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THERMAL REORGANISATION REACTIONS—I

THERMAL CYCLIZATION OF ELEOSTEARATES*†

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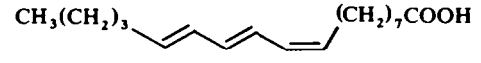
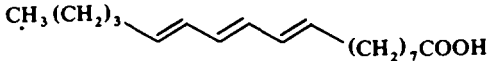
Abstract—Intramolecular thermal cyclization of methyl α- (or β)-eleostearate has been achieved in good yield by the tactical use of sulphur as catalyst. Under relatively mild conditions (~160°), the primary cyclic monomer (methyl cycloeleostearate–I) has been obtained and unambiguously shown to be methyl 5-butyl-1,3-cyclohexadiene-6-caprylate (IV). Under more energetic conditions (~240°) isomers V and VI are formed at the expense of the primary cyclic monomer (IV).

IT IS known[1–3] that thermal treatment of trienic acids, such as α-(I) or β-eleostearic acid (II) results in both intramolecular and intermolecular cyclization, with the latter predominating. In view of possible industrial outlets[4] for the monomeric cyclic products, efforts have been made to increase the yield of such products. A significant contribution was made by Scholfield and Cowan[5] who reported that prolonged alkali isomerization of linolenic acid (III) in ethylene glycol results in a good yield of cyclic monomeric acids. Application[6] of this method to tung oil (oil from kernels of *Aleurites fordii*), the fatty acids of which consist essentially (~80%) of α-eleostearic acid (I), resulted in ~70% of eleostearic acid being converted into cyclic monomeric acids; mere thermal treatment gives no more than 30% conversion.[2]

Structures of products formed by the cyclization of I and/or II, have been discussed[1–3,7] and it has been concluded that the cyclic monomers are dialkyl cyclohexadienes. Structure IV has been postulated[3] for the primary cyclization product (methyl ester) considered as arising from an internal Diels–Alder type reaction.[8] However, isolation of pure cyclic monomers and unequivocal determination of their structures have remained, so far, unaccomplished.

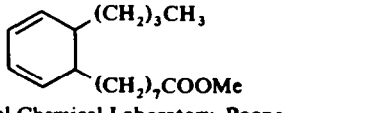


I



II

III



IV

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The present investigation was undertaken with the twin objective of discovering a suitable catalyst for the above cyclization reaction and isolating and characterizing the pure monomeric acids (esters) resulting therefrom.

Sulphur catalysis

For the cyclization of an acyclic conjugated triene to a cyclohexa-1,3-diene, it is obvious that the central olefinic linkage must be *cis*-configurated to permit the attainment of hexagonal geometry necessary for the reaction. Indeed, central-*cis*-configurated conjugated acyclic trienes have been found[9–12] to cyclize efficiently at remarkably mild temperatures (100–150°). Since, in eleostearic acids the central double bond is *trans*-configurated (I, II), it is essential to first isomerize this linkage to permit cyclization. Since, heat alone is a poor agent[13] for such transformations, the low yields of monomeric cyclic acids obtained by earlier workers[1–3] by mere thermal treatment, is readily understood. In view of this, the effect of various catalysts[13, 14] useful in the interconversion of geometrical isomers, on the cyclization reaction was investigated. It may be mentioned that no selective isomerization of the central olefinic linkage is sought for; all that is needed is random isomerization with the anticipation that a species with central *cis*-ethylenic linkage (irrespective of the configuration of other two olefinic bonds) will readily collapse, at the isomerization reaction temperatures, to a cyclic product. Of the various catalysts* investigated (benzoyl peroxide, Se, SeO_2, iodine, flowers of sulphur and 5% Pd-C; 2 mg of catalyst per 1 g of methyl α-eleostearate at 160° for 5 hr), sulphur gave the best results; Se and SeO_2 were also effective, but not to the same extent. The reaction was followed by GLC, which readily separated cyclic monomer (lower retention time) from the linear ester.

Sulphur catalysis was next further investigated for various temperatures (130, 160, 200° and 240°) and reaction times (1–50 hr) to arrive at optimum reaction conditions. Products from many such experiments were fully investigated further by molecular distillation of total product to get yields of monomeric, dimeric and polymeric esters; the monomeric esters were next segregated[3] by urea adduction into cyclic and acyclic products. It was soon found that though the yield of cyclic monomeric ester could be greatly increased by increasing reaction temperature, the nature of the product radically changed as shown by its TLC on $AgNO_3$-silica gel.[16] To study the nature of these products, two diverse reaction conditions (Table 1) were selected, as the monomeric cyclic products from these reactions were quite distinct. The isolation and structure elucidation of major components of these products is discussed below and it will suffice to mention here that the major component from 160°-experiment has been shown to be IV, while the product from 240°-experiment yielded none of IV, but instead was shown to essentially consist of V and VI. Table 2 summarises certain characteristics of these compounds.

