The Rearrangement of Fatty Cyclopropenoids in the Presence of Boron Trifluoride

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The destruction of the cyclopropenoid ring system of methyl 9,10 methyleneoctadec-9-enoate (methyl sterculate) with boron trifluoride etherate has been shown to give a complex mixture of products, including methyl esters of C_{19} allenes (12%), a C_{18} alkyne (11%) and a variety of C_{19} and C_{20} conjugated dienes containing either a methyl or methylene branch. The methylene group lost from the methyl sterculate reactant in the formation of methyl octadec-9-ynoate is incorporated into a second molecule of reactant to yield a mixture of methyl 9-methylene-*trans*-nonadec-10-enoate and the 11-methylene-*trans*-9-isomer.

KEY WORDS: Alkynes, carbon chain reduction and elongation, cyclopropenoid ring opening, dienes, fatty cyclopropenoids, Lewis acid, rearrangement, production of allenes, sterculate, sterculene.

The edible fats cottonseed oil and kapok oil contain the cyclopropenoid compounds 9,10-methyleneoctadec-9-enoic (sterculic) and 8,9-methylene-heptadec-8-enoic (malvalic) acids as glycerides. Fatty cyclopropenoids are known to give ring-opened products when treated with acidic reagents (1), and the most convenient way of destroying the adverse physiological effects associated with the cyclopropenoid ring (2) would be to use acidic earth materials during refining. The fate of the cyclopropenoid ring under these conditions is of interest.

A cursory examination of the isomerization of 9,10-methyleneoctadec-9-ene (sterculene) when treated with alumina (3) suggested the possible formation of ring-opened conjugated dienes, but 50% of the reaction products were polymeric, irreversibly adsorbed or otherwise unidentified materials.

As a preliminary investigation to the examination of the fate of fatty cyclopropenoids in the presence of refining earths, we have used a nonprotonating acidic reagent (boron trifluoride) which permits homogeneous reaction, eliminating the possibility of the formation of irreversibly adsorbed products, and which serves as a model for later studies.

EXPERIMENTAL PROCEDURES

Light petroleum refers to petroleum spirit with a boiling range 40–60°C and ether refers to diethyl ether distilled from phosphorous pentoxide and powdered calcium hydride. Ultraviolet (UV) spectra were recorded with a Pye Unicam SP-8000 (Cambridge, United Kingdom) spectrophotometer (ethanol solutions), and infrared (IR) spectra were obtained on thin films between KBr plates with a Perkin-Elmer (Norwalk, CT) 157G instrument unless otherwise stated [absorptions are only reported where they differ from those of saturated long-chain fatty acid methyl esters (FAME)]. ^{1}H-NMR (nuclear magnetic resonance) spectra were recorded by a Perkin-Elmer R32 (90 MHz) instrument, and samples were dissolved in carbon tetrachloride with 1% of tetramethylsilane as internal reference. Mass spectra were obtained with an AEI MS-9 instrument (Associated Electrical Industries, Manchester, United Kingdom) or by gas chromatography/mass spectrometry (GC/MS) with an AEI MS-30 (Associated Electrical Industries) interfaced to a Pye 104 gas chromatograph.

Analytical gas-liquid chromatography (GLC) was performed on a Philips (Eindhoven, Holland) PV4000 chromatograph fitted with stainless steel, packed columns and a flame-ionization detector (FID). Two stationary phases were used: Apiezon L [APL (Phase Separations Ltd., Deeside, United Kingdom); 2.5% on Gaschrom Q (Phase Separations Ltd.) (125–150 μm); 3000 × 2 mm i.d.; normally at 200°C]; and diethyleneglycol succinate [DEGS; 5% on Chromosorb WHP (125–150 μm) (Phase Separations Ltd.); 2500 × 2 mm i.d.; normally at 170°C]. Nitrogen was used as carrier gas at a flow rate controlled at *ca.* 25 mL/min. A Spectra-Physics (San Jose, CA) Minigrator was used to integrate peak areas and to measure retention times. Retention times are expressed (relative to those of saturated FAME) as equivalent chainlengths (ECL) (4).

