Dimer Acid Structures. The Dehydro-Dimer from Methyl Oleate and Di-t-Butyl Peroxide[1]

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Abstract

The dehydro-dimer of methyl oleate was prepared and its structure determined as a model of a non-ring dimer for reference in studying the structure of other fatty dimer acids.

The dehydro-dimer of methyl oleate is formed by the action of di-t-butyl peroxide on methyl oleate. The reaction is stoichiometric; one mole of DTBP producing one mole of dehydrodimer and two moles of t-BuOH, when excess methyl oleate is used. The dimer was shown to contain two double bonds, and to be formed by carbon-to-carbon linkages predominantly and equally at the 8, 9, 10 and 11 carbons of the oleate monomer segments.

Unsaturation was determined by quantitative hydrogenation and far UV absorption. The points of linkage were established by diagnosis of the positions of the involved tertiary carbons of the hydrogenated dimer 1) by chemical oxidation, and 2) by mass spectrometry. Positions of the double bonds were determined by quantitative ozonization, reductive cleavage followed by gas chromatography of the aldehydes and aldehyde esters. Precise molecular weight of the hydrogenated dimer was determined from the parent mass peak at the expected m/e of 594, confirming the non-ring structure. The unhydrogenated dimer showed a parent m/e peak at the expected value of 590.

The bridging at the 8 and 10 positions is explained as being due to coupling of radicals with limiting resonance structures resulting from loss of a hydrogen atom from the methylene at position 8. The bridging at the 9 and 11 positions is explained as due to coupling of limiting resonance structures resulting from loss of a hydrogen atom from the methylene at position 11.

Mass spectrometric data indicate that the dimerization is a coupling of the expected free radical forms, rather than attack by an oleate free radical on the double bond of an intact oleate molecule, with subsequent loss of hydrogen to form the second double bond in the dimer.

Coupling at the 2-position (α to $COOCH_3$) occurs in not more than 5–10% of the molecules. A small amount of cyclic dimer may be present.

Introduction

IN A STUDY of the polymerization of allyl and vinyl linoleate initiated by di-t-butyl peroxide, Harrison and Wheeler (1) noted the formation of conjugated linoleate structure. They suggested that the t-butoxy radical could remove a hydrogen from the 11 carbon atom of linoleate, that this radical would also have limiting resonance structures with the double bonds in the conjugated 9, 11 and 10, 12 positions, and that these various radicals might couple to give dimers.

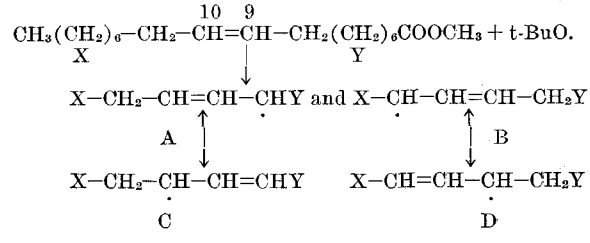
Subsequently, Harrison and Wheeler (2,3) and Clingman and Sutton (4) studied the dimerization of methyl linoleate with di-t-butyl peroxide and confirmed the conjugated structure in the isolated dimer. The dimer contained the four double bonds of the two linoleate segments, and one of the two pairs of the double bonds was conjugated. The remaining pair of non-conjugated double bonds was quite resistant to alkali conjugation, suggesting either a branching at the 11 carbon of a Δ 9,12 linoleate segment, or free radical attack at carbon 8 or 14 (methylenes activated by one adjacent double bond, in contrast to carbon 11 which is activated by two adjacent double bonds). Limiting resonance forms of such radicals would include the doubly methylene interrupted 1,5 diene systems which on coupling would also have the branching at a position between the double bonds.

It was also shown (3) that at low conversions, the product is mostly dimeric and that the reaction is non-catalytic, but essentially stoichiometric in forming one mole of dimer and two moles of t-butanol from one mole of di-t-butyl peroxide.