Essentially same results were obtained with methyl β-eleostearate and tung oil.

Reorganisation at 160°

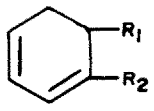
The monomeric, urea non-adducting material from sulphur-catalysed, thermal (160°) treatment of methyl α-eleostearate (Table 1), must, by virtue of its method of

* It may be pertinent to mention that iodine-light-induced isomerization of methyl α-eleostearate has been investigated by Tolberg *et al*,[15] who conclude that the central double bond of a conjugated triene isomerises less readily than the outer two double bonds.

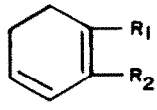
TABLE 1. CYCLIZATION OF METHYL α-ELBOSTEARATE IN PRESENCE OF SULPHUR

No.	Temp. (±2°)	Time (hr)	Yield (%)			
			Monomeric		Dimeric	Polymeric
			Acyclic	Cyclic		
1	160°	5[a]	55	25	10	10
2	240°	1	0	60	20	20

[a] Even after 50 hr at this temp, acyclic material was present in quantity.



V



VI

$R_1 = (CH_2)_3CH_3$

$R_2 = (CH_2)_7COOMe$

TABLE 2. COMPARISON OF SOME CHARACTERISTICS OF METHYL α-ELEOSTEARATE AND ITS CYCLIC ISOMERS

	Cyclo-eleostearate-I	Cyclo-eleostearate-II	Cyclo-eleostearate-III	α-eleostearate
1. Structure	IV	V	VI	I
2. b.p./mm	145°/0·2	145°/0·1	—	148°/0·5
3. n_D^{30}	1·4731	1·4725	1·4772	1·5060
4. RR_f[a]	0·747	0·960	0·533	1·000
5. RRT[b]	0·7	0·7	0·7	1·0
6. $\lambda_{max}^{cyclohexane}$ mμ ($\varepsilon \times 10^{-4}$)	264 (0·324)	266 (0·670)	262 (0·642)	261, 271, 282 (3·70) (5·05) (3·65)
7. IR: diagnostic bands (cm^{-1})	710	700	—	1000(s), 970
8. PMR: vinylic protons	345 (4H, s)	315–355 (3H, m)	341 (2H, essentially s)	310–380 (6H, m)

[a] TLC: $AgNO_3$-SiO_2 gel (0·3 mm layer); solvent, benzene (solvent front, 11 cm); temp 25°.
[b] GLC: Silicone SE-30/Chromosorb W at 250°; carrier gas: H_2 (70 ml/min).

isolation, be essentially free from methyl eleostearate. This was fully borne out from its IR spectrum, which is practically devoid of the 1000 cm^{-1} band, so strong and characteristic[15] in the IR spectra of both α- and β-eleostearates. However, this material displays in the IR a medium intensity band at 970 cm^{-1} (*trans*-disubstituted ethylenic linkage), and in the UV triple peak absorption (258, 268 and 279 mμ), characteristic of conjugated triene absorption. A second treatment with urea did not alter these spectral characteristics. TLC of this product on $AgNO_3$-SiO_2 gel showed three spots (R_f 0·682, 0·655 and 0·509) of which one (R_f 0·509) predominated. These products were

separated by inverted-dry-column-chromatography (IDCC);[18] the structures of two of these are discussed below, while the third (R_f 0·655) was found to be identical with the major product obtained under more vigorous thermal conditions and is discussed in the next section.

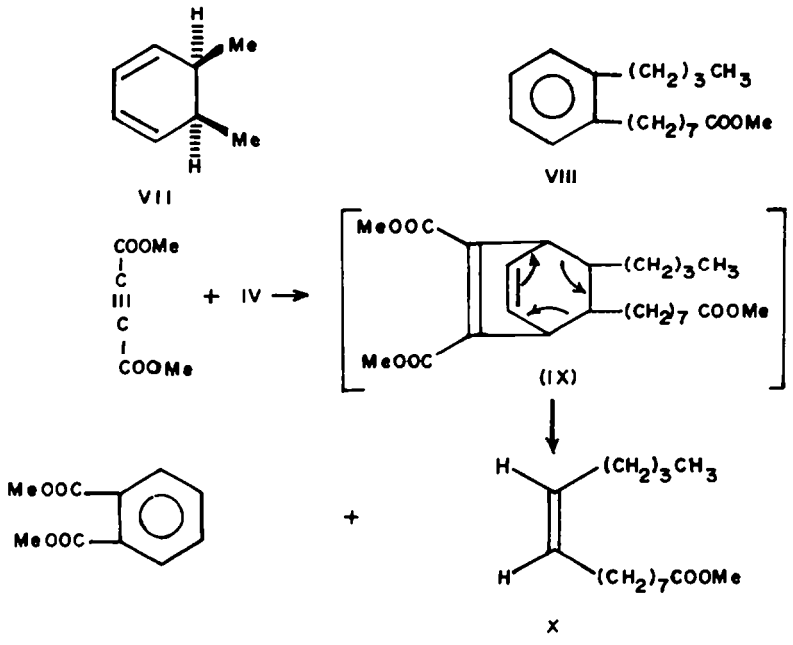
A new geometrical isomer of methyl α-eleostearate. The fastest moving ($AgNO_3$-SiO_2 gel TLC) product, which constitutes ~10% of the total non-adducting material, though TLC pure, was slightly contaminated with an aromatic (PMR) impurity (VIII, ?). In the UV it showed maxima at 258 ($\varepsilon = 1{\cdot}35 \times 10^4$), 268 ($\varepsilon = 1{\cdot}58 \times 10^4$) and 279 mμ ($\varepsilon = 1{\cdot}18 \times 10^4$), typical conjugated triene absorption. Its IR spectrum displays absorption at 970 cm^{-1} (*trans*-disubstituted olefinic bond). In its PMR spectrum a complex multiplet located between 318–370 c/s (olefinic protons, 6H, after correcting for the aromatic impurity) is completely different from the olefinic absorption observed for methyl α(or β)-eleostearate. On catalytic hydrogenation, it furnished methyl stearate. From all these data, it is obvious that this compound is an hitherto unknown geometrical isomer of methyl eleostearate.

