Characterization of Products from Clay Catalyzed Polymerization of Tall Oil Fatty Acids[1]

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ABSTRACT

Products obtained by acid clay catalyzed dimerization of oleic, elaidic, and tall oil fatty acids were characterized. The monomeric products (35% of total) consisted of stearic, octadecenoic (66% *trans*-), and mid chain monomethyl branched acids, both saturated and unsaturated. The polymeric products (65% of total) consisted of linear, alicyclic, aromatic, and polycyclic dimers. The tall oil fatty acid based dimer closely resembled oleic dimer in polycyclic character and linoleic dimer in aromatic and linear structures. Oleic dimers contained the highest linear structural content, while linoleic dimer contained the largest polycyclic content. Alicyclic structures were the principal components of all three products. The monocyclic dimer structures present consisted of six membered ring systems with linoleic and tall oil fatty acid dimers containing the highest aromatic contents.

INTRODUCTION

Monomer acids: Den Otter (1-3) characterized the methylated monomer fraction from the clay catalyzed polymerization of oleic acid. Gas liquid chromatographic (GLC) analysis of the monomer revealed that the normal saturated fatty acids C_8, C_{10}, C_{12}, C_{14}, and C_{18} were present, as well as small amounts of octadecenoic acids. This unsaturated acid fraction was a mixture of *cis*- and *trans*-isomers. GLC analysis indicated no cyclic C_{18} compounds were present. Saturated branched chain acids also were reported based upon GLC and IR spectroscopic data. The saturated branched fatty acids were believed to be monomethyl branched at the hydrocarbon end of the chain, the 16-methyl (iso) isomer being the most likely. The presence of the dimethyl branched saturated fatty acids (neoisomers) with a quarternary carbon atom was postulated but dismissed for lack of evidence.

In this characterization study, the monomer acids from the clay catalyzed polymerization of tall oil fatty acids (TOFA) were examined by NMR and GLC-mass spectroscopic (MS) techniques to determine the nature of the branching present.

Dimer acids: Considerable characterization data on the thermal polymerization of linoleic acid has been reported. Only limited data are available on the clay catalyzed polymerization of linoleic acid. From the latter studies, different dimer acid structures have been proposed. The thermal dimer of *trans-trans*-conjugated linoleic acid was reported by Wheeler and White (4) and Sen Gupta and Scharmann (5,6) to contain a monocyclic structure with two double bonds. Both Wheeler and Sen Gupta concluded that the monocyclic structure was formed by a Diels Alder mechanism and proposed six membered ring structures from the mass spectral fragmentation patterns.

The thermal polymerization of nonconjugated linoleic acid carried out by Wheeler and White (4) and Sen Gupta and Scharmann (5,6) yielded a complex mixture of mono-, bi-, and tricyclic ring structures, with little or no acyclic structures present. The structures proposed by Wheeler (4) were six membered ring systems. The monocyclic structure was formed via a conjugated Diels-Alder mechanism, while the bicyclic structure was formed by a proposed extension of the hydrogen transfer free radical coupling mechanism. Sen Gupta and Scharmann (5,6) proposed structures containing five membered ring systems and presented a logical stepwise mechanism for their formation. Both authors had proposed their structures based upon similar mass spectral fragmentation patterns. Additional evidence is required to resolve these conflicting proposals.

Wheeler, et al., (7) reported on the clay catalyzed polymerization of nonconjugated linoleic acid and provided structural data indicating that the dimer structures contained six membered rings. The clay catalyzed n-linoleic acid polymerization yielded a product containing mono- and bicyclic structures with no acyclic and low levels of tricyclic structures present as determined from mass spectral data. Monocyclic aromatic dimer structures were proposed by Wheeler, et al., (7) from UV and NMR spectroscopic data. The presence of aromatic ring systems confirmed that the six membered ring structures proposed by Wheeler were more plausible than the five membered ring structures proposed by Sen Gupta and Scharmann (5,6).

Few reports on the structure of oleic acid polymers have been published. Ghodssi and coworkers (8) have studied the polymerization of oleic acid at 30 C with boron trifluoride catalyst. Ghodssi, et al., (8) proposed a four membered ring dimer from the presence of peaks at 2.3 (δ) ppm in the NMR spectrum of the product. Dimers obtained from the thermal polymerization of methyl oleate by Sen Gupta (9) consisted of only a monocyclic structure based upon mass spectroscopic data. Sen Gupta (9) indicated that an unequivocal characterization of the ring system was not possible from the NMR and mass spectral data. However, he did propose possible monocyclic dimer structures containing four and five membered rings. The evidence presented suggested that four membered rings were unlikely. Den Otter (1-3) reported on the clay catalyzed polymerization of oleic acid. While the major characterization data from this study were upon the monomer fraction, atomic refraction data were obtained upon the dimer fraction to determine the number of ring systems present. Den Otter (1-3) concluded that the dimer structures contained a single ring system. He did not present any data to determine the ring size but did propose a six membered structure as feasible.

