ough mixing, the flask and a blank prepared as above but without ethyl crotonate were placed in a water bath at the desired temperature.

Periodically, 5-ml. aliquots were withdrawn, added to solutions of 3 ml. of acetic acid in 10 ml. of 20% potassium iodide, and the liberated iodine titrated with *ca.* 0.11 *N* sodium thiosulfate.

Results of a typical run (benzene at 30°) are shown.

| Time (hr.) | 0 | 2.5 | 5.5 | 21.5 | 29 |
|---|---|---|---|---|---|
| [Peracid] (moles/l.) | 0.500 | 0.465 | 0.425 | 0.290 | 0.255 |

After 30 hr., the blank still had 0.492 mole/l. of peracid.

Experiments with *trans*-stilbene were run in the same way, except that initial concentrations were usually about 0.05 *M* because of the lower solubility of the *trans*-stilbene.

# A Re-examination of the Polymerization of Sterculic Acid.
## I. Reaction of Sterculene with Acetic Acid

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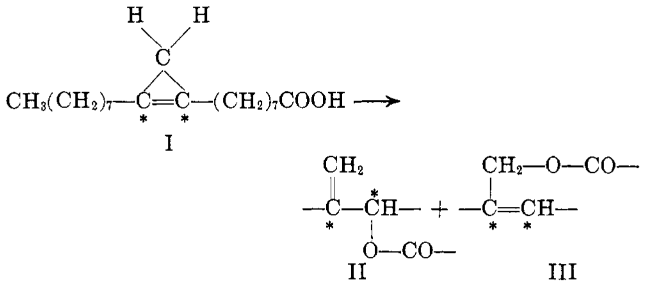
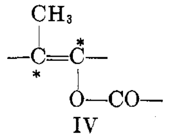
The reaction of sterculene (1,2-di-*n*-octylcyclopropene, V) with acetic acid gave 9-acetoxy-10-methyleneoctadecane (VI), 9-acetoxymethyl-9-octadecene (VII), and 9-acetoxy-10-methyl-9-octadecene (VIII).

Sterculic acid (I) polymerizes with destruction of the cyclopropene ring and formation of a polyester.[1–3] A similar reaction occurs with acetic acid, and from permanganate–periodate oxidations of the reaction products, the structures II and III were inferred to be present in the mixture as well as in the polymer.[3] The olefinic carbon atoms in I and its reaction products are starred.



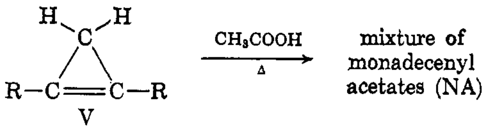
Although Faure and Smith[2] noted an increase in the infrared absorption at 7.72 μ, which they attributed to methyl groups, Rinehart, *et al.*,[3] found no chemical or spectroscopic evidence for the enol ester group IV.



$-\overset{\mathrm{CH_3}}{\underset{*}{C}}=\overset{*}{\underset{\mathrm{O-CO-}}{C}}-$

IV

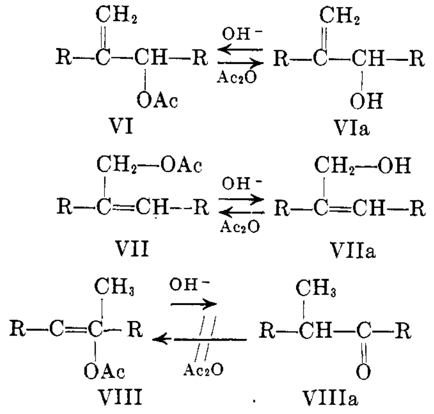
Earlier work in this laboratory on gas chromatography (g.l.c.) of the methyl esters of the acids produced by saponification of the sterculic acid polymer suggested that structure IV is present in the polymer.[4] The availability of sterculene[5] (V) prompted us to reinvestigate the problem because the products expected from V and acetic acid would be more amenable to chromatography and yield simpler compounds on degradation than those derived from I.



