

Fig. 7. Simulated isotopic effect in an automatic manometric apparatus.

try is the requirement of continuous attendance—equilibrating levels, reading and recording. Not only does our new system automatically perform these operations, but it also obviates still another disadvantage of manometry, that of “dead” or uncirculated gas space. This restriction limits the applicability of the manometer for experiments involving gas exchange, such as oxygen and carbon dioxide in photosynthesis or isotopic exchange experiments involving hydrogen, deuterium and tritium gas (2). The use of a flow-through syringe eliminates this unmixed gas volume and mercury vapor contamination. In addition, eliminating the need for reading glass burets makes possible applications well above or below atmospheric pressures.

The circulating gas system also makes this arrangement amenable to monitoring procedures for radioactivity as illustrated here, or for mass spectrometry as previously described (2). A variety of other monitoring procedures may be suggested, such as paramagnetic oxygen analysis or abridged IR spectro-

photometry for carbon dioxide and other gases. To take advantage of the numerous monitoring possibilities, the equipment was made mobile by cart-mounting. This arrangement permits moving the system to special MS, GLC, radioactive or other laboratories. Also readily apparent are application to routine and repeated gas absorption investigations as are involved in evaluating catalysts for activity and selectivity (8).

Many components in the system may be fabricated in a local glass or metal shop. At present, the pressure sensor (Trans-Sonics, No. E2821) (5) must be purchased and is the most costly part of the automation due to its high sensitivity and miniaturization. However, simpler types are available (6) and are now being evaluated (3).

#### ACKNOWLEDGMENTS

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## Dimer Acid Structures. The Thermal Dimer of Methyl 10-*trans*, 12-*trans*, Linoleate<sup>1</sup>

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#### Abstract

Thermal dimerization of the conjugated 10-*trans*, 12-*trans* linoleate (250C, 5 hr) produced a dimer whose structure is shown to be that of the Diels-Alder reaction between two molecules of monomer, with one molecule acting as diene, and either one of the two double bonds of the second molecule acting as dieneophile. This produces four skeletal isomers of a tetrasubstituted (1,2,3,4) cyclohexene structure with  $\alpha$ - $\beta$  unsaturation on one chain. The isomers formed depend on whether the 10 or the 12 double bond acts as dieneophile, and whether the monomers add “head to head” or “head to tail.” Evidences for the structures include chemical analyses, ozonolysis, nuclear magnetic resonance, IR and UV spectrometry and particularly mass spectrometry of the distilled dimer, of the completely hydrogenated dimer, and of the aromatized dimer formed by catalytic dehydrogenation. The hydrogenated dimer can be separated into two components by TLC. These are probably related to “head to head” vs. “head to tail” addition.

#### Introduction

IT WAS PREVIOUSLY SHOWN (1) that the conjugated *trans* linoleate isomer, 10-*trans*, 12-*trans* linoleate was polymerized by heat at a much faster rate than normal 9-*cis*, 12-*cis*, linoleate, or alkali conjugated (9-*cis*, 11-*trans* plus 10-*trans*, 12-*cis*) linoleate. The reaction was second order, and the ratio of dimer to trimer was quite high, compared to other linoleate isomers.

It was suggested that the dimerization was a Diels-Alder addition, with one of the double bonds of one molecule acting as dieneophile, adding to the conjugated diene of the second molecule. The rapid rate of reaction of the *trans-trans* isomer was in accord with other data on 1,4 disubstituted 1,3 dienes. Four isomeric skeletal structures would be expected: (10 refers to the 10 double bond acting as dieneophile; A means that carboxy-containing groups are on adjacent carbons). Isomers due to *cis*, *trans* isomerism on the cyclohexene ring are also possible.