Methyl oleate in the presence of linoleate was shown to similarly polymerize or copolymerize (3), and methyl stearate was also shown to be polymerized by di-t-butyl peroxide (4). The dimerization of oleic acid by di-t-butyl peroxide has been patented (5). In the case of methyl stearate, it was suggested that the methylene α to $COOCH_3$ might be attacked (4). The suggested structures of these dehydropolymers were based on proposed mechanisms deduced from the properties indicated, and by analogy to similar reactions on other olefins.

The present study is on the structure of the dehydrodimer of methyl oleate. The presence of two double bonds in the dimer was shown by quantitative hydrogenation and far UV absorption. Double bond positions were determined by ozonization, reductive cleavage and GLC analysis of the aldehydes and aldehyde esters. The position of joining between the two oleate segments was determined by oxidative cleavage at the tertiary carbons involved and by mass spectrometry. Joining was found to be predominantly and equally at positions 8,9,10 and 11, with 5–10% at position 2, α to $COOCH_3$.

The proposed mechanism is as follows:



The free radical species A,B,C and D couple randomly to form dimer, resulting in 10 species of dimer, AA, AB,AC,AD,BB,BC,BD,CC,CD and DD. These dimers would be jointed equally at positions 8,9,10 and 11 of the oleate segments of the dimers, and on hydrogena-

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TABLE I

	Stage I	Stage II	Stage III
DTBP/oleate (molar)	0.123	0.129	0.102
Residual Dimer			
% Yield [a]	95.0	92.9	96.5
n^{30}_D	1.4663	1.4662	1.4659
% *Trans* [b]	57.1	56.8	56.0
I.V. (Wijs)	100.3	103.4	97.7
I.V. (Kaufman)	61.4	62.1	61.0
Dimer/Trimer (6)	2.9	2.9	2.7
Monomer			
n^{30}_D	1.4487	1.4484	1.4489
% *Trans* [b]	1.5	3.7	3.6
I.V. (Wijs ½ hr)	81.0	77.4	74.0
I.V. (Kaufman)	80.2	75.5	72.6

[a] Basis, 1 mole di-t-butyl peroxide gives one mole of dimer.
[b] As methyl elaidate.

tion would give dimers of the following general structure:

$$\begin{array}{l} CH_3(CH_2)_m-CH-(CH_2)_n-COOCH_3 \\ \qquad\qquad\quad | \\ CH_3(CH_2)_m-CH-(CH_2)_n-COOCH_3 \\ \qquad\qquad\quad \uparrow \\ \qquad\qquad\quad 8,9,10,11 \\ m+n=15 \end{array}$$

Experimental

Preparation of Dehydrodimer of Methyl Oleate. Methyl oleate (Hormel) 287 g (0.97 mole), di-t-butyl peroxide 18.0 g (0.123 mole) were heated under nitrogen with stirring at 135C for 48 hr. Volatiles were stripped under vacuum (0.05 mm) up to 80C pot temperature, with the receiver in dry ice. Loss of volatiles was 17.7 g. Collected condensate was 14.2 g (theoretical t-butanol = 18.2 g). Gas-liquid chromatography (GLC) of the condensate showed only 4.2% acetone in the recovered t-butanol.

The residual product was stripped of monomer under vacuum (0.05 mm) to 250C pot temperature. Yield of residual dimer was 23.4% of starting oleate (95% of theoretical for 1 mole dimer per mole of di-t-butyl peroxide).

The recovered monomer was similarly treated with di-t-butyl peroxide, and the monomer from this second stage was again similarly treated. The results on these three stages of polymerization are summarized in Table I.

A composite of the residual dimers from the three stages was distilled in an alembic molecular still to give a distilled dimer fraction (7,8).

Figure 1 shows the results of the distillation and the dimeric ester fraction selected as pure dimer for structure studies. This dimer fraction showed the following analyses: I.V. (Wijs) = 112.7; I.V. (Kaufman) = 65.7; % *trans* = 62.1 (as elaidate) (1.24 *trans* double bonds per mole); k_{232} mμ (peak) = 2.2; k_{232} after alkali isomerism = 1.9; % monomer = 5.5; mol wt = 507 (theory = 591); % C = 76.7; % H = 11.8 (theory, % C = 77.2, % H = 11.9).

