showed 1.15 mmol of chloride per gram of resin. BOC[7] derivatives of L-Ala, nitro-L-Arg, β-BZL-L-Asp, S-*p*-methoxy-BZL-L-Cys, γ-BZL-L-Glu, L-Gly, L-Ileu, L-Leu, ε-CBZ-L-Lys, L-Met, L-Phe, L-Pro, O-BZL-L-Ser, O-BZL-L-Thr, L-Trp, O-BZL-L-Tyr, and L-Val were esterified to the resin by refluxing 20 g of chloromethylated resin, 20 mmol of derivative, 18 mmol of triethylamine, and 50 ml of ethanol for 46 hr. An equal weight mixture of all of the resin-derivative preparations was treated with acetic acid–anhydrous HCl (1 *M*) for 30 min and washed extensively and dried from ethanol. This mixture was used for all experiments, so that a representative collection of blocking groups was always present. The hydrolyses were performed in sealed glass tubes which were frozen by liquid nitrogen and thawed several times on a vacuum line before sealing. These "anaerobic" conditions seem to give higher recoveries of all of the amino acids. HF reactions were carried out in the apparatus described by Robinson and Kamen[8] which is similar to that described by Sakakibara, *et al.*[9]

Registry No.—Hydrogen chloride, 7647-01-0; hydrogen fluoride, 7664-39-3.

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(7) Abbreviations: BOC = *t*-butyloxycarbonyl, CBZ = carbobenzyloxy, BZL = benzyl (ethers and esters).

(8) A. B. Robinson and M. D. Kamen, Symposium on Cytochromes, Osaka, Japan, 1967.

(9) S. Sakakibara, Y. Shimonishi, Y. Kishida, M. Okada, and H. Sugihora, *Bull. Chem. Soc. Jap.*, **40**, 2164 (1967).

Synthesis of *trans*-3,*cis*-5-Tetradecadienoic Acid (Megatomoic Acid), the Sex Attractant of the Black Carpet Beetle, and Its Geometric Isomers[1]

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The sex attractant of the black carpet beetle, *Attagenus megatoma* (Fabricius), was identified[2] as *trans*-3,*cis*-5-tetradecadienoic acid (I), to which we assign the trivial name, megatomoic acid. The synthesis of megatomic acid and its geometric isomers, *cis*-3,*cis*-5- (II), *cis*-3,*trans*-5- (III), and *trans*-3,*trans*-5-tetradecadienoic acid (IV) is described herein.

$C_8H_{17}CH{=}CH{-}CH{=}CHCH_2COOH$

trans-3,*cis*-5 (I)
cis-3,*cis*-5 (II)
cis-3,*trans*-5 (III)
trans-3,*trans*-5 (IV)

Megatomic acid was synthesized by the sequence shown in Scheme I based on the procedure described by Celmer and Solomons.[3] The *cis*-3,*cis*-5 isomer (II) also resulted.

(1) (a) Supported by the U. S. Department of Agriculture under Contract No. 12-14-100-7786(51). (b) Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, N. Y. 13210.

(2) R. M. Silverstein, J. O. Rodin, W. E. Burkholder, and J. E. Gorman, *Science*, **157**, 85 (1967).

The sequence in Scheme II produced *cis*-3,*cis*-5-tetradecadienoic acid (II) and *cis*-3,*trans*-5-tetradecadienoic acid (III).

trans-3,*trans*-5-Tetradecadienoic acid (IV) was prepared by isomerization with iodine[3] of the *trans*-3,*cis*-5- or *cis*-3,*trans*-5-methyl esters, followed by hydrolysis.

Since none of the isomers (II–IV) nor the by-products resulting from the synthesis of megatomic acid masked its attractiveness, the crude mixture was submitted for large-scale field testing. Analytical samples of all the isomeric acids were prepared by mild alkaline hydrolysis of the corresponding methyl esters, which were isolated by gas chromatography and shown to be homogeneous on several substrates of different polarities. The acids were re-esterified with diazomethane to verify that only a negligible amount of isomerization occurred during the hydrolysis.

