Industrial Chemical Uses of Polyunsaturated Fatty Acids[1]

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ABSTRACT

Production of vegetable, animal and marine oils containing more than about 40% unsaturated fatty acids totaled 15,000 million pounds in 1968, almost on the scale of petrochemical production. The greater share (64%) of this nonfossil oil production was directed toward food uses, the remainder toward industrial and animal feed uses. The variety of chemical reactions carried out on these unsaturated fatty acid products include hydrogenation, interesterification, dimerization, sulfation, formation of nitrogen compounds, epoxidation, alkaline cleavage and oxidative ozonolysis. Some of these reactions have been developed at Utilization Research and Development Divisions of the Agricultural Research Service, U.S. Department of Agriculture. Research is continuing in developing new reactions for potential industrial application. An example is reductive ozonolysis of unsaturated fatty esters to produce monofunctional aldehydes and bifunctional aldehyde esters.

INTRODUCTION

Most scientists readily acknowledge the mammoth proportions of the petroleum industry and of its offshoot, the petrochemical industry. Yet probably few are aware of the comparable magnitude of the industry concerned with oils from nonfossil sources. The 1967 production of petroleum crude products for chemical conversion in the United States was 54,000 million pounds, 70% of it consisting of aliphatic hydrocarbons, at an average value of 3 cents/lb. Although production of nonfossil oils is less, it still amounted to 15,000 million pounds in 1968 at values ranging from 3 cents to 39 cents/lb (Table I). Such nonfossil oils include vegetable, animal and marine oils; they are liquid at ordinary temperatures because of their high proportion of unsaturation. Soybean oil and tallow predominate in the United States, but tall oil and cottonseed oil follow closely.

TABLE I

Production and Price for Unsaturated Fatty Acid Sources

Oil or fat	1968 Production, million lb USA (1)	1968 Production, million lb World (2)	1970 Price for crude product, USA cents/lb (3)
Soybean	6150	11,080	12
Tallow and grease, edible	538		---
Tallow and grease, inedible	4745	9310	7
Sunflower seed	---	7950	---
Peanut	209	7010	15
Cottonseed	1115	4830	13
Rapeseed	---	3690	17
Olive	---	2954	38
Palm	97[a]	2880	13
Fish	171	2440	12
Linseed	307	1720	11
Sesame seed	---	1320	39
Castor	133[a]	820	15
Corn	453	530	15
Safflower	86[a]	470	17
Tung	32[a]	268	24
Whale	40[a]	200	15
Oiticica	---	78	17
Tall oil	1239	---	3
Vegetable oil foots	265	---	6

[a] Consumption in selected products. Production figures are withheld to avoid disclosing figures for individual companies.

Most of these oils contain various proportions of oleic, linoleic and linolenic acids, but some contain unusual acids such as ricinoleic, erucic and eleostearic (Table II). Tall oil deserves special mention because of its rapid growth in the past 15-20 years. Its name is derived from the Swedish "tallolja" (pine oil), and it is a byproduct of the sulfate-pulp industry. Distilled tall oil contains 14-37% rosin and 60-85% unsaturated fatty acids, which comprise roughly 50% oleic, 40% linoleic and 6% conjugated acid. These acids are present as the free acid and not as the glyceride.

An overall picture will be drawn for (a) the consumption and use patterns for these oils and for their unsaturated fatty acids; (b) their industrial reactions; (c) the utilization research areas under investigation by the Agricultural Research Service of the U.S. Department of Agriculture; and (d) reductive ozonolysis, an aspect of the oil research at the Northern Regional Research Laboratory. Monounsaturated as well as polyunsaturated fatty acids will be discussed because for most uses it is impractical to separate these acids.

OIL CONSUMPTION AND USES

By far the greatest market for vegetable oils lies in

TABLE II

Oil Composition[a]

Oil or fatty acids	Composition, wt % Oleic	Linoleic	Linolenic	Other
Vegetable oils				
Castor	3	4	---	89[b]
Corn	27	59	1	---
Cottonseed	17	53	---	---
Crambe	17	9	6	60[c]
Linseed	19	15	57	---
Oiticica	6	---	---	78[d]
Olive	52	15	1	---
Palm	38	10	---	---
Peanut	51	31	---	---
Perilla	13	14	64	---
Rapeseed	17	13	5	56[c]
Safflower	13	78	---	---
Soybean	22	55	8	---
Sunflower	14	75	---	---
Tall oil	48	37	---	---
Tung	8	4	3	80[e]
Animal fats				
Butter fat	32	2	1	8
Lard	43	9	---	5
Tallow	44	2	---	---
Marine fats and oils				
Herring	24	1	---	44[f]
Menhaden	17	1	---	32[f]
Sperm whale	24	5	2	12[f]

[a] Only those sources having more than 40% total unsaturates are listed.
[b] Ricinoleic acid.
[c] Erucic acid.
[d] Licanic (4-keto-9,11,13-octadecatrienoic) acid.
[e] Eleostearic acid.
[f] Various C_{18} to C_{24} polyunsaturated fatty acids.