Adsorption column chromatography was performed on a glass column (400 × 20 mm i.d.) of silicic acid [Merck, Darmstadt, Germany; Kieselgel 60, 63–210 μm (30 g)] filled as a slurry. Thin-layer chromatography (TLC) was performed on commercially prepared layers of silicic acid (Merck; Kieselgel $60F_{254+366}$; 0.25 mm thick). These were normally developed in light petroleum/acetone/ether (18:1:1) and examined under UV (254 nm) to detect FAME having conjugated unsaturation. After spraying with dichlorofluorescein (sodium salt; 0.1% in EtOH) and drying, other types of FAME were visualized under UV (386 nm) as fluorescent yellow spots. Layers for argentation TLC were prepared from silicic acid (Merck; Kieselgel $60PF_{254+366}$) with $AgNO_3$ (2%), applied as an aqueous slurry 0.6 mm thick to clean glass plates. After drying at ambient temperature in the dark (18 h), layers were activated in an oven before use (100°C, 1 h).

Catalytic hydrogenation of FAME (10–20 mg) was performed with Adam's catalyst (1 mg) in glacial acetic acid (5 mL). The solution of hydrogenated lipid was diluted with water (10 mL), extracted into light petroleum (3 × 5 mL), washed with aqueous $NaHCO_3$ (10 mL) and water (10 mL), dried (Na_2SO_4), and the solvent was removed under reduced pressure.

Oxidative cleavage of unsaturated methyl esters was carried out by a modified von Rudloff method (5). The sample of FAME (10 mg) in 2-methylpropan-2-ol (10 mL) was shaken (2 h) with the oxidant solution (97.5 mM $NaIO_4$, 2.5 mM $KMnO_4$) (5 mL) and 1% K_2CO_3 solution (10 mL). After reaction, powdered $NaHSO_3$ was added to just discharge the purple color. The products were extracted with ether (4 × 2.5 mL), and the combined extracts were washed with water (3 × 3 mL) and dried (Na_2SO_4), and the ether was removed with minimum application of reduced pressure. The residue was refluxed for 2 min with 14% BF_3 in MeOH (3 mL). When cool, water and excess $NaHCO_3$ were added, and the methyl esters were extracted with light petroleum/ether (9:1) (3 × 5 mL). The combined extract was washed with water (10 mL), dried (Na_2SO_4) and evaporated to 0.5 mL. Oxidation products were identified and quantitated by GLC on two

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stationary phases (APL at 100 and 150°C; DEGS at 100 and 170°C).

Isolation of methyl sterculate. Methyl sterculate was isolated from the methyl esters prepared from the seed fat of *Sterculia foetida* by urea clathration, followed by crystallization (−50°C) and recrystallization (−40°C) from methanol. The isolate (10 g) was purified by column chromatography to remove polar material. The column was eluted with pentane (800 mL), and the solvent was removed under reduced pressure to give pure sterculate (9 g; 98.5% by HBr titration) (6).

Purification of boron trifluoride etherate. Technical boron trifluoride etherate (48% BF_3 w/w; 300 mL) was stirred (18 h) at ambient temperature with powdered calcium hydride (5 g) and phosphorous pentoxide (5 g). The mixture was distilled under reduced pressure (350°C; 5.3 mm Hg), and the clear, colorless distillate was sealed and protected from light before use.

Reaction of methyl sterculate with boron trifluoride etherate. Boron trifluoride etherate in ether (12% BF_3 wt/vol 67 mL) was added dropwise with stirring to a solution of methyl sterculate (3.1 g) in ether (33 mL) in a dried flask, from which atmospheric moisture was excluded. After 24 h in the dark at ambient temperature (*ca.* 17°C), the flask was placed in an ice bath and rapidly stirred while water (100 mL) was added through a double-surfaced condenser. The lipids were extracted into light petroleum (100 mL), washed with water (2 × 100 mL) and aqueous $NaHCO_3$ (100 mL), dried (Na_2SO_4) and refrigerated. Removal of solvent under reduced pressure gave a light yellow oil. TLC of the products gave three dark spots under UV light (254 nm) (R_f 0.15, 0.37 and 0.54) and three fluorescent yellow spots after spraying with dichlorofluorescein and viewing under 366 nm illumination (R_f 0.26, 0.45 and 0.58). Catalytic hydrogenation resulted in the consumption of 1.2 moles of H_2 per 308 g of products. GLC of the hydrogenation products gave ECL: APL 17.8 (0.4%), 18.00 (15.8), 18.33 (21.3), 18.77 (0.7), 18.99 (0.4), 19.47 (6.0), 19.95 (3.1) and 20.19 (5.1).