Hydrogenation of Pure Dimer Fraction. Hydrogenation was performed in a Parr shaker-type hydrogenator at room temp and 50 psi pressure, with a test gauge permitting estimation to 0.1 psi. Catalyst was saturated with hydrogen before addition of sample. The 250 ml pressure bottle was calibrated with pure methyl oleate as a standard. The catalyst used was a 10% Pd on charcoal (Baker), solvent was ethanol (50 cc/g ester). The oleate standard hydrogenated rapidly (95% in ¼ hr, 98.2% in ½ hr) with 5% (of ester) catalyst.

The methyl dimerate hydrogenated much more slowly—when 100% weight of catalyst (10% Pd) based on the weight of dimer was used, hydrogenation was 70% complete in ⅙ hr, 95% in 4½ hr, complete

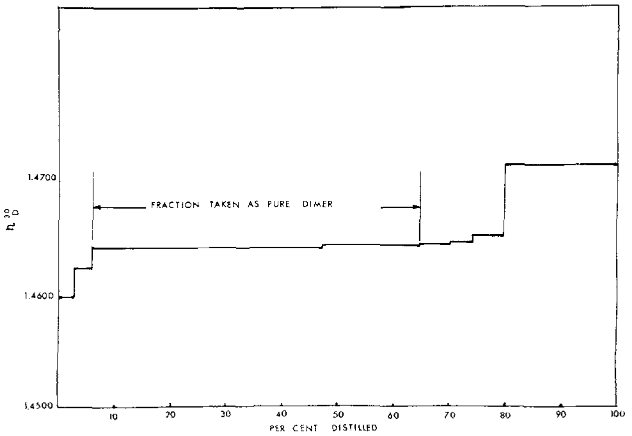


FIG. 1. Distillation of composite residual methyl dimerate.

over night (18 hr). The hydrogen absorbed corresponded to 1.95 moles per mole of dimer. The recovered hydrogenated methyl dimerate showed: I.V. = 0.3, mol wt = 527 (theory 595); % C = 76.7; % H = 12.1 (theory, % C = 76.7, % H = 12.5).

The Double Bonds in Methyl Dimerate. The hydrogenation data presented above indicate very nearly two double bonds per mole of methyl dimerate. Iodine Values (I.V.) indicate 1.5 (Kaufman) or 2.5 (Wijis) double bonds per mole.

Far UV absorption confirmed the presence of ca. two double bonds per mole. Non-conjugated olefins absorb at 180–190 mμ (9). Methyl oleate was found by us to have ϵ = 11,000 at 183 mμ (max) and elaidate showed ϵ = 11,400 at 186 mμ (max). The unhydrogenated methyl dimerate showed ϵ = 19,800 at 189 mμ (max), corresponding to 1.76 double bonds per mole. The hydrogenated methyl dimerate showed no absorption from 180–250 mμ.

After this paper had been presented to the AOCS 1963 Spring Meeting, arrangements were made through Orville Privett. The Hormel Institute, to determine the double bond positions of the unhydrogenated methyl dimerate. Their method of quantitative ozonization, reductive cleavage, and GLC analysis of the aldehydes and aldehyde-esters was applied to the unhydrogenated methyl dimerate. Their data, calculated to mol % showed 26% C_8 aldehyde; 30% C_9 aldehyde; 21% C_8 aldehyde-ester and 22% C_9 aldehyde-ester.

No significant amount of aldehydes or aldehyde-esters of other chain lengths were noticed. These results confirm the double bond positions required by the postulated mechanism.

The unhydrogenated dimer showed only a small amount of UV absorption corresponding to conjugated diene, but this value was not increased on heating with alkali as in determining normal linoleate. This suggests that most of the double bonds are separated by two or more carbons, and/or that bridging occurs on intermediate carbons.