Methyl cyclo-eleostearate-I (IV). The product which was least mobile on TLC, was obtained in major yield (~65% of the mixture) and, in view of the rather mild reaction conditions for its genesis, was anticipated to be the primary cyclic monomer IV. This has, indeed, been found to be so.

Its spectral characteristics (Table 2), especially the vinylic proton count (PMR), clearly support structure IV; a very close analogy is provided by *cis*-5,6-dimethyl-1,3-cyclohexadiene (VII), for which λ_{max} 261 mμ (ε 4100), δ olefinic protions, 4H singlet at 5·88 ppm, have been recorded.[10] In conformity with this the compound, on catalytic hydrogenation, absorbed two moles of hydrogen to give a fully saturated (tetranitromethane test) derivative. On catalytic dehydrogenation or more conveniently on being refluxed with dichloro-dicyano *p*-benzoquinone (DDQ)[19] in benzene, aromatization readily occurred to give the benzene derivative VIII: λ_{max} 257 (sh), 263 ($\varepsilon = 310$) and 272 mμ ($\varepsilon = 242$); IR: aromatic ring 1620, 1500 cm^{-1}; 1,2-disubstituted benzene 760 cm^{-1}; PMR: 4H singlet at 422 c/s.[20] The mass spectrum of VIII is distinguished by the parent peak at $m/e = 290$ (42%) and the base peak at $m/e = 105$ (*O*-xylyl ion); other strong peaks due to fragmentation of a substituted benzene are the tropylium ion peak at $m/e = 91$ (38%) and other homologous fragments at $m/e = 119$ (26%), $m/e = 133$ (22%) and $m/e = 147$ (15%).[21]

Clear-cut chemical proof for the structure IV was obtained by application of Alder–Rickert reaction.[22] When the cyclic ester was heated with dimethyl acetylenedicarboxylate at 200° for 2 hr only two fragments were formed, which were neatly separated by urea-fractionation into a paraffinic compound forming the clathrate and an aromatic compound from urea-filtrate. The former was identified (IR, PMR, Mass and, catalytic hydrogenation) as the expected methyl myristoleate (X),[23] that should result from the retrodiene reaction as shown in IX. The second fragment was readily identified (IR, mixed GLC, hydrolysis) as the expected dimethyl phthalate. The formation of only these two cleavage products is compatible only with the structure IV for the compound in question.

It is known[24] that photoirradiation of 1,3-cyclohexadienes often results in its equilibration with the open-chain valence-isomer. In case of the primary cyclic monomer (IV) photoequilibration should result in formation of an eleostearate (for remarks on stereochemistry, see below); it may be noted that only structure IV can



lead to an eleostearate, other structures such as V and VI will result in branched-chain trienic esters. Photoirradiation of IV resulted in the development of 1000 cm^{-1} band (IR), typical of eleostearates. The acyclic isomer was separated (urea-adductation) and identified as a methyl eleostearate by catalytic hydrogenation to methyl stearate. This valence isomerization, provides another proof for the correctness of structure IV.

Given the precise stereochemistry of the starting acyclic triene, the stereochemistry of the cyclic product arising from an electrocyclic process is predictable by Woodward–Hoffmann rules[25] and, this has been experimentally corroborated in certain cases.[10, 11] However, as already stated, conversion of methyl eleostearate into IV requires conditions under which geometrical isomerism about the olefinic linkages becomes possible and thus, the geometry of the starting triene remains no longer definitive and this in turn obscures the derivation of the stereochemistry of the cyclic monomeric ester IV and consequently that of the methyl eleostearate arising from IV by photoirradiation.

