

Dimer Acid Structures: Cyclic Structures of Clay Catalyzed Dimers of Normal Linoleic Acid, 9-*cis*, 12-*cis*-Octadecadienoic Acid

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Abstract

The clay catalyzed dimer of linoleic acid has been examined by mass spectrometry of the unhydrogenated, the partially hydrogenated and completely hydrogenated dimer. The results show that monocyclic, bicyclic and tricyclic structures are present. Monocyclic structures predominate, bicyclic structures are also prominent, and tricyclic structures are relatively minor. The monocyclic structure is believed to arise from a Diels-Alder type addition reaction. The bicyclic structure may result from a free radical coupling followed by intramolecular ring closure. The monocyclic structure in the unhydrogenated dimer appears to be mostly a benzene ring with saturated and unsaturated side-chains. It probably is formed by hydrogen transfer from the Diels-Alder cyclohexene structure first formed. Little, if any, of the Diels-Alder dimer structure as such is present. The catalytic linoleate dimer has a higher ratio of monocyclic to bicyclic dimer than does the noncatalytic (thermal) dimer made from normal (nonconjugated) linoleate, while the thermal dimer of a conjugated *trans-trans* linoleate is exclusively monocyclic. It is suggested that the clay catalyzes conjugation and hence favors the Diels-Alder reaction, and then catalyzes hydrogen transfer to aromatize the cyclohexene ring.

Introduction

Noncyclic dimers of methyl linoleate, oleate and stearate have been made by a free radical coupling mechanism. The free radicals were produced by hydrogen abstraction from monomer by the *t*-butoxy radical resulting from thermal dissociation of di-*t*-butyl peroxide at 130 C (where subsequent ring formation was largely absent). Their structures have been reported (1-3).

A monocyclic dimer of the classical Diels-Alder structure has been made by noncatalytic thermal dimerization of the pure 10,12-*trans-trans*-conjugated linoleate (4).

A bicyclic dimer was shown to be the principal structure which resulted when a noncyclic dehydrolinoleate was heated to temperatures (290 C) at which linoleate polymerizes at a reasonable rate (5).

Noncatalytic thermal polymerization of normal (nonconjugated 9,12) linoleate has been shown to result in mono-, bi- and tricyclic structures (5). The monocyclic dimer was shown to be of the Diels-Alder structure. The bicyclic dimer was believed to result from rapid intramolecular ring closure to form two rings from a noncyclic dehydrolinoleate type dimer. The noncyclic dehydrolinoleate dimer intermediate was believed to be formed by a hydrogen transfer reaction between two molecules of linoleate to produce two linoleate radicals which then coupled

to form the noncyclic dehydrolinoleate dimer, which rapidly underwent ring closure to the bicyclic structure.

The tricyclic dimer, apparently present in smaller amounts was suggested as resulting from an intramolecular alkylation reaction of a double bond in the bicyclic dimer.

The proof of the number of rings in these dimers was by mass spectrometry of the dimers (as methyl esters) after complete saturation of their double bonds, and determining their parent mass peaks (exact molecular weights to the nearest mass unit).

Thus a saturated noncyclic C₃₆ dimer acid ester has a molecular weight or mass of 594, a saturated monocyclic dimer has a molecular mass of 592, a saturated bicyclic dimer 590, and a saturated tricyclic dimer 588.

It can be seen that each ring formed results in a molecular mass of two units less (two hydrogens less) compared to the structure with one less ring, if there are no double bonds.

Mass spectrometry of the unhydrogenated as well as of the hydrogenated dimers also gave information as to their structure because of the pattern of fragments observed in the mass spectrum.

Clays are known to catalyze the polymerization and isomerization of unsaturated fatty acids and esters (6).

They probably function in part by catalyzing the isomerization of normal linoleate to the faster-polymerizing conjugated forms. They also may catalyze the dimerization of the conjugated linoleate (7).

This paper reports some results on the ring structures of clay catalyzed dimers of linoleic acid.

