TABLE II

Physical Constants and Chemical Characteristics of Pistacia Seed Oil
(Mean values of 12 samples of each species)

Determination	*P. Terebinthus L.*			*P. Lentiscus L.*		
	Max	Mean	Min	Max	Mean	Min
Specific gravity at 25C	0.9141	0.9115	0.9081	0.9165	0.9094	0.9023
Refractive Index at 40C	1.4627	1.4619	1.4619	1.4631	1.4622	1.4613
Free fatty acid %	18.3	6.5	2.2	17.3	9.7	2.1
Unsaponifiable matter %	0.75	0.66	0.60	0.88	0.79	0.70
Saponification value	195.1	192.3	191.8	193.5	193.4	193.3
I.V. (Hanus)	90.2	89.2	88.7	88.9	87.2	85.5
Thiocyanogen value	70.5	69.9	69.3	69.5	69.4	69.3
Titer of fatty acids (°C)	27.2	26.9	26.7	30.8	30.3	30.1
Saponification value of fatty acids	202.5	202.2	202.0	202.3	202.0	201.4
Avg mol wt of fatty acids	277.7	277.4	277.0	278.6	277.8	277.3
Glycerides composition %						
Olein	58.8	56.3	53.4	60.9	57.7	55.5
Linolein	24.8	23.6	22.7	23.8	21.7	19.6
Saturated and unsaponifiable	21.7	20.1	18.1	20.7	20.6	19.5

TABLE III

Composition of Pistacia oil in hypothetically pure triglycerides

Sample No.	1		2	
Method	Cd 7-58	Cd 2-38	Cd 7-58	Cd 2-38
Linolenin	0.2		0.3	
Linolein	24.2	24.4	23.4	23.3
Olein	53.7	54.1	54.9	56.2
Saturated and unsaponifiable	21.9	21.5	21.4	20.5

As the chemical characteristics of the oils analysed show, the Greek Pistacia oils have the same composition as those reported from other areas.

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

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Abstract

Previous work by Sutton, and by Harrison, McCaleb and Wheeler has shown that methyl stearate is converted to dimers plus higher polymers by the action of di-*t*-butyl peroxide. The latter suggested that in the dimer, there was considerable linkage at carbon 2, the carbon α- to the $COOCH_3$ group, since the dimer ester was incompletely saponified by the usual procedures.

Further proof of α-linkage is now presented. A fraction which is predominantly α-,α'-linked dimer was isolated as the nonpolymeric cyclic anhydride (α-,α'-dicetyl succinic anhydride) by molecular distillation from the linear polymeric non-α-linked polyanhydride. The isolated cyclic anhydride appeared identical with a synthetic α-,α'-dicetyl succinic anhydride, whose synthesis is described.

The original dimer ester, the α-,α'-cyclic anhydride fraction, and the dimethyl ester derived from it, were examined by mass spectrometry. The expected mol wt were confirmed by the parent ion peaks. Fragmentation patterns indicated appreciable α-linkage in the original dimer ester, and almost exclusive α-linkage in the ester from the isolated cyclic anhydride. Aside from preference for the α-position, joining appears to be randomly distributed.

Introduction

THE DIMERIZATION of methyl oleate by the action of di-*t*-butyl peroxide (dehydro-dimerization) has been studied (1), and the dimer structure was shown to be predominantly the result of joining of two moles of methyl oleate at carbons 8,9,10 and 11, with a small amt (5–10%) of joining at the 2 position (α- to $COOCH_3$). The mechanism was considered to be that of hydrogen abstraction by the *t*-butoxy radical from the CH_2's at carbon 8 and carbon 11 adjacent to the double bond, followed by coupling of the free radicals at C_8 and C_{11}, as well as the limiting resonance forms with free radicals at C_{10} and C_9. The dimerization was essentially stoichiometric, one mole of dimer resulting from one mole of di-*t*-butyl peroxide and producing 2 moles of *t*-butanol. The ratio of dimer to higher polymers was rather high (3:1).