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[1] Presented at the ISF-AOCS World Congress, Chicago, September 1970.

[2] No. Market. Nutr. Res. Div., ARS, USDA.

TABLE III

1968 Consumption of Oils and Fats in Edible Products, USA, (1) millions of lb

Oil or fat	Baking or frying fat	Salad or cooking oil	Margarine	Other	Total
Soybean	1842	2036	1240	43	5161
Cottonseed	248	541	70	44	903
Lard	601	0	166[a]	b	767
Tallow, edible	487	0	166[a]	b	653
Corn	10	242	179	8	439
Peanut	21	157	b	b	201
Palm	b	b	b	b	97[c]
Safflower	4	b	45	b	69
Others	b	b	b	b	17
					8307

[a] Total for lard and edible tallow.
[b] Consumption figures are withheld to avoid disclosing figures for individual companies.
[c] Total for both edible and inedible products.

various edible products, including baking or frying fats, salad or cooking oils and margarine (Table III). These outlets consume 5161 millions pounds of soybean oil out of a total of 8307 million pounds of all vegetable oils, or 62%.

Consumption of oils in inedible uses amounted to 4700 million pounds in 1968 (Table IV), or 36% of total oil consumption. Although soybean oil is used, tallow and tall oil predominate in the inedible field, especially tallow for feed and both for fatty acids. Tallow is also in demand on a large scale for soaps and for fatty acids. Alkyds and resins and plastics are the major nonfood markets (250 million pounds in 1968) for soybean oil. More and more soybean oil is going into coatings while the amount of linseed oil has declined drastically.

According to the Fatty Acid Producers' Council, the production of unsaturated fatty acids, mainly from tall oil, totaled 570 million pounds in 1969 (Table V). There are five major outlets for tall oil fatty acids, distributed as indicated in Table VI.

TABLE IV

1968 Consumption in Inedible Products, USA, (1) millions of lb

Oil	Consumption in major applications	Total consumption
Edible oils		
Soybean[a]	Paints, 79; resins, 102	250
Cottonseed	---	7
Lard	Lubricants, 12	25
Tallow	---	8
Peanut	---	5
Palm	---	---
Safflower	Paints, 13; resins, 4	19
Others	Resins, 19; lubricants, 5	39
		353
Inedible oils		
Tallow	Feed, 1011; soap, 639; fatty acids, 573; lubricants, 92	2478
Tall oil	Fatty acids, 1144; paints, 18; soap, 9; lubricants, 9	1288
Linseed	Paints, 122; resins, 19; lubricants, 7	194
Castor	Paints, 13; lubricants, 8	133
Vegetable oil foots	Fatty acids, 82	123
Sperm	Lubricants, 19	40
Tung	Paints, 22; resins, 6	32
Fish	Paints, 6	30
Others	---	39
		4357
	Overall total	4710

[a] According to USDA (4), nonfood uses for soybean oil totalled 492 million pounds for the year beginning October, 1968. Foots and loss amounted to 243 million pounds; foots are largely consumed in animal feeds and industrial soaps.

The U.S. Tariff Commission has given data for some specific compounds of unsaturated fatty acids (Table VII) (6).

INDUSTRIAL REACTIONS

Many industrial uses cited for vegetable oils depend upon a chemical reaction being carried out on the oil or fatty acid. Some of the more noteworthy reactions are outlined here. For a more thorough treatment consult the literature listed in References 53-59.

Hydrogenation

Partial hydrogenation is an essential reaction in the production of food items (margarine, salad and cooking oils and shortening), as well as of industrial chemicals. A general reaction can be written in the following way for oleic, linoleic and linolenic acids if it is recognized that extensive geometric and positional isomerizations have occurred in

TABLE V

1969 Production of Unsaturated Fatty Acids[a]

Fatty acid	Iodine value	1969 Production, million lb
Oleic (red oil)	b	130.9
Animal[c]	36-80	32.5
Vegetable or marine	<115	8.9
Unsaturated	116-130	17.7
Unsaturated	>130	9.3
Tall oil[d]	b	174.2
Tall oil[e]	b	196.5
		570.0

[a] Fatty Acid Producers' Council.
[b] Iodine value not defined for these acids.
[c] Animal fatty acids other than oleic.
[d] Tall oil fatty acids containing more than 2% rosin acids.
[e] Tall oil fatty acids containing less than 2% rosin acids.