Experimental Section

The spectra were recorded on the following instruments unless otherwise noted: ir, Perkin-Elmer 137; uv, Perkin-Elmer 202; mass, CEC 103; nmr, Varian T 60 (60 Mc). The nmr spectra were obtained in CCl_4 and the chemical shifts are in τ values using TMS as an internal standard. The abbreviations "s, d, q, and m" denote "singlet, doublet, quartet, and multiplet," respectively. Gas chromatography (glc) was done on a Varian Aerograph 205 equipped with a hydrogen flame detector; a 1:20 splitter and N_2 make-up gas were used for preparative runs. Glc substrates were obtained from Applied Science Laboratory, Inc., State College, Pa.

1-*n*-Tridecen-4-yn-3-ol (V).—This compound was prepared in 56% yield from 1-decyne and acrolein according to the procedure of Celmer and Solomons.[3] The crude product was distilled at 114–117° (0.9 mm). Ir (λ^{film}, μ) 3.0 (OH), 3.25 (olefinic CH) 4.45 (C≡C), 6.03 (C=C), 9.8 (C—OH), 10.1 and 10.8 (vinyl).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.4. Found: C, 80.0; H, 11.5.

1-Bromo-*cis*- and -*trans*-2-tridecen-4-yne (VI).—A mixture of 3-bromo-1-tridecen-4-yne and 1-bromo-2-tridecen-4-yne resulted from the reaction of V with phosphorus tribromide according to the procedure of Celmer and Solomons.[3] Ir (λ^{film}, μ) 4.5 (C≡C), 10.15 and 10.8 (vinyl), 10.5 (*trans* -CH=CH-).

The 3-bromo compound was converted to VI when the mixture was heated under nitrogen at 117° for 75 min. Distillation though a Claisen head at 0.15 mm (bath temp 95–110°) afforded a 75% yield of VI.

Anal. Calcd for $C_{13}H_{21}Br$: C, 60.7; H, 8.2. Found: C, 61.0; H, 8.5.

The *cis* and *trans* isomers of VI were obtained in a ratio of 1:2 by glc fractionation (SE 30, 4% on Chromosorb G, 60–80 mesh, 0.9 m × 7 mm i.d. Pyrex, 160°, 50 cm³ He/min) with fractions collected: at 20 min ir (λ^{film}, μ) 4.50 (C≡C), 8.3, 13.1 (*cis*-CH=CH-); and 25 min ir (λ^{film}, μ) 4.50 (C≡C), 8.3 and 10.5 (*trans* -CH=CH-).

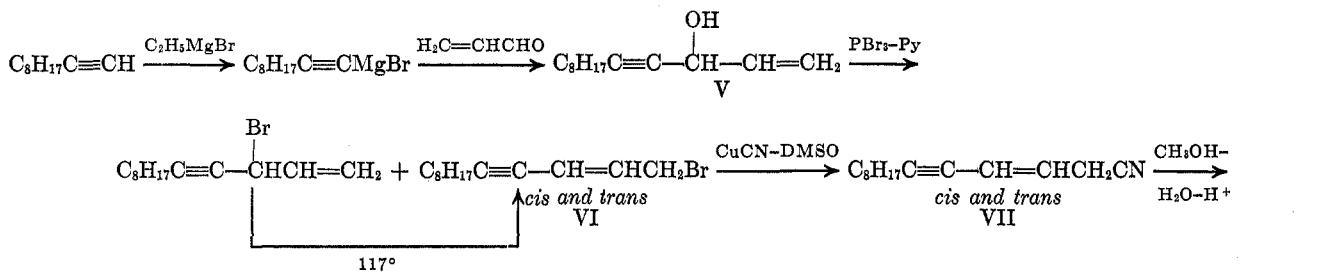
1-Cyano-2-*cis*- and -*trans*-tridecen-4-yne (VII).—A solution of 140 g (0.54 mol) of VI in 70 ml of dimethyl sulfoxide (dried over Linde 4X molecular sieves) was added dropwise over 20 min to a stirred suspension of 55.7 g (0.62 mol) of cuprous cyanide in 300 ml of dimethyl sulfoxide. The reaction mixture was stirred without external heating for 1 hr, at 40° for 1 hr, and finally at 85° for 2 hr. After cooling, the mixture was diluted with water and extracted with hexane. The extract was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was distilled through a Claisen head at 0.1 mm (bath temp 110–130°) to give 72 g (66% yield) of VII.

