Dimer Acid Structures. The Thermal Dimer of Normal Linoleate, Methyl 9-cis, 12-cis Octadecadienoate[1]

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Abstract

The thermal dimer (290C) of normal methyl linoleate and its hydrogenated form have been examined by mass spectrometry. Parent mass peaks of the hydrogenated dimer show the presence of monocyclic, bicyclic, and tricyclic structures.

The monocyclic structure is formed via the conjugation-Diels-Alder mechanism.

The bicyclic structure is best explained by an extension of the hydrogen transfer free radical coupling mechanism. The noncyclic dehydrodimer resulting from free radical coupling undergoes a relatively rapid intramolecular cyclization to a bicyclic structure, probably by an interval Diels-Alder reaction. A model noncyclic dehydro-linoleate dimer was shown to give a bicyclic dimer as the predominant structure under thermal dimerization conditions.

The tricyclic dimer may result from intramolecular alkylation of the bicyclic structures.

Introduction

THE STRUCTURES of two types of dimer have been shown in previous studies: one, a noncyclic dehydrodimer; the second, a Diels-Alder addition structure.

The first type is illustrated by the dehydrodimer of methyl oleate, which is a noncyclic dimer with two double bonds, one in each oleate segment, with joining of the two oleate segments by a single bond at positions 8, 9, 10, and 11 (1). It is made at 135C by the action of the t-butoxy radical from di-t-butyl peroxide on methyl oleate. In the mass spectrograph it gave a single parent peak of mass $M = 590$, corresponding to no ring and two double bonds and gave a strong M/2 peak because of cleavage of the branched bond joining the two oleate segments.

The hydrogenated form of this dimer showed the correct parent mass of 594 for a noncyclic saturated structure. It also gave a strong M/2 peak since the same branched structure was present.

Dehydrolinoleate has also been made similarly from normal linoleate and shown to contain conjugated linoleate segments (ca 50% or more) and four double bonds (2). The noncyclic structure of this dimer was recently confirmed by mass spectrometry.

These dehydrodimers are formed at 125–135C so that ltitle, if any, secondary ring closure reactions occur.

The second type of established dimer structure is the Diels-Alder structure which results from thermal polymerization of a pure methyl 10-t, 12-t conjugated linoleate (3). The 10- or 12-double bond of one molecule acts as dienophile to add 1,4 to the conjugated diene of a second molecule to give a 1,2,3,4-tetra-substituted cyclohexene dibasic acid ester, which gave a single parent mass peak, $M = 588$, corresponding to one ring and two double bonds. This dimer also gave a strong M/2 peak on account

of a reverse or retro-Diels-Alder, as has been observed with other analogous Diels-Alder adducts. It also showed preferential loss of the groups in the 2,3 positions. On hydrogenation, this dimer gave a single parent peak of $M = 592$, corresponding to one ring and no double bonds. This saturated dimer did not give an M/2 peak since it was no longer a Diels-Alder adduct structure as such.

With these known behaviors of the two model dimer structures, one may conclude that a strong M/2 peak both before and after hydrogenation indicates a noncyclic dehydrodimer structure; a strong M/2 peak before hydrogenation, but no strong M/2 peak after hydrogenation indicates a Diels-Alder adduct structure; and a parent peak of 594 of a saturated dimer indicates a noncyclic dehydrodimer structure, and its absence denotes the lack of this structure.

The relationship of molecular masses of C_{36} dimer methyl esters to possible structures as to the number of double bonds and number of rings as shown in Table I will be valuable in following the subsequent discussions.

The bottom figure in each column is for the saturated dimers (no double bond) where 594 indicates no ring, 592 one ring, 590 two rings, etc. A saturated dimer of mass 592 with one ring could come from an unsaturated monocyclic dimer of mass 590 with one double bond or from a monocyclic dimer of mass 588 with two double bonds, etc. Similarly a saturated dimer of mass 590 would have two rings and could come from a bicyclic dimer of mass 588 with one double bond or from a bicyclic dimer of mass 586 with two double bonds, etc. Thus the mass spectrum of a saturated dimer tells exactly the number of rings in the structure and, combined with the mass spectrum of the unsaturated dimer from which it was derived, may give important clues as to the nature of the unsaturated dimer.