TABLE VI

Tall Oil Fatty Acid Uses, 1967 (5)

Use	Consumption, million lb
Coatings	79
Dimer acid	40
Soaps	33
Flotation agents	29
Epoxy tallates	20
Others	67
	268

TABLE VII

Production, Unit Value and Industrial Use for Selected Unsaturated Fatty Acids (6)

Unsaturated fatty acid derivative	1967 Production, million lb	1967 Unit value, dollars/lb	Industrial use[a]
Tallow			
Salt, potassium	45.2	—	SAA
Salt, sodium	533.1	0.13	SAA
Glyceride, sulfated, sodium salt	10.0	0.13	SAA
Amine			
Tallow alkyl amine	5.2	0.24	SAA
Hydrogenated tallow alkyl amine	2.6	0.28	SAA
Ethoxylated tallow alkyl amine	1.3	0.55	SAA
N-(Tallow alkyl) trimethylene diamine	3.6	0.30	SAA
Bis(hydrogenated tallow alkyl) dimethyl ammonium chloride	20.7	0.24	SAA
N-Methyl *bis*(hydrogenated tallow alkyl) amine	2.8[b]	0.27	SAA
	624.5		
Oleic acid			
Salts			
Sodium	1.8	0.20	SAA
Potassium	1.1	0.23	SAA
Acid, sulfated, disodium salt	9.7	—	SAA
Esters			
Alkyl	11.0	0.21-0.28	PLA
Alkyl, sulfated, sodium salt	7.9	0.28	SAA
Anhydrosorbitol esters (including ethoxylated esters)	11.7	0.38-0.42	SAA
Diethylene and polyethylene glycol esters	6.9	0.29-0.35	SAA
Glycerol monooleate	2.5	0.36	SAA
Amides			
Ethylene diamine, monoethoxylated	4.6[c]	—	SAA
Diethanolamides	2.0	0.30-0.65	SAA
Amines			
Oleylamine	1.8	0.43[c]	SAA
N-Oleyl trimethylene diamine	1.6	0.37	SAA
Alcohol			
Oleyl alcohol, ethoxylated	3.6	0.52	SAA
Tall oil			
Salts			
Sodium	10.0	—	SAA
Potassium	11.7	—	SAA
Other	7.8	0.23-0.48	DRI
Acids, sulfated sodium salt	0.8	0.24	SAA
Esters			
Polyethylene glycol esters	8.5	0.17	SAA
Anhydrosorbitol monoester	0.6	—	SAA
Amides			
Diethanolamides	0.4	—	SAA
Epoxy			
2-Ethylhexyl epoxytallate	9.7[b]	0.24	PLAST
Octyl epoxytallate	15.1	0.26	PLAST
Miscellaneous			
Soybean oil, sulfated, sodium salt	0.3	0.36	SAA
Soybean alkyl amine, ethoxylated	0.9	0.37	SAA
Soybean oil, epoxidized	62.1	0.26	PLAST
Castor oil, ethoxylated	4.3	0.33	SAA
Castor oil, sulfated, sodium salt	7.0	0.33	SAA
Sperm oil, sulfated, sodium salt	6.5	0.17	SAA
Sperm oil, sulfurized	23.0[c]	—	LUB
Azelaic acid esters	17.5	0.29	PLA
Sebacic acid esters	11.5	0.50-0.59	PLA
Erucamide	1.1	1.25	

[a] SAA, surface active agents; PLA, plasticizers; DRI, driers for surface coatings; PLAST, plasticizer-stabilizer; LUB, lubricating oil additives.
[b] Sales.
[c] Year of 1966.

the partially hydrogenated product (G = glyceride):