Anal. Calcd for $C_{14}H_{21}N$: N, 6.9. Found: N, 6.9.

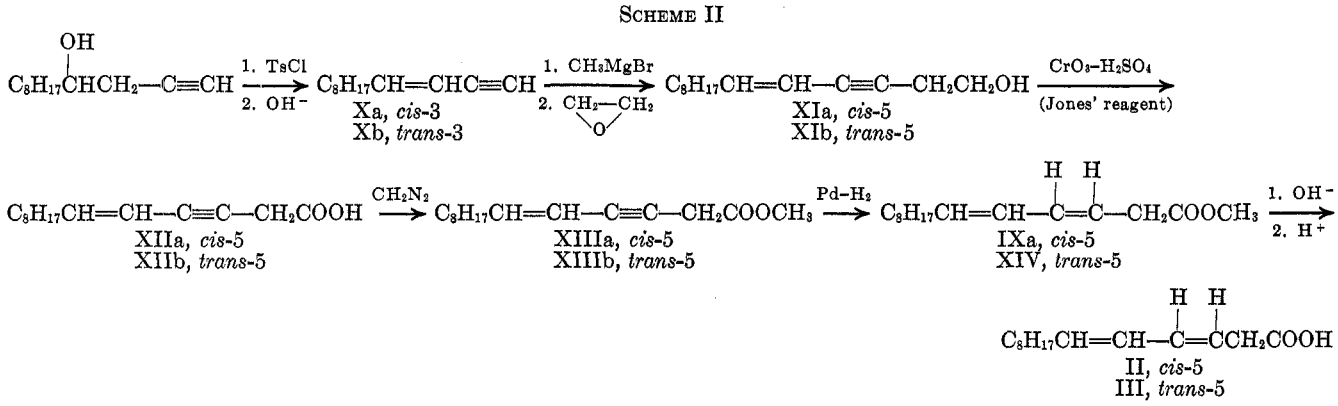
The *cis* and *trans* isomers of VII were obtained in a ratio of 1:2 by glc fractionation (Carbowax 20M, 10% on Gas Chrom Q, 60–80 mesh, 0.6 m × 8 mm i.d. Pyrex, 170°, 100 cm³ He/min) with fractions collected at 45 min and 100 min. The 45 min peak showed: ir (λ^{film}, μ) 4.44 and 4.51 (C≡C) and 13.7 (broad. *cis* -CH=CH-); nmr 4.3 (m, CH=CH) and 6.7 (d, $-CH_2CN$).

(3) W. D. Celmer and I. A. Solomons, *J. Amer. Chem. Soc.*, **75**, 3430 (1953).

SCHEME I



SCHEME II



The 100 min peak showed ir (λ^{film}, μ) 4.44 and 4.51 (C≡C) and 10.5 (*trans* -CH=CH-); nmr 4.2 (m, -CH=CH-) and 6.9 (d, $-CH_2CN$).

Methyl *cis*- and *trans*-3-Tetradecen-5-ynoate (VIII).—A slow stream of hydrogen chloride was bubbled into a solution of 32 g (0.157 mol) of VII in 84 ml of methanol and 6 ml of water. The resulting heat of solution caused the solvent to reflux. After the temperature had subsided (10 min), the reaction solution was treated with 15 ml of water, warmed on a steam bath for 15 min, and poured into an excess of cold water. The solution was extracted with pentane. The extract was washed successively with water, sodium bicarbonate solution, and water, dried over sodium sulfate, and concentrated under reduced pressure. The product was distilled through a Claisen head at 0.1 mm (bath temp 90–130°) to give 32 g (86% yield) of VIII.

The *cis* and *trans* isomers of VIII were obtained in one fraction by glc fractionation (Carbowax 20M, 10% on Gas Chrom Q, 60–80 mesh, 0.6 m × 8 mm i.d. Pyrex, 170°, 100 cm³ He/min, R_t 50–80 min). This fraction comprised 80% of the total. Ir (λ^{film}, μ) 4.51 (C≡C), 5.74 (C=O), 8.0, 8.3, 8.6 (C—O, methyl ester), 10.45 (*trans* -CH=CH-).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.2; H, 10.2 Found: C, 76.6; H, 10.7.