The present work is a further study of the structure of this dimer. It confirms the proposed cyclohexene structure expected from a Diels-Alder addition. The principal points in this structure proof are: 1) correct C & H analyses and mol wt; 2) mass spectrometry

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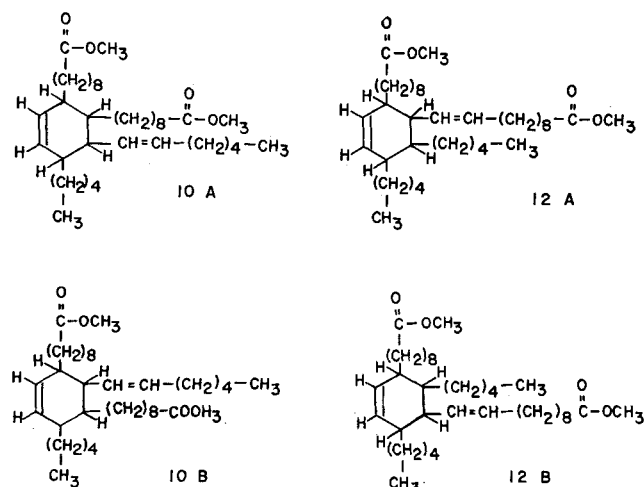


FIG. 1. Possible skeletal structures of dimers.

shows a single parent peak at theoretical mass of 588 for one ring and two double bonds; 3) mass spectrometry of the completely hydrogenated dimer shows a single parent peak at theoretical mass of 592 for one ring, no double bonds; 4) the unhydrogenated dimer shows a strong mass peak at  $M/2$  of 294, due to reversal of the Diels-Alder reaction under electron impact, as known for other adducts (2) whereas the hydrogenated dimer does not show any prominent peak at  $M/2$ , since it is no longer a Diels-Alder adduct as such; 5) the fragmentation patterns of both the unhydrogenated and the hydrogenated dimer are in agreement with structures of a Diels-Alder adduct; 6) ozonolysis of the distilled dimer gives hexaldehyde and the  $C_{10}$  aldehyde-ester as principal cleavage products; and 7) the dimers can be catalytically dehydrogenated to aromatic structures.

### Experimental

**Preparation of Distilled Dimer.** Methyl 10-*trans*, 12-*trans* linoleate was dimerized as previously described (1) using a 6-hr reaction time at 250C. The crude dimer was fractionally distilled in an alembic still (3) to give a main distilled dimer fraction which analyzed as follows: % C = 77.5; % H = 11.7 (Theory: % C = 77.5; % H = 11.7). Mol wt = 520 (vapor osmometer) (Theory = 588). % Monomer = 5.4. IR spectroscopy showed a typical spectrum of a

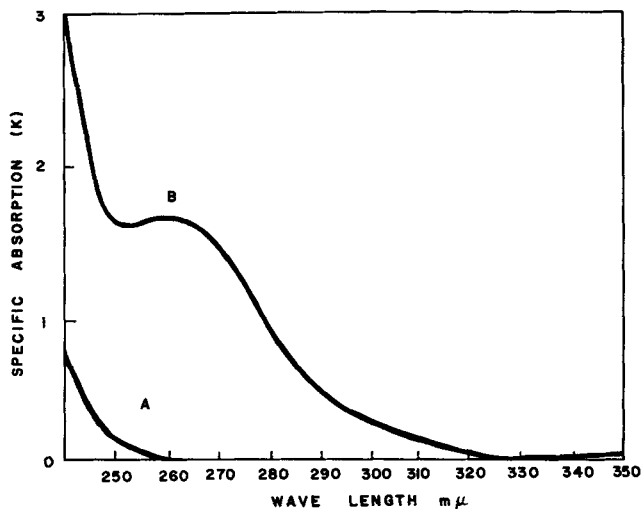


FIG. 2. UV absorption of dimers. A = Distilled Dimer. B = Dehydrogenated Dimer.