Conjugation-Diels-Alder Mechanism

This is the most commonly mentioned mechanism for thermal dimerization of normal linoleate (4).

Normal linoleate is thermally isomerized to 9,11 or 10,12 conjugated linoleate and then acts as a diene, adding to a double bond of a normal (or conjugated) linoleate which acts as a dieneophile to give a monocyclic dimer with two double bonds. This dimer of mass 588 would be similar in structure to the model dimer of 10,12 linoleate, differing only in the size of side-chains and position of unsaturation. It should give a strong M/2 peak before hydrogenation but no prominent M/2 peak after hydrogenation to mass 592.

TABLE I
Relationship of Mass to Number of Rings (R) and Number of Double Bonds (DB) of C_{36} Dimer Methyl Esters

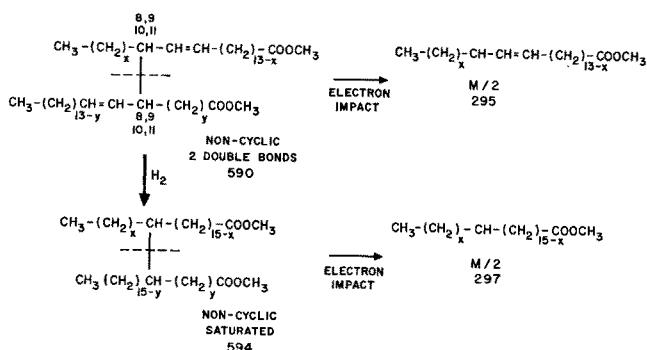| Mass = 594		592		590		588		586	
R	DB	R	DB	R	DB	R	DB	R	DB
0	0	0	1	0	2	0	3	0	4
		1	0	1	1	1	2	1	3
				2	0	2	1	2	2
						3	0	3	1
								4	0

FIG. 1. Mass spectrographic properties of a model dehydro-dimer type of dimer structure.

Bimolecular Hydrogen Transfer Free Radical Mechanism

This has been proposed by Rushman and Simpson (5). It suggested the bimolecular reversible transfer of a hydrogen from the C_{11} methylene of one molecule to the carbon of a double bond of a second molecule. This would result in equal numbers of free radicals R_1 and R_2. They also indicated that the radical R_1 would have limiting resonance forms in which the two double bonds would be conjugated. The R_2 with only one double bond, which is nonallylic to the free radical, would not have limiting isomeric resonance forms of any significance. They wrote the dimerization reaction as a coupling of radicals R_1 and R_2 (presumably randomly) to give the dimer. There were no comments on the resulting structures. A simple coupling of such radicals would obviously give a noncyclic dehydrodimer type of structure.

Although they recognized that thermal linoleate dimers are cyclic and have essentially no conjugation, they did not comment on the fact that their mechanism would require some subsequent reaction to explain these facts.

It should be noted that R_1, resultnig from loss of a hydrogen, would have a mass of 293 and R_2, resulting from a gain of a hydrogen, would have a mass of 295. Random coupling should result in dimers $R_1 + R_1$ (586), $R_1 + R_2$ (588), and $R_2 + R_2$ (590) in the ratio of 1/2/1.

