an intermediate for 6/9 nylon, useful in fibers, monofilaments, molded articles, wire coatings and other applications where water resistance superior to ordinary 6/6 nylon is needed. Azelaic acid is also useful as a modifier to impart improved properties to conventional terephthalic acid-ethylene glycol polyesters.

SEBACIC ACID C-10

Occurrence

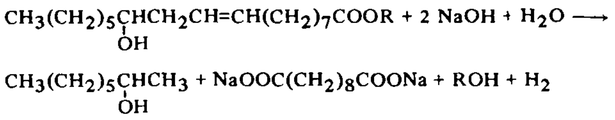
Sebacic acid is the common name for decanedioic acid, $HOOC(CH_2)_8COOH$. It does not occur in nature as such but is obtained from castor oil by a series of chemical reactions.

Properties

Sebacic acid exists as colorless leaflets melting at 134.5 C. It distills at 295 C/100 mm and at 232 C/10 mm. Heating to 360 C is required before appreciable amounts of carbon dioxide are evolved. Its thermal stability is greater than any of its lower homologs. It is only 0.1% soluble in water at room temperature but is easily soluble in hot water.

Preparation

Sebacic acid has been prepared by the oxidation of stearic acid with nitric acid, the oxidative cleavage of undecylenic acid, and by the caustic fusion of castor oil, sodium ricinoleate or other ricinoleic acid derivative. Castor oil is most commonly used. A laboratory conversion of castor oil with sodium hydroxide has been described (17). Methods of producing sebacic acid by heating castor oil with aqueous sodium hydroxide at around 250 C under pressure have been patented (18,19). Improved yields are claimed if the reaction is conducted in the presence of sodium nitrate (20), lead compounds (21), lead and barium compounds (22), nickel and barium compounds (23) or mineral oil (24). The reaction products are disodium sebacate and octanol-2:



$$CH_3(CH_2)_5\underset{OH}{CH}CH_2CH{=}CH(CH_2)_7COOR + 2\ NaOH + H_2O \longrightarrow$$

$$CH_3(CH_2)_5\underset{OH}{CH}CH_3 + NaOOC(CH_2)_8COONa + ROH + H_2$$

The mixture is distilled to remove capryl alcohol (octanol-2), acidified with sulfuric acid, and the sebacic acid extracted.

Commercial Production

Sebacic acid is produced commercially by the treatment of castor oil with alkali as described above.

Reactions

Sebacic acid undergoes the various reactions typical of the carboxyl group. Distillation at 340 C in a stream of carbon dioxide gives nonanoic acid, a little cyclononanone and an unsaturated fatty acid.

Uses

Sebacic acid has long been established as polyvinyl chloride plasticizers in the form of dioctyl sebacate and linear polyesters. Dioctyl sebacate was the forerunner in the field of synthetic ester lubricants for jet aircraft. Nylon 6/10 is a specialty polyamide used where high moisture resistance is required such as signal wire coating, toothbrush bristles, and certain molded articles. It is also useful as a modifier for dimer polyamides where improved flexibility and oxidation resistance is needed.

UNDECANEDIOIC ACID C-11

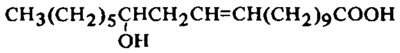
Properties

This acid crystallizes from water as plates. Melting point is given as 110 C and 124 C. Solubility in water at 20 C is 0.014%. It dissolves with difficulty in hot water.

Preparation

It is obtained as a coproduct along with dodecanedioic acid by the oxidation of 12-ketostearic acid, by the oxidation of 12-hydroxystearic acid by concentrated nitric acid at 70 C (25), and by fusion of 12-ketostearic acid with sodium hydroxide at 325 C in the presence of cadmium oxide (25).

Lesquerolic acid, a higher analog of ricinoleic acid, is a relatively newly discovered hydroxyacid present in lesquerella seed oil:



$$CH_3(CH_2)_5\underset{OH}{CH}CH_2CH{=}CH(CH_2)_9COOH$$

On oxidation with potassium permanganate-sodium periodate, it yields undecanedioic acid (26).

Undecanedioic acid is also produced as a minor component along with mixed dibasic acids of shorter chain length by dilute nitric acid oxidation of oleic acid, cottonseed fatty acids, or castor oil. The acid is not produced commercially.

Reactions

It undergoes normal carboxyl group reactions. Distillation of the thorium salt at 350-400 C/30-40 mm gives cyclodecanone.

Uses

It could be useful in esters, polyesters and polyamides, but these have not been developed.

DODECANEDIOIC ACID C-12

Properties

It crystallizes as needles from hot water, m.p. 127 C, and distills at 245 C/10 mm. Solubility in water is 0.005% at 23 C and 0.113% at 100 C.

