hand, dodec-2,4-dienal in the current work has been consistently found in linoleate and in most of the fats. The possibility has been considered that undec-2,4-dienal and dodec-2,4-dienal might be mistaken for one another, but this is not believed to be the case (4). It may be that both compounds are present but approach trace amounts in proportion to the other aldehydes (12). Heating the oxidized butterfat produced over 17% 2-alkanone class consisting of C_5, C_7, C_9, C_{11}, C_{13}, and C_{15} ketones. These compounds are not due to oxidation as their formation in heated fresh butterfat has been described by Patton and Tharp (17).

Composition of volatile monocarbonyl compounds found in the more highly unsaturated peanut, soybean, and linseed oils is shown in Table V. Amounts of the major characteristic aldehydes reflect the larger proportions of linoleic and linolenic acids in these oils.

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Ozonization of Soybean Oil. The Preparation and Some Properties of Aldehyde Oils[1]

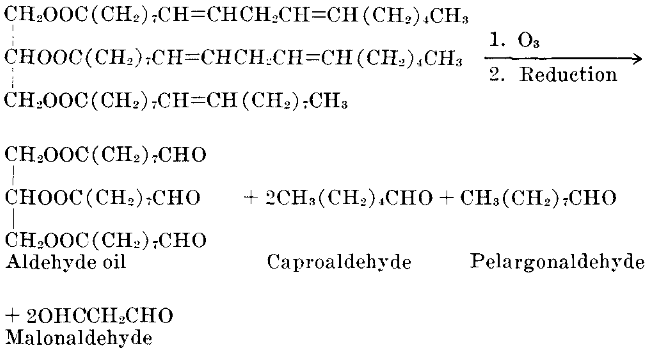
E.H. PRYDE, D.E. ANDERS, H.M. TEETER, J.C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

A polyaldehydic product called aldehyde oil was prepared by the ozonization of soybean oil, followed by reductive decomposition of the ozonolysis products. Reductive decomposition by chemical means gave 85–90% yields of carbonyl in the aldehyde oil. Catalytic reduction gave 75–80% yields. Partially-hydrogenated soybean oil gave more efficient results than did unhydrogenated oil. The polyfunctional aldehyde oil was found to undergo condensation reactions with phenolic compounds, urea, amines, and polyols to give cross-linked polymers.

OZONE IS ONE of the most attractive reagents for carrying out oxidative cleavage of unsaturated fatty materials because of its relatively low cost, its availability, and the quantitative nature of the reaction. Either carboxylic acids or aldehydes may be obtained, depending upon whether oxidative or reductive decomposition of the ozonolysis products is carried out. Oxidative cleavage has been successfully applied on a commercial scale to the production of pelargonic and azelaic acids from oleic acid (1). Reductive cleavage for the production of fatty aldehydes possibly would be of equal commercial interest because of the versatility of the aldehyde group in chemical reactions. An attractive aldehydic product is the glyceride of azelaic semi-aldehyde, obtained by the ozonization of an unsaturated oil. The polyfunctionality of this compound makes it useful in a variety of cross-linking and resin-forming reactions. The one mention in the literature (2) describes it only as a brown, viscous oil. It was obtained *en route* to the preparation of azelaic acid from castor oil by hydroxylation with hydrogen peroxide, cleavage with lead tetra-acetate, followed by oxidation with hydrogen peroxide, then by saponification.

This paper describes a relatively simple method of preparing an aldehyde oil in good yield from soybean oil and also describes some of its properties. The effects of solvent and the method of reduction were studied in some detail in order to obtain high yields.

The course of the reaction may be illustrated with an idealized triglyceride structure for soybean oil:



$$\begin{array}{l} CH_2OOC(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CHOOC(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CH_2OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array} \xrightarrow[\text{2. Reduction}]{\text{1. } O_3}$$

$$\begin{array}{llll} CH_2OOC(CH_2)_7CHO & & & \\ | & & & \\ CHOOC(CH_2)_7CHO & + 2CH_3(CH_2)_4CHO & + CH_3(CH_2)_7CHO & \\ | & & & \\ CH_2OOC(CH_2)_7CHO & & & \\ \text{Aldehyde oil} & \text{Caproaldehyde} & \text{Pelargonaldehyde} & \end{array}$$

$$+\ 2OHCCH_2CHO$$
Malonaldehyde

In addition to the linoleic and oleic acids indicated in the formula, palmitic, stearic, and linolenic acids are also present but to a lesser extent. From 100 lbs. of the soybean oil used in these experiments, there would be obtained theoretically 31.8 lbs. of volatile aldehydes, 16.0 lbs. of malonaldehyde, and 67.5 lbs. of aldehyde oil.