Separation of fractions from the reaction products. The FAME products (3 g) in light petroleum were separated by adsorption column chromatography, the following four fractions (A-D) being eluted by mixtures of light petroleum with increasing levels of ether (typical results): A (250 mL of 2% ether; 250 mL of 3% ether) 1.4 g; B (200 mL of 5% ether) 0.9 g; C (100 mL of 10% ether; 200 mL of 20% ether) 0.2 g; D (250 mL of 30% ether) 0.5 g.

Separation of fraction A. Preparative GLC was conducted on a Pye Unicam 105 automatic instrument fitted with a packed column (2100 × 9 mm i.d.) of OV-101 silicone oil [17% on Chromosorb WHP (150–177 μm)]. Portions of Fraction A (20 mg each) were injected onto the column and separated isothermally at 220°C with nitrogen carrier gas (100 mL/min). One percent of the eluate was monitored by FID to actuate the collection of peaks in separate convoluted glass traps. The condensed fractions of FAME were rinsed out of the traps with light petroleum, and the solvent was removed under reduced pressure. Of the four subfractions obtained (A1, A2, A3, A4), A3 and A4 required no further purification.

Separation of subfraction A1. The two components A1.1 and A1.2 were isolated by argentation TLC (light petroleum/chloroform, 1:3). The two fluorescent bands (irradiation 254 and 366 nm) (R_f 0.4 and 0.6) were recovered from the layers, and the FAME were eluted with ether.

Separation of subfraction A2. Argentation TLC (light petroleum/chloroform, 1:1) gave three bands of recovered components, A2.1, A2.2, A2.3, and the FAME were eluted with ether.

RESULTS AND DISCUSSION

Treatment of methyl sterculate with highly purified boron trifluoride etherate was slow at ambient temperature but resulted in complete destruction of the cyclopronenoid ring in some 24 h. GLC of the extracted reaction products showed at least eight types of compounds to be present, representing 52% of the total product mixture, and UV analysis indicated conjugated diene systems to an extent of some 20% [*cf.* 64% from sterculene (3)]. IR spectra disclosed the presence of a carbonyl group and possibly allenic, in addition to ethenoid unsaturation (ν_{max} 1710, 1950, 3020, 1630, 965, 880, 720, cm^{-1}).

Catalytic hydrogenation followed by MS and GLC analysis revealed the presence of methyl esters of C_{18}, C_{19} and C_{20} compounds. TLC of the original product mixture on silicic acid showed the presence of at least six components, and column chromatography was used to obtain four fractions—A (47%), B (31%), C (6%) and D (16%)—in increasing order of polarity. This communication is concerned with the identification of the reaction products found in fraction A. Later fractions contain high quantities of oligomeric material.

Fraction A was completely volatile under GLC conditions and was separated into four subfractions (A1–4) by preparative GLC. Some of these subfractions were not composed of unique structures, and in those cases further separation was necessary. Subfraction A1 was separated into two components (A1.1 and A1.2) by argentation TLC. Component A1.1 gave an R_f at 0.5, intermediate between those of methyl stearate and methyl oleate, suggesting the presence of a *trans*-alkene or an allene group (ECL: APL 17.73, DEGS 18.80). On catalytic hydrogenation, two moles of hydrogen were absorbed, and GLC of the hydrogenated products gave a single peak at an ECL of 18.30 on both APL and polyester (DEGS) stationary phases, suggesting a mid-chain methyl-substituted stearate (7). The MS of this product showed it to be composed of a mixture of methyl 9-methyloctadecanoate [1] and the 10-methyl isomer [2] (M^+312) with two pairs of α-cleavage ions which identify the position of the branching (8) [1] *m/z* 185, 157; [2] 199, 171). The IR spectrum of A1.1 showed a weak absorbance at ν_{max} 1950 cm^{-1} (nonterminal allene).