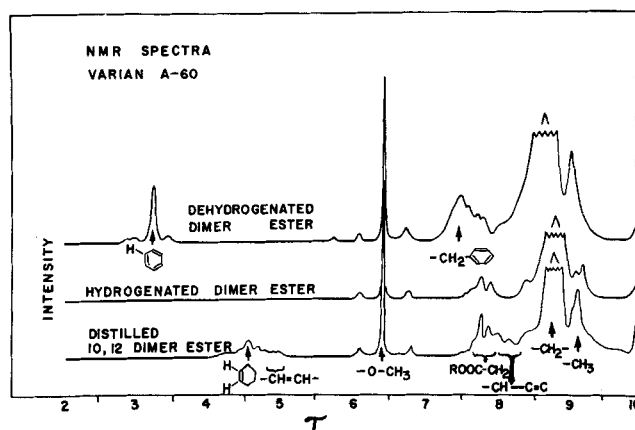


FIG. 3. NMR of dimers.

fatty methyl ester, with an isolated *trans* double bond peak at 10.27  $\mu$  (slightly shifted from the usual 10.32  $\mu$ ) whose intensity was ca. 36% of elaidate. A very weak band at 6.00  $\mu$  due to C=C stretching, and a very weak band at 10.32  $\mu$  due to *cis* unsaturation were also seen. UV spectroscopy showed virtually no absorption in the aromatic region (Fig. 2).

**Hydrogenation of Distilled Dimer.** The distilled dimer (2 g) was hydrogenated in glacial acetic acid (5 cc) with PtO<sub>2</sub> catalyst (1.0 g) at 150C and 1000 psi for 34 hr. The hydrogenated ester was recovered by dilution with CHCl<sub>3</sub>, filtering from catalyst and evaporation. Since IR analysis indicated considerable free acid (acidolysis by acetic acid), the product was re-esterified with methanol plus H<sub>2</sub>SO<sub>4</sub> catalyst. The recovered ester (80% recovery) showed no free carboxyl by IR analysis. Iodine value was 0.1. % C = 77.5; % H = 12.3 (Theory: % C = 77.0; % H = 12.2). % Monomer = 0.4. Mol wt = 544 (vapor osmometer) (Theory = 592).

**Dehydrogenation of Distilled Dimer.** To distilled dimer (0.46 g) was added 0.10 g 10% Pd on charcoal (Baker) in a small flask equipped for bubbling with CO<sub>2</sub> and collecting the evolved gas over 50% aqueous KOH. The flask was heated to 280C in an air bath while bubbling with CO<sub>2</sub>. The evolution of gas decreased from 0.27 cc/min at the beginning to 0.03 cc/min at the end of five hr, when heating was stopped. The product was recovered by dissolving in CHCl<sub>3</sub>, filtering and evaporating to give a 74% wt recovery of the dimer ester. The evolved gas, collected over 50% KOH was equivalent to 1.4 moles/mole of dimer. However, mass spectrometry of the gas indicated only 31% hydrogen, the remainder being largely methane, presumably formed by hydrogenolysis of the COOCH<sub>3</sub> group which was lost to a considerable extent (ca. 38%) according to IR spectrometry. IR also indicated that the dehydrogenated dimer had lost essentially all of the *trans* unsaturation (10.27 or 10.34  $\mu$ ) and *cis* unsaturation (3.32), and that poly-substituted benzene (12.17  $\mu$ ) structure had been formed, either 1,4 or 1,2,3,4.

UV absorption in the aromatic region was greatly increased, to  $k_{262\mu} = 1.7$  or  $\epsilon = 996$  for mol wt of 586 (Fig. 2). This appears somewhat high for an aromatic C<sub>36</sub> ester, but suitable standards are not available, and background absorption was not subtracted. Mass spectrometry also indicated aromatization (cf. below).

**Ozonolyses of Distilled Dimer.** Through the courtesy of Orville Privett of The Hormel Institute, the double bond positions of side chains of the unhydrogenated dimer ester were determined by them, with