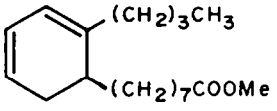
Methyl cyclo-eleostearate-I reacts sluggishly (cf. methyl α-eleostearate[26]) with maleic anhydride to give a liquid product. A solid crystalline adduct (m.p. 142–143°) could be prepared, though in low yield, with *p*-phenylazomaleinanil[27] in presence of $AlCl_3$.[28]

Reorganisation at 240°

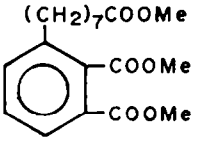
It is clear from Table 1 that sulphur-catalysed thermal treatment of methyl α-eleostearate at elevated temp (240°) furnishes the urea-non-adducting material in a considerably enhanced yield (60%). TLC analysis ($AgNO_3$-SiO gel) of the product revealed three compounds having R_f's 0·364, 0·655 (major) and 0·680. The mixture was resolved by IDCC and the fastest moving compound (~15%) was identified (IR and PMR) as the *ar*-monomer (VIII); the other two have proved to be new isomers of methyl cycloeleostearate-I.

Methyl cycloeleostearate-II (V). This product (R_f 0·655) constitutes ~75% of the total urea-non-adducting material. That, it must be a close relative of IV is obvious from its UV and IR data (Table 2). Furthermore, since the vinylic region in its PMR spectrum integrates for three protons, structure V or its positional isomer XI is dictated.

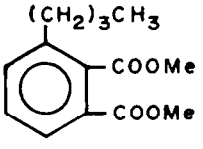
Application of the retro-Diels–Alder reaction to this isomer, as described for IV, provided clear-cut evidence in favour of V. Thus, *in situ* addition-cleavage with dimethyl acetylenedicarboxylate gave a product, the PMR spectral characteristics of which are clearly in accord with XII (derived from V) and not with XIII (derived from XI):



XI



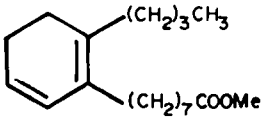
XII



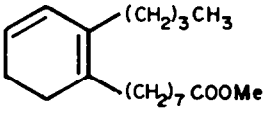
XIII

CH_2 of the C-chain, 10H broad singlet at 80 c/s; CH_2COOMe, 2H triplet at 133 c/s (J = 6 c/s); *ar*-CH_2, 2H triplet at 155 c/s (J = 6 c/s); CH_2-COOMe, 3H singlet at 217 c/s; two *ar*-COOMe, 6H singlet at 231 c/s; three vicinal aromatic proton, 3H, typical AB_2 type multiplet located between 435–475 c/s. This defines the structure of methyl cycloeleostearate-II as V.

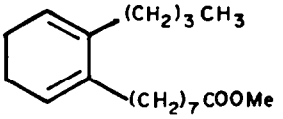
Methyl cycloeleostearate-III (VI). The compound with R_f 0·364 is also clearly a cyclohexadiene (UV, Table 2). Its PMR spectrum shows in the vinylic proton region only a 2H signal, essentially a singlet with a shoulder, 341 c/s) and this finding limits the possible structures to VI, XIV and XV; an 8H singlet at 122 c/s (four allylic CH_2) further supports this. Again, retro-diene reaction with dimethyl acetylenedicarboxylate proved invaluable. The product from this reaction shows, in its PMR spectrum, an AB



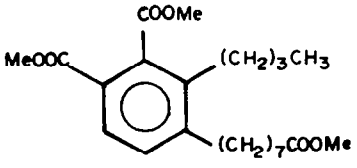
VI



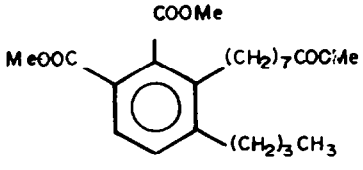
XIV



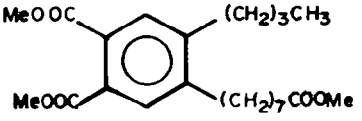
XV



XVI



XVII



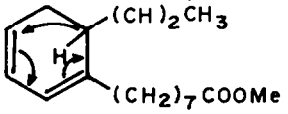
XVIII

quartet centred at 445 c/s (J = 8 c/s, $J_{AB}/\delta_B - \delta_A$ = 0·258) and assignable to two isolated ortho-coupled aromatic protons. Of the three possible structures (XVI, XVII and XVIII) for the retro-diene reaction product, the PMR data are in accord

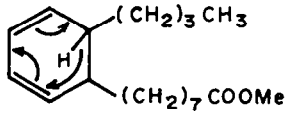
with only XVI/XVII. An IR band at 855 cm^{-1} (1,2,3,4-substituted benzene) further supports this conclusion. Thus the possibility of XV for the parent diene can be ruled out. The subtle difference between XVI and XVII renders spectroscopic distinction between them difficult. However, mechanistic considerations (*vide infra*) clearly favour structure VI.