While the various investigators employed different dimerization conditions for oleic acid or its methyl ester, they concluded that monocyclic structures were the major components present. However, considerable uncertainty remains as to the actual dimer structures present.

EXPERIMENTAL PROCEDURES

The oleic acid used consisted of 78% oleic; 12%, palmitoleic; and 10%, other fatty acids, as determined by GLC. The elaidic acid used had the following composition: 60% elaidic (*trans*); 20%, oleic (*cis*); 4%, stearic; and 7%, other fatty acids. A 97% TOFA mixture contained 52%, oleic acid; 45%, linoleic acids; 1.5%, rosin acids; and 1.5%, unsaponifiables. The acids were polymerized by heating at 250 C with 4% Alabama blue clay (a montmorillonite) containing 1 meq of lithium hydroxide for 4 hr using 80 psi

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steam. Typical reaction product yields from the polymerization were 65% polymerized acids and 35% monomer by wt.

At the completion of the reaction, the product was treated with phosphoric acid (15% of the wt of the clay catalyst) to remove inorganic cations. The cation complexes were removed by filtration, and the crude polymerized fraction was stripped of monomer by thin film evaporation.

Hydrogenation of the monomer fraction was carried out with 1% Girdler G-53 (a reduced nickel catalyst supported on Kieselguhr) for 3-4 hr at 160 C and 90 psi hydrogen. The yield was 97.5%.

An enriched branched octadecanoic acid sample was obtained by low temperature recrystallization of stearic acid from an acetone solution of the hydrogenated monomer. The stearic acid was removed by filtration, and the acetone was removed from the filtrate by evaporation.

Polymerized fractions were hydrogenated using 0.1% of 5% palladium on carbon for 6 hr at 250 C and 500 psi hydrogen.

For GLC analysis, the methyl esters of the monomer and dimer acids were prepared by the diazomethylation procedure of DeBaer and Backer (10). Separation of the methyl esters of the monomer acids was performed at 210 C with ca. 40 ml/min helium flow through a 12 ft x 1/8 in. 12% free fatty acid phase on 100-120 mesh Chromosorb W HP column. The GLC-MS analysis was carried out on a Beckman GC-4 chromatograph coupled to a Hitachi RMU-6 mass spectrometer by a Watson-Biemann separator.

Spectra of the methylated dimer acids introduced through the heated inlet of the Hitachi mass spectrometer at 250 C were obtained at 70 ev. The molecular ion peak intensities in the dimer region (m/e 586-594) were measured and normalized. The percent *trans*-monoenoic acid content of the monomer fraction was determined by a standard AOCS method (11) utilizing IR spectroscopy.

The NMR spectra were obtained (as 50% deuterochloro form solutions) on a Varian model A-60 60 MHz NMR spectrometer. A spectrum amplitude of 80 was necessary to observe the aromatic and olefinic protons of the dimers. However, a spectrum amplitude of 4 was employed to obtain an entire spectrum.

UV analyses of the hydrogenated oleic dimer and the hydrogenated TOFA dimer in methanol were performed using a Cary model 14 UV spectrometer and 1 cm quartz cells.

Gel permeation chromatographic analyses were performed on a 3/8 in. diameter 17 ft Bio Beads SX-2 column in a Waters model 502 liquid chromatograph equipped with a refractive index detector and using tetrahydrofuran solvent. Preparative isolation of pure dimer was carried out on a 1 in. diameter 8 ft column packed with Sephadex LH-20 and using dimethyl formamide solvent. These liquid chromatographic methods have been reported previously by Harris, et al. (12).

RESULTS AND DISCUSSION

Monomer acids from tall oil polymerization: The monomer fraction from tall oil was found to be a mixture of octadecanoic and octadecenoic acids with relatively small amounts of heptadecanoic and nonadecanoic acids. This information was obtained from a consideration of the molecular ions observed for the methyl esters derivatives. Gel permeation chromatography revealed that the monomer fraction contained low levels of fatty acid dimers.

The ester number of the monomer fraction, which is the difference between acid and saponification numbers, was 14. This indicated that low levels of esters were present. IR spectroscopic analysis of the monomer indicated that lactones may be present, since a carbon-oxygen stretching vibration at 1780 cm^{-1} was evident. Therefore, some or all of the esters could be lactones.