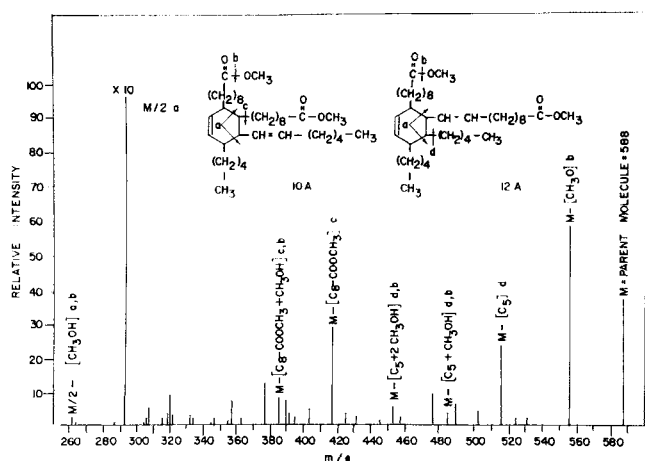


FIG. 4. Mass spectrum of distilled dimer.

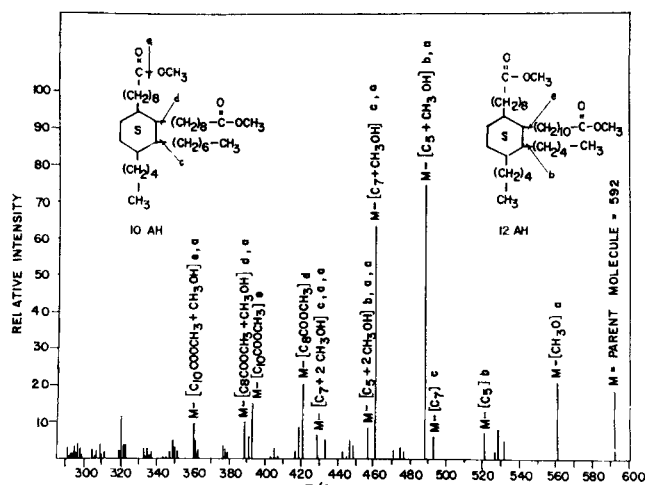


FIG. 5. Mass spectrum of hydrogenated dimer.

their method of quantitative ozonization, reductive cleavage and GLC analysis of the resulting aldehydes and aldehyde esters (4). They reported that the expected  $C_6$  aldehyde and the  $C_{10}$  aldehyde ester were the highly predominant products of cleavage, observed in the molar ratio of 1.15 (hexaldehyde) to 1.0 ( $C_{10}$  aldehyde ester), confirming the double bond positions expected for the proposed Diels-Alder structures.

**Nuclear Magnetic Resonance of Dimers.** The NMR spectra of the dimers (Fig. 3) agreed well with the postulated structures. The distilled, unhydrogenated dimer showed bands corresponding to hydrogens on ring double bonds as well as non-cyclic double bonds, and also showed  $CH_2$ 's adjacent to double bonds. The hydrogenated dimer showed no bands related to double bonds. The dehydrogenated dimer showed bands corresponding to aromatic hydrogens as well as  $CH_2$ 's attached to an aromatic ring.

**Mass Spectrometry of Distilled Dimer.** Mass spectra were determined as previously reported (5). The significant portion of the spectrum of the distilled dimer is shown in Figure 4.

The parent peak at  $m/e = 588$  corresponds to the expected  $C_{36}$  dimer structure with two double bonds and one ring.

The base peak is at 294 or  $1/2\%$  of the mass of the parent molecule. This strongest peak presumably results from reversal of the Diels-Alder addition (2c), under electron impact as is seen with both butadiene and isoprene dimers (2a,2b). This peak is so strong that it would have to be multiplied by 10 to be on the same scale as the other peaks shown. Weak peaks at  $M/2 - CH_3O = 263$  and  $M/2 - [CH_3OH + H] = 262$  are related to this same mode of cleavage. The peak at  $M - CH_3O$  ( $m/e = 557$ ) is quite prominent, but not of direct diagnostic value.

Peaks related to loss of the saturated  $C_5H_{11}$  side chains are: 1)  $M - C_5H_{11} = 517$ ; 2)  $M - (C_5H_{11} + CH_3OH) = 485$ ; and 3)  $M - (C_5H_{11} + 2CH_3OH) = 453$ .