It is obvious that cyclic isomers V and VI arise from the primary methyl cycloeleostearate-I (IV) by further thermal rearrangement. This is fully supported by the results of further thermal (non-catalytic) treatment of pure IV. At 160° (2 hr), the primary monomer remained essentially unchanged, while at 200° (2 hr) remarkably clean isomerization to methyl cycloeleostearate-II (V) occurred. More drastic thermal treatment (240°, 2 hr) furnished a mixture consisting essentially of V (~20%) and VI (~80%). At 280° (2 hr) a complex mixture of several compounds resulted.

It is clear from the above that rearrangement takes place in the sequence IV → V → VI. These transformations are 1,5-sigmatropic shifts[25, 29] involving hydrogen migration. Since the structure of methyl cycloeleostearate-II is well-secured as V, it follows



XIX



XX

that methyl cycloeleostearate-III, arising from V *via* XIX, must be represented by VI. However, it is not clear why IV rearranges preferentially to V, since the alternate pathway (XX) to XI would appear to be equally probable.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to fraction b.p. 60–70°. Solvent extracts were dried over anhydrous Na_2SO_4.

IR spectra were taken on a Perkin–Elmer Infracord model 137-E, either as smears (liquids) or in Nujol (solids). UV spectra were recorded on a Perkin–Elmer Spectrophotometer, model 350, in cyclohexane (unless otherwise stated). PMR spectra were scanned on a Varian A-60 instrument as 10–15% solns in CCl_4 and values are reported in c/s from internal TMS standard. The mass spectrum was recorded on a CEC type 21-110 B mass spectrometer at 70 ev.

GLC were performed on the Wilkens Aerograph A-350-B instrument with a 5 ft × 0·25" in column using 20% silicone SE-30 as stationary phase on Chromosorb W (60–80 mesh) using H_2 as carrier gas at a suitable flow rate (30–100 ml/min).

TLC were carried out on silica gel (200 mesh) containing 15% gypsum as binder. Visualization of zones after development was by I_2-vapours or by spraying with conc H_2SO_4 and heating the plates at 110°.

Methyl eleostearates

Methyl α-eleostearate. This was prepared by esterification of α-eleostearic acid,[30] m.p. 49°, with (a) CH_2N_2-Et_2O-MeOH[31] (b) MeOH-*p*-toluenesulfonic acid[32] or by methanolysis[33] of α-tung oil.

Methyl β-eleostearate. This was prepared by esterification of β-eleostearic acid,[1] m.p. 70–71°, by the above methods. The pure ester had λ_{max} 268 mμ ($\varepsilon = 5{\cdot}7 \times 10^4$).

Thermal reorganisation at 160°

(a) *Using pure methyl α-eleostearate.* Methyl α-eleostearate (44 g) and S (88 mg) were taken in a pyrex glass tube (160 mm × 32 mm), sealed under vacuum and immersed in a preheated oil bath held at 160°. After 5 hr the thermal product was distilled in a 2"-rotafilm molecular still* at 160°/100 mμ yielding the

* Supplied by A. F. Smith Co., Rochester, N.Y. (USA)

monomer as a pale yellow oil (34·3 g). The residue (7·4 g) on redistillation at 260°/70 μ gave the dimer as a golden yellow liquid (4·5 g, 10%).

The monomer (34 g) in MeOH (30 ml) was treated with urea (170 g) in MeOH (700 ml) at 50° and left at room temp (25°) for 15 hr. The adduct was filtered, the filtrate concentrated to 300 ml and kept in the refrigerator for 24 hr. The slightly turbid filtrate was taken to dryness on the waterbath, treated with water (500 ml), extracted with ether (200 ml × 2), washed with water, dried and evaporated to a light brown oil (12·5 g). Distillation as before at 150°/70 μ gave the urea-filtrate monomer as a colourless oil (10·5 g, 25%).

(b) *Using pure methyl β-eleostearate.* Methyl β-eleostearate (44 g) in presence of S (88 mg) was thermally treated at 160°/5 hr as in (a). The heated product was distilled in the rotafilm still at 160°/150 μ to separate the monomer distillate (36·5 g) from a residue (5·2 g). Redistillation of the latter at 250°/50 μ yielded the dimer (3·4 g, 8%). The monomer distillate (36 g) was fractionated by the urea-inclusion method when the filtrate gave 10·4 g of monomer.

(c) *Using tung oil.* Three evacuated sealed tubes, each containing α-tung oil (66 g) and S (132 mg), were heated at 160° for 5 hr in a preheated oil bath. The heated oil (198 g) was subjected to methanolysis by refluxing for 1·5 hr with a soln of Na (1·2 g) in dry MeOH (90 ml). Usual work up followed by distillation at 150°/200 μ gave the monomer (165 g) which on segregation with urea gave 39 g of non-complexing material; IR spectrum: 970(m) and 710 (s) cm^{-1}.