Preparation

It is obtained by various oxidation methods from 12-keto and 12-hydroxystearic acids as a coproduct along with undecanedioic acid as described in the previous section, conveniently prepared by the ozonolysis of cyclododecene (27-29). The latter is obtained by the partial hydrogenation of 1,5,8-cyclododecatriene, the cyclic trimer of butadiene. Alternately, the triene can be completely hydrogenated to cyclododecane which is then oxidized to dodecanedioic acid.

Commercial Production

Produced in multimillion pound quantities by the oxidation of cyclododecane in two steps. Various methods are used to convert initially to cyclododecanone or cyclododecanol or a mixture of the two which is oxidized further in a second step, commonly by nitric acid. This sequence is used by DuPont and is similar to their well known method for producing adipic acid from cyclohexane.

Reactions

When dodecanedioic acid is refluxed with acetic anhydride, a polymeric anhydride is formed (30). Heating of the thorium salt gradually to 500 C gives a small yield of cycloundecanone.

Uses

DuPont's synthetic polyamide fiber, Quiana, is derived from dodecanedioic acid and bis(p-aminocyclohexyl)-methane (31). Other polyamides have been prepared.

BRASSYLIC ACID C-13

Occurrence

Brassylic acid is the common name for tridecanedioic acid, $HOOC(CH_2)_{11}COOH$. It appears to occur naturally only in the form of oxidation precursors.

Properties

Brassylic acid is a solid, melting at 113 C, and crystallizing as needles from dilute alcohol. Its solubility in water at 24 C is 0.004%.

Preparation

13-Docosenoic acid (erucic acid) occurs in rapeseed oil and mustard seed oil. Erucic acid can be cleaved oxidatively to brassylic acid by all of the methods used to oxidize oleic acid to azelaic acid.

Commercial Production

Brassylic acid has been produced on occasion in pilot quantities by the ozonolysis of erucic acid followed by oxidative cleavage, the same method used to produce azelaic acid on commercial scale.

Reactions

Like other dibasic acids in this series of C-8 and above, brassylic acid forms a polymeric anhydride when refluxed with acetic anhydride. Molecular distillation of the polymer forms an unstable monomeric anhydride (30).

Uses

Polyamides derived from brassylic acid, nylon 6/13 and nylon 13/13, are not commercial, but their properties have been extensively investigated (32,33). These results suggest commercial possibilities if erucic acid became available at a lower price.

CARBOXYSTEARIC ACID C-19

Occurrence

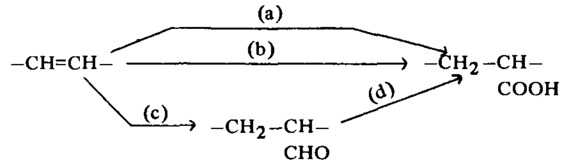
Carboxystearic acid is a C-19 dicarboxylic acid which does not occur naturally. It consists primarily of 9- and 10-carboxystearic acids, with some other isomers also present.

Properties

The isomeric carboxystearic acid mixture is either a viscous liquid or a low melting solid depending on the method of preparation. It can exist in the solid form because of a narrower distribution of isomers. The effect of the branched carboxyl group on melting point can be seen by comparison with the melting point of 118 C for straight chain nonadecanedioic acid.

Preparation

Oleic acid has been converted to carboxystearic acid by three main routes, all of which involve reaction of carbon monoxide at the double bond.



(a) Koch reaction with CO and water, catalyzed by strong acid (34); (b) Reppe reaction with CO and water, catalyzed by $Ni(CO)_4/NiI_2$; (c) Oxo reaction with CO/H_2, catalyzed by $Ni(CO)_4$ followed by (d) Oxidation (35).

Extensive isomerization of the double bond occurs during reaction so that numerous positional isomers are produced besides the simple 9- and 10-addition products.

Commercial Production

Carboxystearic acid has been offered in experimental quantities by several companies, but it has not been commercialized.

Reactions

The two carboxyl groups exhibit the various typical reactions except that the side chain carboxyl is only ca. 1/25 as reactive as the terminal carboxyl. Because of the hindered position of the side chain carboxyl group, it is difficult to force the esterification of that group to completion. This difference in reactivity leads to synthetic opportunities not possible when the two carboxyl groups are equivalent as in azelaic acid. Esterification of one mole of azelaic acid with one mole of methanol yields large amounts of dimethyl azelate, monomethyl azelate and azelaic acid. The same reaction with carboxystearic acid gives primarily methyl carboxystearte only. The other monomethyl ester can be obtained by preparing the dimethyl ester and hydrolyzing with one mole of base to give carbomethoxystearic acid.

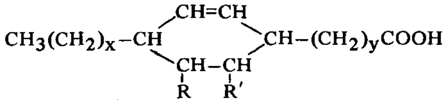
Uses

Several polyesters, polyamides and ester plasticizers from carboxystearic acid have been patented, but none have found commercial use.