The fact that the unhydrogenated methyl dimerate shows 1.25 *trans* double bonds per mole (62.4% *trans*) suggests that *cis-trans* equilibration is fairly complete during the life of the free radicals. Since the recovered monomer had very little *trans* content, there is very little reversal to form olefin monomer from the free radical.

Location of Branching or Joining Points in Methyl Dimerate: Oxidative Cleavage. The method of Cason, et al. (10), for determining the location of a branch in a saturated carbon chain was applied to the hydro-

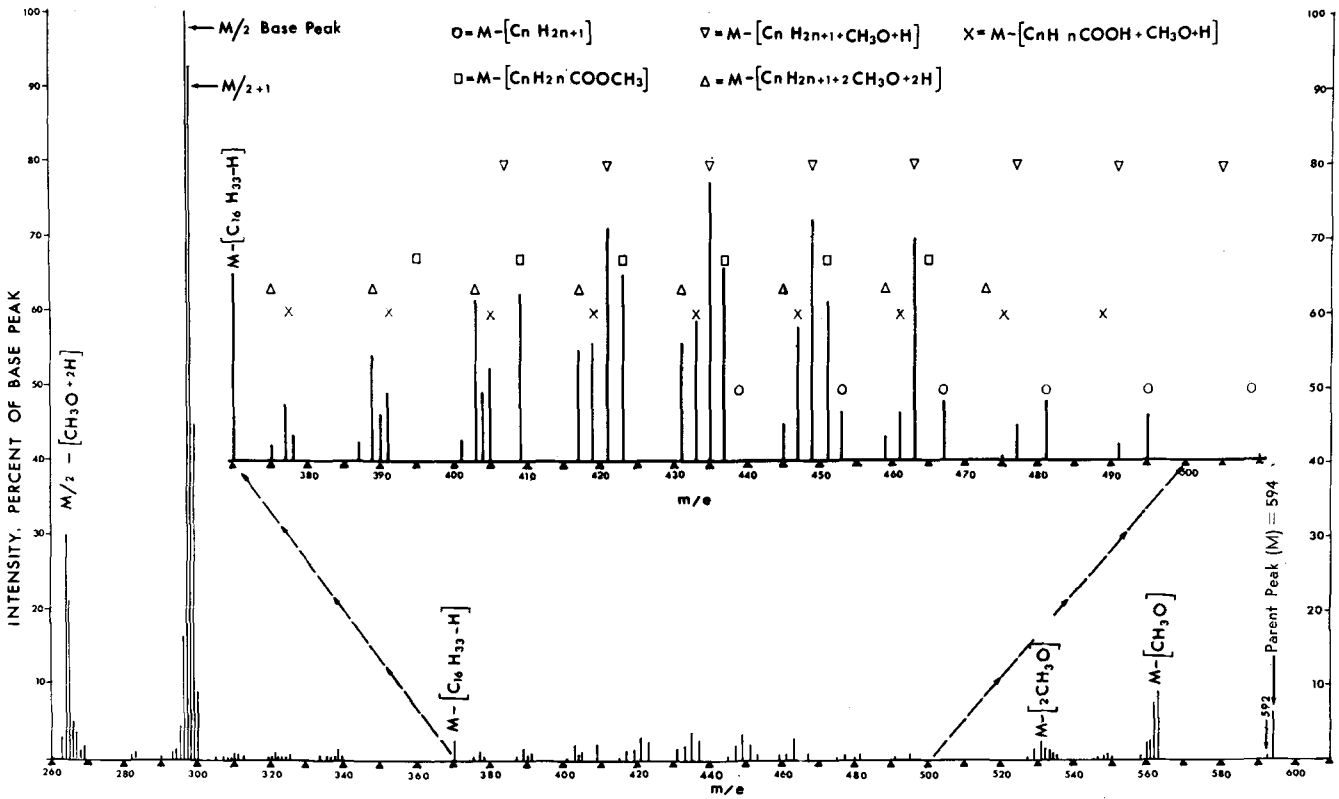


FIG. 2. Mass spectrum of hydrogenated methyl dimerate.