(d) *Using total tung oil esters* (80% *eleostearate*). Three tubes, each containing the ester (66 g) and S (132 mg), and sealed under vacuum, were thermally treated as in (c). The combined thermal products were distilled at 130°/40 μ to furnish the monomer (170 g) and a residue (20·6 g). The monomer (170 g) was repeatedly adducted with urea and the fourth filtrate gave a non-adducting material (22·1 g) with IR bands at 970(m) and 710(s) cm^{-1}. TLC ($AgNO_3$-SiO_2 gel, benzene: essentially 3 spots having R_f's 0·682, 0·655 and 0·509). This product (12·8 g) was subjected to IDCC on $AgNO_3$-SiO_2 gel (600 g; 20 × 6·5 cm) using benzene as developer. Pooling by TLC screening furnished four fractions. (1) 0·0140 g: highest R_f (rejected); (2) 0·989 g: a new geometrical isomer of eleostearate; (3) 3·761 g: methyl cycloeleostearate-II (slightly impure); (4) 7·096 g: least R_f, methyl cycloeleostearate-I.

A new geometrical isomer of methyl eleostearate

This product (colourless liquid, b.p. 150°/0·1 mm; 220 mg) was hydrogenated over pre-reduced PtO_2 (24 mg) in AcOH till no more H_2 was consumed (45 ml). The isolated product (219 mg) was purified by urea-inclusion to furnish a solid (52 mg) on regeneration from the adduct by treatment with dil HCl. Recrystallization of this material from MeOH gave white platelets m.p. 37–38°, identified as methyl stearate (mixed m.p., IR and mixed GLC).

Methyl cycloeleostearate-I (IV)

IR spectrum (smear): CH=CH (3049, 1587–1640 cm^{-1}), 710(s) cm^{-1}. PMR spectrum: CH_2—$\underline{CH_3}$ (distorted tr 55 c/s), allylic H and $\underline{CH_2}COOMe$ (133 c/s, distorted tr 4H), $COOCH_3$ (3H s, 216 c/s) and olefinic H (4H s, 345 c/s). (Found: C, 78·70; H, 10·63. $C_{19}H_{32}O_2$ requires: C, 78·07; H, 10·96%).

Hydrogenation. The above compound (106 g) in glacial AcOH (10 ml) on quantitative hydrogenation over Adams' catalyst (25 mg) consumed nearly 2 mole equiv (19 ml) of H_2 at 32°/715 mm. The tetrahydro-derivative is a colourless liquid b.p. 160°(bath)/0·1 mm, n_D^{30} 1·4621, TNM test: -ve. IR spectrum: featureless below 1000 cm^{-1}. (Found: C, 75·68; H, 11·92. $C_{19}H_{36}O_2$ requires: C, 75·97; H, 12·76%).

Methyl ar-cycloeleostearate (VIII)

(a) Compound IV (832 mg) and 10% Pd-C (200 mg) were heated at 240–250°, under N_2, for 3 hr. The cooled product was diluted with light petroleum, filtered and evaporated. The residue was purified by IDCC over silica gel (IIB, 144 g, 20 × 3·6 cm) using benzene-light petroleum (4:1) as developer. The pure fraction, b.p. 170°/0·25 mm, was a colourless liquid, n_D^{30} 1·4882; PMR spectrum: CH_2-$\underline{CH_3}$ (58 c/s, distorted tr), $\underline{CH_2}COOMe$ (2H tr 133 c/s), *ar*-$\underline{CH_2}$ (4H tr 156 c/s), $COOCH_3$ (3H s 215 c/s) and aromatic H (4H s 422 c/s). (Found: C, 78·83; H, 10·64. $C_{19}H_{30}O_2$ requires: C, 78·57; H, 10·41%).

(b) Compound IV (0·876 g) in dry benzene was treated with DDQ (0·881 g) and refluxed for 5 hr on a waterbath. The reaction mixture was cooled, diluted with light petroleum (100 ml), filtered and the filtrate evaporated. The liquid residue (0·717 g) was filtered through a small column of Al_2O_3 and distilled to give VIII (0·6 g).