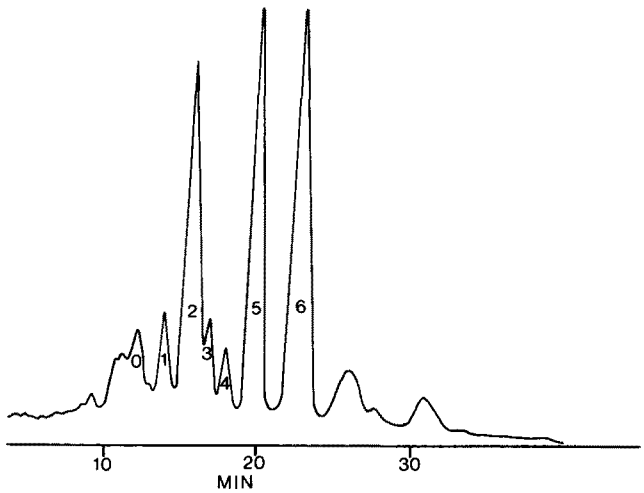

FIG. 1. Gas chromatogram of monomer acids from tall oil fatty acids polymerization.

GLC analyses of the methylated monomer and the monomer after hydrogenation were obtained to determine the octadecanoic acids present. The chromatogram for the methylated monomer acids is shown in Figure 1. Peaks 5 and 6 in the monomer were found to have similar retention times to stearic and oleic acids, respectively. Peak 6, the major monomer peak, disappeared on hydrogenation with half being converted to stearic acid, peak 5, and the rest being converted to peak 2. Since branched isomers are known to elute prior to the linear homologues (1-3, 13), it was concluded that peak 2 was a branched octadecanoic acid. Consequently, half of the octadecenoic acid represented by peak 6 was a linear isomer, and the rest was branched. Den Otter (1-3) had found no evidence for branched unsaturated fatty acids in monomer from oleic polymerization. However, the octadecenoic acid content of his monomer fraction was less than 1%. The octadecenoic acid level of the tall oil monomer was ca. 25%.

IR analysis showed that the monomer fraction contained 15% isolated *trans*-isomers (11). Peak 6, which represented 22% of the monomer, was the only peak that disappeared upon hydrogenation. Therefore, it was concluded that octadecenoic acids represented by this peak were two-thirds *trans*-isomers. Evidence for *cis-trans*-isomerization occurring during clay catalyzed polymerization has been reported by Den Otter (1-3).

Experiments were conducted to develop more specific information on the nature of the octadecanoic acid isomers present. Previous work (13) has demonstrated that the GLC retention times of saturated fatty acids are dependent upon chain length. Octadecanoic acids with ethyl or dimethyl branching would be expected to elute between normal hexadecanoic and heptadecanoic acids, while the monomethyl analogues would elute between normal heptadecanoic and octadecanoic acids. In the monomer fraction, the majority of the branched octadecanoic acids was found in the latter category, as shown in Figure 1. Therefore, it is likely that the majority of the acids are monomethyl branched isomers.

An enriched sample of the branched isomers of octadecanoic acid was obtained by low temperature crystallization of stearic acid from the hydrogenated monomer. NMR data on this enriched sample indicated that 6.9 methyl protons were present relative to the carboxylic acid proton. Therefore, there were 2.3 methyl groups/carboxylic acid or 1.3 branched methyl groups/acid molecule present in the enriched branched octadecanoic acid fraction. This suggested that the majority of these branched isomers was monomethyl branched with the presence of some ethyl or

TABLE I

Equivalent Chain Lengths (ECL) by Gas Chromatography for Methyl Esters of Monomethyl Branched Octadecanoic Acids

Tall oil monomer		Branched isomers	
Gas chromatographic peak number	ECL FFAP column[a]	ECL BDS column[b]	Methyl position
2	17.28	17.32-17.39	5-12
3	17.48	17.45	13
4	17.62	17.56	14

[a]Present work. FFAP = free fatty acid phase.
[b]See reference 13.

TABLE II

Mass Spectral Analysis of Branched Stearates

Stearate	Fragment ratio[a] M-29/M-31/M-43	Source
Normal	28/45/100	b
	20/46/100	c
16-Methyl (iso)	11/15/100	b
	15/19/100	c
	16/16/100	d
	15/20/100	e
15-Methyl (anteiso)	40/20/100	b
14-Methyl	15/21/100	e
10-Methyl	14/29/100	d
9-Methyl	22/29/100	c
	23/30/100	d
3-Methyl (β)	12/121/100	d

[a]M = molecular ion peak.
[b]Present work.
[c]See reference 15.
[d]Calculated from reference 16.
[e]Calculated from spectra reported by Ryhage and Stenhagen (14).

dimethyl branched isomers possible. It was unlikely that branching larger than ethyl was present due to the absence of components eluting prior to palmitic acid in the chromatogram.