The present study shows that the thermal dimer of methyl linoleate at 290C is predominantly a mixture of structures with one, two, and three rings. The monocyclic structure is best explained by the conjugation-Diels-Alder mechanism. The bicyclic structure is best explained by an extension of the
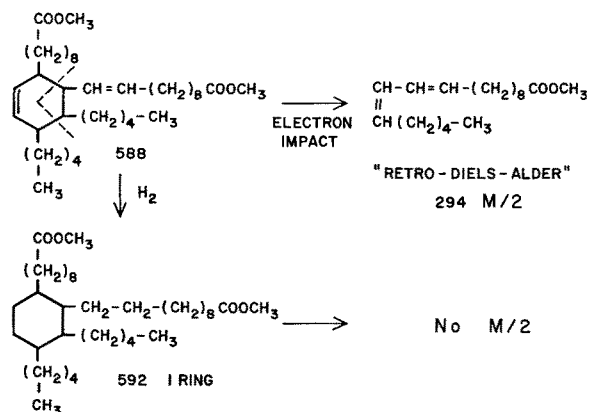

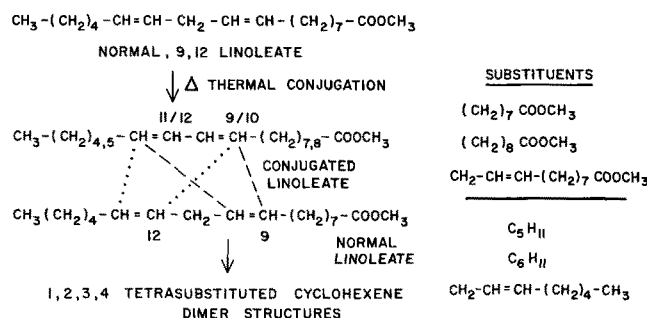FIG. 2. Mass spectrographic properties of a model Diels-Alder type of dimer structure.

FIG. 3. Conjugation-Diels-Alder mechanism of thermal dimerization of normal linoleate.

free radical coupling mechanism with a rapid intramolecular cyclization.

Experimental

Thermal Dimer of Methyl Linoleate

This was made by heating in an evacuated sealed tube for 48 hr at 290C, followed by fractional molecular distillation in an alembic still to remove monomer and trimer, as previously described (6). Analysis: mol. wt. = 554 (588); % C = 76.7 (77.5); % H = 11.2 (11.7); % monomer = 0.6.

Hydrogenated Thermal Dimer

This was made by hydrogenation in acetic acid with PtO_2 catalyst, 150C, 1000 psi, 72 hr with re-esterification of free acid formed by acidolysis (1). Analysis: mol. wt. =548 (592); % C = 77.2 (77.5); % H = 12.1 (12.2); I.V. = 2.8; % monomer = 0.1.

In addition to the large 48-hr sample, small samples (2 g) were similarly polymerized at 290C for 1, 2, 4, 8, 16, and 32 hr and analyzed for monomer, dimer, and trimer as well as for composition of monomer. Mass spectra were run on the whole sample since dimer parent peaks were the principal items of interest. Peaks were seen only at 588 and 586, and the ratio of 588/586 was very close to 2, as it was on the pure isolated 48-hr dimer (cf. below).

The 4-hr and the 8-hr samples were hydrogenated as above, and mass spectra were obtained. Peaks were seen only at 592, 590, and 588 in about the same ratio as in the hydrogenated 48-hr. dimer (cf. below).

Mass Spectrum (1) of 48-Hour Dimer Sample

This is shown in Figure 5. The parent peak $M_1=$ 588 is 2.1 times as intense as the parent peak $M_2=$ 586. A mass of 588 could result from a Diels-Alder dimerization or from the free radical coupling of $R_1 + R_2$ as previously mentioned. The following

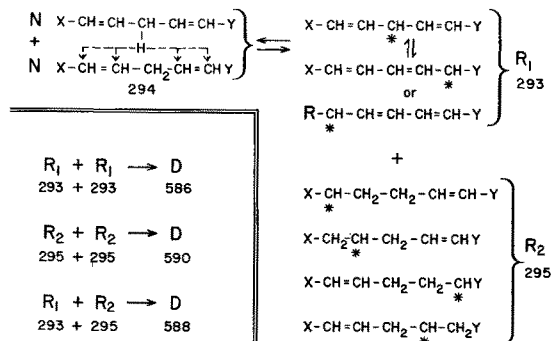FIG. 4. Bimolecular hydrogen transfer free radical mechanism of dimerization of normal linoleate.