R (in this and succeeding diagrams) = $n\text{-}C_8H_{17}$–

When sterculene was heated with acetic acid, a mixture was obtained from which the reaction product was separated by distillation. The product was a mixture of nonadecenyl acetates (NA) that gave two peaks on g.l.c. and two spots on thin layer chromatography (t.l.c.). Saponification (calcd. for $C_{19}H_{37}$-OAc, 324; found, 321 and 322) gave a mixture (NA, $OH^-$) that showed two different peaks on g.l.c. and three different spots on t.l.c. Acetylation of NA,$OH^-$ gave a product (NA,$OH^-$,Ac) that showed the original two peaks on g.l.c. plus the smaller one in the NA,$OH^-$ diagram (Fig. 1), and the original two spots on t.l.c. plus the smaller one of highest $R_f$ given by the NA,$OH^-$ mixture (Fig. 1). The saponification equivalent of NA,$OH^-$,Ac (345) indicated that a portion of the saponified nonadecenyl acetate mixture could not be reacetylated to an ester.

These results suggested that at least three components were present in NA: the methyleneacetoxy derivative VI and the acetoxymethyl derivative VII, on the basis of previous results,[3] as well as the enol acetate derivative VIII.



The infrared spectrum of NA,$OH^-$ corroborated this supposition. A small band at 5.83 μ indicated the presence of a ketone such as VIIIa in the mixture of alcohols VIa and VIIa.

NA was ozonized in methylene chloride and the resulting solution decomposed with zinc in aqueous acetic acid. The aqueous fraction from the ozonolysis

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[1] J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

[2] P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

[3] K. L. Rinehart, Jr., S. I. Goldberg, C. L. Tarimu, and T. P. Culbertson, *J. Am. Chem. Soc.*, **83**, 225 (1961).

[4] J. C. Masson, Ph.D. thesis, University of Arizona, 1959.

[5] H. W. Kircher, *J. Am. Oil Chemists' Soc.*, **41**, 4 (1964).

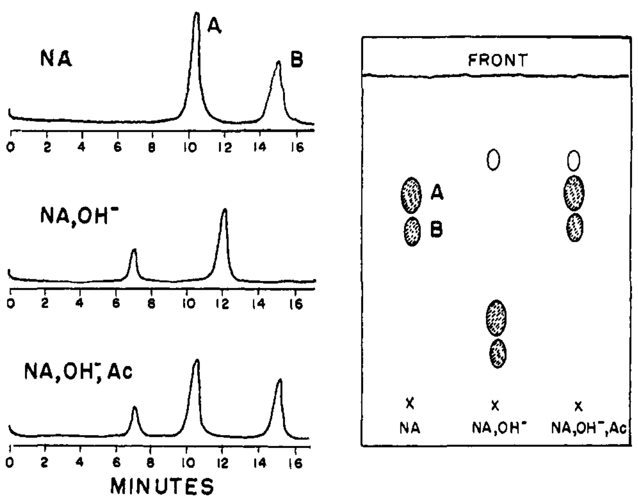

Fig. 1.—G.l.c. (left) of the nonadecenyl acetate mixture (NA) and its hydrolytic (Na,OH$^-$) and reacetylated (NA,OH$^-$,Ac) products (Aerograph Hy-Fi, 190°, 1 atm. He, 10-ft. ethylene glycol succinate column); t.l.c. (right): filled circles, 1% potassium permanganate spray; empty circles, 2,4-dinitrophenylhydrazine hydrochloride or 50% sulfuric acid sprays.