The production of aldehydes (Table I) was measured by reaction with hydroxylamine hydrochloride.

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[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

TABLE I

The Ozonization of Soybean Oil

Exp. No.	Solvent[a]	Ozonization			Total carbonyl yield % before isolation	Yield of volatile aldehydes	Aldehyde oil			Yieldof water-soluble aldehyde
		Temp. °C.	Consumed, % of theory	Not consumed, % of theory			Crude yield	Carbonyl yield	Carbonyl content	
	A. Chemical Reduction					%	%	%	mmoles/g.	%
1	Methylene chloride	−20	125	2.9	45	44	112	78	3.00	......
2	Methanol	+14	135	3.1	48	55	94	77	3.57	......
3	Ethanol	+ 8	124	2.7	59	78	101	86	3.69	2.0
4	*n*-Butanol	+14	120	4.2	54	68	115	86	3.28	......
5	Methylene chloride (55)–methanol (45)	−15	130	3.2	60	49	102	91	3.91	8.0
6	Ethyl acetate (80)–methanol (20)	−11	127	3.0	56	55	100	92	4.00	......
6A[b]	Ethyl acetate (80)–methanol (20)	−18	117	4.7	51	76	109	100	4.02	......
7[c]	Methylene chloride (55)–methanol (45)	− 9	129	2.1	75	63	114	91	3.48	......
8[d]	Methylene chloride (55)–methanol (45)	− 4	129	3.1	84	79	105	85	4.36	......
	B. Catalytic Reduction									
9	Ethyl acetate	−20	120	3.4	44	....	......	....	......	......
10	Methylene chloride[e]	−64	102	3.3	47	....	......	....	......	......
11	Ethyl alcohol	+10	117	3.0	54	81	115	72	2.70	4.4
12	Isopropyl alcohol	− 3	116	4.5	55	85	124	79	2.79	1.8
13	Ethyl acetate (80)–acetic acid (20)	−11	118	4.0	57	....	107	76	3.10	......
14	Methyl acetate (80)–methanol (20)	−20	154	2.9	69	70	102	68	2.88	24.9

[a] Except where noted a concentration of about 10 wt. % of soybean oil in the solvent was used.
[b] The concentration of soybean oil in the solvent was increased to 30 wt. %.
[c] Margarine.
[d] Triolein.
[e] The methylene chloride was replaced with methanol before hydrogenation.

Analysis for aldehydes on the solution containing all reduction products is reported as the total carbonyl yield before isolation. Because of the loss of malonaldehyde, which is subject to ozone attack, the maximum production of useful carbonyl compounds should be about 57 mole %, or 31.8 + 67.5 = 99.3 weight % (see method of yield calculation in Experimental). The expected carbonyl yield of 57 mole % was about the value actually obtained with the soybean oil under optimum conditions. In isolating the reaction products, no attempt was made to separate pelargonaldehyde, caproaldehyde, and propionaldehyde; these are reported as volatile aldehydes. Crude yields and carbonyl yields of the products are based on the weight and carbonyl content theoretically expected, respectively. In some experiments, carbonyl analyses were made on the aqueous solutions and are reported as yield of water-soluble aldehyde, chiefly malonaldehyde.

Factors Affecting Ozonization

Solvent. Reactive solvents in general, such as methanol, ethanol, and acetic acid, are superior to nonreactive solvents (4). The alkoxy- or acyloxyhydroperoxides formed are easily reduced or oxidized and lead to a minimum of by-products. Methanol is a good solvent for the ozonization of methyl oleate (3). The total carbonyl yield before product isolation is as high as 92% when methanol is the solvent, and the isolated yield of the methyl ester of azelaic semialdehyde is 88%.

In the ozonization of soybean oil, methanol gives a relatively low carbonyl yield in the aldehyde oil comparable with that obtained with the nonreactive solvent methylene chloride. This low yield results from the relative insolubility of the oil in methanol to give a two-phase system. The ozonolysis products, which are soluble, were present in solution in much higher concentration than the oil and hence were subject to oxidation. Both ethanol and *n*-butanol were better solvents and gave better results. Butanol presents some disadvantages because of the difficulty in separating layers during washing operations. Best results (aldehyde oil carbonyl yields of 90% or better) were obtained when a good solvent (methylene chloride or ethyl acetate) was used in combination with methanol. In all the experiments listed in Table II, chemical reduction of the ozonolysis products was used.

