80 μl of 1 was placed in a reservoir at the cold end of the tube and a 0.1-mm vacuum was applied through a trap cooled to −78°. Gentle warming was applied to the sample to facilitate distillation into the hot tube. Collection of the major product gave a colorless liquid: ir 3070, 3060, 3015, 2960, 2915, 2895, 2835, 1795, 1745, 1600, 1490, 1360, 855, and 690 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.53; H, 8.17.

Synthesis of 2.—To a slurry of 6.12 g (0.054 mol) of potassium *tert*-butoxide and 18 g (0.1 mol) of 1,1-diphenylethylene in 75 ml of *n*-pentane held at −10° was added dropwise a solution of 5.12 g (0.054 mol) of 3-chloro-3-methyl-1-butyne[13] in 20 ml of *n*-pentane. Following the addition the slurry was allowed to warm to room temperature and 100 ml of water was added. The layers were separated and the organic material was washed with five 150-ml portions of water, dried over anhydrous sodium sulfate, and concentrated at the water pump to give 21 g of a red oil. Chromatography of 2.0 g of the oil on silica gel using hexane as eluent led to the recovery of 1.5 g of 1,1-diphenylethylene and 0.3 g of 2. A value of 246.140713 was obtained in a precise mass measurement (calcd for $C_{19}H_{18}$: 246.140844).

Pyrolysis of 2.—2 (100 mg) was dissolved in 500 μl of CCl_4 and sealed in a medium-walled nmr tube under nitrogen. Heating the sample at 80° for 19 hr caused complete rearrangement to **4**, which was purified by chromatography on a 1 ft × 0.5 in. column of basic alumina: ir 3080, 3060, 3030, 2970, 2930, 2905, 1795, 1600, 1490, 1440, 1365, 1095, 1070, 855, 775, 750, and 685 cm^{-1}. A value of 246.140713 was obtained in a precise mass measurement.

Registry No.—**1**, 4544-23-4; **2**, 30800-74-9; **3**, 30896-86-7; **4**, 30800-58-9.

(13) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

Mononitration of Methyl Abieta-8,11,13-trien-18-oate

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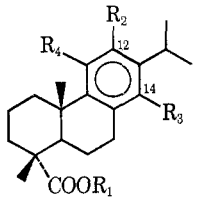
Aromatic substitution reactions on abieta-8,11,13-trien-18-oic acid, dehydroabietic acid (**1a**), and the corresponding methyl ester **1b** have been the subject of a number of investigations. Although monosulfonation at C-12,[1-3] monobromination at C-12,[4] and monoacetylation[2,5] at C-12 and at C-14 (75% C-12) have been reported, attempted mononitration has failed to produce the desired results, yielding instead the 12,14-dinitro derivative **1c**[6] and **1d**.[7] Also an attempt to produce a mononitro derivative *via* nitration of the 12-sulfonic acid and subsequent hydrolysis of the sulfonic acid group failed at the second step.[4] The 14-nitro derivative **1e** has been prepared from methyl 12,14-dinitroabieta-8,11,13-trien-18-oate (**1d**) by selective reduction of the 12-nitro group to the amine **1f** followed by deamination[4,8] and by nitration of the 12-amino compound **1g** followed by deamination.[4,9]



1

	R_1	R_2	R_3	R_4
a	H	H	H	H
b	CH_3	H	H	H
c	H	NO_2	NO_2	H
d	CH_3	NO_2	NO_2	H
e	CH_3	H	NO_2	H
f	CH_3	NH_2	NO_2	H
g	CH_3	NH_2	H	H
h	CH_3	NO_2	H	H
i	CH_3	H	H	NO_2

The work cited indicates that the 12 position is more reactive than the 14 position. We, therefore, decided to investigate anew the feasibility of direct mononitration of methyl abieta-8,11,13-trien-18-oate (**1b**). We hoped to obtain the 12-nitro derivative **1h**, which we believe would be a useful synthetic intermediate. We were encouraged also by the advent of positionally selective nitration procedures in recent years. Acetic acid, for instance, is the solvent of choice for positionally selective nitrations of fluoranthene[10] and naphthalene[11] (mixed acids), acenaphthene[12] (nitric acid), and octaethylporphyrin[13] (fuming nitric acid). Nitric acid in nitromethane is also positionally selective.[11] Mechanistic considerations have been discussed[11,14] but will not be reviewed here.

We attempted mononitration of **1b** with the above procedures and found, uniformly, that under the usual mild conditions no reaction occurred. By increasing time or temperature complex mixtures were obtained which were relatively free of both starting material and the desired product, as shown by the aromatic region of their nmr spectra. The conclusion reached was that the substrate **1b** was not sufficiently reactive toward these reagents under the usual conditions.