TABLE II
Thermally Polymerized Linoleate (290C)

Hr.	Monomer %	Dimer %	Trimer %	Monomer composition					Ratio 588/586 peaks
				N %	Cct %	Ctt %	01 %	X %	
0 (orig.)	100.0	....	....	99.0	1.0	0	0	0	....
1	99.0	1.0	0	97.6	1.7	0.4	0.3	0	....
2	97.9	2.2	0	97.4	1.5	0.8	0.2	0.1	1.8
4	96.3	3.7	0	95.8	2.1	1.6	0.3	0.2	1.8
8	87.9	10.0	2.0	94.2	2.4	2.5	0.7	0.2	1.7
16	76.2	17.2	5.6	86.6	5.0	5.6	2.4	0.4	1.9
32	45.6	38.5	15.9	77.1	6.9	7.3	8.0	0.7	2.0

facts indicate that it is caused by a Diels-Alder dimerization to a considerable extent: a) a strong $M_1/2 = 294$ peak (1.2×588 intensity) which disappears on hydrogenation (cf. below); b) a strong peak at $M_1 - 267 = 321$, corresponding to the simultaneous loss of the two groups in the 2,3 positions of the Diels-Alder dimer structure with hydrogen transfer (also seen in the model dimer of conjugated 10,12 linoleate); c) relatively strong peaks corresponding to loss of the expected alkyl groups on the cyclohexene ring: $M_1 - C_5H_{11} = 517$, $M_1 - C_6H_{13} = 503$, $M - C_8H_{15} = 477$; d) relatively strong peaks corresponding to loss of the ester-containing side-chains: $M_1 - (CH_2)_7COOCH_3$, $M_1 - (CH_2)_8 COOCH_3$, and $M_1 - CH_2CH = CH - (CH_2)_7 - COOCH_3$.

Many of these peaks are accompanied by peaks at 2 mass units less, presumably similarly related to the $M_2 = 586$ peak.

Mass Spectrum of Hydrogenated Dimer

This is shown in Figure 6. The major parent peaks at 592, 590, and 588 correspond to saturated dimers with one, two, and three rings.

The $M_1 = 592$ peak corresponds to the monocyclic dimer expected from the Diels-Alder dimerization. The following facts indicate that the M_1 is attributable to this structure: a) absence of strong $M_1/2 = 296$ peak; b) relatively strong peak at $M_1 - 271 = 321$ corresponding to loss of the two groups in the 2,3 positions of the Diels-Alder adduct with hydro-

gen transfer; preferential loss of these groups was also seen in the hydrogenated model 10,12 linoleate dimer; c) relatively strong peaks owing to loss of CH_3OH plus alkyl groups: $M_1 - (C_5H_{11} + CH_3OH) = 489$, $M_1 - (C_6H_{13} + CH_3OH) = 475$, $M_1 - (CH_7H_{15} + CH_3OH) = 461$, $M_1 - (C_8H_{17} + CH_3OH) = 447$; and d) relatively strong peaks corresponding to the loss of ester-containing side-chains: $M_1 - (CH_2)_7COOCH_3 = 435$, $M_1 - (CH_2)_8 COOCH_3 = 421$, $M_1 - (CH_2)_{10}COOCH_3 = 393$.

The C_5H_{11}, C_6H_{13}, and C_8H_{17} alkyl groups and the $(CH_2)_7COOCH_3$, $(CH_2)_8COOCH_3$, and $(CH_2)_{1u}COOCH_3$ would be expected in the Diels-Alder dimer if the 9- or 12- double bond of unconjugated linoleate acted as dieneophile. If the C_{10} double bond of 10,12 conjugated isomer acted as dieneophile, the C_7 alkyl group would also be expected; and if the C_{11} double bond of the 9,11 conjugated isomer acted as dieneophile, the $(CH_2)_9COOCH_3$ group would also be expected.