genated dimer acid. This chromic acid oxidation cleaves the tertiary carbon-carbon linkages of a branched position quite preferentially, compared to secondary or primary linkages, except when the branching is gamma or closer to the carboxylic acid group. The mono- and dibasic acids resulting from this cleavage were analyzed as methyl esters by GLC, and ranged in chain length from 4–10 carbons with a peak at 7 carbons, corresponding to branching at carbons 5–11 inclusive, with a maximum at carbon 8, according to the dibasic acid chain length. It was shown by similar oxidation of pure oleic acid that in addition to cleavage at the double bond to give C_9 dibasic acid, there was some chain length degradation to give 15–20% C_8 dibasic and monobasic acids and smaller amounts of C_4, C_5, C_6 and C_7 mono- and dibasic acids, with no acids above C_9. In view of this, the results on the dimer acid indicate branching to be largely from carbon 7–8 to carbon 11. Mass spectrometry confirmed this in a more definite manner.

Mass Spectrometry of Dimers. The mass spectrometer used was Consolidated Engineering Model 21-103-C with an all-glass high temp inlet system described by one of us (11). An inlet temp of 275C, ionizing voltage 70 v, current 10 μ amp, Isatron temp of 250C was used. Scans run at 5 and 10 min after introduction of sample were identical, indicating thermal stability under conditions used. Eight replicates run at intervals over two months gave relative peak heights which agreed within 5% on all peaks, except that one peak (M/2) on one sample was very weak, apparently due to a transient instrumental effect, since the peak was unsymmetrical. Response of parent peak per unit of weight (sensitivity) was reproducible to ±10%.

The excellent review by Ryhage and Stenhagen (12) on the mass spectrometry of lipids outlines many of the modes of fragmentation of fatty acids and derivatives, especially as affected by branching of the chains. The preferred cleavage at branched positions was a particularly useful principle in interpreting the spectra of the dehydrodimers.

Unhydrogenated dimer showed a single parent peak M, at m/e = 590, as expected for a carbon-carbon linked dimer with two double bonds. The parent peak was weak, since there are many bonds where cleavage could occur. One which is *particularly* prone to cleavage is the bond joining the two oleate fragments, since this linkage is between two tertiary carbons, and is allylic to two double bonds. Very strong peaks were seen at 295 (base peak, M/2) and 294 (hydrogen rearrangement).

Preferential loss of alkane fragments C_7H_{15} and C_8H_{17} would be expected, since these are the only hydrocarbon groups which are attached to a tertiary carbon and are at the same time allylic, according to the proposed structure. Peaks which are prominent relative to adjacent members of the series were seen at m/e 477 and 491, corresponding to loss of C_7H_{15} and C_8H_{17} from the parent mass of 590.

Similarly, loss of $C_6H_{12}COOCH_3$ and $C_7H_{14}COOCH_3$ would be prominent, since these are similarly the only groups of this type which are attached to tertiary carbons and which are also allylic. Prominent peaks relative to adjacent members of the series were seen at m/e 447 and 433, corresponding to loss of these radicals from the parent mass.

A moderate peak at m/e 370, which is 220 mass units less than parent mass, may be related to α linkage with loss of $C_{16}H_{31}$ (cf. hydrogenated dimer, below), but should be at M-222 for the usual mode of cleavage of the α-β linkage with hydrogen rearrangement. This anomaly is not explainable at present.

The peak at mass 74 due to $(CH_2COOCH_3 + H)^+$ was strong as is common in non-α-substituted fatty methyl esters (12).