The more reactive but still selective[15,16] nitrating agent acetyl nitrate provided a procedure which yields a mixture of the 12-nitro and 14-nitro derivatives, **1h** and **1e**, respectively. A convenient separation of the mixture by one fractional crystallization in methanol gave a first fraction of almost pure 14-nitro derivative **1e** (20% yield). The 14-nitro derivative **1e** was identical with a sample prepared by the method of Zeiss.[8] This one-step synthesis (20%) compares well in terms of con-

(1) Numbering systems used in the past have been translated into the presently accepted system.

(2) L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.*, **60**, 2631 (1938).

(3) T. Hasselstrom and J. D. McPherson, *ibid.*, **60**, 2340 (1938).

(4) W. P. Campbell and M. Morgana, *ibid.*, **63**, 1838 (1941).

(5) L. F. Fieser and W. P. Campbell, *ibid.*, **61**, 2528 (1939).

(6) L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 159 (1938).

(7) E. S. Hansen and H. H. Zeiss, *ibid.*, **77**, 1643 (1955).

(8) H. H. Zeiss, U. S. Patent 2,803,645 (1957); *Chem. Abstr.*, **52**, 2921 (1958).

(9) The assignment of one nitro group of the dinitro compound (**1c** and **1d**) at C-12 was unambiguous.[2,4] Locating the second nitro group at C-14 was based on the expectation of normal meta orientation. Hansen and Zeiss[7] have pointed out that this assignment is reasonable but not beyond question.

(10) A. Streitwieser, Jr., and R. C. Fahey, *J. Org. Chem.*, **27**, 2352 (1962).

(11) P. G. E. Alcorn and P. R. Wells, *Aust. J. Chem.*, **18**, 1377 (1965).

(12) A. Davies and K. D. Warren, *J. Chem. Soc. B*, 873 (1969).

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(14) G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Amer. Chem. Soc.*, **84**, 3687 (1962).

(15) G. Powell and F. R. Johnson, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1955, p 449.

(16) M. L. Scheinbaum, *Chem. Commun.*, 1235 (1969).

venience with the best three-step synthesis (43%).[8] The nmr spectrum supports the assigned structure. The aromatic region contains an AB quartet with J_{AB} = 9 Hz and $\Delta\nu$ = 9.4 Hz.[17] The coupling constant is satisfactory for ortho protons[18] and $\Delta\nu$ is consistent for two protons meta and para to a nitro group, respectively.[19] Alternative structure **1i** is clearly not allowed by these data.

Concentration of the methanol gave a second fraction which is *ca.* 80% 12-nitro **1h** and 20% 14-nitro **1e** (by nmr). The total material represented a 45% yield of the 12 isomer. Pure 12-nitro **1h** was obtained on further fractional crystallization. The structure of the 12-nitro derivative **1h** was established by nitration to the known 12,14-dinitro derivative **1d**[9] and by catalytic hydrogenation to the known 12-amine **1g**.[4]

The nmr spectrum of **1h** has the methine proton of the isopropyl group downfield from its position in **1b**, **1d**, and **1e**. In view of the known long-range shielding effect of the nitro group[13] we assume that the isopropyl group is in some conformation in which the methine proton is out of the area shielded by the nitro group. The methyls of the isopropyl side chain in both **1h** and **1e** appear as doublets (J = 2 Hz) of a doublet (J = 7 Hz). Decoupling experiments to determine the source of the weaker coupling were not conclusive, but suggested that the $ArCH_2$ protons were responsible.

With the two pure isomers in hand it was shown that the 12-nitro compound **1h** underwent catalytic reduction to the amine **1g** smoothly, while the 14-nitro compound **1e** did not react under the same conditions. This is in accord with the selective catalytic reduction of the 12,14-dinitro compound **1d** cited above.[4,8] These data suggested a separation scheme based on selective reduction from the crude mixture of the 12-nitro compound. This was realized and direct catalytic hydrogenation of the crude mixture of products yielded the 12-amine **1g** in 32% yield and the unreacted 14-nitro compound **1e** in 20% yield.

Experimental Section[20]

Nitration.—To a solution of 3.14 g (0.01 mol) of methyl abieta-8,11,13-trien-18-oate (**1b**) in 30 ml of acetic anhydride at 25° was added dropwise with stirring over 15 min a solution of 0.90 ml of fuming nitric acid (90%) in 1.80 ml of acetic anhydride also at 25°. After the addition was completed the mixture was stirred for 1 hr and poured onto ice. The solid, collected by filtration after hydrolysis of the solvent, was washed with water and air dried to 3.48 g. This crude product had four relatively large peaks in the aromatic region of the nmr spectrum (CCl_4) and at least five smaller peaks in the same region. Integration indicated approximately 27% 14-nitro **1e** and 47% 12-nitro **1h** in the crude product.