These assignments of substituents on the cyclohexene ring from cleavage fragments are complicated by the presence of three prominent parent mass peaks and by the prominent simultaneous loss of methanol with the alkyl side-chains. The preferential simultaneous loss of methanol with substituents in the hydrogenated form compared with the unhydrogenated form was also seen in the model dimer of 10,12 linoleate.

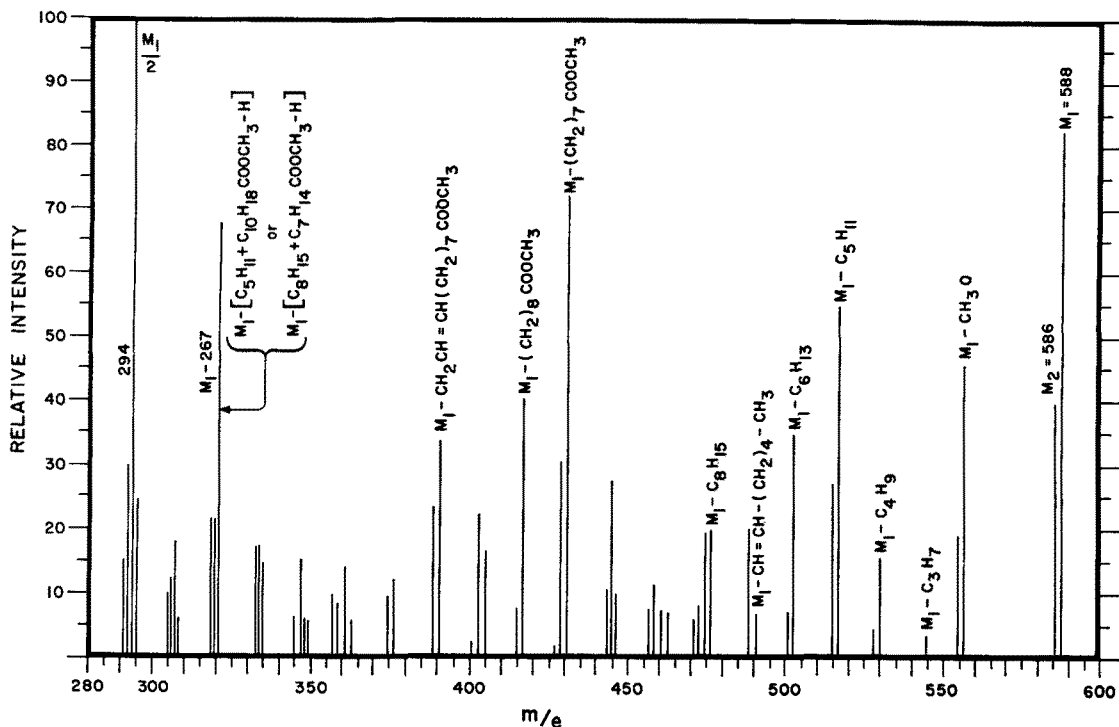The peaks discussed above in relation to the 592

FIG. 5. Mass spectrum of thermal dimer of normal linoleate.

peak were generally accompanied by peaks two and four mass units lower, usually stronger but sometimes weaker (C_6H_{13} and C_8H_{17}) than those related to the 592 peaks. These are presumably related to the 590 and 588 parent mass peaks.