Peaks related to loss of the saturated side chain  $(CH_2)_8COOCH_3$  are: 1)  $M - C_8H_{16}COOCH_3 = 417$ ; and 2)  $M - (C_8H_{16}COOCH_3 + CH_3OH) = 385$ .

A weak peak related to loss of the unsaturated  $-CH=CH-(CH_2)_4CH_3$  side-chain is at  $M - (C_7H_{13} + H) = 490$  is seen.

A weak peak related to loss of the unsaturated  $-CH=CH-(CH_2)_8COOCH_3$  side-chain is at  $M - [C_{10}H_{18}COOCH_3 + H] = 390$  is seen.

Some weak peaks were observed which correspond to elimination of each of the side chains plus the ring

carbon to which they are attached. While double cleavage to eliminate a ring carbon is not generally a favored mode of cleavage, the bonds involved in this case are all to tertiary carbons, and at least one of the two bonds is to an allylic carbon ( $\beta$  to the double bond) which often favors cleavage: 1)  $M - [CH - CH=CH - (CH_2)_4 - CH_3 + H] = 477$ ; 2)  $M - [CH - CH=CH - (CH_2)_8COOCH_3 + H] = 377$ ; 3)  $M - [CH - (CH_2)_4 - CH_3 + H] = 503$ ; and 4)  $M - [CH - (C_2H)_8COOCH_3 + H] = 403$ .

The spectrum below 294 was not of much diagnostic value. The peak at  $m/e = 74$ , usually seen in non- $\alpha$ -substituted esters was present but while it was only at 17% of the intensity the  $M/2$  parent peak, it was rather strong compared to most other peaks. The remainder of the spectrum below 294 contained many peaks corresponding to alkane, carboxymethyl alkane, alkene and carboxy methyl alkene fragments.

**Mass Spectrometry of Hydrogenated Dimer.** The significant portion of the mass spectrum of the hydrogenated dimer ester is shown in Figure 5.

The parent peak  $M$  at  $m/e = 592$  (18% of base peak 74) is correct for a saturated monocyclic  $C_{36}$  dibasic ester.

The base peak of  $m/e = 74$  is the strongest peak, as is often the case with non- $\alpha$ -substituted saturated aliphatic esters which do not have other points of highly preferred cleavage.

In contrast to the unhydrogenated dimer, there is no peak of any prominence at  $M/2 = 296$  or near it.

Peaks corresponding to loss of  $C_5H_{11}$  are: 1)  $M - C_5H_{11} = 521$ ; 2)  $M - (C_5H_{11} + CH_3OH) = 489$ ; and 3)  $M - (C_5H_{11} + 2CH_2OH) = 457$ .

Peaks corresponding to loss of  $C_7H_{15}$  are: 1)  $M - C_7H_{15} = 493$ ; 2)  $M - (C_7H_{15} + CH_3OH) = 461$ ; and 3)  $M - C_7H_{15} + 2CH_3OH) = 429$ .

Peaks corresponding to loss of  $(CH_2)_8COOCH_3$  are: 1)  $M - (CH_2)_8COOCH_3 = 421$ ; and 2)  $M - [(CH_2)_8COOCH_3 + CH_3OH] = 389$ .

Peaks corresponding to loss of  $(CH_2)_{10}COOCH_3$  are: 1)  $M - (CH_2)_{10}COOCH_3 = 393$ ; and 2)  $M - [(CH_2)_{10}COOCH_3 + CH_3OH] = 361$ .

**Mass Spectrometry of Dehydrogenated Dimer.** The dehydrogenated dimer showed a parent peak at  $m/e = 586$ , corresponding to a  $C_{36}$  dibasic ester with one benzene ring. This was very strong compared to other  $C_{36}$  parent peaks. The peak at  $m/e = 588$  of the original dimer ester was essentially absent. A strong peak at 528 was observed. This is probably the parent peak of a dimer molecule in which a  $COOCH_3$  group has