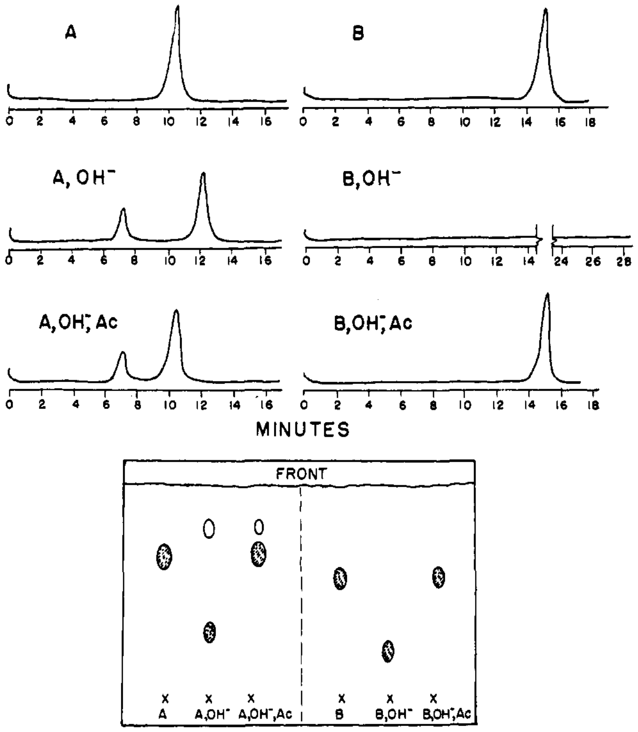

Fig. 2.—G.l.c. (upper left) of A and its hydrolytic and reacetylated products; g.l.c. (upper right) of B and its hydrolytic and reacetylated products; t.l.c. (lower) of the compounds (same g.l.c. and t.l.c. conditions as used in Fig. 1).

contained formaldehyde (from VI); the acid fraction contained only pelargonic acid (from VIII and from over oxidation of VII). The neutral fraction, after acetylation, showed four spots on t.l.c. corresponding in $R_f$ to pelargonaldehyde (from VII), 2-decanone (from VIII), nonyloin acetate (from VI), and 2-ketodecyl acetate (from VII). The neutral fraction was distilled; the first fraction contained pelargonaldehyde and 2-decanone, which were separated with a preparatory g.l.c. column and identified as their 2,4-dinitrophenylhydrazones. The second fraction was mainly 2-ketodecyl acetate and the third, nonyloin acetate, which was identified by hydrolysis to nonyloin. Thus, all of the products expected from the ozonolysis of VI, VII, and VIII were obtained and identified.

NA was separated into the components A and B (Fig. 1) by several distillations through a spinning band column. Hydrolysis and reacetylation of A indicated that it was a mixture of VI and VIII (Fig. 2). Early fractions obtained from a redistillation of A were rich in VIII. The spectra of one such fraction (A-1), its hydrolytic product, and the mixture obtained on reacetylation are shown in Fig. 3. The enol acetate C–O stretching band at 8.25 μ[6] is readily distinguishable from the acetate C–O stretching band at 8.08 μ[7] in A-1; the ketone band at 5.83 μ is seen in the hydrolytic product and the presence of this band as a shoulder on the ester carbonyl band is visible in the spectrum of the reacetylated material.

Permanganate–periodate oxidation[8] of A-1 gave unchanged starting material and nonyloin acetate. Ozonolysis of A-1 yielded 2-decanone, pelargonic acid, and nonyloin acetate. The components of A are therefore VI and VIII.

Hydrolysis of B (Fig. 1) and reacetylation gave the results shown in Fig. 2. G.l.c. of B,OH$^-$ produced no peak; the primary alcohol VIIa did not emerge from the column. The infrared spectrum of B,OH$^-$,Ac was superimposable on that of B; the spectrum of B,OH$^-$ showed no band in the carbonyl region. Permanganate–periodate oxidation of B went to completion to yield pelargonic acid and 2-ketodecyl acetate. B is therefore the acetoxymethyl derivative VII.

It was of interest to determine the ratios of VI, VII, and VIII in the sterculene–acetic acid reaction mixtures at various temperatures and times to see if VIII was produced by rearrangement of a previously formed product. It has been reported[3] that structure II is in 65% of the sterculic acid residues in the polymer and that structure III is in 35% of the residues. Since the three peaks in the chromatogram of NA,OH$^-$,Ac correspond to VIIIa, VI, and VII, respectively (Fig. 1), measurement of the area under these peaks will give an estimation of the relative proportions of VIII, VI, and VII in the nonadecenyl acetate mixture.