Dehydrolinoleate Dimer

This was made by heating methyl linoleate (Hormel) (0.177 mole) with di-t-butyl peroxide (0.0212 mole) at 130C for 72 hr. Most of the unreacted monomer was stripped in an alembic still to a maximum temperature of 130C. The residue was then fractionally distilled in a micromolecular still, operated to isolate the pure dimer fraction (7). The dimer fraction showed 21% conjugated $cis,trans$ and 29% conjugated $trans,trans$ linoleate by IR (8). U.V. showed $k_{236} = 47.0$. Thus the dimer has about 50% of conjugated linoleate segments. The mass spectrum showed a highly predominant parent peak at $M = 586$, with weaker peaks at 584 (0.11×586 intensity) at 582 (0.03×586), and 588 (0.15×586). It also showed a strong peak at $M/2 = 293$ (13×586). Mass 586 corresponds to a noncyclic dimer with four double bonds.

Hydrogenated Dehydrolinoleate Dimer

This was made by hydrogenating the crude stripped dimer, as above (1), then fractionally distilling in the micromolecular still, as above, to get a pure dimer fraction. This saturated dimer showed a highly predominant parent mass peak $M = 594$, with weaker peaks at 592 (0.12×594 intensity), at 590 (0.16×594), and at 588 (0.03×594). It also showed a very strong peak at $M/2 = 297$ (19×594) and at $M/2 + 1 = 298$ (18×594). These data confirm the noncyclic, conjugated structure of dehydrolinoleate, as proposed previously (2).

Intramolecular Ring Closure

Closure of the unhydrogenated dehydrolinoleate dimer was accomplished by heating a 10% solution of it in methyl laurate as inert diluent for 8 hr at 290C. (Normal methyl linoleate would be about 10% dimerized under these conditions.) The methyl laurate was stripped off in vacuo to a maximum temperature of 130C in an alembic still. The residual dimer showed $k_{234} = 5.0$, indicating that the conjugation had mostly disappeared. The mass spectrum of this residual dimer still showed 586 as the highly predominant peak, with less intense peaks at 584 (0.11×586), at 582 (0.065×586), and at 580 (0.04×586).

This residual dimer was hydrogenated and recovered as above (1). The mass spectrum showed a parent mass peak $M = 590$ (2 rings) as the highly predominant peak, with minor peaks at 588 (0.24×590) and at 586 (0.11×590). There was no relatively strong peak at $M/2 = 295$ (0.5×590) compared with the uncyclized hydrogenated dehydrolinoleate, where the peak at $M/2 = 297$ is 19×594 intensity. There was no detectable peak at 594 (no ring) or 592 (one ring).