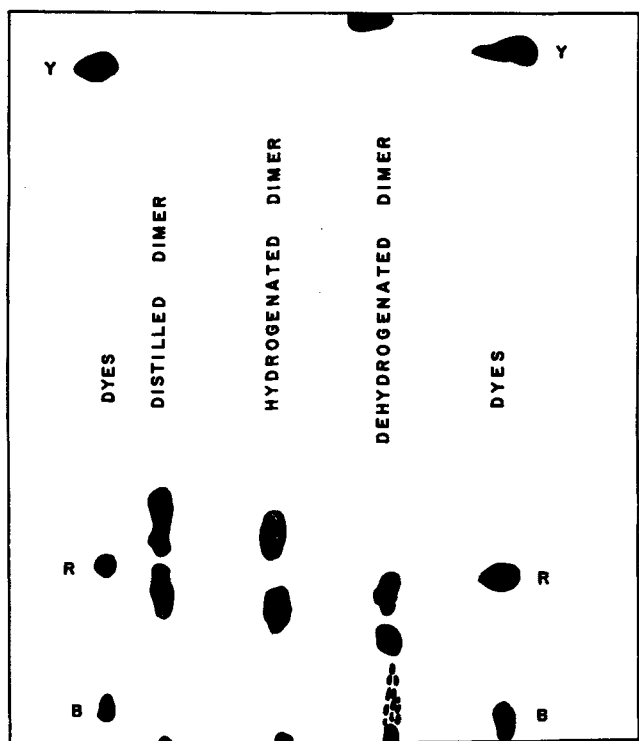


FIG. 6. TLC of dimers.

been replaced by H, since IR analysis indicated a 38% loss of ester C=O.

**Thin Layer Chromatography of Dimers.** The hydrogenated dimer (as well as the original dimer and the dehydrogenated dimer) could be separated into two distinct spots by TLC on neutral Silica gel G with benzene as the ascending developing solvent (Fig. 6).

The slower moving spot of the hydrogenated dimer moved at ca. the same rate as Sudan red G dye. The amt of travel and separation was increased by partially opening the top of the developing jar to cause evaporation at the solvent front. With the red dye as a monitor, a multiple-spotted plate was thus developed until the red dye was at 50–60 mm height. Spraying of a section with dichlorofluorescein showed a slow-moving dimer spot at 45–68 mm and a faster-moving dimer spot at 70–90 mm, each of ca. equal size. The slow moving and fast-moving components were separately recovered from the removed SiO<sub>2</sub> by extraction with methanol for examination by mass spectrometry. The two fractions showed mass spectra essentially identical with one another and with the unfractionated dimer ester.

The two dimer spots from TLC of the dehydrogenated dimer were similarly recovered separately and examined by mass spectrometry. In both samples, the peak at  $m/e = 586$  was the highly predominant dimer peak (a peak at  $m/e = 592$ , ca. 5–10% of 586, and one at  $m/e = 576$ , ca. 3% of 586 were the only other resolved peaks in the dimer region). The peak at  $m/e = 528$ , corresponding to replacement of COOCH<sub>3</sub> with H, was very weak on these samples (2% or less of 586), in contrast with the original dehydrogenated dimer, where it was ca. three times as intense as the peak at  $m/e = 586$ . Apparently, dehydrogenation caused many side-reaction, as evidenced by loss of COOCH<sub>3</sub>, and as indicated by TLC spots at the solvent front and at the base-line with streaking above the base-line. However, the mass spectra of the original dehydrogenated dimer and of the TLC fractions do indicate that dehydrogenation to a substituted