Experimental Procedures

Linoleic acid (Hormel), 275 g, was polymerized with 13.5% of a montmorillonite clay (SiO₂, 57.9; Al₂O₃, 17.0; FeO, 0.17; Fe₂O₃, 2.8; MgO, 2.8; CaO, 1.7; TiO₂, 0.28; SO₃, 0.56; Na₂O, 0.69; K₂O, 0.71; H₂O, 10; pH, 8), in a stainless steel rocking bomb (with stainless steel balls to improve agitation), at autogenous pressure of 130-140 psi at 230 C for 4 hr. The crude acids were recovered by treatment with 1.2 ml of H₃PO₄ at 100 C to liberate acids from any soaps present, filtering under pressure, washing the clay with Skelly C, and evaporation of Skelly C in vacuo. Yield 247 g. Analysis: iodine value (IV), 97.7 (Wijs ½ hr); saponification value, 200.8; acid value, 193.9; monomer, 26.6%; dimer, 59.3%; residual polymer, 14.1% [micromolecular distillation (8)].

The crude dimer acids were converted to methyl esters and fractionally distilled in a centrifugal cyclic molecular still (DPI-CMS-5) with the results shown in Figure 1. A center cut of the dimer was taken which was used as pure dimer for structure studies. Analysis: C, 77.5% (77.5); H, 11.6 (11.7); Mol. Wt.

(VP Osm.), 529 (588); IV, 108.9 (Wijs $\frac{1}{2}$ hr); $N_D^{30} = 1.4767$; $d^{30}_D = 0.9348$.

Hydrogenation of the dimer methyl ester with 5% (based on ester) of 10% Pd on charcoal at room temperature and 50 psi in ethanol (50 vol) reduced the IV to 73. Hydrogenation at 1000 psi at 150 C for 24 hr with 130% (based on ester) of 10% Pd on C in cyclohexane (8 vol) plus methanol (0.4 vol) for 24 hr reduced the IV to 26. Hydrogenation with 44% PtO₂ (based on ester) in glacial acetic acid (2 vol) at 150 C and 1000 psi for 30 hr gave a product with IV 0.0. This hydrogenated ester was re-esterified to convert free acid formed by acidolysis back to methyl ester (4). Analysis: C, 76.5% (77.1); H, 12.3% (12.2); Mol. Wt. = 547 (592); IV, 0.0.

Mass spectra of the distilled dimer and of the hydrogenated dimers were run with the Consolidated Engineering Model 21-103-C mass spectrometer as before (2).

The relative intensities of the parent peaks are shown in Table I, with the strongest parent peak in each spectrum taken as 100. For comparison, the unhydrogenated and hydrogenated forms of the thermal dimers of normal linoleate and 10-*t*-12-*t*-linoleate are also shown. The fragmentation patterns between masses 270 and 600 were even more complex than that previously reported for thermal linoleate and its completely hydrogenated form. A detailed interpretation of the fragmentation patterns will not be attempted at this time. One notable fact was the absence of any relatively strong peak at M/2 (retro-Diels-Alder cleavage) in the hydrogenated or unhydrogenated dimer, relative to adjacent homologous peaks. This is in contrast to the unhydrogenated thermal dimers of 10,12-linoleate and 9,12-linoleate which gave a relatively strong peak at M/2 due to retro-Diels-Alder cleavage by electron impact in the mass spectrometer.

UV absorption of the unhydrogenated catalytic dimer showed aromatic peaks at 270 and 278 m μ . Molar extinction, $E_{270} = 240$ (tangent base-line between 248 and 290 m μ). The sample hydrogenated to IV 26 with Pd/C also showed peaks at 271 and 278 m μ , $E_{271} = 182$ (curved base-line between 245 and 290 m μ). This sample showed less background absorption from 240-270 m μ than the unhydrogenated dimer (Fig. 2).

The completely hydrogenated sample showed practically no UV absorption in the 270-280 region ($E_{271} = 3$).

The nuclear magnetic resonance spectrum of the unhydrogenated sample showed a doublet aromatic peak at 6.7 and 6.8 ppm whose integrated intensity was approximately 1.0 H per mole, using the H of -OCH₃ ester as internal standard. The completely hydrogenated dimer showed no peaks in this region.