Methyl *cis*- and *trans*-3,*cis*-5-Tetradecadienoate (IXa and IXb).—A mixture of 20.0 g (0.085 mol) of VIII (distillate), 2.7 g of Lindlar catalyst (Engelhardt Industries, Inc.), and 210 ml of hexane containing 1.5 ml of pyridine was stirred at 25° under a hydrogen atmosphere. After 2180 ml (0.091 mol) of hydrogen was absorbed (2 hr), the hydrogenation was stopped, the mixture filtered, and the filtrate concentrated to give 20.2 g of product.

Compounds IXa and IXb were obtained pure by glc fractionation (HIEFF-IBP, 10% on Gas Chrom Q, 60/80 mesh, 6 m × 4 mm i.d. Pyrex, 174°, 46 cm³ He/min). IXb was collected at 52–57 min and IXa at 62 to 66 min. These two peaks comprised 65% of the total fraction.

The following data were obtained on IXb: ir (λ^{film}, μ) 3.32 (C=CH), 5.74 (C=O), 6.03, 6.18 (weak, C=C conjugated), 8.00, 8.35, 8.60 (C—O, methyl ester), 9.85, 10.18, 10.54 (characteristic pattern for *cis,trans* conjugated double bonds; the 9.85 band is very weak),[4] 13.90 (weak CH_2 rock); uv ($\lambda_{max}^{pentane}$, mμ) 231.5 (ε 29,000); nmr (100 MHz, CCl_4, τ) 3.55–4.90 (4 H, m, conjugated olefinic), 6.41 (3 H, s, $COOCH_3$), 6.98 (2 H, d, J = 7 Hz $=CHCH_2COOCH_3$), 7.88 (2 H, distorted q, CH_2-$CH_2CH=$), 8.72 [12 H, $(CH_2)_6$], 9.11 (3 H, distorted t, CH_3-CH_2); mass, *m/e* 238 (M^+), 207 (M^+ minus OCH_3), 206 (M^+ minus CH_3OH), 179 (M^+ minus $COOCH_3$), 74 (CH_2COOCH_3 + H). The above spectra of IXb were congruent with those of the methyl ester of megatomoic acid isolated from *Attagenus megatoma*.[2]

The following data were obtained on IXa: the infrared spectrum was essentially the same as IXb except for the absence of the 10.18 and 10.54 μ bands. This is consistent with absorption of *cis,cis* conjugated double bonds:[4] uv ($\lambda_{max}^{pentane}$, mμ) 234 (ε 29,000).

***cis*- and *-trans*-3,*cis*-5-Tetradecadienoic Acid (II and I).**—A solution of 20.8 g (0.087 mol) of the esters IXa and IXb (distillate) in 340 ml of 0.9 *M* potassium hydroxide in methanol containing 10% water was stirred at 25° for 2.5 hr. The solution was diluted with 300 ml of cold water and extracted thrice with 200-ml portions of pentane. The aqueous solution was cooled to 0°, acidified with 6 *N* hydrochloric acid to pH 1.5, and extracted twice with pentane. The pentane solution was washed with water, dried over sodium sulfate, and concentrated under reduced pressure to 12.4 g (64%) of a viscous oil. Ir (λ^{film}, μ) 3.0 to 4.2 (characteristic COOH absorption), 5.83 (C=O), 10.15, 10.5 (characteristic pattern for *cis,trans* conjugated double bonds), 10.7 (broad, carboxylic acid dimer).

A sample of the hydrolysate was methylated with diazomethane in ethyl ether solution. Glc analysis (Carbowax 20 M, 5% on Gas Chrom Q, 3 m × 3 mm aluminum tubing, 170°; 30 cm³ He/min) showed major peaks at 11.3 and 12 min (50% and 22%) which coincided with IXb and IXa, respectively. A sample of the methylated material was fractionated by glc (same conditions as for IXa and IXb) collecting the two major peaks as a single fraction at 50–70 min. The ir spectrum was identical with a mixture of IXa and IXb. This glc fraction was hydrolyzed by the procedure used above and the hydrolysate was evaporatively distilled at 120° (0.05 mm). The distillate gave the following data: ir (λ^{film}, μ) 3.0 to 4.2, 5.83, 6.17 (weak), 6.85, 7.1, 7.8, 8.2, 10.2, 10.5, 10.7 (broad), 12.1, and 13.9; uv (λ_{max}^{hexane}, mμ) 233 (ε 25,000).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 75.0; H, 10.8. Found: C, 75.1; H, 10.9.