Isolation of Methyl 14-Nitrodehydroabietate (1e).—The crude product was dissolved in 125 ml of methanol and the first crop, collected after 1 day at room temperature, weighed 0.75 g,[21] mp 187–190°, 185–190°, 185–189°. One recrystallization from methanol gave 0.61 g,[21] mp 193–194.5°. Concentration of the mother liquor yielded a second crop of less pure material, 0.06 g,[21] mp 184–188°, total yield 19% (lit. mp 194–195°,[4] 192–193.5°;[8] authentic sample prepared by the method of Zeiss[8] had mp 192.5–194.5°). The mixture melting point of authentic sample and sample prepared by one-step mononitration was 193–194.5°. The ir and nmr spectra were identical: ir (CCl_4) 5.8 (C=O), 6.5, 7.3 μ (NO_2); nmr ($CDCl_3$) δ 7.30 (AB quartet, $\Delta\nu_{AB}$ = 9.4 Hz, J_{AB} = 9 Hz, 2 H, Ar), 3.67 (s, 3 H, $-OCH_3$), 2.75 (m, 3 H, $ArCH_2$, ArCH), 1.27 (s, CH_3), 1.22 (s, CH_3), 1.22 [d, J = 6 Hz, $CH(CH_3)_2$, both peaks are further split, J = 2 Hz]. Decoupling (difference frequency = −97 Hz) caused the methyl region to collapse to two peaks at δ 1.22 and 1.27.

Isolation of Methyl 12-Nitrodehydroabietate (1h).—The mother liquor from which the 14-nitro compound **1e** had been obtained was concentrated to 25 ml. After cooling, the precipitate was collected and washed with cold alcohol. The air-dried solid weighed 1.65 g,[21] mp 116–126°, 107–125°, 120–129° (*ca.* 80% 12-nitro by integration of nmr aromatic region). Recrystallization from 95% ethanol yielded 1.13 g[21] (*ca.* 90–95% pure by nmr), mp 123–131°, yield 31%. Three more layers of fractional recrystallization from 95% ethanol afforded pure material (0.63 g) in the head fraction and an additional 0.26 g of material 70+% pure by nmr, mp 123–134°, next to the head fraction. Two more recrystallizations of the head fraction afforded the analytical sample: mp 134.5–136°; ir (KBr) 5.8 (C=O), 6.6, 7.5 μ (NO_2); nmr (CCl_4) δ 7.57 (s, 1 H, Ar), 7.07 (s, 1 H, Ar), 3.63 (s, 3 H, OCH_3), 3.53, 3.42, 3.30, 3.18 (four peaks observed of $-CH(CH_3)_2$ septuplet, 1 H, J = 7 Hz), 2.93 (t, 2 H, $ArCH_2$, J = 6 Hz), 1.25 (s, CH_3), 1.22 (s, CH_3), 1.25 [d, J = 7 Hz, $CH(CH_3)$, both peaks are further split, J = 2 Hz). Decoupling (difference frequency = −126 Hz, methine H) caused the methyl region to collapse to two peaks at δ 1.25 and 1.22. With a difference frequency of −110 Hz ($ArCH_2$) the methyl region collapsed to four peaks at δ 1.20, 1.23, 1.25, and 1.32.

Anal. Calcd for $C_{21}H_{29}O_4N$: C, 70.17; H, 8.13; N, 3.90. Found: C, 70.19; H, 8.12; N, 3.82.

Nitration of Methyl 12-Nitrodehydroabietate (1h).—Methyl 12-nitrodehydroabietate (1h), 0.50 g (*ca.* 85% pure), was nitrated with mixed acids (dinitration procedure of Fieser[6] and of Zeiss[7]). Recrystallization of the crude product from ether afforded a first crop of 0.17 g: mp 188–189° (lit. mp 189–190°,[8] 189–189.5°,[6] 190–191°[7]), mmp 188–189° (authentic sample prepared by method of Hansen and Zeiss[7] had mp 188–189°); ir ($CHCl_3$) 5.8 (C=O), 6.5, 7.35 μ (NO_2) (identical with spectrum of authentic methyl 12,14-dinitrodehydroabietate); nmr ($CDCl_3$) δ 7.58 (s, Ar), 3.68 (s, OCH_3), 2.83 (m, ArCH, $ArCH_2$), 1.32 [d, J = 7 Hz, $CH(CH_3)_2$], 1.27 (s, CH_3), 1.25 (s, CH_3).