The dimerization of methyl linoleate (2,3) and methyl linoelaidate (2) by di-*t*-butyl peroxide has also been studied. The dimer, which contained 4 double bonds, showed considerable amt (ca. 50%) of conjugated dimer. This was explained as resulting from coupling of limiting (conjugated) resonance forms of the free radicals resulting from hydrogen extraction from the active CH_2 at C_{11} between the two double bonds at C_9 and C_{12}.

Dehydrodimerization of methyl stearate has also been reported by Sutton (3), but no structural evidence was given.

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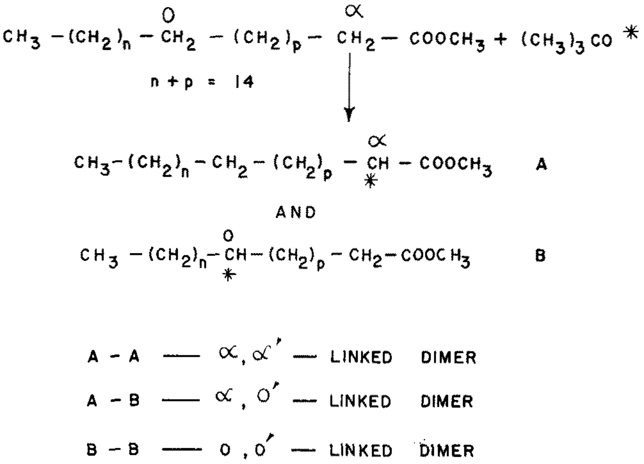


FIG. 1. Dehydrostearate dimer formation. Types of structures.

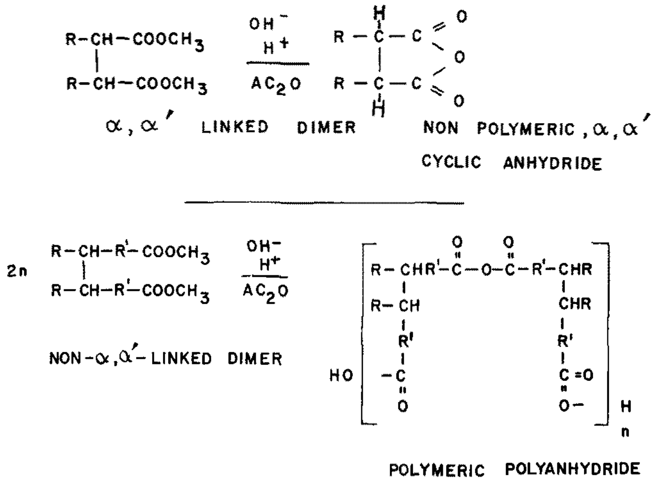


FIG. 2. Formation of polymeric and non-polymeric anhydrides of dehydrostearic acids.

Harrison et al. (4) also reported on the dehydrodimerization of methyl stearate. They noted that the dimer gave a low saponification value, ca. 30% below theory, by the usual method (which gave nearly theoretical values on the dehydrodimer of oleate or linoleate).

They suggested that this was due to an unknown amt of monomer segments linked in the 2 or α-(to $COOCH_3$) position.

The present study presents additional evidence of α-linkage, by mass spectrometry of the distilled dimer and of an isolated fraction of the dimer in which both monomer segments are α-linked. This fraction was isolated by converting the free dimer acids to anhydrides. The α-,α′-linked dimer, being a disubstituted succinic acid, readily formed a non-polymeric cyclic anhydride, while the dimers with linking farther down the chain readily formed linear polymeric anhydrides. Molecular distillation and fractional crystallization of the distillate gave the expected α-,α′-dicetyl succinic anhydride, whose melting point was not depressed by a synthetic product, the synthesis of which is described. Mass spectrometry of the methyl ester derived from the isolated cyclic anhydride fraction compared to the original dehydrodimer showed greatly enhanced peaks related to α-linkage and greatly reduced peaks related to non-α-linkage. Linkage other than α- was apparently random.

Experimental

The dehydrodimer of methyl stearate was that previously reported (4) made by reaction of methyl stearate and di-*t*-butyl peroxide (12 mole %) at 130C for 15 hr. The dimer was separated from monomer and higher polymers by molecular distillation in a cyclic molecular still, distilling at a rotor temp of 150–163C. $\eta_D^{30} = 1.4520$; % C = 76.9; % H = 12.58. Theory, % C = 76.7; % H = 12.54. Sap. value (6) = 133.1. Theory = 188.7.