Mixtures of sterculene and acetic acid were heated at 60, 80, 100, and 120° for various lengths of time and sampled periodically. The samples were hydrolyzed to VIa, VIIa, and VIIIa, reacetylated to VI, VII, and VIIIa, and analyzed by g.l.c. The extent of the reaction and the ratios of the three components were

TABLE I

EXTENT OF THE STERCULENE–ACETIC ACID REACTION AND PRODUCT RATIOS AT VARIOUS TEMPERATURES

| Temp., °C. | Time, hr. | Sterculene reacted, % | Products, %[a] VI | VII | VIII |
|---|---|---|---|---|---|
| 60 | 117 | 88 | 54 (54–57) | 41 (39–41) | 5 (3.6–5) |
| 80 | 96 | 84 | 52 (51–55) | 36 (35–38) | 12 (10–12) |
| 100 | 44 | 83 | 54 (52–55) | 36 (35–37) | 10 (10–13) |
| 120 | 22 | 82 | 51 (48–55) | 33 (33–37) | 16 (13–17) |

[a] The figures in parenthesis represent the range of values observed during the entire reaction, from 10 to 88% completion.

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(6) R. N. Jones and F. Herling, *J. Am. Chem. Soc.*, **78**, 1159 (1956).

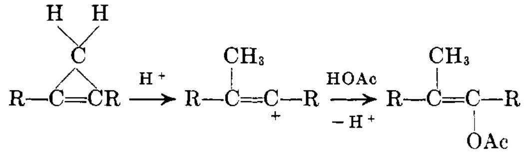
(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(8) R. V. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).

calculated from the areas under each peak and are given in Fig. 4 and Table I.

The amount of VIII in the reaction mixture increased with a rise in temperature at the expense of VI and VII. The ratios of the three components did not vary appreciably during a run at a particular temperature; the product ratio at the beginning of the reaction was about the same as that at the end of the reaction. A concomitant, but slower reaction, was the rearrangement of sterculene,[9] which decreased the extent of the sterculene–acetic acid reaction from 88% at 60° to 82% at 120°.

The mechanism proposed by Rinehart, *et al.*,[3] protonation of one of the olefinic carbon atoms of the cyclopropene ring followed by ring opening and addition of acetate, explains the formation of VI and VII. The formation of VIII cannot proceed by this pathway; it can be rationalized by the less likely protonation of the methylene group in the cyclopropene ring with ring opening and addition of acetate. The



I VIII

constancies of the product ratios at various temperatures and times indicate that VIII is formed from sterculene and acetic acid by an independent route and does not arise by rearrangement of VI or VII.

## Experimental

**Materials and Methods.**—Pelargonaldehyde and 2-decanone were purchased from Calbiochem, Los Angeles, Calif., and pelargonic acid from Distillation Products Industries. Nonyloin was prepared[10] from methyl pelargonate and sterculene, as described previously.[5] G.l.c. was done with a 10-ft. 20% ethylene glycol succinate analytical column and a 5-ft. 20% diethylene glycol succinate preparatory column in the Aerograph Hy-Fi and A-90-C instruments. T.l.c. of the nonadecenyl acetates and alcohols on Silica Gel G (Research Specialties Co.) was done with a solvent composed of petroleum ether (b.p. 60–90°), diethyl ether, and acetic acid in the ratio 180:20:1 (v./v./v.). T.l.c. of the nonadecenyl acetate oxidation products used the same adsorbent and solvents in the ratio 80:20:1. Infrared spectra were obtained in carbon tetrachloride with the Perkin-Elmer 137-C Infracord.

**Nonadecenyl Acetates.**—A mixture of V (35.3 g.) and glacial acetic acid (150 ml.) was stirred for 18.5 hr. under nitrogen at 120°. Excess acetic acid was removed with a rotary evaporator and the residue distilled (72–120° at 0.035 mm.) to yield 41.8 g. of a mixture of rearranged sterculene[9] and product. The former was removed with a spinning band column (75–100° at 0.05 mm.) and the latter distilled (110–120° at 0.04 mm.) to yield 31.7 g. of nonadecenyl acetates (NA, Fig. 1). The infrared spectrum of NA showed strong bands at 5.75 and 8.08 (acetate ester[7]) and weaker bands at 6.05 and 11.03 $\mu$ (*unsym*-disubstituted olefin[7]).