Concentration of the mother liquor gave a second crop of 0.13 g, mp 186.5–188°.

Catalytic Reduction of Methyl 12-Nitrodehydroabietate (1h).—Methyl 12-nitrodehydroabietate (1h), 0.50 g (*ca.* 90% pure), in 20 ml of ethyl acetate and 2 ml of acetic acid with 0.09 g of 83% platinum oxide was treated with hydrogen at room temperature and atmospheric pressure (selective reduction procedure of Zeiss[8]). The crude solid recovered by filtration and evaporation was dissolved in ether and treated with dry hydrogen chloride. The hydrochloride salt was treated with dilute aqueous base to yield 0.34 g (65%) of methyl 12-aminodehydroabietate (1g): mp 135–137° (lit.[5] mp 137–137.5°); ir (KBr) 2.85, 2.95 (NH_2), 5.8 (C=O), 6.1, 6.35, 6.65 μ (Ar); nmr ($CDCl_3$) δ 6.80 (s, 1 H, Ar), 6.58 (s, 1 H, Ar), 3.65 (s, 3 H, OCH_3), 3.50 (broad, 2 H, NH_2), 2.83 (m, 3 H, ArCH, $ArCH_2$), 1.27 (s, CH_3), 1.23 [d, J = 7 Hz, $CH(CH_3)_2$], 1.18 (s, CH_3).

Under the same conditions the 14-nitro isomer **1e** did not consume hydrogen.

Catalytic Hydrogenation of Crude Nitration Mixture.—A solution of 1.00 g of crude nitration mixture in 40 ml of ethyl acetate and 4 ml of acetic acid with 0.10 g of 83% platinum oxide was treated as above.

The crude hydrochloride salt of methyl 12-aminodehydroabietate (1g) was isolated in the usual manner and converted to the free amine 1g, 0.33 g,[21] mp 135–137° (32% yield from methyl dehydroabietate).

The ether mother liquor was concentrated and crude methyl 14-nitrodehydroabietate was recovered, 0.20 g,[21] mp 186–189° (20% yield from methyl dehydroabietate), ir identical with ir of authentic sample.

Registry No.—**1b**, 1235-74-1; **1g**, 30885-12-2; **1h**, 30885-13-3.

(17) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 203.

(18) Reference 17, p 183.

(19) Reference 17, p 175.

(20) Infrared spectra were obtained on a Perkin–Elmer Model 137 spectrophotometer and nmr spectra were obtained from dilute solutions with tetramethylsilane as internal standard using a Varian A-60 spectrometer equipped with a Model V6058A spin decoupler. Melting points were determined in open capillary tubes with a Büchi melting point apparatus and are corrected. Microanalysis was by Scandinavian Microanalytical Laboratory, Box 25, 2730 Herlev, Denmark.

(21) Data given are average for three similar experiments.

Acknowledgment.—We wish to express our thanks to Dr. Horace F. White for helpful discussion of the nmr spectra and to the Portland State University Research Committee for support.

Three-Step Synthesis of Methyl Sterculate[1a]

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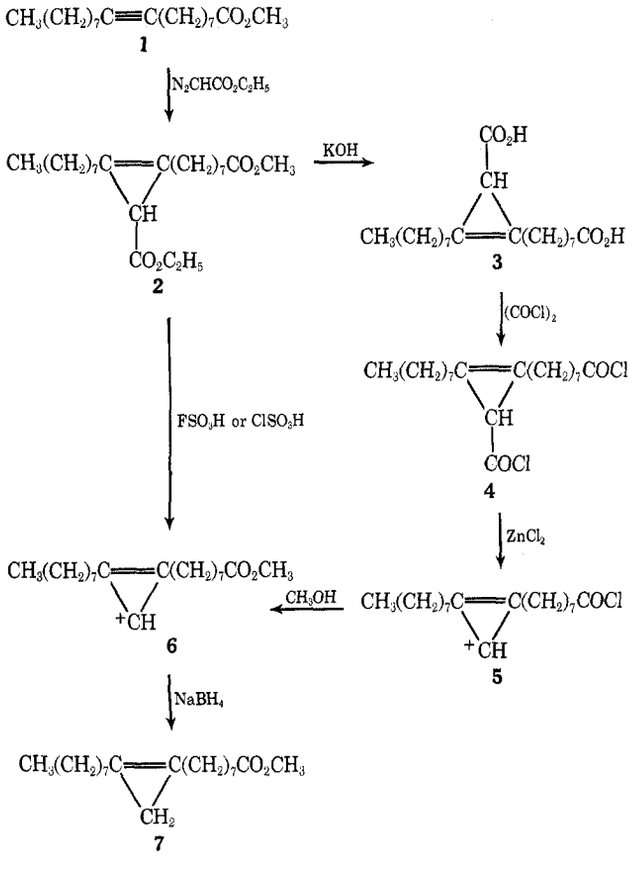
Studies to elucidate details of the metabolism[2,3] of the physiologically important cyclopropenoic acids have made the availability of these acids highly desirable. Several devised syntheses have provided possible routes but the low overall yield realized in these procedures offered no satisfactory solution to the problem.[4-7] Recently, however, Gensler and his associates[7,8] published a method for the synthesis of methyl sterculate with an overall yield in the order of 30%.