Hydrogenated dimer actually proved to be much more fruitful in establishing structure. The mass spectrum of the hydrogenated methyl dimerate above

m/e = 260 is shown in Figure 2. The parent peak M was at 594, the expected mass for a saturated dimer with one carbon-to-carbon linkage joining the two C_{18} chains. A small 592 peak (ca. 8% as intense as 594) could indicate a small amount of ring structure or the loss of two (tertiary?) hydrogens by electron impact. Peaks at $M-CH_3O$ and $M-CH_3OH$, and $M-2CH_3O$ are seen, and would be expected for the methyl ester of a dibasic acid. The spectrum below m/e 260 showed the strong m/e 74 peak (87% of base peak) common to non-α-substituted methyl esters, and the expected series of alkane and of carbomethoxyalkane peaks which were not of diagnostic value.

Cleavage at the bond joining the two chains is very pronounced, the peak at mass 297 M/2 being the strongest peak (base peak) in the spectrum. This is expected, since this is a bond between two tertiary carbons. The almost equally strong peak at 298 as well as lesser peaks at 299, 300, 296 and 295 must be due to hydrogen rearrangements as well as isotope effect. Peaks at M/2-32 and M/2-33 are related to the same cleavage, with simultaneous loss of CH_3OH and $CH_3OH + H$.

The series of peaks between 360 and 520 proved to be most informative in determining the position at which the two C_{18} chains are joined. This section of the spectrum is shown on an expanded scale in the in the insert in Figure 2.

One homologous series at 495,481,467 and 453 were of equal intensity, with no homologous peaks on either side of the series. This series corresponds to loss of C_7H_{15}, C_8H_{17}, C_9H_{19} and $C_{10}H_{21}$, from the parent mass of 594, indicating joining at atoms 8,9,10 and 11.

A second series of peaks of equal intensity was at masses 451,437,423 and 409, corresponding to loss of $C_6H_{12}COOCH_3$, $C_7H_{14}COOCH_3$, $C_8H_{16}COOCH_3$ and $C_9H_{18}COOCH_3$ from the parent mass of 594, again indicating joining at carbons 8,9,10 and 11.

A third series of peaks of equal intensity was at m/e 463,449,435 and 421. These correspond to loss of $C_nH_{2n+1} + CH_3OH$ from the parent mass of 594, where n = 7,8,9 and 10, again indicating the points of joining to be at carbons 8,9,10 and 11. Weak peaks at 477 and 491 correspond to joining at carbons 12 and 13.

A fourth series of peaks of equal intensity was at m/e 431,417,403 and 389. These correspond to loss of $C_nH_{2n+1} + 2CH_3OH$ from the parent mass of 594, where n = 7,8,9 and 10, again indicating the poins of joining to be at carbons 8,9,10 and 11. Weak peaks at 445 and 459 correspond to joining at carbons 12 and 13.

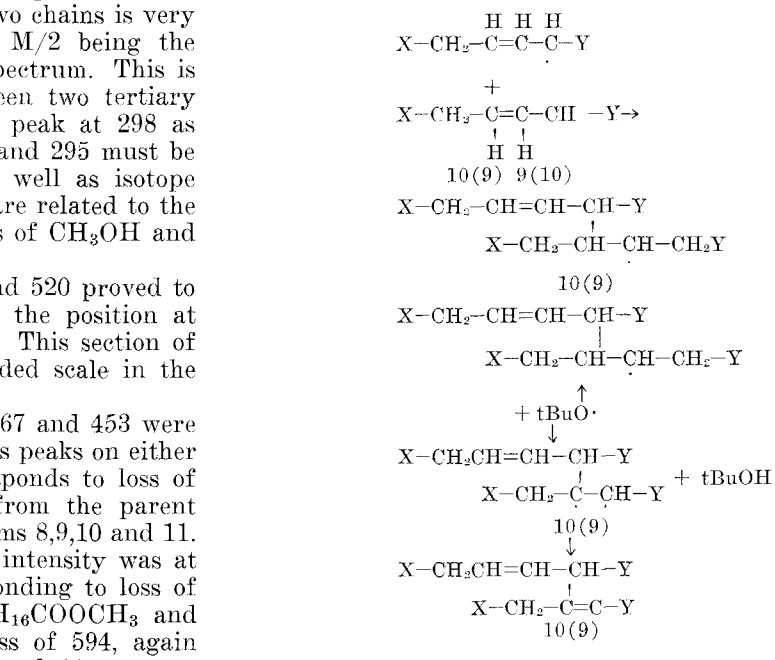
A fifth series of peaks at m/e 419,405,391 and 377, corresponds to loss of $C_nH_{2n}COOCH_3 + CH_3OH$ from the parent mass of 594, where n-= 6,7,8, and 9, again indicating joining at carbons 8,9,10 and 11.