Similar results, obtained when the ozonolysis products were reduced catalytically with hydrogen, were not as clear-cut as with chemical reduction because of lower yields. In this series isopropyl alcohol is equivalent to ethyl alcohol, but hydrogenation at atmospheric pressure was difficult to achieve. Reduction took place more readily at 40 p.s.i.g.

Alcohol as the solvent is clearly superior in obtaining high carbonyl yields but has the minor disadvantage of causing increased consumption of ozone. Such solvents as methylene chloride, acetic acid, and water have been reported to be essentially unreactive to ozone whereas methanol does react (5). However reaction of ozone with carbon-carbon unsaturation is so rapid that very little of the ozone reacts with the solvent. In these experiments consumption of ozone exceeded by about 25% the amount expected on the basis of the unsaturation.

TABLE II

Effect of Solvent on Carbonyl Yield in the Aldehyde Oil (Chemical Reduction)

Exp. No.	Solvent	Total carbonyl yield before isolation	Aldehyde oil, carbonyl yield
		%	%
1	Methylene chloride	45	78
2	Methanol	48	77
3	Ethanol	59[a]	86
4	*n*-Butanol	54	86
5	Methylene chloride (55)–methanol (45)	60[b]	91
6	Ethyl acetate (80)–methanol (20)	56	92

[a] Includes 2% water-soluble aldehydes.
[b] Includes 8% water-soluble aldehydes.

The concentration of oil in solvent was 10 wt. % in the majority of experiments. Equivalent results were obtained at 30 wt. % (Exp. 6A, Table I).

Reduction Method. Previously it had been found that catalytic reduction of the ozonolysis products from methyl oleate with 10% palladium-on-charcoal gave carbonyl in lower yields than did reduction with zinc and acetic acid (3). This difference was confirmed with soybean oil (Table III). In spite of

TABLE III

Catalytic *versus* Chemical Reduction

Exp. No.	Method of reduction	Solvent	Aldehyde oil	
			Carbonyl yield	Carbonyl content
			%	*mmoles/g.*
6	Chemical	Ethyl acetate (80)–methanol (20)	92	4.00
14	Catalytic	Methyl acetate (80)–methanol (20)	77	3.04

lower yields, catalytic reduction has the advantages of simpler operation and of a cheaper reducing agent. Using a catalyst results in the partial oxidation of the ozonolysis products to a carboxylic ester (6) so that the kind but not the degree of polyfunctionality is changed.

Polyunsaturation. Although polyunsaturated fatty acids present in soybean oil should give malonaldehyde upon ozonization, the malonaldehyde itself is apparently attacked by ozone to give various acidic compounds. This attack of ozone on malonic acid has been described as leading to a mixture of products including tartronic acid, mesoxalic acid, oxalic acid, and carbon dioxide (7). The active methylene group in malonaldehyde should result in a similar series of reactions; the carbonyl groups also are subject to oxidation. Although no attempt was made to isolate and identify these oxidation products, observations were made on the amount of acid formed at various degrees of ozonization (Table IV). A similar determination on methyl oleate indicated only a relatively small amount of acid. Attempts to minimize acid formation by reducing ozone consumption below about 125% of the theoretical amount resulted only in incomplete ozonization of the soybean oil.

TABLE IV

Acid Formation Resulting from Ozonization of Soybean Oil (Catalytic Reduction)

Exp. No.	Ozone, % of theory consumed	Yield of acid
		%
15[a]	118	2.7
16	94	12.9
17	98	16.5
18	127	22.2
19	151	31.1

[a] Methyl oleate.

In another, more successful attempt to increase efficiency of ozone utilization a partially hydrogenated soybean oil (a margarine) was utilized. The conversion of unsaturation to carbonyl compounds was increased from 60 to 75%, and, when triolein was used, the conversion increased to 84% (Table V).

Properties of Aldehyde Oils

Physical Properties. Several physical properties of the aldehyde oils are listed in Table VI. In general, color varied from light yellow to brown and depends upon at least three different factors: a) degree of polyunsaturation in the original oil—the greater the polyunsaturation the darker the oil; b) method of reducing the ozonolysis products—catalytic hydrogenation, in general, gave lighter products than did chemical reduction; c) temperature to which the oil is subjected—temperatures in excess of 150°C. during removal of the volatile aldehydes resulted in dark products.