A vital sequence in their synthesis was the decarbonylation of **2** to **7** *via* the corresponding biacid chloride **4**.

We have now developed an alternate method (reaction **2** → **7**) for a direct decarbonylation of **2** by employing either fluorosulfonic or chlorosulfonic acids[9] and we have arrived at the final methyl sterculate **7** in a three-step synthesis (60–65% yield). Fluorosulfonic acid in methylene chloride reacted upon 9,10-(carbethoxymethano)-9-octadecenoate and the reaction proceeded with gas evolution and formation of cyclopropenium cation ester **6**. The obtained yield as a function of the amount and the concentration of the reagent are given in Table I.

TABLE I

DETERMINATION OF THE PER CENT DECARBONYLATION OF THE CYCLOPROPENIUM CARBONYL BY FLUOROSULFONIC ACID AT ROOM TEMPERATURE[a]

Amount of FSO_3H, mmol	FSO_3H in CH_2Cl_2, *M*	Cyclopropeniod diester, mmol	Decarbonylation,[b] %
5.25	0.28	5.25	
5.25	0.53	5.25	
5.25	1.72	5.25	10
34.58	1.72	5.25	25
43.74	4.37	5.25	20
43.74	17.50	5.25	100

[a] The extent of decarbonylation was followed by monitoring the disappearance of the cyclopropenium carbonyl absorption at 1730 cm^{-1} after complete work-up of the solution. [b] Reaction time 1 hr.

The analogous reaction with a solution of chlorosulfonic acid in methylene chloride was difficult to predict. In that respect, the difference in performance between chlorosulfonic and fluorosulfonic acids may be due to the high ionizing power and low nucleophilicity of the latter.[10] However, when chlorosulfonic acid was added without any previous dilution it performed better than fluorosulfonic acid and the reaction proceeded and afforded cyclopropenium cation ester. We elected to use fluorosulfonic acid in methylene chloride as our standard decarbonylation reagent.

Experimental Section

Melting points and boiling points are uncorrected. Elementary analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill. Infrared analyses were made in CCl_4 solution on a Beckman 1R-7 spectrophometer. All nmr spectra were taken on a Varian A-60A instrument as saturated solutions in chloroform-*d*, using tetramethylsilane as the internal standard. Chemical shifts are reported in τ units (τ 10.00 for tetramethylsilane). Glpc analyses were carried out on a Barber-Coleman Model 5000 equipped with a flame ionization detector. The column (6 ft × 1/8 in. glass) was packed with 10% EGS on Chromosorb W 60–80 mesh. The temperature was 175° and the helium flow was 45 ml/min.

Methyl Stearolate (**1**).—Stearolic acid, mp 45.5–46.0°, was synthesized according to the method of Butterfield and Dutton.[11] Methyl stearolate prepared with diazomethane gave a single peak on glpc with a relative retention time of 1.90 (methyl stearate 1.00).

(1) (a) Abstracted in part from a thesis submitted by J. L. Williams to the University of Illinois, Aug 1970, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Tuskegee Institute, School of Veterinary Medicine, Tuskegee Institute, Ala. 36088.

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(8) W. J. Gensler, M. B. Floyd, R. Yanase, and K. W. Pober, *ibid.*, **92**, 2472 (1970).

(9) Decarbonylation with sulfur trioxide in sulfuric acid, fluorosulfonic acid, or chlorosulfonic acid was demonstrated for several short aliphatic and aromatic cyclopropenium carbonyls [D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967)]. Also, the possibility that this kind of decarbonylation could be applied to their compounds was suggested by Gensler, Floyd, Yanase, and Pober (see ref 8).

(10) A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, **91**, 5637 (1969).

(11) R. O. Butterfield and H. J. Dutton, *J. Amer. Oil Chem. Soc.*, **45**, 635 (1968).