However, this series has three adjacent higher homologous peaks at 433,447 and 461, corresponding to joining at carbons 5,6 and 7. The peaks in this whole series are not equal in intensity as in the other four series, the peaks at 419,433 and 447 being 50–80% stronger than the others. No satisfactory assignment can be given at this time to those at 433,447 and 461, in view of the preponderance of evidence from the other four series.

Discussion

The four series, each containing members of essentially equal intensity, indicating joining at carbons 8,9,10 and 11 substantiate the proposed mechanism; viz., equally probable attack by the t-butoxy radical to remove a proton from carbons 8 or 11 to give a free radical, with coupling of these and their resonance-equivalent structures (with a free radical at carbons 9 and 10), giving equal probability of coupling at positions 8,9,10 and 11.

Another possible mechanism would be formation of the free radicals as above, equally probable at carbons 8,9,10 and 11, followed by addition of this radical to the 9,10 double bond of an intact oleate, with subsequent loss of tertiary hydrogen from the resulting dimer free radical to give the second double bond found in the dimer:



However, this mechanism would give joining only at the 9 or 10 position on one of the two oleate segments of the dimer, and would result in a ratio of 1:3:3:1 for positions 8,9,10 and 11 respectively as the overall points of coupling of the oleate segments. In view of the essentially equal intensities of the four members of each series of fragment peaks corresponding to joining at positions 8,9,10 and 11, this mechanism appears unlikely, and radical coupling appears to be the predominant mechanism.

A peak at m/e 370 is moderately strong, and corresponds to loss of 224, or $C_{16}H_{33}-H$ from the parent mass of 594. This cleavage, with hydrogen rearrangement, would be expected of a dimer with a linkage α to $COOCH_3$, i.e., on carbon 2. This would be a reasonable possibility since hydrogens on the α methylene might be expected to be somewhat activated, but probably not as much as those adjacent to a C=C double bond. Clingman and Sutton (4) suggested that α as well as random coupling might occur with methyl stearate.

In a study to be published later, the dehydrodimer of methyl stearate was found to have a peak at m/e 370 which was 1.5 times as strong as that observed with the hydrogenated dehydro-oleate dimer. Furthermore, a fraction of this dehydrostearate dimer was obtained which was much richer in α linkage. This was isolated by forming the anhydride of the crude dehydrostearic acid and molecularly distilling the cyclic α,α' linked dimer anhydride from the polymeric non-α,α' linked dimer. This fraction, converted to methyl ester, showed a peak at m/e 370 which was 20 times as strong as that of the hydrogenated dehydro-

oleate. The amount of alpha linkage is, therefore, not more than 5–10% in the dehydro-oleate dimer ester. In view of this fact, attack at other non-activated methylenes is probably quite small in extent.

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Cyclic Fatty Acids from Linolenic Acid[1]

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Abstract

Linolenic acid of 95% purity was heated with excess alkali in ethylene glycol to produce cyclic fatty acids. Reaction variables, which are associated with the cyclization reaction and which were investigated, included solvent-to-fatty-acid ratio, catalyst concentration, and reaction temperature, headspace gas (N_2 or C_2H_4), and headspace gas pressure.