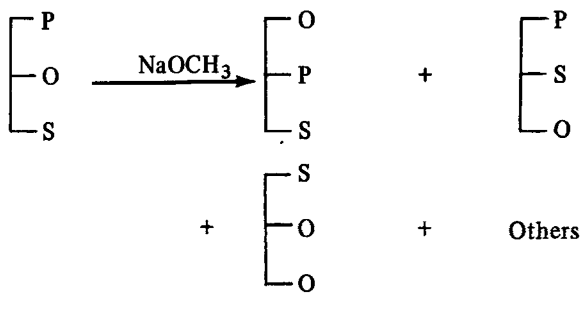
$$GOOC(CH_2)_7(CH{=}CHCH_2)_m(CH_2)_nCH_3 \xrightarrow[\text{catalyst}]{H_2}$$

$$GOOC(CH_2)_x(CH{=}CHCH_2)_y(CH_2)_zCH_3$$

where m=1, 2 or 3; n=0, 3 or 6; 3m+n=9;
y=0, 1 or 2; x+3y+z=16

Interesterification

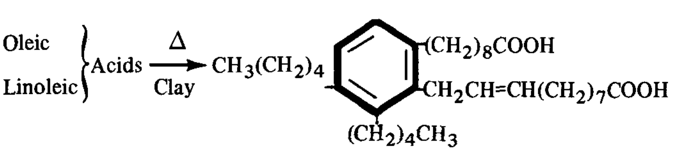
This reaction gives a modified product having a suitable melting range for shortening.



P = palmitic, S = stearic, O= oleic

Dimerization

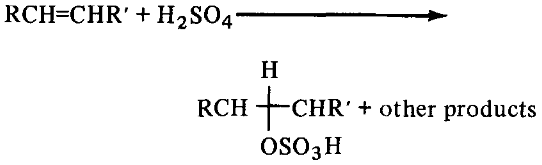
Dimer and trimer acids have found outlets in many different commercial applications, most important of which are the dimer acid polyamides used in epoxy adhesives and resins, heat sealing resins and printing inks (7). These acids are also used in making polyesters for polyurethane foams and in making lubricants, corrosion inhibitors and alkyds. They are generally produced by heating oleic acid or tall oil fatty acids over a clay catalyst (8):



Dimer acid
+ other products

Sulfation

Reaction of sulfuric acid with the double bond is an important one in producing textile lubricants, wetting agents and a fat-liquoring agent for leather. At mild temperatures, sulfation predominates; at higher temperature, sulfonation occurs.



$$RCH{=}CHR' + H_2SO_4 \longrightarrow RCH\underset{OSO_3H}{\overset{H}{-}}CHR' + \text{other products}$$

Nitrogen Compounds

Conversion of unsaturated fatty acids to amides, nitriles and saturated amines may be illustrated as follows:

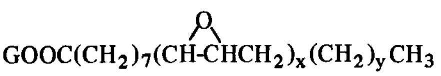
1. $RCOOH + NH_3 \xrightarrow{\Delta} RCONH_2 + H_2O$
2. $RCONH_2 \xrightarrow[\text{Catalyst}]{\Delta} RC{\equiv}N + H_2O$
3. $RC{\equiv}N \xrightarrow{H_2,Ni} RCH_2NH_2$

Amides serve as antiblock agents, as solvents and in waterproofing; nitriles, in low temperature plasticizers and yarn lubricants; and amines, as intermediates for surface active agents and oil flotation.

Epoxidation

Epoxidized oils useful as a combination plasticizer and stabilizer for poly(vinyl chloride) and as an active reactant for making resins are prepared according to the scheme:

$$GOOC(CH_2)_7(CH{=}CHCH_2)_x(CH_2)_yCH_3 \xrightarrow[H^+]{H_2O_2}$$



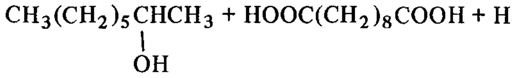
$$GOOC(CH_2)_7(\overset{O}{CH\text{—}CH}CH_2)_x(CH_2)_yCH_3$$

$$x = 2 \text{ or } 3,\ 3x + y = 9$$

Alkaline Cleavage

Heating ricinoleic acid or castor oil in the presence of caustic produces sebacic acid, valuable as an intermediate for plasticizers, for polyamides such as nylon-6/10 and for lubricants.

$$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH \xrightarrow[250\ C]{NaOH,\ H_2O}$$



$$CH_3(CH_2)_5\underset{OH}{CH}CH_3 + HOOC(CH_2)_8COOH + H_2$$

Oxidative Ozonolysis

Azelaic acid is produced by oxidative ozonolysis of oleic acid and is used for making poly(vinyl chloride) plasticizers and lubricants. Pelargonic acid, the other cleavage product, is valuable for making jet engine lubricants.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[RCOOH]{O_3} \left[\begin{array}{c}\text{Ozonolysis}\\ \text{products}\end{array}\right] \xrightarrow[\Delta]{O_2}$$

$$CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$$

UTILIZATION RESEARCH

Research on unsaturated vegetable and animal fats and oils is carried out by the Agricultural Research Service of the U.S. Department of Agriculture at five different locations (Table VIII). Research on fish oils is conducted by the U.S. Bureau of Commercial Fisheries. A few examples of utilization research accomplishments adopted by industry at sometime or another will be cited here, but no attempt will be made to document them completely. Lists of publications and patents are available from each of the five Divisions. A categorized list of NU publications is available from the Oilseed Crops Laboratory of the Northern Division. Selected investigations will illustrate current activities.