[1]

[2]

No UV absorption maximum was observed above 210 nm. The mass spectrum gave the expected molecular ion (*m/z*

308) and fragment ions consistent with an unsaturated FAME.

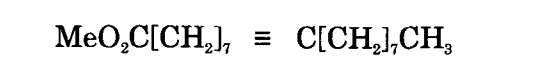
Permanganate-periodate oxidation (5) followed by methylation and GLC identification of the fragments showed the presence of methyl octanoate and methyl 9-oxodecanoate (from 3), and dimethyloctadioate and decan-2-one (from 4).

[3]

[4]

Thus, A1.1 was composed of a mixture of two isomeric allenic esters, methyl 9-methyloctadeca-9, 10-dienoate [3] and methyl 10-methyloctadeca-8,9-dienoate [4]. The 90 MHz ^{1}H-NMR spectrum of A1.1 confirmed the presence of a methyl-substituted allene (9). The allenic protons (δ4.9) coupling with the methyl and methylene protons attached to the allenic center would be expected to yield a ten-peak multiplet of intensity ratios 1:3:9.5:14:19:19:14:9.5:3:1; eight major peaks were observed in approximately the calculated ratio.

Argentation TLC of component A1.2 suggested that this material has a complexing constant similar to that of methyl oleate (R_f 0.4). Catalytic hydrogenation (2 moles of hydrogen) gave a product that had an ECL of 18.0 when subjected to GLC examination on both APL and DEGS stationary phases, suggesting methyl stearate. GLC of A1.2 on the same two phases gave ECLs of 17.84 and 20.10, respectively, confirming the presence of more than one unit of unsaturation. However, the IR spectrum gave no indication of the presence of unsaturation, and no absorption maximum was observed in the UV region above 207 nm. Permanganate-periodate oxidation followed by methylation and GLC gave only two products, methyl nonanoate and dimethyl nonadioate, indicating that the two units of unsaturation were located between C_9 and C_{10} of the C_{18} chain. Thus A1.2 was composed entirely of methyl octadec-9-ynoate (5), the ring methylene group having been lost from the methyl sterculate starting material. The ECLs given above for A1.2 confirm the identity of the product, and the MS gave the expected molecular ion (*m/z* 294) and a fragmentation pattern identical to that of an authentic sample of methyl octadec-9-ynoate. The 90 MHz ^{1}H-NMR spectrum was also consistent with this structure [5] (10–12).



[5]

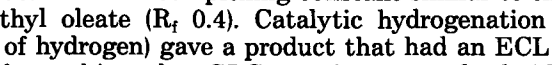
Subfraction A2, obtained by preparative GLC, was also a mixture, which was separated into three components by argentation TLC. The R_f of the component A2.1 was coincident with that of methyl stearate, that of A2.2 was between methyl stearate and methyl oleate and the R_f of component A2.3 was identical with that of methyl oleate. From its TLC properties, it appeared that component A2.1 was a saturated methyl ester (R_f 0.6), and this was confirmed by its failure to absorb hydrogen. Insufficient material was available for NMR studies, but IR spectra of both the ester and the parent acid indicated the presence of a cyclopropane ring (ν_{max} 3055, 1020 cm^{-1}) (13), and GLC properties were identical to those of an authentic specimen of methyl *cis*-9,10-methylene octodecanoate [6] (ECL: APL 18.58, DEGS 19.42). The MS fragmentation pattern was substantially the same as that published for [6] (14).