Monomethyl position in branched octadecanoic acids: Ackman (13) had reported that the methyl esters of the 5-methyl to 12-methyl isomers of branched fatty acids could not be separated on packed or capillary columns but that the 13- and 14-methyl isomers could be separated. A comparison of the equivalent chain lengths for the methyl branched octadecanoic acids present in the monomer fraction with the equivalent chain lengths of known monomethyl branched isomers reported by Ackman (13) is shown in Table I. These GLC data indicate that peak 2 could be a mixture of several mid chain branched isomers and that peaks 3 and 4 could be the 13- and 14-methyl branched isomers.

GLC components eluting prior to normal heptadecanoic acid were not analyzed by mass spectroscopy. Based upon equivalent chain lengths, however, it is likely that these minor components are ethyl or dimethyl branched octadecanoic acids.

GLC/MS was employed to establish the relative position of the methyl group of the branched octadecanoic acids. Methylated monomer peaks 2-5 each showed the same general fragmentation pattern and were confirmed to be saturated octadecanoic fatty acid methyl esters. There were no significant differences in the relative intensities of the fragmentation patterns of these four components. Differences in relative peak intensities for different isomers were observed in the spectra of Ryhage and Stenhagen (14).

TABLE III

Gas Liquid Chromatographic-GLC/MS Analysis of Monomer Acids Branched and Straight Chain C_{18} Saturated Acids

Gas chromatographic peak number	Fragment ion ratio[a] (M-29/M-31/M-43)
2	28/30/100
3	19/30/100
4	45/42/100
5	27/53/100

[a]M = molecular ion peak.

TABLE IV

Relationship of Mass to Number of Rings (R) and Number of Double Bonds (DB) of C_{36} Dimer Esters-Maximum Possible Structures[a]

Mass (m/e)	594	592	590	588	586
Total R and DB	0	1	2	3	4
Number of rings	Number of double bonds				
0	0	1	2	3	4
1		0	1	2	3
2			0	1	2
3				0	1

[a]Previously reported by Wheeler and White (4).

However, there was no pattern which could be used to distinguish between mixtures of mid chain branched isomers and mixtures of end chain branched isomers. In this study, the GC/MS conditions employed faster scan speeds and different instrument parameters than those conditions of Ryhage and Stenhagen (14) using a heated inlet system. This may have had some effect upon the relative peak intensities. It was concluded that a comparison of the entire mass spectra of these isomers did not aid in establishing the relative position of methyl branching in the monomer components.

Campbell and Naworal (15) had reported that normal, mid chain, and end chain branched fatty esters could be distinguished by ratios of selected fragment ions, namely those fragmentations resulting from M-29, M-31, and M-43. The ratios obtained in this laboratory compared favorably with literature data (14-16) (Table II). It was concluded that the literature ratios could be used in lieu of experimental ratios. It was not possible to identify specific mid chain isomers from these ratios due to their similarity, e.g. 9- and 10-methyl isomers. Mass spectroscopy was useful only in establishing whether the methyl branching occurred near the carboxyl or hydrocarbon end of the chain or near mid molecule.

The fragment ion ratios of the branched acids in the monomer fraction are shown in Table III. The fragment ion ratio of peak 5 confirmed the earlier GLC retention time data that this component was stearic acid. The fragment ion ratios for peak 2 and peak 3 were similar to the 9- and 10-methyl isomers. Therefore, these two chromatographic peaks were assumed to consist of mid chained methyl branched isomers. The ratios observed for peak 4 also suggested mid chain branching. None of the branched methyl isomers in the monomer had mass spectral fragmentation patterns similar to the (β) 3-methyl or (anteiso) 15-methyl isomers. GLC-MS data suggested that the monomethyl branched isomers in the monomer fraction were mid chain and not end chain isomers.

Dimer acids: The dimerization products from the clay catalyzed polymerization of oleic and elaidic acid mixtures were examined to determine the dimer structures present. The polymerization product of a TOFA mixture of oleic (52%) and linoleic (45%) acids also was examined to determine its dimer structure.

TABLE V

Trimer Content of Dimer Acids as Determined by Gel Permeation Chromatography

Fatty acid dimer	Percent trimer
Tall oil A	0
Tall oil B	3
Oleic	6
Elaidic	9

The molecular ion region of the mass spectrum can be used to determine the number of ring systems and double bonds present in dimer structures. From the fragmentation pattern of the mass spectrum, the length of the side chains attached to the ring systems can be determined.