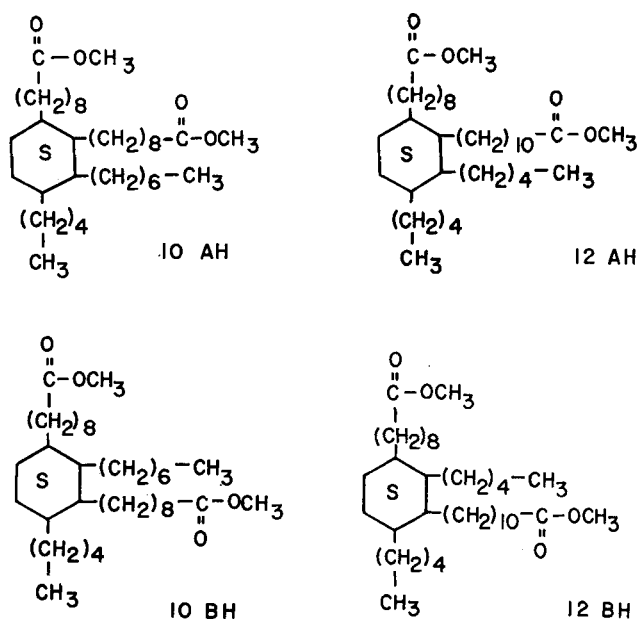


FIG. 7. Possible skeletal structures of hydrogenated dimers.

benzene occurred, that some of this dehydrogenated dimer came through unscathed, and was separated by TLC into two fractions.

### Discussion

Chemical analyses, ozonolysis, NMR and mass spectrometric data in particular confirm the structure of the thermal dimer of methyl 10-*trans*, 12-*trans* linoleate to be that of a Diel-Alder adduct with one molecule acting as diene and one of the double bonds of the second molecule acting as dieneophile, to give a tetrasubstituted cyclohexene structure with a double bond in the  $\alpha$ - $\beta$  position to the ring. Hydrogenation to the saturated one-ring structures, and dehydrogenation to the tetrasubstituted benzene structures further confirm the proposed structures.

The hydrogenated forms of the four postulated skeletal isomers are shown in Figure 7.

If one assumes that these four isomers are formed in equal quantities, the ratio of C<sub>5</sub> alkyl to C<sub>7</sub> alkyl groups is 6 to 2, and the ratio of (CH<sub>2</sub>)<sub>8</sub>COOCH<sub>3</sub> to (CH<sub>2</sub>)<sub>10</sub>COOCH<sub>3</sub> groups is also 6 to 2. One might expect peaks proportional to the relative amounts of the groups. However in the mass spectra, the peaks related to loss of C<sub>5</sub> alkyl are only slightly higher than those related to loss of C<sub>7</sub> alkyl, and the same relation is true of (CH<sub>2</sub>)<sub>8</sub>COOCH<sub>3</sub> vs. (CH<sub>2</sub>)<sub>10</sub>COOCH<sub>3</sub>. If one assumes that groups in the "crowded" 2,3 positions are much more easily eliminated than those in the "flanking" 1,4 positions, then the observed intensities are close to expectations, since the ratio of C<sub>5</sub> to C<sub>7</sub> alkyl and of (CH<sub>2</sub>)<sub>8</sub>COOCH<sub>3</sub> to (CH<sub>2</sub>)<sub>10</sub>COOCH<sub>3</sub> in the 2,3 positions is 2:2 in each case. Synthesis of a suitable pure reference compound to verify this speculation would be interesting.

Since these dimers could be separated by TLC into two distinct spots instead of one elongated spot for most dimers, we offer the following speculation about their possible structures. On the basis of the proposed structures, the following pairs of structural types could account for the two separate species observed by TLC of the hydrogenated dimers: 1) "head to head" or adjacent, 1,2- RCOOCH<sub>3</sub> chains vs. the 1,3- position (10AH + 12AH) vs. (10BH + 12BH); 2)  $\Delta$ 10 vs.  $\Delta$ 12 acting as dieneophile, (10AH + 10BH)

vs. (12AH + 12BH); and 3) *cis*, *trans* isomers of the cyclohexane ring substituents.

The second possibility,  $\Delta 10$  vs.  $\Delta 12$  as dieneophile can be eliminated because of the identity of the mass spectra of the two fractions and the original material, since  $\Delta 10$  as dieneophile would give *no*  $-(\text{CH}_2)_{10}\text{COOCH}_3$  group, while  $\Delta 12$  as dieneophile would give *no*  $-(\text{CH}_2)_6\text{CH}_3$  groups on the cyclohexane ring. Since both of these groups were found in the same amt in both fractions and original dimers, this explanation is untenable.