Alder–Rickert reaction with IV

A mixture of IV (1·161 g) and dimethyl acetylenedicarboxylate (1·21 g) was heated under N_2 in an oil bath

at 130° (1 hr) and then at 200° (1 hr). Distillation of the reaction mixture gave a pale yellow liquid b.p. 66–140°/2 mm (mostly at 118°). This material was adducted with urea (10 g) in MeOH (60 ml) and the ppt. filtered after 15 hr at 0°. The adduct, after washing with urea-saturated MeOH (10 ml), was decomposed with water (50 ml), extracted with ether (30 ml × 4), washed with water (25 ml), evaporated to a clear liquid (309 mg) and distilled to furnish *methyl myristoleate* (X) as a colourless oil b.p. 116–118°/2 mm, n_D^{30} 1·4425; IR spectrum: *cis*-CH=CH— (3000, 1650 and 710 cm^{-1}); PMR spectrum: CH_2—C$\underline{H}_3$ (distorted triplet 55 c/s), allylic H and C$\underline{H}_2$COOMe (6H m 120–145 c/s), COOC$\underline{H}_3$ (3H s 217 c/s) and CH_2·C$\underline{H}$=C$\underline{H}$·CH_2 (2H tr 320 c/s). (Found: C, 74·64; H, 11·77. $C_{15}H_{28}O_2$ requires: C, 74·95; H, 11·74%). X (130 mg) was hydrogenated in glacial AcOH over 10% Pd-C (200 mg) to furnish the dihydro compound which was hydrolysed with 10% methanolic KOH (10 ml) by refluxing for 1 hr. Usual work-up and recrystallisation from dil EtOH gave white platelets m.p. 52–53°, undepressed on admixture with authentic myristic acid of m.p. 53°.

The urea-filtrate mentioned above was worked up and the distilled product (451 mg) b.p. 145–147°/10 mm, identified as dimethyl phthalate (IR, mixed GLC).

Photolysis of IV

Compound IV (1 g) in pure cyclohexane (30 ml) was taken in a quartz tube fitted with a condenser and irradiated for 3·5 hr with UV light from a high-pressure 125-watt Hanovia Hg-lamp kept at a distance of 5 cm from the solution. IR bands of the photoproduct: 710 cm^{-1} and between 950–1000 cm^{-1} (2 new bands). The material was segregated by adduction with urea (12 g) in hot MeOH (50 ml) and cooling to 0° (16 hr). The crystalline adduct was decomposed with water and the new eleostearate isomer distilled: colourless oil b.p. 150°/0·2 mm (261 mg); TLC ($AgNO_3$—SiO_2 gel, benzene): single spot R_f 0·682; IR spectrum (smear): 1000 and 975 and 950 cm^{-1}; UV spectrum: triple absorption with λ_{max} 271 mμ ($\varepsilon = 3{\cdot}97 \times 10^4$). On hydrogenation with prereduced PtO_2 in AcOH at 30°/715 mm, this compound (95 mg) consumed 27 ml of H_2 (equiv to 3 moles). The isolated product (93 mg) was hydrolysed with 10% methanolic KOH (10 ml) at reflux (2 hr); the acid (87 mg) on recrystallisation from MeOH furnished stearic acid, m.p. and mixed m.p. 68–69°.

Maleic anhydride adduct of IV

Freshly recrystallised maleic anhydride (260 mg) in benzene (20 ml) was treated with IV (878 mg) and the greenish yellow soln refluxed for 24 hr. The cooled reaction mixture was washed with water (15 ml × 4) and evaporated to a gummy mass, which still showed the presence of some starting diene by TLC. This material, which refused to crystallise, was hydrolysed with 10% methanolic KOH (25 ml) by refluxing for 2 hr. The crude acid (1·03 g) was esterified with CH_2N_2 in Et_2O—MeOH and the product purified by chromatography over SiO_2 (30 g; 15 × 2·5 cm). The pure triester (976 mg) was eluted with benzene and distilled: colourless viscous liquid b.p. 165–180°/0·2 mm; PMR spectrum: olefinic protons (2H, complex m 359–390 c/s). (Found: C, 69·11; H, 9·37. $C_{25}H_{40}O_6$ requires: C, 68·77; H, 9·24%).

The triester from the maleic anhydride adduct[34] (m.p. 64–65°) of α-eleostearic acid was prepared: b.p. 175–190°/0·2 mm; PMR spectrum: olefinic protons (4H, complex m 300–354 c/s). (Found: C, 69·52; H, 9·35. $C_{25}H_{40}O_6$ requires: C, 68·77; H, 9·24%).

p-*Phenylazomaleinanil adduct of* IV

p-Phenylazomaleinanil (98 mg) in dry benzene (10 ml) was treated with anhyd $AlCl_3$ (10 mg) and a soln of IV (101 mg) in the same solvent (5 ml) added. After refluxing for 42 hr the reaction mixture was washed with dil HCl (10 ml × 3), followed by water (10 ml × 3), dried and evaporated. The residue (178 mg), which indicated 3 spots on TLC, was fractionated by IDCC over SiO_2 gel (Gr. I, 25 g; 20 × 1·4 cm) with benzene as developer. The pure adduct (87 mg) was recrystallised from C_6H_6—MeOH to furnish orange silky needles m.p. 142–143°; IR spectrum: COOMe (1745 and 1200 cm^{-1}), anil C=O (1710 cm^{-1}). (Found: N, 7·27. $C_{35}H_{43}O_4N_3$ requires: N, 7·38%).