TABLE 1

Permanganate-Periodate Oxidation of Fraction A2.2

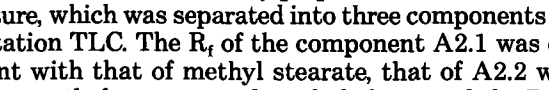
Fragments identified by gas-liquid chromatography	Origin of fragments	%
C^a_{10} 9-oxo + C^a_7 mono^b	9-Me$\Delta^{9,11}$ [7]	44
C_9di^c + C_7mono	10-Me$\Delta^{9,11}$ [7a]	
C_7di + C_9mono	9-Me$\Delta^{7,9}$ [8]	30
C_7di + 2-decanone	10-Me$\Delta^{7,9}$ [8a]	
C_8di + C_8mono	9-Me$\Delta^{8,10}$ [9]	22
C_8di + C_8mono	10-Me$\Delta^{8,10}$ [9a]	

^{a}Carbon number of parent acid.
^{b}mono = Monobasic parent acid.
^{c}di = Dibasic parent acid; 9-oxo = 9-oxo monobasic parent acid.

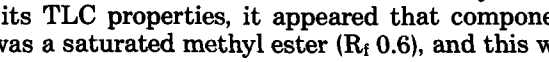


[6]

The argentation-TLC properties of isolate A2.2 suggest the presence of an allene, conjugated diene or *trans*-alkene function (R_f 0.5). UV absorption (λ_{max} 240 nm; ε_{240} 26,000) indicated the presence of a conjugated diene system substituted with three or four alkyl groups (15) (M^+ at *m/z* 308), and the IR spectrum supported this view [ν_{max} 3020, 960 (*trans*=CH), 1650, 1620 (C=C), 1378 (CH_3 branch), 865, 845, (R^1R^2C=CHR^3)]. GLC of the hydrogenated products from A2.2 (2 moles of hydrogen) gave an ECL of 18.30 for both the APL and the DEGS phases, indicating a C_{18} chain with an additional mid-chain methyl group, and MS showed the presence of 9-methyl and 10-methyl octadecanoates. Examination of the methylated permanganate-periodate oxidation products from A2.2 by GLC showed a variety of fragments (Table 1), indicating that A2.2 was a mixture of isomeric conjugated dienes with the mid-chain methyl group in either the 9- or the 10-position. The predominance of methyl heptanoate and methyl 9-oxodecanoate indicated that the major component of A2.2 was methyl 9-methyloctadec-9-11-dienoate [7].



[7]



[7a]

Table 1 shows the origin of the oxidation fragments and indicates that A2.2 was composed largely of the 9-methyl $\Delta^{9,11}$ [7] and 10-methyl $\Delta^{9,11}$ [**7a**] isomers (44%), the 9-methyl $\Delta^{7,9}$ [8] and 10-methyl $\Delta^{7,9}$ [**8a**] isomers (30%), and the 9-methyl $\Delta^{8,10}$ [**9**] and 10-methyl $\Delta^{8,10}$ [**9a**] isomers (22%).

$$MeO_2C[CH_2]_5\ CH = CH - \overset{\overset{CH_3}{|}}{C} = CH[CH_2]_7CH_3 \qquad [8]$$

10-Me isomer [8a]

$$MeO_2C[CH_2]_6CH = \overset{\overset{CH_3}{|}}{C} - CH = CH[CH_2]_6CH_3 \qquad [9]$$

10-Me isomer [9a]

The NMR spectrum of the isolate confirmed the presence, in admixture, of methyl groups attached to the termini and to the middle of the conjugated diene system (3H singlet at δ 1.70 and 1.74, respectively). The diversity of the conjugated diene species present was illustrated by the complexity of the spectrum in the δ5.0–6.4 region (3H multiplet). Coupling constants of 15 Hz, and possibly 8 Hz, were discernible in this region, indicating *trans* and possibly *cis*-substituted double bonds. The GLC of simple conjugated FAMEs on APL as stationary phase, where volatility considerations dictate chromatographic characteristics, has shown that *trans-trans* isomers have ECLs of about one unit higher than corresponding *cis-cis* isomers [19.4, 18.6, respectively (16)]. The ECL found for isolate A2.2 was 18.60, as opposed to 19.38 for isolate A3, which we suggest was composed entirely of *trans-trans* isomers. However, the possibility of *cis-cis* isomers being major components was rejected on spectroscopic grounds. It is concluded that isolate A2.2 is composed of *cis-trans* and/or *trans-cis* isomers of a mixture of conjugated dienes [7–9]. This view is supported by argentation-TLC where isolate A2.3 (*cis-cis* compounds) showed greater silver ion complexing ability than A2.2, again suggesting *cis-trans/trans-cis* configurations for the components of this isolate.