"DIACID" C-21

Occurrence

The C-21 dicarboxylic acid discussed here has the structure



$x + y = 12$
$R = H, R' = COOH$ or $R = COOH, R' = H$

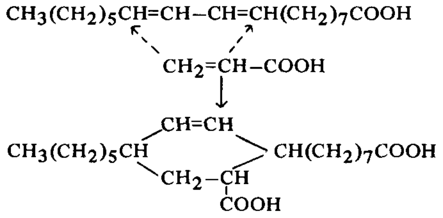
It does not occur naturally.

Properties

This acid is a viscous liquid, insoluble in water and soluble in many common organic solvents. The terminal carboxyl group has a pKa of 6.4, and the ring carboxyl group has a pKa of 7.15.

Preparation

Diacid is prepared by the Diels-Alder addition of acrylic acid to a conjugated linoleic acid (36-39). Ordinary 9,12-linoleic acid also undergoes the condensation when conducted under conditions which also isomerize the linoleic acid to mainly 10,12- and 9,11-linoleic acid, which then reacts. The isomerizing agent can be iodine (40), palladium (41) or sulfur dioxide (41).



Commercial Production

The acid is produced by the Westvaco Corporation, starting with tall oil fatty acids, in quantities somewhere in the range of 2-10 million pounds per year. They have given the product the commercial name of "Diacid." The linoleic acid component of the tall oil fatty acids undergoes sequentially in one pot conjugation and Diels-Alder condensation by heating with acrylic acid and ca. 1% iodine at 250 C (40). The linoleic acid component is almost completely converted. Therefore, the unreacted oleic acid, which is stripped off, contains less than 1% of polyunsaturates. The Diacid still residue can be used as such or distilled in thin film equipment.

Reactions

Diacid has an aliphatic double bond in the ring and thus undergoes all the typical double bond reactions of cyclohexene as well as the usual carboxyl group reactions. The terminal carboxyl group is about ten times as reactive as the ring carboxyl and also has greater acid strength. Therefore, it is possible to prepare various monoesters, monoamides, monosalts, etc. by selective reaction of the terminal carboxyl group. The other monoderivative can be obtained by, for example, partial hydrolysis of the diester to leave the ring carboxyl group esterified. Diacid will yield polyesters and polyamides, but molecular weights are lower than obtained from other dicarboxylic acids because of the reduced reactivity of the ring carboxyl group.

Uses

Various uses for Diacid have been reviewed (42). Probably the most important use so far has been in alkali metal soaps for various cleaning and detergent formulations

(43,44). Much higher solid contents are possible in these soaps as compared to the comparable coconut fatty acid soaps.

Other uses are as rust inhibitors for hydrocarbons (45), epoxy esters (46), soaps for SBR latex foam stabilization (47) and soaps for polyethylene emulsions (48).

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New Applications for Fatty Acids and Derivatives[1,2]

M. WEISS, Gross & Co., Newark, NJ, **R. ROSBERG**, and **N.O.V. SONNTAG**,
Southland Chemical Division, Dallas TX (and **S. ENG**, Glyco Chemicals, Inc., Painesville, OH)[1]

ABSTRACT

The early development of the American fatty acid industry during 1900-1920 is usually associated with the use of stearic acid in candles for lighting purposes. Today, the use of stearic acid in candle manufacture continues; the volume consumed for this application is not small, but the use is for ornamental, decorative or festival purposes, only incidentally for emergency lighting purposes. When one consideres that most candles consist of 10-20% stearic acid, which improves among other things, the appearance, burning qualities and stiffness of the candle, the volume consumed is appreciable. More than that, the growth rate in this use is impressive. In 1965, it has been estimated that the volume of double-pressed stearic acid that found its way into candles was 3.5 million pounds. Today (1979) it is conservatively estimated that from 10-12 million pounds are utilized for this purpose. Innovations, such as the development of dripless candles, achieved by the incorporation of a somewhat larger proportion of stearic acid to the external wax coat, are now possible uses. Concrete and asphalt are examples of much-used large tonnage materials of construction which have disadvantages in use that can be at least partially or significantly improved through the incorporation of stearic acid or certain other fatty chemicals. An excellent example of the tailor-making of fatty acid derivatives to satisfy an almost desperate need is provided by the development of derivatives suited for the retardation of water evaporation from reservoirs in arid areas. In 1966 it was estimated that the evaporation from large lakes and reservoirs in 17 western states was equivalent to 14 million acre feet, an amount which could ordinarily supply 84 million people annually. The design of water insoluble long chain organic compounds with a hydrophilic group at one terminal position gives products capable of forming monomolecular films which are uniquely suited to solve this problem. Fatty alcohol ethoxylates are only one approach among several.

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[1] Paper presented at Short Course by S. Eng, Glyco Chemicals, Inc., Painesville, Ohio.

[2] Representatives of A. Gross Candle Co. (Linden, NJ), Faroy, Inc. (Houston, Texas) and Old Harbor, Inc. (Hyanis Port, MA) supplied part of the information used in this paper.