Yields of cyclic acids were improved by increasing solvent ratio (1.5–6 wt basis), reaction temperature (225–295C), and catalyst concentration (10–100% excess). With nitrogen the optimum catalyst concentration was about 100% excess, but when ethylene was used, no increase was obtained beyond 50% excess catalyst. Yields of polymeric acids produced in the reaction generally decreased as cyclic acid yields increased, except in one instance.

Higher yields of cyclic fatty acids were obtained with ethylene than with nitrogen under all comparable conditions, and increasing the ethylene pressure to as high as 500 psi improved the yield. Ethylene adds to the conjugated double bonds and is believed to give C_{20} fatty acids having a 1,4-disubstituted monoene ring in the chain. The maximum yield of monomeric cyclic acids from 95% linolenic acid was 84.6%, the balance being polymeric and unreacted monomeric acids. Monomeric acids from this test contained 95% cyclic acids.

Introduction

IN A PREVIOUS PAPER (4) it was demonstrated that the linolenic acid fraction of linseed oil can be converted to a cyclized structure under proper reaction conditions. Linolenic acid of 95% purity, prepared at this laboratory from linseed fatty acids by liquid-liquid extraction as reported by Beal et al. (2), was cyclized with ethylene glycol as the solvent and sodium hydroxide as the catalyst. These reactions were conducted with either nitrogen or ethylene under various pressures in the reactor headspace. Increased yields of cyclic acids have been reported by conducting the cyclization reaction with linseed oil in the presence of ethylene (1). Ethylene enters into the reaction to form a cyclized C_{20} fatty acid. In the present studies, undertaken to determine optimum conditions for producing cyclic acids from linolenic acid, substantially increased yields were again obtained with ethylene.

Reaction conditions, such as solvent ratio, catalyst concentration, temperature, reactor headspace gas, and gas pressure, were varied to determine their effects on the yield of cyclic fatty acids.

Experimental

A 2-liter Parr autoclave equipped with stirrer and sample tube was used for all reactions. Figure 1 is a flowsheet (of the method used) for determining percentage of cyclic and polymeric ester yields. The autoclave was charged with ethylene glycol, NaOH, and linolenic acid. The headspace was evacuated and filled with either nitrogen or ethylene gas. Solvent ratios of 6,3, and 1.5 to 1 (wt basis); temperatures of 225,250,275, and 295C; ethylene gas pressures of 150,300, and 500 psi (before heating); and excess

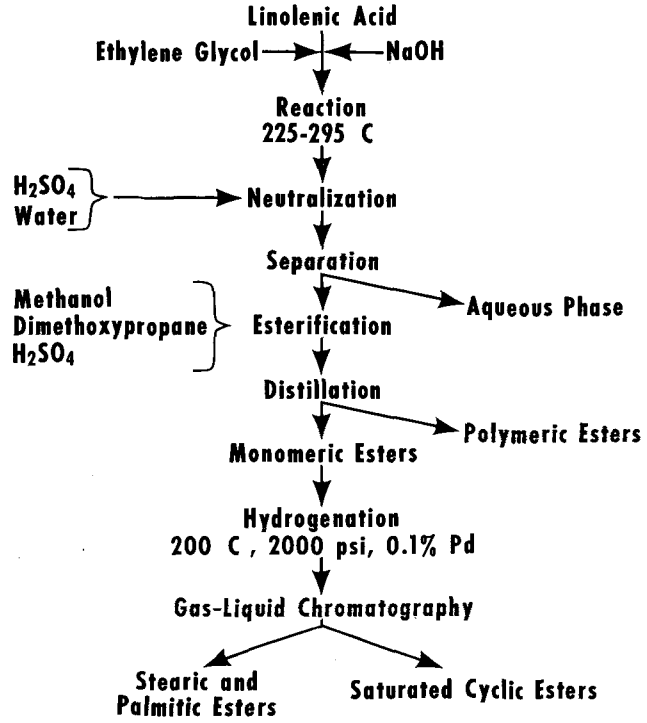

FIG. 1. Flow sheet for determining percentage of cyclic and polymeric ester yields.

[1] Presented at AOCS meeting, New Orleans, 1962.
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