Table IV summarizes the large number of ring and double bond structural combinations possible for C_{36} dimer methyl esters. Complete hydrogenation of the dimer acids greatly simplifies interpretation of the mass spectral data since each molecular ion is then representative of the ring system alone. For example, mass 590 could be attributed to 3 dimer structures in an unhydrogenated dimer. However, after hydrogenation, only a saturated bicyclic dimer structure is possible for mass 590. In this study mild palladium on carbon hydrogenation was used, which did not reduce any aromatic ring systems. Therefore, if aromatic monocyclic dimers were present with no aliphatic unsaturation, a molecular ion of 586 would be observed after mild hydrogenation. The presence of a noncyclic structure would show a molecular ion of 594 in the mass spectrum after hydrogenation. Saturated and aromatic monocyclic dimer structures would have mol wts of 592 and 586, respectively. The presence of any bicyclic structures would be represented by a molecular ion of 590.

An examination of the mass spectra of oleic dimer, elaidic dimer, and TOFA dimers before and after mild hydrogenation was made to determine the dimer structures present. Graphic representations of the dimer molecular ion regions of these dimers are compared in Figure 2 with those of clay catalyzed linoleic dimer (7).

The mass spectrum of clay catalyzed oleic dimer after hydrogenation revealed that significant amounts of noncyclic dimer structure (m/e 594) and monocyclic structure (m/e 592) were present. Some monocyclic aromatic dimer structure (m/e 586) also was present.

A comparison of the mass spectra of the hydrogenated and unhydrogenated oleic dimer revealed that appreciable amounts of aliphatic unsaturation were present in these dimer structures. These data indicated that clay catalyzed oleic dimer consisted chiefly of unsaturated noncyclic and monocyclic (alicyclic and aromatic) dimer structures.

A comparison of the dimer molecular ion region of the mass spectra of oleic and elaidic dimers revealed that no significant differences in dimer structural composition existed between products based upon *cis*- and *trans*-isomers. Therefore, the stereochemistry at the 9,10 double bond had no discernible effect upon the structural distribution of the dimers in the clay catalyzed polymerization reaction of the monoenoic acids.

An examination of the mass spectrum of clay catalyzed TOFA dimer after mild hydrogenation indicated that the saturated (m/e 592) and aromatic (m/e 586) monocyclic dimer structures were the major components present. Considerably smaller amounts of noncyclic dimer structures (m/e 594) were found in the TOFA dimer than in the oleic and elaidic dimers. Most of the noncyclic dimer structures present in the unhydrogenated oleic, elaidic, and TOFA dimers contain unsaturation.

The dimer molecular ion regions of clay catalyzed oleic, elaidic, and TOFA dimers were compared with those of thermal and clay catalyzed linoleic dimers. Only minor

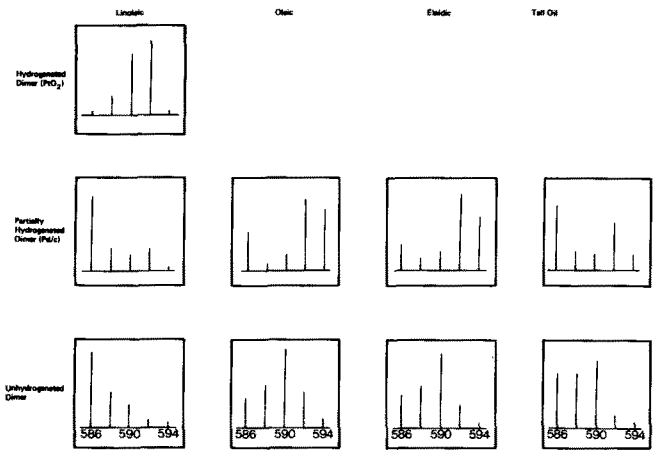

FIG. 2. Molecular ion region of mass spectra of clay catalyzed dimers.

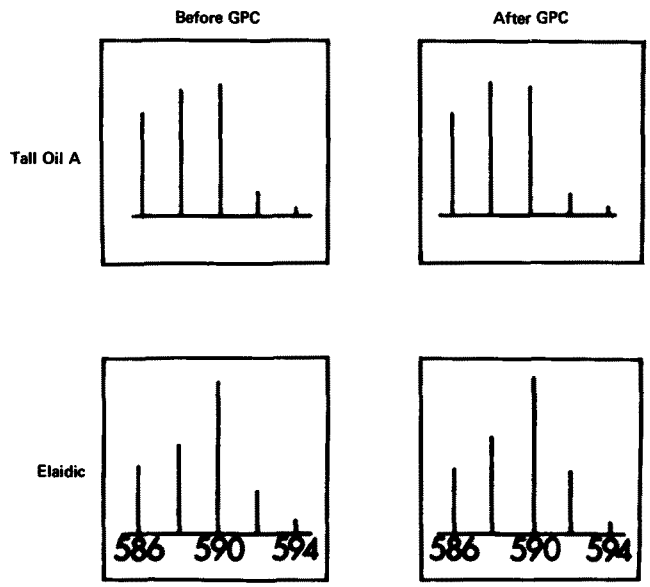

FIG. 3. Molecular ion region of mass spectra of clay catalyzed dimers before and after preparative gel permeation chromatographic (GPC) analysis.