Thermal reorganisation at 240°

Total tung oil esters (100 g) and S (200 mg) were taken in a flask fitted with a special adaptor consisting of a long tube provided with a gas inlet tube at the lower part while the upper end was connected to a Hg-valve. Purified N_2 was passed at a steady rate for 15–20 min at room temp and the flask next immersed in a bath at 240°. The heating was continued for 1 hr while N_2 was kept bubbling. The thermal product was distilled in the molecular still at 130°/50 μ to yield the monomer distillate (67 g). The residue (28·7 g) on redistillation at 240°/50 μ furnished the dimer (20·5 g).

The monomer distillate (67 g) was fractionated by treatment with urea (330 g) in dry MeOH (1 l.) in the usual way to furnish the filtrate-monomer as a pale yellow oil (32 g). This mixture was subjected to IDCC on $AgNO_3$—SiO gel (450 g, 20 × 5·5 cm) using light petroleum benzene (1:2) as developer and 7 cuts (TLC monitoring) were made as follows: (1) 0·132 g: highest R_f (rejected); (2) 0·899 g: *ar*-cycloeleostearate (VIII); (3) 0·757 g: VIII + cycloeleostearate-II (V); (4) 2·062 g: Cycloeleostearate-II (V); (5) 0·279 g: (V) (slightly impure); (6) 0·201 g: (V) + cycloeleostearate-III (VI); (7) 0·312 g: Cycloeleostearate-III (VI).

Methyl cycloeleostearate-II (V)

Colourless liquid b.p. 145°/0·1 mm. (Found: C, 78·48; H, 11·08. $C_{19}H_{32}O_2$ requires: C, 78·07; H, 10·96%).

Alder–Rickert reaction with V. Compound V (226 mg) was reacted with dimethyl acetylene-dicarboxylate (230 mg) at 110° for 0·5 hr and then at 200° for 1 hr (N_2 atmos). After distilling off a forerun b.p. 65–68°/2 mm (116 mg, unreacted reagent) the residue was separately distilled in a bulb tube at 100 mμ to furnish XII as a pale yellow liquid; IR spectrum: COOMe (1750, 1290 cm^{-1}), benzenoid absorption [1600, 1490 and 775 cm^{-1} (1,2,3-trisubstitution)]; UV spectrum: λ_{max} 276 mμ (ε = 2050). (Found: C, 65·45; H, 7·60. $C_{19}H_{26}O_6$ requires: C, 65·12; H, 7·48%).

Methyl cycloeleostearate-III (VI)

Light yellow liquid b.p. 160° (bath/50 μ; IR spectrum (smear): CH=CH (3000, 1600 cm^{-1}); COOMe (1750, 1180 cm^{-1}); PMR spectrum: CH_2—$C\underline{H}_3$ (unsymmetrical triplet 54 c/s), $C\underline{H}_2$ of C-chain (14H, broad 78 c/s), allylic $C\underline{H}_2$ (8H, essentially a s, 122 c/s), $C\underline{H}_2COOMe$ (133 c/s, partially buried under allylic $C\underline{H}_2$ resonance), $COO\underline{Me}$ (3H s, 216 c/s) and olefinic H (essentially a 2H-s 341 c/s). (Found: C, 77·91; H, 11·19. $C_{19}H_{32}O_2$ requires: C, 78·07; H, 10·96%).

Alder–Rickert reaction with VI. A mixture of VI (201 mg) and dimethyl acetylenedicarboxylate (250 mg) was heated at 120° for 0·5 hr and then at 210° (1 hr) under a blanket of N_2. Excess reagent was removed as a low-boiling fore-run, b.p. 100° (oil bath)/2 mm and the residue distilled at 0·1 mm. Further purification of the reddish brown distillate by IDCC on SiO_2-gel (25 g, 20 × 1·3 cm) using light petroleum-benzene (1:2) as developer furnished a central cut as a light yellow liquid of XVI; PMR spectrum: CH_2—CH_3 (distorted broad tr 56 c/s), $C\underline{H}_2$ of C-chain (14H, broad s 81 c/s), $C\underline{H}_2COOMe$ (2H tr 133 c/s), *ar*-$C\underline{H}_2$ (4H, unsymm tr, 158 c/s), $COO\underline{Me}$ (3H, s 215 c/s), *ar*-$COO\underline{Me}$ (6H, s 228 c/s) and *ortho*-coupled aromatic protons (2H, AB-qu 445 c/s, J = 8 c/s, $J_{AB}/\delta_B-\delta_A$ = 0·258); IR spectrum: COOMe (1750, 1280 cm^{-1}); benzenoid absorption [1600, 1490, 855 cm^{-1} (1,2,3,4-tetrasubstitution)]; UV spectrum: λ_{max} 277 mμ (ε = 1797). (Found: C, 68·82; H, 8·86. $C_{23}H_{34}O_6$ requires: C, 67·95; H, 8·43%).

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