Results and Discussion

The parent mass peak pattern of the completely hydrogenated catalytic dimer shows the presence of monocyclic (mass 592, strongest peak), bicyclic (mass 590), and tricyclic structures (mass 588). The very weak peak at 586 would correspond to a saturated tetracyclic structure or it could be due to a trace of tricyclic monoene, bicyclic diene, or monocyclic aromatic structure with saturated side chains. The latter is probably the most reasonable.

This same general pattern, with different ratios of mono-, di- and tricyclic structures was seen in the hydrogenated noncatalytic thermal dimer of nor-

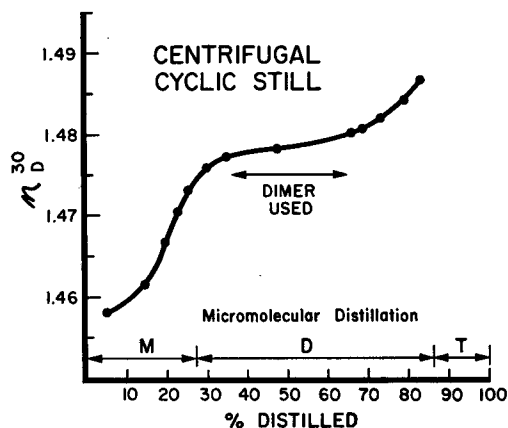


Fig. 1. Molecular distillation of crude dimer methyl esters.

mal linoleate. The catalytic linoleate dimer showed monocyclic structure (592 = 100%) as predominant, according to parent peak heights, with the bicyclic (590) structure next (78%) and the tricyclic (588) structure least (19%). In contrast, noncatalytic thermal dimer showed bicyclic structure as predominant (590 = 100%) followed by monocyclic (55%) and tricyclic (45%).

Accurate determination of actual amounts of mono-, di-, and tricyclic structures is difficult because of lack of pure standards for determining sensitivities of parent peak response. A best estimate, based on response of the model monocyclic saturated dimer of 10-*t*,12-*t*-linoleate, is 50-60% monocyclic, 40-30% bicyclic and 9-10% tricyclic structure in the saturated catalytic linoleate dimer.

The UV and NMR evidence for aromatic structure indicates that the clay catalyst may act as hydrogen transfer catalyst to aromatize a substituted cyclohexene structure to a substituted benzene structure. The persistence of the 586 peak as the predominant peak on partial hydrogenation with Pd/C catalyst (Table I, 1,2,3) suggests that this peak is due extensively to a substituted benzene ring with saturated side chains. The UV and NMR spectra also indicated

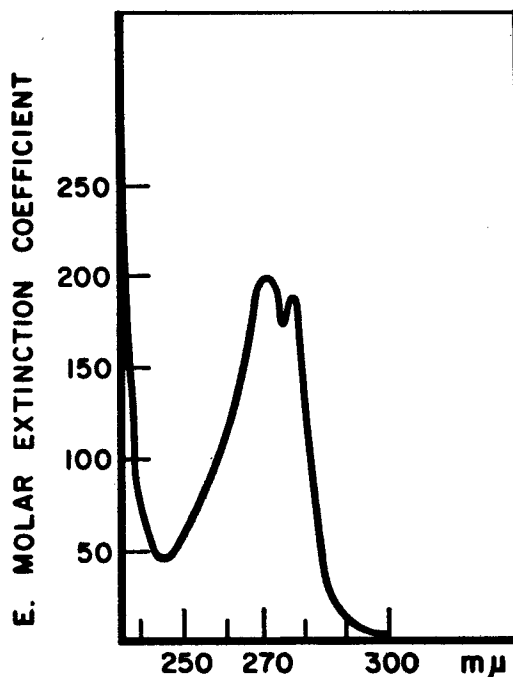


Fig. 2. Ultraviolet absorption of Sample 3, Table I.