Isolation of α-,α′-Dicetyl Succinic Anhydride. A 6.5-g portion of the distilled dimer was saponified for 2 hr at 235C with 4.5 x theory of a 10% KOH solution in diethylene glycol. The product was diluted with 2 vol of 50% ethanol, acidified with excess 6N HCl and extracted with ether (2 x 100 cc) and Skelly C (5 x 100 cc). The combined extracts were washed free of HCl, dried over Drierite and solvent removed, finally under water pump vacuum on the steam bath.

IR scan of the products indicated the presence of cyclic anhydride (peaks at 5.57 μ and 5.32 μ), free acid (5.8 μ) and noncyclic or open-chain anhydride (5.73 μ). The product was refluxed with acetic anhydride (5 g/g product) for 4 hr and recovered by stripping off the acetic anhydride under vacuum. IR still indicated a mixture of anhydrides and some free acid. Ca. 0.5 g was distilled in a micromolecular still (5) at 3–6 μ pressure, collecting the fraction which distilled at 190–250C block temp as cyclic dimer anhydride. This fraction was recrystallized twice from Skelly B to give 50 mg of a product mp 49.5–50.8C. This product showed the expected IR bands for a cyclic anhydride (5.32 μ and 5.57 μ) and was free of non-cyclic anhydride (5.73 μ) or free acid (5.8 μ). Its IR curve was essentially identical with that of a synthetic α-,α′-dicetyl succinic anhydride, and mixed melting points showed no depression.

Methyl Ester from Cyclic Anhydride Fraction of Dehydrodimer of Methyl Stearate. A 4-mg sample of the distilled presumably cyclic anhydride was sealed in a glass ampule with 2 cc methanol and 0.1 mg *p*-toluene sulfonic acid and heated in a steam bath for 48 hr. The methyl ester (3.9 mg) was isolated by crystallization from methanol at −10C. It melted at 57–9C. IR analysis confirmed the presence of methyl ester and the absence of acid and anhydride structures.

Synthetic α-,α′-Dicetyl Succinic Anhydride. The synthesis was by coupling of diethyl bromocetyl malonate with diethyl sodiocetyl malonate, saponification, decarboxylation of the bis-malonic acid and dehydration of the disubstituted succinic acid to the anhydride. Diethyl cetylmalonate made according to Organic Syntheses (7) was converted to the bromoderivative by bromination in 3 parts of CCl_4 with 100% excess bromine for nine hr on a steam bath. The product, recovered by stripping off solvent, HBr and excess bromine analyzed 15.5% Br (Theory = 16.9% Br).

Sodiomalonate was made from diethyl cetylmalonate (16 g 0.041 mole) by reaction with a solution of 1.0 g (0.043 mole) of sodium in 23 g absolute methanol and distilling off excess methanol. To the sodio derivative, 18 g (0.042 mole) of the diethyl bromo cetyl malonate was added. The mixture was stirred for 1.5 hr, let stand for 15 hr and then filtered from the NaBr with added filter aid. Yield was 28 g ester (89% theory).

This ester was saponified by heating 20 g (0.027 mole) with 10 g (0.18 mole) KOH in 100 cc diethylene glycol at 230–240C for 4.5 hr. The mixture was cooled to 50C, poured into 1 liter warm water and acidified with excess dilute H_2SO_4. Product was extracted with

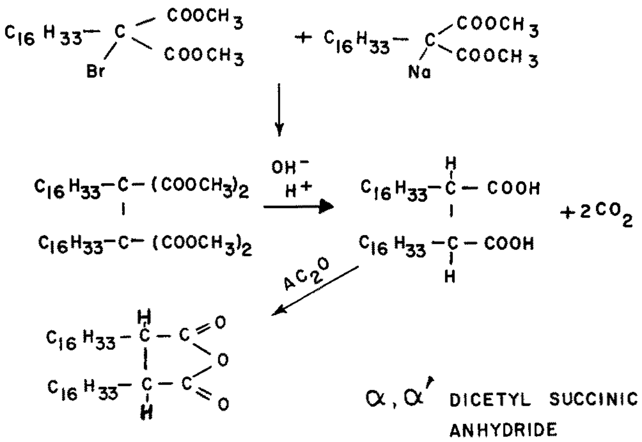


FIG. 3. Outline of synthesis of α-,α′-dicetyl succinic anhydride.