Discussion

The rather strong $M/2$ peak in the unhydrogenated dimer and its absence in the hydrogenated dimer, plus the fragmentation patterns, strongly suggest the Diels-Alder addition mechanism for the monocyclic dimer. Although the $M/2$ peak was quite strong, it was not nearly as strong relative to parent molecular peak (1.2×588 intensity) as was the case of the dimer from pure conjugated 10,12 linoleate, where the peak at $M/2 = 294$ was 27×588 intensity. The lesser relative intensity of the $M/2$ peak of the thermal dimer of normal linoleate may result from the fact that, when it undergoes retro-Diels-Alder cleavage, only one conjugated linoleate is formed plus one nonconjugated linoleate whereas retro-Diels-Alder reaction of the dimer from 10,12 linoleate would give two conjugated linoleates with greater resonance stabilization. The amount of the monocyclic Diels-Alder dimer present is not easily determined since parent peak sensitivities depend on structure. If one assumes that the hydrogenated
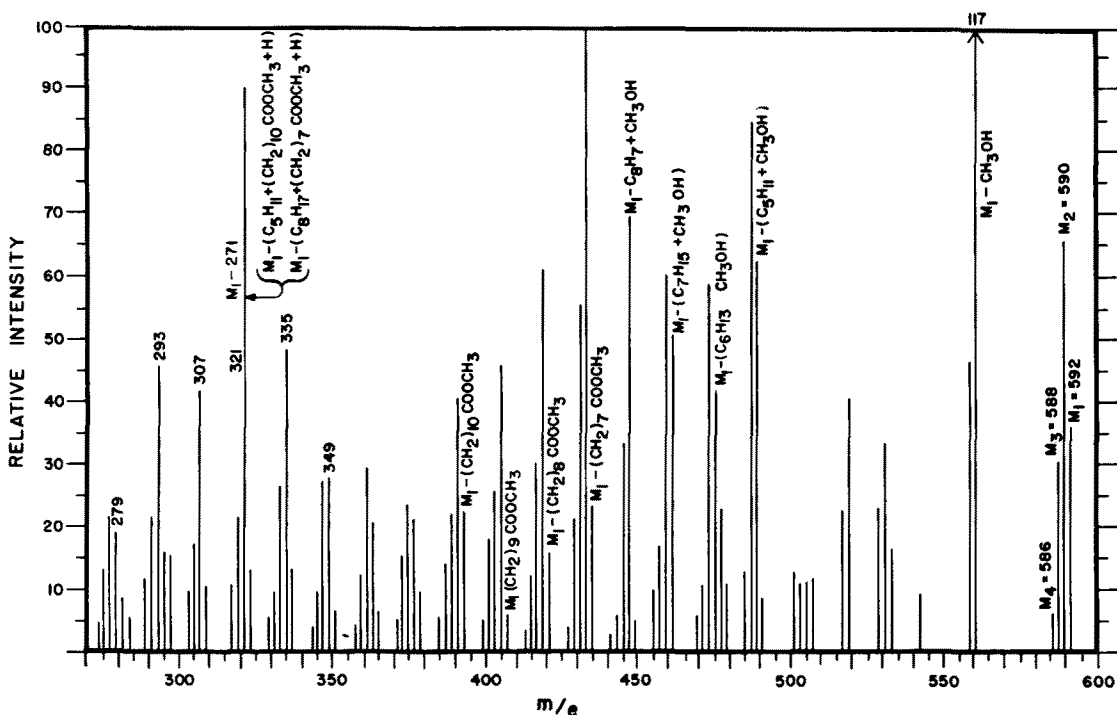

FIG. 6. Mass spectrum of hydrogenated thermal dimer of normal linoleate.

CH$_3$-(CH$_2$)$_4$-CH=CH-CH=CH-CH-(CH$_2$)$_7$COOCH$_3$

CH$_3$(CH$_2$)$_4$ CH=CH-CH=CH-(CH$_2$)$_7$COOCH$_3$

Δ

NON-CYCLIC DIMER , 586
4 DOUBLE BONDS

COOCH$_3$
(CH$_2$)$_7$

CH$_3$-(CH$_2$)$_4$ —(CH$_2$)$_7$COOCH$_3$

(CH$_2$)$_4$
CH$_3$

BICYCLIC DIMER 586
2 DOUBLE BONDS

H$_2$

COOCH$_3$
(CH$_2$)$_7$

CH$_3$-(CH$_2$)$_4$ (CH$_2$)$_7$-COOCH$_3$
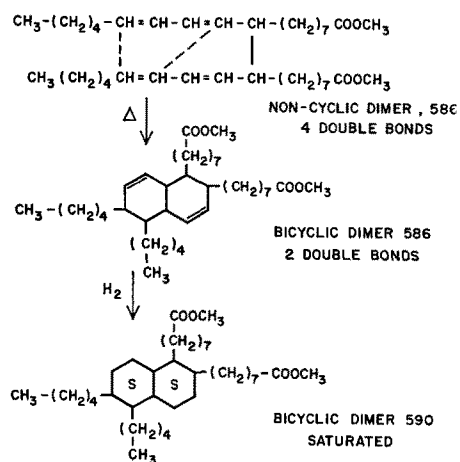
(CH$_2$)$_4$
CH$_3$

BICYCLIC DIMER 590
SATURATED

FIG. 7. Intramolecular cyclization of a dehydrolinoleate dimer.

dimer of the model 10,12 linoleate may be used as a standard, then the 48-hr dimer would have only about 32% of monocyclic dimer structure (by relative parent peak intensities of 592 of the hydrogenated dimers, run the same day and under the same conditions). It is interesting to note that the hydrogenated 4-hr and 8-hr samples (Table II, 3.7 and 12% conversion) had essentially the same ratio of 592 to 590 peaks as the 48-hr sample, indicating that the monocyclic Diels-Alder structure is formed in the early stages of dimerization.