Isolate A2.3 also had a high molar absorbtivity at 240 nm (ε_{240} 26,000) and, although quantitative catalytic hydrogenation was not possible because of insufficient sample, MS of the isolate and of the hydrogenation products showed that two moles of hydrogen were absorbed (M^+ at *m/z* 308 and 312, respectively). The GLC and MS characteristics of the hydrogenation products indicated the presence of an octadecanoate with a methyl group at the 9- and 10-positions as before, with the 10-methyl isomer predominating in this case. The IR spectrum of the isolate A2.3 showed a new absorption band at ν_{max} 740 cm^{-1} [close to the normal skeletal $-(CH_2)_n-$ at 720 cm^{-1}], which was much stronger than in *cis* monounsaturated fatty esters, indicating the possibility of *cis-cis* conjugation; this was supported by the argentation-TLC characteristics. Permanganate-periodate oxidation of the isolate, followed by methylation and GLC identification of the fragments, showed the presence of dimethyl-heptadioate and decan-2-one, indicating the presence of methyl 10-methyl $\Delta^{7,9}$ octadecadienoate [**8a**] in the isolate to an extent of some 60%, and methyl heptanoate and methyl 9-oxodecanoate, suggesting the presence of the 9-methyl $\Delta^{9,11}$ isomer [7] to an extent of some 20%. That the isomers in this isolate were in the *cis-cis* configuration was supported by GLC studies (ECL: APL 18.69, DEGS 20.56) and by NMR spectra, which showed a 1-H quartet at δ5.24 (J 8.0 Hz) and a 2-H multiplet at δ6.00 (J 9.0 Hz) corresponding to those calculated for a *cis-cis* $-R^1(Me)C{=}CH{-}CH{=}CHR^2$ system. Thus, isolate A2.3 was composed substantially of *cis-cis* isomers of methyl 10-methyloctadeca-7,9-dienoate [**8a**] with a secondary constituent methyl 9-methyloctadeca-9,11-dienoate [7] and minor quantities of other isomers.

Subfraction A3, isolated by preparative GLC, exhibited IR and UV absorption properties characteristic of conjugated dienoic FAME [ν_{max} 3020, 1660, 1620, 1378 (Me branch), 960 (strong, *trans*=CH)cm^{-1}; λ_{max} 235 nm]. Examination of the products of catalytic hydrogenation (2 moles of hydrogen) by GLC and MS showed the presence of methyl 9- and methyl 10-methyloctadecanoates, as in the case of the previous isolate. Permanganate-periodate oxidation showed the isolate to be composed mainly of 9-methyl and 10-methyl octadeca-8,10-dienoates [**9,9a**], *i.e.,* with the side-chain methyl group in the middle of the diene system (50%), and equal quantities of the 9-methyl $\Delta^{9,11}$ isomer [**13**], and the 10-methyl $\Delta^{7,9}$ isomer [**14a**]. That the isolate was substantially composed of *trans-trans* unsaturation was confirmed by the high UV molar extinction coefficient (ε_{235} 30,500), characteristic of such fatty acids/esters (15), and by the high ECL obtained by GLC on APL as stationary phase (19.35) and DEGS (21.31) (16). The NMR spectrum was consistent with the structural features indicated, showing superimposed multiplets in the δ5.2–6.3 region (J 15 and 13 Hz) characteristic of *trans-trans* conjugation, predominantly of the type $R^1CH{=}C(Me)CH{=}CHR^2$. Thus, isolates A2.2, A2.3 and A3 are substantially composed of *cis-trans*, *cis-cis* and *trans-trans* isomers, respectively, of a variety of conjugated dienoic esters with a methyl substituent attached to one of the unsaturated carbon centers [7–**9a**].