amounts of noncyclic structures (m/e 594) were found in clay catalyzed TOFA and linoleic dimers, as well as thermal linoleic dimers (4). Only clay catalyzed oleic and elaidic dimers were found to contain any appreciable amounts of noncyclic dimer structures. Clay catalyzed linoleic dimer contained larger amounts of bicyclic structures than oleic and elaidic dimers.

The presence of trimers in the fatty acid dimer samples was thought to be a potential source of interference to the mass spectroscopic investigation of dimers. The fatty acid dimer samples did contain low levels of fatty acid trimers as shown in Table V. These trimer contents were determined as wt percentages by gel permeation chromatography.

To establish the effect of trimers upon the mass spectroscopic investigation of dimers, preparative isolation of pure dimers was carried out on a Sephadex LH-20 column, and the resulting trimer-free dimer fractions were examined by MS. A trimer-free production TOFA dimer (tall oil A) was examined before and after gel permeation chromatography to determine if any changes occurred in the molecular ion region distribution. No differences in the mass spectra were observed (Fig. 3). Similarly, a trimer-free dimer fraction was isolated from elaidic dimer. Again, the dimer molecular ion region distribution was unchanged by chromatographic separation (Fig. 3). The presence of up to

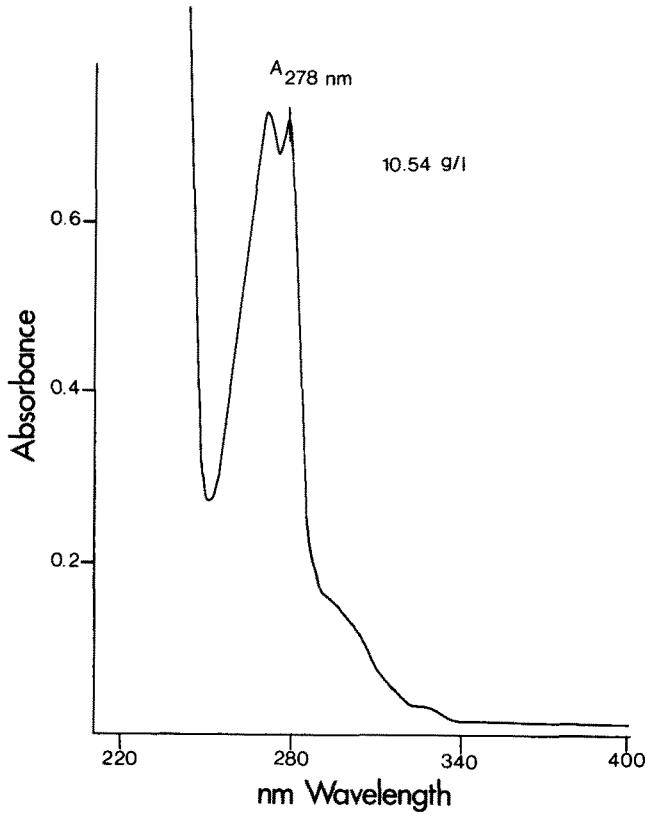

FIG. 4. UV spectra of hydrogenated clay catalyzed oleic dimer.

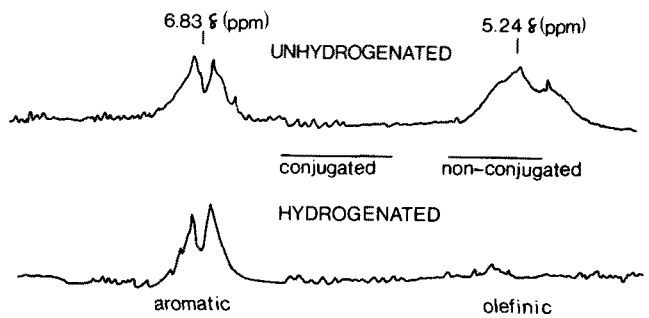

FIG. 5. Aromatic and olefinic protons in the NMR spectra of tall oil fatty acid dimer.