The bicyclic dimer, indicated by the 590 parent mass peak in the hydrogenated dimer, is best explained by the free radical coupling theory, with subsequent rapid intramolecular cyclization. The dehydro-linoleate synthesized from normal linoleate is a model of the dimer which would result from coupling of R$_1$ + R$_1$ according to the free radical coupling theory. The fact that it did cyclize to a predominantly bicyclic structure shows that this mechanism is possible. The particular dehydrodimer structure shown in Figure 7 has two conjugated linoleate segments, resulting in two fused cyclohexene rings. If one of these segments were the nonconjugated form of R$_1$, joined at C$_{11}$, then intramolecular Diels-Alder cyclization would result in a cyclobutane ring fused to the cyclohexene ring. If free radicals were formed by loss of hydrogen from linoleate at C$_8$ or C$_{14}$ (2) and these radicals or their limiting resonance forms were coupled with a conjugated segment (R$_1$), bicyclic dimers could be formed with four- and five-membered rings fused to the cyclohexene ring.

As mentioned earlier, the 588 peak of the unhydrogenated dimer could be caused in part by coupling of R$_1$ + R$_2$ of the free radical mechanism. If this occurred, this conjugated noncyclic triene dimer must also undergo intramolecular cyclization to a bicyclic dimer since noncyclic structure was absent (no 594 peak in hydrogenated dimer). Such bicyclic

dimers could have cyclopentane or cyclohexane rings fused to the cyclohexene ring.

The possible bicyclic structures mentioned above are those which give 1,2 or a,β fusion of the second ring to the cyclohexene ring that is formed by intramolecular Diels-Alder cyclization. By adding the conjugated diene in the "opposite" head-to-tail vs. head-to-head sense, rings of 5,6,7, or 8 carbons fused 1,3 or a,γ to the cyclohexene ring are theoretically possible. Since mass spectrometry would not be expected to differentiate the ring size in such polycyclic structures, the ring sizes and structures of these polycyclic dimers are not established with the present data.

The absence of dimer of mass 590 in the unhydrogenated dimer indicates that there is no coupling of R$_2$ + R$_2$ = 590, as originally proposed by Rushman. There is no obvious mechanism by which such a dehydrodimer of mass 590 would form a cyclic dimer of mass less than 590.

A possible explanation for the absence of dimer of mass 590 in the unhydrogenated dimer is that radical R$_2$, which is not appreciably stabilized by allylic resonance, would preferentially abstract a hydrogen atom from a normal linoleate (and generate an R$_1$ radical) and thus become an oleate isomer, which is actually observed in the monomers of partially polymerized linoleate (cf. Table II and Ref. 6). Thus for each oleate isomer formed, an additional R$_1$ radical would be formed, which would be available for reacting with another R$_1$ to give a 586 mass dimer or with R$_2$ to give a 588 mass dimer.

The tricyclic dimer indicated by the 588 peak in the hydrogenated dimer might arise by an intramolecular alkylation reaction of an exocyclic double bond of the bicyclic dimer. No speculation as to possible structures of these tricyclic dimers is offered.

The weak peak at 586 in the hydrogenated dimer could be attributable to any one of three possibilities or combinations of them: a saturated tetracyclic dimer, a tricyclic dimer with one double bond (the hydrogenated dimer had an I.V. = 2.8), and a monocyclic benzene ring with saturated substituents (UV could detect no aromatic structure). The second explanation seems most likely.

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