The Eastern Laboratory has developed epoxidized oils valuable as plasticizer-stabilizers for poly(vinyl chloride), biodegradable detergents from tallow alcohol sulfates and α-sulfoacids, vinyl ester polymers and copolymers and potential lubricants and surface active agents from phenylstearic acid. Investigations on epoxidation, vinyl monomers, peroxy acids, hydroxy acids and γ-stearolactone, carboxystearic acid, alkyl 9(10)-phosphonostearates and sulfur compounds were summarized in 1963 (9). Later investigations include reactions of iospropenyl esters (10), surface active properties of sulfated alkanolamides (11), flame resistant polyurethane foams from hypohalogenated glycerides (12) and potential lubricant additives from *N*-sulfonylaziridine derivatives (13).

The Southern Laboratory has developed water resistant, intumescent fire retardant paints from tung oil (14,15) and acetoglycerides for food coatings (16). The acetoglycerides have potential use as plasticizers for synthetic resins including polyvinyl resins (17); and epoxidized acetoglycerides, as stabilizer-plasticizers for vinyl chloride-containing resins (18). Plasticizers based on *N,N*-dimethylamides (19) and other *N,N*-disubstituted amides (20) have been made, and sucrose ester emulsifiers have been prepared by interesterification in the absence of a solvent (21). This process should make possible the preparation of linoleates of high functionality useful as drying oils.

The Western Laboratory has developed castor oil-based rigid urethane foams (22,23) including some with flame resistant properties (24). Other studies are 10-hydroxydecanoic acid by alkaline cleavage of ricinoleates (25), diol ricinoleates from dihaloalkanes for polyurethanes (26), catalytic dehydrogenation of methyl ricinoleate (27) and of methyl 12-hydroxystearate (28,29), synthesis of some acrylate esters of ricinoleates (30), chemical modificiation of high oleic safflower oil (31), rates of reaction of hexahalocyclopentadienes with long chain olefins (32) and a thermal isomerization equilibrium between conjugated and unconjugated unsaturated keto esters (33).

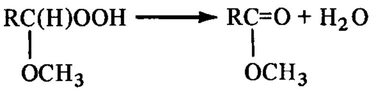
The Northern Laboratory has developed dimer acid and polyamides and polyesters therefrom, inactivation of metal contaminants in edible oils, selective hydrogenation of edible oils, linseed emulsions for paint and concrete treatment and crambe oil and erucic acid for various industrial purposes. Current reports include hydroformylation of unsaturated fatty esters (34), reactions of azelaaldehydic esters obtained by reductive ozonolysis (35), diisocyanate-modified polyesteramides for protective coatings (36), potential lubricant additives of plasticizers from 1,2-cycloaddition of haloalkenes to conjugated fatty esters (37), homogeneous hydrogenation of polyunsaturates to *cis*-monounsaturates with chromium carbonyl (38) and homogeneous catalytic conjugation of polyunsaturated also by chromium carbonyls (39).

REDUCTIVE OZONOLYSIS

Although oxidative ozonolysis is a well-known industrial reaction, reductive ozonolysis has not yet reached industrial scale. Such nonacceptance may be ascribed to a lack of understanding the reaction, high reactivity of the aldehydic products, poor yields, but most of all to a lack in demonstrated utility for the products. Such products include pelargonaldehyde and methyl azelaaldehydate when reductive ozonolysis is applied to methyl oleate. For several years, this reaction and potential areas for industrial application have been investigated at the Northern Laboratory.

All ozonolyses are performed in two steps, the first step being common to both oxidative and reductive ozonolyses (40). To produce acids, the ozonolysis products are oxidized; for aldehydes, they are reduced. Both solvent and reducing agent profoundly affect the results of ozonolysis. Solvents may be protolytic and react with the intermediate zwitterion or nonprotolytic and nonreactive. The reducing agent may be hydrogen in the present of a catalyst or it may be some other chemical reagent.