9% trimer did not interfere in the mass spectroscopic investigation. Thus, while gel permeation chromatography was effective in isolating trimer-free dimer acids, it was not necessary for reliable mass spectral data to be obtained when less than 9% trimer was present.

A striking feature of the clay catalyzed dimers was the presence of monocyclic aromatic structures as shown by the molecular ion at m/e 586. However, to confirm the presence of an aromatic monocyclic dimer structure, UV and NMR spectroscopic analyses were performed.

UV analysis of the hydrogenated oleic and TOFA dimers confirmed that aromatic monocyclic dimer structures were

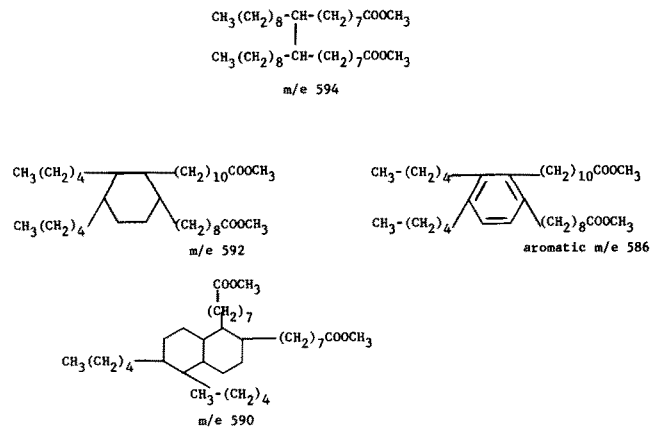

FIG. 6. Structures of saturated and aromatic fatty acid dimers as methyl esters.

present. The UV spectrum of hydrogenated oleic dimer is shown in Figure 4. Calculations were made from the UV spectrum to estimate the aromatic content of the dimer structures. These data are shown in Table VI. The unavailability of pure monocyclic aromatic dimers led to the choice of two tetramethyl benzenes as model compounds. The model compounds, like the proposed monocyclic aromatic dimers, are tetra substituted and should provide a reasonable estimate of the aromatic content of the dimer. The average molar absorptivity of 697 $\frac{\text{liters}}{\text{mole x cm}}$ at 278 nm was calculated from the literature spectra.

The aromatic dimer contents of the hydrogenated oleic and TOFA dimers were found to be 4 and 17%, respectively. Clay catalyzed linoleic dimer was calculated to contain 26% aromatic dimer after palladium on carbon hydrogenation. This content was calculated from the UV spectra obtained by Wheeler, et al., (7) and utilizing the molar absorptivity data from the tetramethyl benzene models. The latter was calculated for comparison purposes. The aromatic content of the unhydrogenated oleic and TOFA dimers could not be determined by UV spectroscopy due to the high background absorption present in these dimers.

NMR analyses were performed on the unhydrogenated oleic and TOFA dimers. The integrated intensities of the aromatic protons in the hydrogenated and unhydrogenated dimers were found to be similar using a spectrum amplitude of 80 (Fig. 5). It should be noted that the high spectrum amplitude was necessary to observe these protons, since they represent only a small portion of the total number present in these dimer structures. Since the aromatic proton intensities were similar before and after hydrogenation, the aromatic contents of the unhydrogenated dimers were concluded to be similar to those of the hydrogenated dimers.

No conjugated olefinic bonds existed in the unhydrogenated dimers as evidenced by the lack of protons in the 5.8-6.5 (δ) ppm region of the spectra. NMR also confirmed that the double bonds in the aliphatic side chains were reduced completely by the hydrogenation, since no olefinic protons appeared in the spectrum. The lack of conjugated

TABLE VI

Determination of Monocyclic Aromatic Dimer Content of Dimer Acids by UV Spectroscopy

Hydrogenated dimer	Absorbance 278 nm	Molar[a] concentration	Concentration aromatic[b] dimer g/liter	Total concentration g/liter	Percent aromatic dimer
Oleic	0.536	7.7×10^{-4}	0.43	10.54	4
Tall oil	0.232	3.3×10^{-4}	0.18	1.10	17

[a]Based upon the average molar absorptivity of 697 liters/mole x cm at 278 nm. Calculated from Sadtler reference UV spectra 355 and 6956.
[b]Based upon the mol wt of 558 for the monocyclic aromatic dimer acid.

double bonds in the unhydrogenated dimers also was confirmed by an examination of the conjugated diene region of the UV spectra.

The NMR splitting pattern of the aromatic protons in the TOFA dimer was an unresolved quartet. This would be expected for an AB spin pattern for adjacent protons in the proposed tetra substituted aromatic system (17). The relative intensities of the integrated aromatic protons indicated that the oleic dimer contained less aromatic content than the TOFA dimer. This was consistent with the UV data.