**Saponification.**—Two samples of NA (4.445 and 3.600 g.) were hydrolyzed at 60–70° for 3 hr. with 1 *N* potassium hydroxide in ethanol (30 ml.). Titration of the samples and a blank with 0.510 *N* hydrochloric acid gave saponification equivalents of 321 and 322 (calcd. for $C_{19}H_{37}OAc$, 324). The isolated hydrolytic products (7.10 g.; NA,OH$^-$, Fig. 1) had infrared absorption bands at 2.72 and 9.5 (alcohol[7]), 6.05 and 11.03 (*unsym*-disubstituted olefin[7]), and at 5.83 $\mu$ (ketone[7]).

**Reacetylation.**—The hydrolyzed nonadecenyl acetates (6 g.) were acetylated with pyridine and acetic anhydride (15 ml. each)

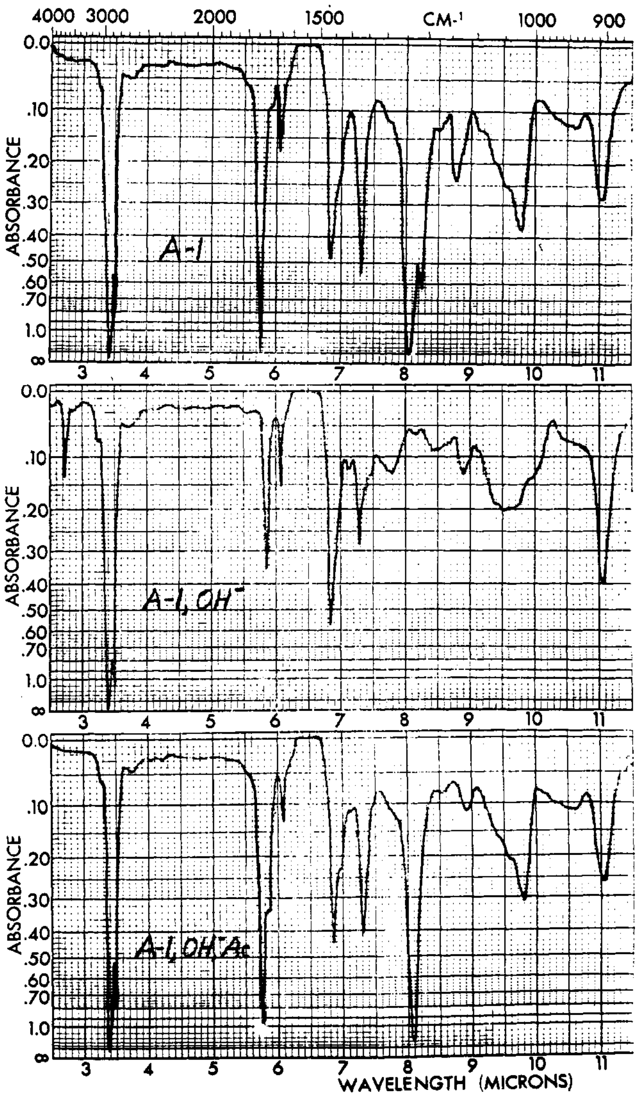


Fig. 3.—Infrared spectrum (top) of A-1, a mixture of VI and VIII; spectrum (middle) of A-1,OH$^-$, a mixture of VIa and VIIIa; spectrum (bottom) of A-1,OH$^-$,Ac, a mixture of VI and VIIIa.

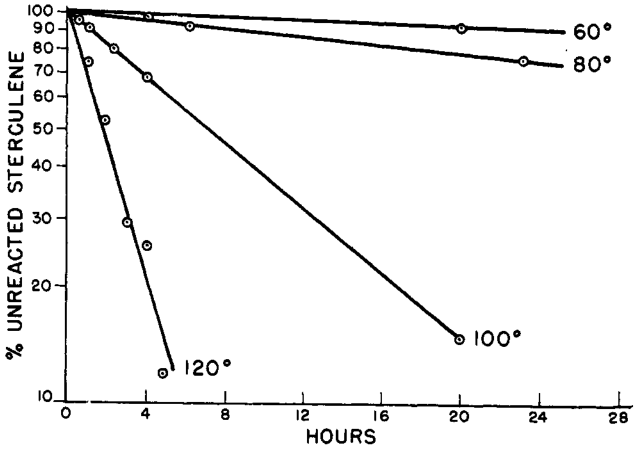


Fig. 4.—Reaction of sterculene and acetic acid at various temperatures.