Skelly B and recovered by evaporation to give 13.2 gm residue which was stripped at 205–211C at 1 mm. The distillate (8 g) proved to be stearic acid. The residue was 4 g. One gram of this residue was distilled in the micromolecular still to give 0.3 g distilling in the C_{36} temp range (235–244C block temp). This was crystallized from Skelly B to give a product which melted at 44.8–49.5C which did not depress the mp of the cyclic anhydride derived from the dehydrodimer of methyl stearate. IR spectra of the two products were identical, except that the synthetic product showed a slight amount of free acid which might account for its slightly lower melting range.

Mass Spectrometry of Dimers. Mass spectra of the distilled dehydro-stearate dimer ester, the cyclic anhydride fraction derived from it and the methyl ester made from the cyclic anhydride were determined with a Consolidated Eng. Model 21-103-C mass spectrometer equipped with an all glass, high temp inlet, as previously described (1,8).

Mass spectrum of distilled dimer ester from M/e = 260–600 is shown in Figure 4. The parent peak at M/e = 594 is correct for a C_{36} saturated non-ring dimer.

The fact that cleavage occurs readily at branched carbons (9) was most useful in interpreting the mass spectra. Peaks indicating a generally branched structure are: 1) M/2 = 297 and M/2 + 1 = 298, corresponding to cleavage between the tertiary carbons which join the two monomer segments (whether at an α- or other position). With the M/2 + 1 peak (hydrogen transfer) taken as the base peak, the M/2 peak is about 60% as intense; and 2) $M/2-CH_3OH$ = 266 corresponds to the same cleavage with simultaneous cleavage of methoxy group.

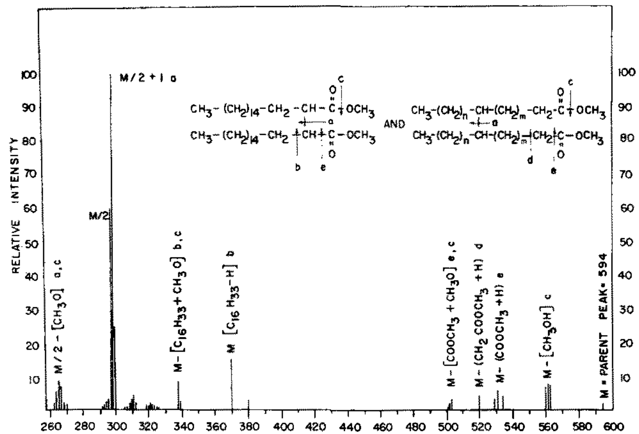


FIG. 4. Mass spectrum of distilled dehydrostearate dimer.

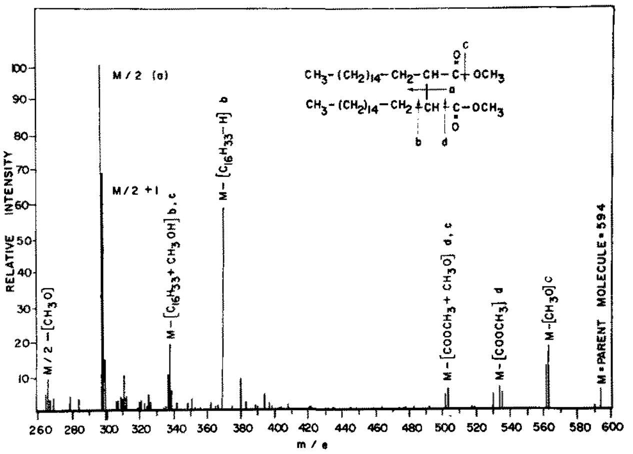


FIG. 5. Mass spectrum of dimer ester from cyclic anhydride.