Viscosity of the aldehyde oils followed a pattern similar to their color development. Molecular weight determinations by freezing-point depression measurements in benzene gave results higher than theoretical. Condensation of volatile aldehydes with the aldehyde oil or self-condensation of the aldehyde oil in the aldol type of reactions could account for the increases in color, viscosity, and molecular weight.

Resin-Forming Reactions. A number of exploratory tests were made on the aldehyde oils to determine the reactivity and the kind of products that might be expected in typical condensation reactions. Generally, a soft, flexible, insoluble, and infusible solid was obtained.

Aldehyde oil reacted fairly readily with phenol under alkaline conditions. Under acidic conditions it reacted with phenol only with difficulty but did rapidly with resorcinol. If excess resorcinol were present, a hard, brittle, solid resin was obtained in contrast to the usual rubbery gel. When a hard, fusible resin from pelargonaldehyde and resorcinol was further treated with aldehyde oil, a flexible, insoluble, and infusible resin was formed.

Although pelargonaldehyde gave no apparent reaction with urea, aldehyde oil gave a reaction almost immediately. An orange, rubbery gel was obtained with various reactant ratios.

Reactions with polyols were carried out with acetal oils, and with potassium acid sulfate as a catalyst. Hexamethylene glycol gave products ranging from nontacky, brittle, and soluble solids to tacky and in-

TABLE V

Effect of Polyunsaturation (Chemical Reduction)

Exp. No.	Glyceride	Iodine value	Solvent	Carbonyl conversion
				%
5	Soybean oil	131.7	Methylene chloride (55)–methanol (45)	60
7	Margarine	88.4	Methylene chloride (55)–methanol (45)	75
8	Triolein	84.4	Methylene chloride (55)–methanol (45)	84

TABLE VI

Physical Characteristics of Aldehyde Oils

Exp. No.	Material	Source	Method of reduction	Physical Characteristics			
				n_D^{30}	Mol. wt.	Gardner viscosity	Gardner color
8	Aldehyde oil	Triolein	Chemical	1.4632	666	D	4
7	Aldehyde oil	Margarine	Chemical	1.4617	666	G	8
11	Aldehyde oil	Soybean oil	Catalytic	1.4605	800	E	9
12	Aldehyde oil	Soybean oil	Catalytic	1.4579	640	I	12
3[a]	Aldehyde oil	Soybean oil	Chemical	1.4695	800	R	15
3[b]	Dimethyl acetal oil	Soybean oil	Chemical	1.4620	870	O	18+

[a] A duplicate run of Experiment No. 3.

[b] Prepared from Experiment No. 3a.

soluble products, depending upon the reactant ratio.

An aldol condensation occurred almost immediately when the aldehyde oil was treated with an amine, such as *n*-octyl amine, ethylene diamine, piperidine, melamine, and aniline. These condensation products were rubbery, insoluble, and infusible gels. Mixtures of pelargonaldehyde with aldehyde oil were condensed in the presence of diamines to form soluble products, which could then be cross-linked with the further addition of aldehyde oil.

Heat alone also caused aldehyde oil to form a brown, insoluble, and infusible but soft resin.

It is quite evident from these reactions that the polyfunctionality of aldehyde oils is sufficient to cause cross-linking (Table VII). This property, in addition to the possibility of giving internally plasticized resins, suggests that aldehyde oil might be used as a cross-linking and modifying agent for a variety of condensation resins.

TABLE VII

Functionality *versus* Carbonyl Content of Aldehyde Oil

Source	Carbonyl content	Number of aldehyde groups/mol.
A. As free aldehyde	*meq./g.*	
Theoretical	5.41	3.00
Triolein [a]	4.36	2.41
Soybean oil [a]	4.00	2.22
Soybean oil [b]	3.60	2.00
B. As dimethyl acetal		
Theoretical	4.34	3.00
Soybean oil [a]	3.04	2.10
Soybean oil [b]	2.90	2.00

[a] Actual sample.
[b] Calculated carbonyl content to give a functionality of 2.

Experimental

Materials. The refined and bleached, but not deodorized, soybean oil used was purchased from the A.E. Staley Manufacturing Company. Partially-hydrogenated soybean oil (margarine), not deodorized and containing no added metal-inactivating agent, was supplied by Swift and Company. Pure methyl oleate (IV = 85.3, $n_{D}^{30.2}$ = 1.4483), obtained from Applied Science Laboratories, was converted to the triolein needed. Excess (30%) methyl oleate and glycerol were heated in the presence of 0.3% sodium methoxide for 18 hrs. at 150–160°, for 12 hrs., at 175–200° and 23–50 mm. of mercury pressure, and finally for 16 hrs. at 180° and 0.25 mm. of mercury. The triolein had the following characteristics: $n_{D}^{30.2}$, 1.4655; I.V., 84.4; triglyceride by chromatography on a silica gel column, 97.4%; isolated *trans* double bond by infrared, about 5%; sap. equiv., 302.