at room temperature for 18 hr. Water was added to the reaction mixture and the products (NA,OH$^-$,Ac, Fig. 1) were extracted with petroleum ether (b.p. 30–60°) and distilled (115–120° at 0.05 mm.). Two samples were saponified as above to give saponification equivalents of 345 and 345. On the basis of this value, 94% of NA,OH$^-$,Ac was the acetates VI and VII and 6% was the ketone VIIIa. The infrared spectrum of NA,OH$^-$,Ac was

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[9] T. Shimadate, H. W. Kircher, J. W. Berry, and A. J. Deutschman, Jr., *J. Org. Chem.*, **29**, 485 (1964).

[10] V. L. Hansley, *J. Am. Chem. Soc.*, **57**, 2303 (1935).

almost superimposable on that of NA, a small shoulder on the ester carbonyl band (ketone) was discernible in NA,OH$^-$,Ac, and a small band at 8.8 $\mu$ (enol acetate*) in NA was missing in NA,OH$^-$,Ac.

**Ozonolysis.**—NA (20.35 g., 0.063 mole) in methylene chloride (250 ml.) was cooled to −45°. Ozone (0.15 mole) was passed through the solution over 2.5 hr. after which the temperature had risen to −32°. The solution was purged with nitrogen, warmed to room temperature, and added to a suspension of zinc dust (20 g.) in 50% aqueous acetic acid (200 ml.). The mixture was heated on a boiling water bath 1 hr. and the residue in the flask extracted with petroleum ether. The aqueous phase from the extraction was combined with that which had steam distilled with the methylene chloride and was treated with methone (20 g.) in ethanol (150 ml.). The next day the methone derivative of formaldehyde was obtained (5.94 g., 0.0202 mole) m.p. and m.m.p. 189.5–190°, lit.[11] m.p. 189°.

The petroleum ether phase was extracted with aqueous alkali. The alkaline solution was acidified and extracted with ether to yield an acid (1.40 g.), a portion of which was converted to the methyl ester with 7% boron trifluoride in methanol. G.l.c. of the ester showed only methyl pelargonate. The *p*-toluidide of the acid was prepared,[12] m.p. 81–81.5°, m.m.p. (with the *p*-toluidide of pelargonic acid) 82–84°, lit.[12] m.p. 84°.

The remaining petroleum ether phase was evaporated to leave a residue (18.4 g.) which showed six spots on t.l.c., some of which were suspected to be deacetylated oxidation products. The mixture was acetylated with pyridine and acetic anhydride (20 ml. each) to yield a product that showed only four spots on t.l.c. It was distilled; the first fraction (b.p. 91–114° at 26 mm., 2.25 g.) was composed of 70% pelargonaldehyde and 30% 2-decanone (by g.l.c.). These were separated on a preparatory column and the 2,4-dinitrophenylhydrazones of each were prepared: 2-decanone 2,4-DNP, m.p. and m.m.p. 73.5–74.5°, lit.[13] m.p. 73–74°; pelargonaldehyde 2,4-DNP, m.p. and m.m.p. 105–106°, lit.[14] m.p. 105–106°.

The second fraction from the distillation (b.p. up to 90° at 0.05 mm., 4.73 g.) crystallized in the receiver. It was recrystallized from methanol and identified as 2-ketodecyl acetate, m.p. 55.5–56.5°, lit.[3] m.p. 55.5–55.8°; infrared bands at 5.68 and 8.13 (acetate ester) and 5.75 $\mu$ (ketone).

The third fraction (b.p. 145–155° at 0.015 mm., 8.95 g.) had the same retention time on g.l.c. and $R_f$ on t.l.c. as synthetic nonyloin acetate. A portion (5.2 g.) was hydrolyzed with alcoholic potassium hydroxide and the product crystallized from ethanol to yield 3.74 g. of nonyloin, m.p. 45–46.5°, m.m.p. 47–48°, lit.[10] m.p. 44°.