TABLE I
Parent Mass Peaks of Linoleate Dimers

Sample	Dimer (IV)	Parent peak of various masses relative to strongest peak = 100							
		592	590	588	586	584	582	580	578
1	Cat. Lin., ^a unhydrogenated (109)		28	44	100	70	24	19	5
2	Cat. Lin., ^a Pd/C, 50 psi, 25 C (73)	14	20	41	100	77	11	3	..
3	Cat. Lin., ^a Pd/C, 1000 psi, 150 C (26)	22	15	19	100	15	12	4	..
4	Cat. Lin., ^a PtO ₂ , 1000 psi, 150 C (0.0)	100	78	19	2
5	Therm. Lin., ^a unhydrogenated	100	48
6	Therm. Lin., ^a PtO ₂ , 1000 psi, 150 C (2.8)	55	100	47	11
7	Therm. 10-12-Lin., ^b unhydrogenated	100
8	Therm. 10,12-Lin., ^b PtO ₂ , 1000 psi, 150 C (0.1)	100
	R + DB ^c	1	2	3	4	5	6	7	8
	1R + nDB: n =	0	1	2	3	4	5	6	7
	2R + nDB: n =		0	1	2	3	4	5	6
	3R + nDB: n =			0	1	2	3	4	5
	1 Benzene R + n(DB + R): n =				0	1	2	3	4

^a Normal 9,12-linoleate.

^b 10-*t*,12-*t*-linoleate.

^c R, rings; DB, double bonds.

aromatic structure in these partially hydrogenated dimers and its absence in the completely hydrogenated dimer. The marked decrease of the 586 peak and a corresponding increase in the 592 in the completely hydrogenated sample (Table I, 4) would be consistent with the idea that the 586 peak is largely due to a benzene ring with saturated side chains. The decrease in peaks below 586 on hydrogenation with Pd suggests cyclic structures (either benzenoid or alicyclic) with double bonds in the side chains which are more easily saturated than the cyclic double bonds. These may be formed by hydrogen transfer by the catalyst. Monomer as well as dimer may be the hydrogen acceptor. The 590 peak in the unhydrogenated dimer (absent in thermal linoleate) could be due to hydrogenation of the exocyclic double bond of a Diels-Alder monocyclic dimer (mass 588), by hydrogen transfer.

The absence of a relatively strong M/2 peak in the unhydrogenated catalytic dimer indicates that there is very little if any of the Diels-Alder monocyclic structure as such in contrast to the thermal dimers which showed strong M/2 peaks due to retro-Diels-Alder cleavage. It is suggested that the monocyclic dimer is originally formed by the conjugation-Diels-Alder mechanism and that this monocyclic Diels-Alder structure is isomerized by double bond position isomerization as well as by hydrogen transfer by the action of the clay catalyst. These isomerized structures would no longer be of actual Diels-Alder structure and would not undergo retro-Diels-Alder cleavage.

The clay probably acts as a catalyst in several ways: (a) as a conjugation catalyst; (b) as a hydrogen transfer catalyst; (c) as a catalyst for the double bond isomerization of dimer, both positional and *cis-trans*; (d) as a catalyst for the Diels-Alder addition reaction; (e) possibly as an alkylation catalyst to

cause ring formation by intramolecular alkylation with an exocyclic double bond.

The relatively greater proportion of monocyclic dimer in the catalytic dimer of normal linoleate compared to the thermal dimer of normal linoleate suggests that the Diels-Alder mechanism is favored by the catalytic action of the clay catalyst in preference to the hydrogen transfer free radical mechanism proposed for the formation of the predominantly bicyclic structure found in thermal dimer of normal linoleate (4). The higher temperature and longer reaction time required for noncatalytic thermal dimerization of normal linoleate would favor the free radical mechanism, compared to a system which contained a catalyst for formation of conjugated isomers which could dimerize via the Diels-Alder addition.

The spectroscopic data on the catalytic dimers strongly indicate that the monocyclic dimer is a six-member ring, as would be expected from a Diels-Alder mechanism. The nature and size of the second and third rings in the bicyclic and tricyclic dimers cannot be deduced from data available at present.

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