TABLE VIII

Composition of Soybean Oil

Fatty acid component	Mole %
Palmitic	10.9
Stearic	3.3
Oleic	26.0
Linoleic	53.6
Linolenic	6.2

Iodine value: Calcd. from GLC, 131.4. Found, 131.7.
Sap. equiv.: Calcd. from GLC, 290.0. Found, 296.2.

Method of Yield Calculation. Yields of aldehyde oil were calculated on the basis of the actual composition of the soybean oil as determined by gas-liquid phase chromatography (GLC, on 10% Craig succinic polyester on Chromosorb at 175°). Compositions of the original soybean oil and the aldehyde oil derived from it are given in Tables VIII and IX.

TABLE IX

Theoretical Composition of Aldehyde Oil
(Based on Soybean Oil Composition)

Component	Mole %
Palmitic	10.9
Stearic	3.3
Azelaic semi-aldehyde	85.8

Molecular weight = 600
Carbonyl value = 4.29 mmoles g.

Constants for Dimethyl Acetal Oil

Molecular weight = 719
Carbonyl value = 3.58 mmoles/g.

The aldehydes theoretically produced from one mole (889 g.) of soybean oil include, as shown in Table X: propionaldehyde (0.186 mole, 10.8 g.), caproaldehyde (1.608 moles, 161.2 g.), pelargonaldehyde (0.78 mole, 111.0 g.), malonaldehyde (1.98 moles, 142.8 g.), and aldehyde oil (1.0 mole, 600 g.). In terms of carbonyl functions, 28.3 mole % of the carbonyl formed should appear as aldehyde oil, a like amount as volatile aldehydes, and 43.4 mole % as malonaldehyde. The theoretical yield of aldehydes other than malonaldehyde is then about 57%. In Experiment No. 3 (Table I) 28.9 g. (0.15 mole of unsaturation corresponding to 300 mmoles of carbonyl) of soybean oil gave 11.6 g. of volatile aldehydes containing 5.32 mmoles carbonyl/g., and 19.5 g. of aldehyde oil containing 3.74 mmoles carbonyl/g. The forerun (18.8 g.) also contained 0.40 mmoles carbonyl/g. From these data the following calculations can be made:

TABLE X

Theoretical Yields of Aldehydes (other than Aldehyde Oil) Produced from Soybean Oil
[Based on 1 Mole (889 g.) of Soybean Oil]

Fatty acid origin	Composition, mole %	Aldehyde produced, moles/mole soybean oil			
		C_3	C_6	C_9	Malonaldehyde
Oleic	26.0	....	....	0.78	....
Linoleic	53.6	....	1.608	....	1.608
Linolenic	6.2	0.186	....	....	0.372
Total moles		0.186	1.608	0.78	1.980
Total grams		10.8	161.2	111.0	142.8
Lbs./100 lbs. SBO		1.2	18.1	12.5	16.0

Crude yield of aldehyde oil =

$$\frac{19.5 \times 889}{600 \times 28.9} \times 100 = 100\% \text{ of theory}$$

Yield of carbonyl in aldehyde oil =

$$\frac{19.5 \times 3.74}{300 \times 0.283} \times 100 = 86\% \text{ of theory}$$

Carbonyl yield of volatile aldehydes =

$$\frac{(18.8 \times 0.4\ +\ 11.6 \times 5.32)}{300 \times 0.283} \times 100 = 81\% \text{ of theory}$$

The yield of aldehyde oil could exceed 100% for several reasons: a) condensation of the volatile aldehydes with the aldehyde oil at high pot temperatures, b) incomplete removal of volatile aldehydes, and c)