The third explanation (*cis*, *trans* isomers) cannot be disregarded, but appears less attractive than the first because *cis*, *trans* equilibration with respect to the cyclohexane ring appears possible in view of the conditions of polymerization and hydrogenation. If this occurred, one would expect that the predominant forms would be those with the least steric interference of groups, namely the all-equatorial, tetrasubstituted chair form of the cyclohexane ring (with adjacent groups *trans* to one another). Further, if the same structural feature is responsible for separa-

tion of the dehydrogenated dimer into two spots, then it cannot be *cis*, *trans* isomerism, since substituents on benzene cannot have *cis* or *trans* relationships.

By elimination, the first explanation, "head to head,"  $\alpha$ - or 1,2 adjacent positions of  $-\text{RCOOCH}_3$  groups vs. "head to tail,"  $\beta$ - or 1,3 positions appears to be correct for the structures of dimers in the separated spots.

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## Preparation of Partial Glycerides by Direct Esterification<sup>1</sup>

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### Abstract

A previously described procedure for the direct esterification of diglycerides without interesterification occurring has been evaluated for the preparation of mono- and diglycerides. The esterifications were accomplished with *p*-toluenesulfonic acid catalyst and with continuous removal of water of esterification by azeotropic distillation. The effect of such variables as unsaturation, chain length, mode of addition of solvent and reaction temp on the composition and yield of glycerides was observed. Chemical and chromatographic analyses were used to determine the composition of the glycerides and their component fatty acids and to detect the presence of isomeric glycerides. Simple esterification of 1-monostearin with oleic acid at 80C yielded as much as 72.3% diglycerides, and esterification of glycerol with stearic acid at 100C yielded up to 70.1% monoglycerides, each calculated on a glyceride basis. It is concluded that simple esterification predominates with some intra- and interesterification occurring.

### Introduction

MONO- AND DIGLYCERIDES are usually prepared by the reaction of fat or fatty acids with glycerol in the presence of an alkaline catalyst (6,7,13). The reaction products at equilibrium are a mixture of free glycerol and mono-, di- and triglycerides, relative proportions of which can be calculated, for practical purposes, on the assumption that the esterified hydroxyl groups are distributed in a random manner among all the available hydroxyl groups (8). Even though the primary and secondary hydroxyl groups in glycerol have different activities (4,5), the calculated compo-

sitions are in reasonably good agreement with the experimental data.

The monoglyceride content of reaction products made commercially from  $\text{C}_{16}$ - $\text{C}_{18}$  fatty acid oils without benefit of molecular distillation usually does not exceed 60% by wt, calculated on a total glyceride basis. This percentage is set by the proportion of glycerol miscible with the glycerides at the max permissible temp, ca. 250C. Even with short reaction times at these temp, some polyglycerols and other undesirable byproducts form. The max percentage of diglycerides which can be formed by the random interesterification of  $\text{C}_{16}$ - $\text{C}_{18}$  fatty acid oils is ca. 49%, calculated on the total wt of glycerides (8).

Commercially, monoglyceride products of over 90% purity are prepared by molecular distillation. Diglyceride products can be prepared in a similar manner. Monoglyceride products of high purity also might be prepared by fractional crystallization from solvents (9).

Since the time of Berthelot (3), many investigations of the preparation of mono- and diglycerides by esterification and interesterification have been conducted. The highest yields of monoglycerides prepared by interesterification have been obtained by the use of a mutual solvent for glycerides and glycerol (16,17,24, 25). On interesterifying in a pyridine solution one part by wt of hydrogenated soybean oil with one part of glycerol, Mattil and Sims (20) obtained 78% monoglycerides, calculated on a glyceride basis. Franzke and Kretzschman (11) reported monoglyceride yields up to 90% by the catalytic glycerolysis of natural fats in pyridine solution.

The preparation of mono- and diglycerides by direct esterification has not been a preferred process because it was generally concluded that esterification was always accompanied by interesterification, which includes acidolysis, alcoholysis and ester interchange,

<sup>1</sup> Presented at the AOCs Meeting, Toronto, 1962.

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