Methyl azelaaldehydate may be obtained in about 90% yield when methyl oleate is ozonized in methanol and the ozonolysis products are reduced with zinc and acetic acid (41). A less costly reducing agent is hydrogen. However, when the same ozonolysis products are catalytically hydrogenated over palladium on charcoal, the yield of methyl azelaaldehydate is only about 70% and dimethyl azelate is formed in about 25% yield (42). Dimethyl azelate forms because the methoxy hydroperoxide ozonolysis product decomposes on the catalyst surface:



$$\underset{\displaystyle \mathrm{OCH_3}}{\mathrm{RC(H)OOH}} \longrightarrow \underset{\displaystyle \mathrm{OCH_3}}{\mathrm{RC{=}O}} + \mathrm{H_2O}$$

It is noteworthy that chain degradation, which has been observed during either oxidation or reduction of other types of ozonolysis products, does not occur.

There are at least three ways to minimize hydroperoxide decomposition, probably all of which involve some modification of the catalyst's surface and activity. The first employs methanol containing 10% pyridine as an ozonolysis and hydrogenation solvent. Pyridine reduces the dimethyl azelate formation to 5-10%, prevents acetal formation and inhibits hydrogenation of residual double bonds (42,43).

Decomposition of methoxy hydroperoxide can also be minimized by a palladium on calcium carbonate catalyst that has been poisoned with lead acetate (Lindlar catalyst) (44). Here again, basic conditions, this time supplied by the support, inhibit acetal formation. The lead acetate inhibits double bond hydrogenation.

TABLE VIII

Location of Government Utilization Research on Unsaturated Fat and Oil Commodities

Commidity	USA production, 1968, million lb	Location[a]
Soybeal oil	6150	NU
Tallow, grease and lard	5283	EU
Cottonseed oil	1115	SU
Linseed oil	307	NU
Fish and whale oil	211	BCF
Peanut oil	209	SU
Castor oil	133[b]	WU
Safflower oil	86[b]	WU
Sunflower oil	---	RRC
New crops[c]	---	NU

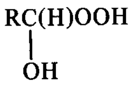
[a] Utilization research is carried out at five Regional Research Laboratories of the Agricultural Research Service, U.S. Department of Agriculture: Northern Utilization Research and Development Division (NU), Peoria, Illinois 61604; Eastern Utilization Research and Development Division (EU), Philadelphia, Pennsylvania 19118; Southern Utilization Research and Development Division (SU), New Orleans, Louisiana 70119; Western Utilization Research and Development Division (WU), Albany, California 94710; and the Richard B. Russell Agricultural Research Center (RRC), (formerly the Southeastern Agricultural Research Laboratory SEU), Athens, Georgia 30601. This new facility is now being staffed and research programs are being implemented. Research on fish oils is carried out at the U.S. Bureau of Commercial Fisheries (BCF), Seattle, Washington.

[b] Consumption in selected products.

[c] New crops research includes the high erucic crambe oil from *Crambe abyssinica*.

The third method employs an ozonolysis solvent consisting of an equimolar mixture of an alcohol and a carboxylic acid (45). The carboxylic acid is preferably acetic acid, but the alcohol can be methyl, ethyl, *n*-butyl alcohol or even 2-methoxyethanol. Hydrogenation proceeds quickly with palladium on charcoal at atmospheric pressure to produce aldehydes in excellent yields (>90%). With this solvent combination, acetal formation can be a problem unless the temperature during both steps is maintained below 15-20 C. Deviation from equimolarity in either direction increases the amount of hydroperoxide decomposition to ester.

The three preceding ozonolyses were all carried out in organic solvents. A more economic ozonolysis medium is water. Surprisingly, water acts as a reactive solvent and is an effective ozonolysis medium for unsaturated fatty esters when the water is present as a water in oil emulsion (46,47). Depending upon hydrogenation conditions and catalysts, aldehyde yield may be as high as 89%. Decomposition of the peroxidic ozonolysis products, probably hydroxy hydroperoxides,



$$\underset{\displaystyle \mathrm{OH}}{\mathrm{RC(H)OOH}}$$

also occurs during hydrognation, but the product is a carboxylic acid and not an ester. The byproduct is removed by an alkaline wash.

The aldehydic products have been investigated for a number of purposes, some of which would seen to have considerable merit, e.g., low temperature plasticizers for poly(vinyl chloride) (48), as intermediates for nylon-9 synthesis (49) and as starting materials for several types of coatings (50-52).

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