**Separation of NA into A and B (Fig. 1).**—The products from two sterculene–acetic acid reactions were combined (57.5 g.) and fractionated through a 20-in. spinning band column at 0.05 mm. Nine fractions were obtained (0.5 ml./hr.), the first (6.7 ml.) was largely forerun, fractions 2–5 (43.5 ml.) were 70–90% A, and fractions 6–9 (14.1 ml.) were 85–90% B. Fractions 2–5 were combined and redistilled to yield a fraction (A-1, 15.1 ml.) consisting only of A and enriched in the enol acetate derivative VIII. Fractions 6–9 were redistilled to yield a fraction (5.6 ml.) consisting only of B.

**Identification of A.**—Alkaline hydrolysis (A,OH$^-$) and reacetylation (A,OH$^-$,Ac) of 1 ml. of A-1 gave the chromatographic and spectroscopic data shown in Fig. 2 and 3. A solution of sodium periodate (6.85 g.), potassium permanganate (0.085 g.), and sodium bicarbonate (1.27 g.) in water (800 ml.)[8] was added to A-1 (1.30 g.). *t*-Butyl alcohol (250 ml.) was added to enhance the solubility of A-1 in the aqueous solution. The mixture was stirred for 44 hr., acidified, and extracted with petroleum ether. The extract was dried and evaporated to yield the oxidation products (1.62 g.). G.l.c. of the products showed no 2-decanone; t.l.c. showed unchanged starting material and nonyloin acetate.

A solution of A-1 (8.40 g.) in glacial acetic acid (175 ml.) was ozonized and worked up as described above to yield a product (7.76 g.). From this, pelargonic acid (1.61 g.) was obtained by alkaline extraction; it was identified by g.l.c. of its methyl ester and as its *p*-toluidide, m.p. 81–82°. 2-Decanone (0.45 g.) was distilled from the mixture (b.p. 90–91° at 10 mm.) and characterized as its 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 74–74.8°. The remaining material had the chromatographic behavior of nonyloin acetate on g.l.c. and t.l.c. Component A was therefore a mixture of VI and VIII. Both of these were oxidizable with ozone, but only VI could be degraded by the permanganate–periodate procedure.

**Identification of B.**—Alkaline hydrolysis of 1 ml. of B gave an alcohol (B,OH$^-$, Fig. 2) that did not pass through the g.l.c. column, which explains why only two peaks were observed on g.l.c. on the NA,OH$^-$ mixture. It showed a single spot on t.l.c.; reacetylation of the alcohol gave an ester (B,OH$^-$,Ac) that had the same chromatographic behavior and whose infrared spectrum was superimposable on that of B. A portion (1.36 g.) of B was oxidized by the permanganate–periodate procedure given above to yield a product (1.80 g.) that contained no starting material. It was separated into an acid fraction (0.55 g.) and a neutral fraction (1.01 g.). The former contained only pelargonic acid by g.l.c. of its methyl ester, *p*-toluidide m.p. and m.m.p. 82–84°. The latter was crystallized from methanol to yield 2-ketodecyl acetate, m.p. 55.8–56°, lit.[3] m.p. 55.5–55.8°. Component B is therefore VII.

**Reactions of Sterculene and Acetic Acid at Various Temperatures.**—The two reagents (1 ml. each) were placed in 4-ml. screw cap vials under nitrogen and placed in oil baths held at 60–65°, 80–85°, 100–105°, and 120–127° by hot plates. The reaction mixtures at the higher two temperatures became homogeneous within 1 hr.; those at 60 and 80° remained as two phases for almost 2 days. Six samples of 10 drops each were removed from the vials periodically and added to alcoholic potassium hydroxide; the hydrolyzed materials were reacetylated with pyridine and acetic anhydride and isolated from the water-diluted reaction mixtures. When two phases were present, the vials were vigorously shaken before the samples were removed to get a representative quantity of both phases. Ten microliters of the products from the esterifications was analyzed with the Aerograph A-90-C instrument.

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(11) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(13) C. Jutz, *Ber.*, **91**, 1867 (1958).

(14) W. F. Huber, *J. Am. Chem. Soc.*, **73**, 2730 (1951).