TABLE XI

Aldehyde Oil Condensations

Reactant	Mole ratio[a]	Catalyst	*Reaction time and mean* temperature	Product[b] resin
Phenol	0.5	$(COOH)_2$	10–24 hrs. at 150°	Soft gel
Phenol	0.5	Na_2CO_3	5 hrs. at 150°	Soft gel
Resorcinol	0.5	$(COOH)_2$	½ hr. at 150°	Soft gel
Resorcinol	1.0	$(COOH)_2$	½ hr. at 150°	Hard gel
Pelargonaldehyde-resorcinol resin	......	$(COOH)_2$	1½ hrs. at 140°	Flexible gel
Urea	0.5–2	None	10 min. at 120°	Soft gel
Hexamethylene glycol	0.5	$KHSO_4$.	1 hr. at 135°	Tacky gel
Hexamethylene glycol	1.5	$KHSO_4$	1 hr. at 140°	Brittle solid
Hexamethylene glycol	2.0	$KHSO_4$	1½ hrs. at 150°	Soft solid
Pelargonaldehyde-aldehyde oil resin (EDA catalyst)	......	......	1 hr. at 100°	Soft gel

[a] Moles of reactant per mole of aldehyde present in the aldehyde oil.
[b] All products described as a gel were insoluble and infusible solids.

formation of acetals. The third is the most probable cause of high-oil yields in these experiments.

Procedure

The general ozonization procedure employed has been previously described in some detail (3). Of all the experiments summarized in Table I, one suffices to illustrate chemical reduction of the ozonolysis products and another, to illustrate catalytic hydrogenation.

Chemical Reduction. Triolein (150 g., 0.498 mole of unsaturation) was dissolved in a solution of 800 ml. of methanol in 1,000 ml. of methylene chloride. Oxygen containing 1.24 mmoles of ozone per liter of oxygen was passed through the solution, which had been cooled to—4°C. at a rate of about 2.8 l./min. for 190 min. The end-point of the reaction was determined as the point at which the ozone concentration in the exit gases from the reactor began to rise as determined by the Welsbach ozone meter. The amount of ozone that was unreacted and found to have passed through the reactor was 15 mmoles, corresponding to 3% of the amount of ozone theoretically expected to be absorbed. The amount of ozone absorbed by the reaction mixture was 129% of the theoretical. The ozonolysis products were reduced with zinc powder (75 g.) and glacial acetic acid (150 ml.). The excess zinc and the precipitated zinc salts were removed by filtration. The solution was evaporated under a slight vacuum to a volume of about 500 ml. Water (350 ml.) and methylene chloride (250 ml.) were added, and the layers were separated. The aqueous layer was extracted twice more with methylene chloride, and the extract then gave a negative test for carbonyl. The methylene chloride solution was washed first with water, then with diluted sodium bicarbonate solution, and again with water, backwashing each wash with a small amount of methylene chloride. The combined methylene chloride solutions were dried and evaporated. The residue weighed 202 g. and contained 4.15 mmoles of carbonyl per gram for a carbonyl yield of 84%. The volatile aldehydes were then removed under vacuum. There were recovered 15.1 g. of material in a dry ice trap containing 0.39 mmoles of carbonyl/g., 54.7 g. of volatile aldehydes containing 6.33 mmoles of carbonyl/g., and 86.2 g. of residue containing 4.36 mmoles of carbonyl/g. Yield of carbonyl as volatile aldehydes was 79%, crude yield of aldehyde oil was 105%, and the carbonyl yield in the aldehyde oil was 85%.

Catalytic Hydrogenation. Soybean oil (28.9 g., 0.15 mole of unsaturation) was dissolved in 250 ml. of absolute ethanol. Oxygen containing 1.12 m moles of ozone per liter of oxygen was passed through the solution, which had been chilled to 10°C., at a rate of about 1.81 l./min. for 89 min. The end-point of the reaction was determined by the same means as before. The amount of ozone found to have passed through the reactor was 3.0% of the theoretical amount. The amount of ozone absorbed by the reaction mixture was 117% of the theoretical. The solution and vapor space above the solution were flushed with nitrogen, and 0.20 g. of 10% palladium-on-charcoal catalyst was added. Hydrogenation was carried out at atmospheric pressure and room temperature for about 7 hrs., at the end of which time the test for peroxide was negative. A solution of hydrogen iodide in glacial acetic acid was used for this test. The use of isopropyl alcohol as a solvent required a pressure of 40 p.s.i.g. of hydrogen to obtain a product free of peroxide. The solution was filtered, then washed in much the same manner as before to remove small amounts of malonaldehyde. If this step was omitted, the aldehyde oil product was considerably darker in color. There was obtained 12.8 g. of volatile aldehydes and 21.38 g. of aldehyde oil. The total yield of carbonyl in the volatile aldehydes was 81%, the crude yield of aldehyde oil was 115%, and the carbonyl yield of the aldehyde oil was 72%.

Resin-Forming Reactions. These were carried out on a small scale on a purely exploratory basis and are summarized in Table XI.

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