From the above characterization evidence, the six membered ring systems proposed by Wheeler, et al., (7) are the most plausible dimer structures for the clay catalyzed dimer acids. Figure 6 shows the proposed saturated and aromatic dimer structures present after hydrogenation. Mass spectral fragmentation ions found for oleic and TOFA dimers could be attributed to the proposed side chains on the rings of the dimer structures. The major mass spectral fragmentation ions in the 300-594 mass region of these dimers were similar to those previously reported for thermal linoleic dimers (4-6).

Ghodssi, et al., (8) proposed the presence of four membered ring dimer structures for BF_3 polymerized oleic acid. The multiplet in the 2.3 (δ) ppm region of the NMR spectrum of the BF_3 catalyzed oleic dimer was interpreted by Ghodssi as being indicative of a cyclobutyl ring system. However, the methylene protons α to the carboxylic acid also absorb in this region (18). For example, stearic and oleic acids contain peaks in this region, but their structures are linear. Therefore, the cyclobutyl ring system proposed by Ghodssi for oleic dimer structures is unlikely.

Evidence from this study verifies the presence of aromatic ring systems. The presence of the aromaticity indicates that six membered rings are present and suggests that the five membered ring structures proposed by Sen Gupta and Scharmann (5,6,9) are unlikely. Therefore, the structures proposed in Figure 6 are the most probable in these clay catalyzed dimers.

A comparison of mass spectral data obtained for thermal methyl oleate dimer (9) and clay catalyzed oleic acid dimer was made. Only monocyclic structures were reported for thermal oleate dimer, whereas clay catalyzed oleic dimer was found to contain chiefly acyclic and monocyclic structures.

In summary, the estimated contents of the dimer structures present in clay catalyzed oleic, elaidic, and TOFA dimers were compared with clay catalyzed linoleic dimer (7) and are shown in Table VII. The percent monocyclic aromatic dimer contents are the most reliable, since they are based upon UV analysis.

TABLE VII

Structural Composition of Clay Catalyzed Fatty Acid Dimers

Structure	Linoleic	Tall oil	Oleic and elaidic
Linear	5	15[a]	40[a]
Monocyclic-aromatic	25	20	5
Nonaromatic	30	50[a]	50[a]
Polycyclic	40	15[a]	5[a]

[a]Based upon uncalibrated mass spectral data.

The remaining contents are based upon uncalibrated mass spectral molecular ion intensities and are less reliable estimates due to the lack of mass spectral response data. As would be expected, the TOFA dimer, a product of the clay catalyzed polymerization of a 50% oleic and 45% linoleic acids mixture, was found to contain an estimated dimer structural content between that of linoleic and oleic-elaidic dimers.

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REFERENCES

1. Den Otter, M.J.A.M., Fette Seifen Anschrichm. 72:667 (1970).
2. Den Otter, M.J.A.M., Ibid. 72:875 (1970).
3. Den Otter, M.J.A.M., Ibid. 72:1056 (1970).
4. Wheeler, D.H., and J. White, JAOCS 44:298 (1967).
5. Sen Gupta, A.K., and H. Scharmann, Fette Seifen Anstrichm. 70:86 (1968).
6. Sen Gupta, A.K., and H. Scharmann, Ibid. 70:265 (1968).
7. Wheeler, D.H., A. Milum, and F. Lin, JAOCS 47:242 (1970).
8. Ghodssi, S.M.A., J. Petit, and H. Valot, Bull. Soc. Chim. Fr. 1461 (1970).
9. Sen Gupta, A.K., Fette Seifen Anstrichm. 69:907 (1967).
10. DeBaer, T.J., and H.J. Backer, Rec. Trav. Chim. 73:229 (1954).
11. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third Edition, AOCS, Champaign, Ill., 1964, Method Cd 14-61.
12. Harris, W.C., E.P. Crowell, and B.B. Burnett, JAOCS 50:537 (1973).
13. Ackman, R.G., J. Chromatog. Sci. 10:243 (1972).
14. Ryhage, R., and E. Stenhagen, Arkiv. Kemi. 15:291 (1960).
15. Campbell, I.M., and J. Naworal, J. Lipid Res. 10:589 (1969).
16. United Kingdom Atomic Energy Authority, "Mass Spectral Data Sheets," Nos. 3294-7, United Kingdom Atomic Energy Authority, Aldermaston, Reading, United Kingdom.
17. Bible, R.J., "Interpretation of NMR Spectra," Plenum Press, New York, pp. 82-4.
18. Frost, D.J., and J. Barzilay, Anal. Chem. 43:1317 (1971).

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