Peaks which indicate α-branching or linking of monomer segments are: 1) $M-[C_{16}H_{33}-H] = 370$. This peak, and 2) the related peak, $M-[C_{16}H_{33}+CH_3O] = 338$ are quite strong compared to other homologous peaks in this region corresponding to loss of shorter chains (i.e. branching at positions farther from the $COOCH_3$ group), suggesting that these are random, with a low individual incidence of occurrence.

Peaks which indicate branching or linking at non-α-positions are: 1) $M-[CH_2COOCH + H] = 520$; and 2) a very strong peak at $[CH_2COOCH_3 + H] = 74$. This 74 peak is often the strongest one in non-α-substituted fatty acid methyl esters. In this case, the 74 peak was slightly stronger than (108% of) the base peak at M/2 + 1.

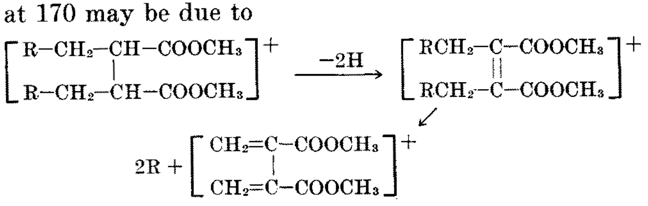
The spectrum of the anhydride derived from the distilled dimer is not shown, since it did not give as much information as the dimethyl ester derived from it. It did show a parent peak at the expected mass of 548, and showed a peak at 324 due to loss of $(C_{16}H_{33}-H)$.

Mass spectrum of the dimer ester from the isolated cyclic anhydride from M/e = 260–600 is shown in Figure 5. The following differences from the whole distilled dimer show the much greater amount of α-linkage: 1) much stronger peak at $M-[C_{16}H_{33}-H] = 370$ (58% vs. 16%); and 2) much stronger peak at $M-[C_{16}H_{33}+CH_3O] = 338$ (19% vs. 8%).

The following differences show the greatly decreased amt of non-α-linkage: 1) a much weaker peak at $M-[CH_2COOCH_3 + H] = 520$ (0.5% vs. 5%); and 2) a much weaker peak at $CH_2COOCH_3 + H = 74$ (16% vs. 108%).

There were small peaks at mass 383 (4%), and 397 (3%) corresponding to loss of $C_{15}H_{31}$ and $C_{14}H_{29}$, which could be due to a small amt of β- or γ-linkage of one segment to the α-position of the other segment resulting in 6 or 7 membered cyclic anhydrides.

Several peaks appeared in the mass spectrum of the α-,α′-linked dimer which would not be readily predicted, but which can be rationally explained: A peak at 170 may be due to

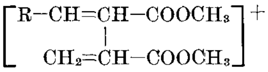


$$\left[\begin{array}{l} R{-}CH_2{-}CH{-}COOCH_3 \\ \qquad\quad\;\; | \\ R{-}CH_2{-}CH{-}COOCH_3 \end{array}\right]^+ \xrightarrow{-2H} \left[\begin{array}{l} RCH_2{-}C{-}COOCH_3 \\ \qquad\;\; \| \\ RCH_2{-}C{-}COOCH_3 \end{array}\right]^+ \swarrow \quad 2R + \left[\begin{array}{l} CH_2{=}C{-}COOCH_3 \\ \qquad\;\; | \\ CH_2{=}C{-}COOCH_3 \end{array}\right]^+$$

M/e = 170

Where $C_{15}H_{31} = R$

A peak at 380 is explainable from the same intermediate losing only one R with hydrogen transfer to give



$$\left[\begin{array}{l}\mathrm{R{-}CH{=}CH{-}COOCH_3}\\ \qquad\quad |\\ \quad\mathrm{CH_2{=}CH{-}COOCH_3}\end{array}\right]^{+} \quad \mathrm{C_{16}H_{33} = R}$$

Discussion

While the intensity of various fragmentation peaks relative to the base peak cannot be related strictly quantitatively to the amt of structures in different dimers giving rise to the peaks, the mass spectrographic data given above, taken as a whole, are an elegant confirmation and extension of the chemical evidence for considerable α-linkage, and for the identity of the α-,α'-linked dimer isolated via the cyclic anhydride. Linkage at positions other than α- appears to be random.