The MS of subfraction A4 showed a molecular ion at *m/z* 322, consistent with the molecular formula of a dienoic methyl ester of a C_{20} carboxylic acid, and gave a fragmentation pattern characteristic of such esters. The UV absorption spectrum (λ_{max} 232 nm; ε 24,000) and the properties of the compound on argentation-TLC confirmed the presence of a conjugated diene system. GLC gave a single peak on both APL (ECL 19.5) and DEGS (ECL 21.05) stationary phases. The products from catalytic hydrogenation (2 moles hydrogen) gave a single GLC peak of ECL 19.30 on both the above phases, suggesting methyl nonadecanoate with a mid-chain methyl group. MS of the products confirmed this assignment and revealed a mixture of 9-methyl and 11-methyl nonadecanoates (M^+ at *m/z* 326; fragments at *m/z* 213, 185, 157). The IR spectrum of the isolated subfraction showed absorption bands characteristic of an end-chain methylene group (ν_{max} 3080, 880 cm^{-1}) and a *trans*-ethenoid center (ν_{max} 3010, 963 cm^{-1}); a conjugated diene system was clearly visible

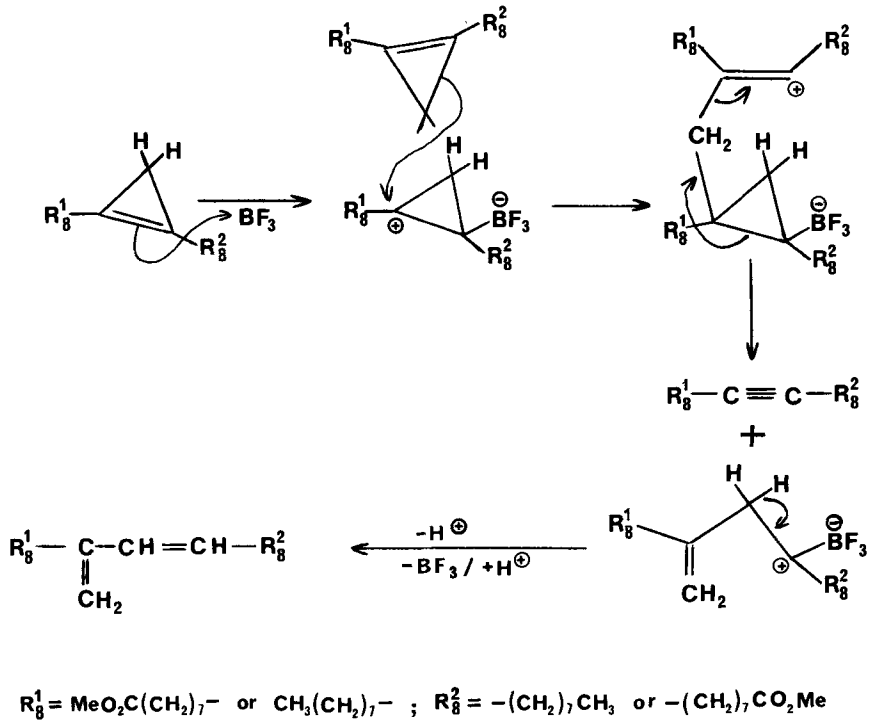


FIG. 1. Rationalization of the formation of the C_{18} alkyne and the C_{20} diene from the C_{19} sterculate.

at ν_{max} 1650, 1610 cm^{-1}; no broadening of the skeletal $-(CH_2)_n-$ band at 720 cm^{-1} was observed, suggesting the absence of *cis* unsaturation. That this isolate was composed of a mixture of methyl nonadecenoates with a conjugated side-chain methylene group in the 9- or 11-position was confirmed by permanganate-periodate oxidation, a technique that also located the position of the second double bond. Only methyl nonanoate and dimethylnonadioate were identified, indicating that the isolate was composed of a mixture of methyl 9-methylene-*trans*-10-nonadecenoate [**10**], and the 11-methylene-*trans*-9-isomer [**11**]. The NMR spectrum confirmed this assignment, being typical of an unsaturated fatty acid methyl ester but showing the resonance of the side-chain methylene group (2-H singlet) at δ4.78 and the *trans*-ethenoid protons (2-H multiplet) in the δ5.90 region (J 15 Hz).