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The Geometric Isomers of Conjugated Octadecadienoates from Dehydrated Methyl Ricinoleate

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Abstract

The dehydration of methyl ricinoleate by heating *in vacuo* in the presence of $KHSO_4$ resulted in the formation of the following conjugated octadecadienoates expressed as a percentage of the final product: *cis, trans (trans, cis)*, 14.3; *cis, cis*, 11.2; *trans, trans*, 7.3. The isomers contained the double bonds predominantly in the 9,11 position but the possible presence of traces of 8,10 and other conjugated isomers is not excluded. Using urea "inclusion" fractionation and low temp crystallization from acetone methyl, *cis*-9, *cis*-11-octadecadienoate was isolated.

The methyl esters of commercially dehydrated castor oil fatty acids on the other hand, contained the following percentages of conjugated octadecadienoate isomers: *cis, trans (trans, cis)*, 20.3; *cis, cis*, 8.0; *trans, trans*, 5.4. From these mixtures conc of *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates were prepared by fractional distillation and low temp crystallization. It was found that the conjugated octadecadienoates consisted of mixtures of positional isomers with double bonds mainly in the 8,10 and 9,11 positions with lesser amounts in the 7,9 and 10,12 positions.

Introduction

CONJUGATED *cis, cis*-octadecadienoic acids have not been reported as constituents of natural products, but *cis*-9, *cis*-11- and *cis*-10, *cis*-12-octadecadienoic acids (1) as well as the methyl esters of the latter (2) have been synthesised using acetylenic intermediates. In addition, we have shown that during dehydration of methyl ricinoleate, not only are *trans, trans*- and *cis, trans (trans, cis)*-octadecadienoates produced in agreement with the results of previous investigations by Jackson, Paschke, Tolberg, Boyd and Wheeler (3), using dehydrated castor oil, but there also are formed *cis, cis* conjugated isomers (4). The purpose of the work now reported was to elucidate the position of the double bonds in the conjugated *cis, cis* isomers and to reinvestigate in the light of the new techniques and knowledge the related conjugated isomers previously examined by other investigators (3,5,6).

Our interest in the present work stems from a general project to investigate more closely the wide range of isomeric octadecadienoic acids found in ruminant fats. Using Reiser's observation (7) that sheep rumen contents hydrogenate linolenic acid in linseed oil to linoleic acid, workers in the Fats Research Division have shown (8) that in pasture fed ruminants, the main dietary fatty acid, linolenic acid, is converted into *trans* and positional isomers of linoleic acid, as well as into oleic acid isomers and stearic acid.

Procedures

Gas-Liquid Chromatography. The GLC analyses were made at 207C using packed columns (254 x 0.65 cm I.D.) with argon as carrier gas in conjunction with the ionising detector described by Lovelock, James and Piper (9). The determination of the retention times relative to methyl stearate was as described by Gerson (10). (Throughout the composition of the methyl esters is expressed as moles % on the assumption that the detector response is proportional to the mol wt.) As a guide to the composition of the fractions obtained during the separation of the conjugated octadecadienoates, the relative retention volumes given by Farquhar, Insull, Rosen, Stoffel and Ahrens (11) were generally used. In addition, the data provided by Beerthuis, Dijkstra, Keppler and Recourt (12) assisted in locating the peaks corresponding to the *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates. Two types of liquid phase comprising a) 20% (w/w) diethylene glycol adipate (DEGA), and b) 5% (w/w) Apiezon L (ApL) were applied with 30–80 mesh celite (British Drug Houses Ltd., Poole, England) as the solid support.

Infrared Spectrophotometry. Pure methyl elaidate prepared as described by Jart (13) was used as a standard in the determination of the amt of *trans* double bonds. The melting point of the purified elaidic acid used to prepare methyl elaidate was 43.6–43.8C as compared with 43.8–44.0C recorded by Jart (13). An approx measure of the concn of conjugated *trans, trans* isomers was obtained by comparing the ratios of *trans* absorption at 986 cm^{-1} (3) to the absorption at 1450 cm^{-1} corresponding to the deformation fre-