$$MeO_2C[CH_2]_7 - \overset{\overset{CH_2}{\|}}{C} - CH = CH[CH_2]_7CH_3 \qquad [10]$$

$$MeO_2C[CH_2]_7CH = CH - \overset{\overset{CH_2}{\|}}{C}[CH_2]_7CH_3 \qquad [11]$$

Quantitative GLC showed that Fraction A was composed of some 25% of the allenes [**3**] and [**4**] (12% of the total products of the reaction between methyl sterculate and boron trifluoride etherate), 23% of the alkyne [**5**] (11%), 1% of the cyclopropanoid [**6**], 20% of the 9-methyl- and 10-methyl-*cis-trans*, *trans-cis* and *cis-cis* conjugated dienoic esters [**7–9a**] (9%), 20% of the *trans-trans* isomers of [**7–9a**] (9%) and 10% of the 9-methylene- and 11-methylene-*trans* conjugated dienoic esters [**10** and **11**] (5%). It is evident that isolates A2.2, A2.3 and A3, being C_{18} conjugated dienes with the methyl substituent at the termini and in the middle of the diene system, correspond to the products tentatively identified by Shimadate *et al.* (3) from their reaction between sterculene and aluminum oxide. They also recognized the presence of a conjugated diene containing a side-chain methylene group but suggested that it was a C_{19} compound rather than the related C_{20} compounds found in this work [**10,11**]. It is now evident that at least some of the ozonolysis products found by Shimadate *et al.* [caprylaldehyde (C_8), 2-decanone, methyl caprylate (C_8), methyl pelargonate (C_9)] were probably derived from allenes and alkynes, as well as from conjugated dienoic compounds.

The surprising discovery of a high concentration of methyl octadec-9-ynoate in our isolated products, arising from loss of the ring methylene group from the methyl sterculate reactant, was of some concern until the lost carbon atom was later found in the chain-lengthened conjugated dienes of sub-fraction A4 [**10,11**]. The transfer of the methylene group, after ring-opening by the acidic reagent, can be rationalized as in Figure 1.

REFERENCES

1. Rosie, D.A., and G.G. Shone, *J. Chem. Soc., Perkin Trans. 1, 1972*:1750 (1972).
2. Shone, G.G., *Proc. Nutrition Soc. 25*:37 (1966).
3. Shimadate, T., H.W. Kircher, J.W. Berry and A.J. Deutschman, Jr., *J. Org. Chem. 29*:485 (1964).

4. Miwa, T.K., K.L. Mikolajczak, F.R. Earle and I.A. Wolff, *Anal. Chem. 32:*1739 (1960).
5. von Rudloff, E., *Can. J. Chem. 34:*1413 (1956).
6. Rosie, D.A., and G.G. Shone, *Analyst, (London) 94:*677 (1969).
7. Hammonds, T.W., and G.G. Shone, *Ibid. 91:*455 (1966).
8. McCloskey, J.A., and J.H. Law, *Lipids 2:*225 (1967).
9. Chamberlain, N.F., *Anal. Chem. 31:*56 (1959).
10. Purcell, J.M., and Susi Heino, *Ibid. 40:*571 (1968).
11. Bohlmann, F., D. Shumann, H. Bethke and C. Zdero, *Chem. Ber. 100:*3706 (1967).
12. Stenhagen, E., S. Abrahamsson and F.W. McLafferty, *Registry of Mass Spectral Data,* Vol. 3, Wiley, New York, 1974, p. 1833.
13. Hopkins, C.Y., *J. Am. Oil Chem. Soc. 45:*781 (1968).
14. Wood, R., and R. Reiser, *Ibid. 42:*318 (1965).
15. Pitt, G.A.J., and R.A. Morton, in *Progress in the Chemistry of Fats and Other Lipids,* Vol. 4, Pergamon Press, London, 1957, p. 228.
16. Gunstone, F.D., and M.S.F. Lie Ken Jie, *Chem. Phys. Lipids 4:*131 (1970).

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