(4) A. Butenandt, E. Hecker, M. Hopp, and W. Koch, *Justus Liebigs Ann. Chem.*, **658**, 39 (1962).

cis-3- and *trans*-3-Dodecen-1-yne (X).—A solution of 32 g (0.095 mol) of *p*-toluenesulfonic esters of 1-dodecyn-4-ol and 1,2-dodecadien-4-ol (prepared from nonanal and propargyl bromide by the method of Butenandt, *et al.*[4]), 7 g of potassium hydroxide, 30 ml of water, and 150 ml of ethanol was refluxed under nitrogen for 75 min, cooled, and extracted twice with 200-ml portions of pentane. The pentane solution was washed with water, dried over sodium sulfate, and concentrated to give 14 g (90%) of yellow oil. This product was flash-distilled at 5 mm and fractionated by glc [Carbowax 20M, 20% on Chromosorb P, 10–60 mesh, 2.4 m × 12.7 mm (i.d.) stainless steel tubing, 115°, 350 cm³ helium per min] to give 6.2 g of *cis*-3-dodecen-1-yne (Xa) at 46 to 66 min (99.8% pure) which had ir (λ^{film}, μ) 3.1 (C≡CH), 3.32 (C=CH), 13.5 (*cis* -CH=CH-). The yield of *trans*-3-dodecen-1-yne (Xb) was (2.4 g) (98% pure) at 67–87 min and had ir (λ^{film}, μ) 3.1 (C≡CH), 3.32 (C=CH), 10.4 (*trans* -CH=CH-).

Anal. Calcd for $C_{12}H_{20}$, Xa: C, 87.7; H, 12.3. Found: C, 88.0; H, 12.4. Xb: C, 87.7; H, 12.3. Found: C, 87.6; H, 12.4.

cis-5-Tetradecen-3-yn-1-ol (XIa).—A mixture of 1.25 g (0.0076 mol) of *cis*-3-dodecen-1-yne (Xa), 2 ml of anhydrous ethyl ether, and 2.8 ml (0.0084 mol) of methylmagnesium bromide (3 *M* in ethyl ether) was refluxed under N_2 with stirring for 1.5 hr with ethyl ether added at intervals to compensate for evaporation. The reaction mixture was cooled with an ice bath and a solution of 0.9 ml (0.02 mol) of ethylene oxide in 4 ml of ethyl ether was added. After 5 min, 15 ml of benzene was added to the gel that had formed, the ethyl ether was boiled off, and the mixture was refluxed for 2 hr under nitrogen, during which time the gel disappeared and a dark red solution resulted. The solution was cooled and poured into ice water containing 2 g of ammonium chloride. The mixture was extracted twice with ethyl ether. The organic solution was washed with water, dried over magnesium sulfate, and concentrated. The residue was distilled evaporatively at 105° (0.05 mm), and 0.8 g of distillate was collected. A portion of this was fractionated (Carbowax 20 M, 5% on Chromosorb G, 60–80 mesh, 0.9 m × 9.4 mm aluminum tubing, 177°, 100 cm³ He/min) and the major peak (90%) was collected at 10 to 18 min. Ir (λ^{film}, μ) 3.05, 3.32, 9.55, 13.5.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.7; H, 11.6. Found: C, 80.4; H, 11.7.

trans-5-Tetradecen-3-yn-1-ol (XIb).—This was prepared from Xb with the same procedure used to prepare XIa. The distillate had ir (λ^{film}, μ) 3.05, 3.32, 9.55, and 10.4 (*trans* -CH=CH-).

Methyl *cis*-5-Tetradecen-3-ynoate (XIIIa).—Chromic acid solution[5] (1.1 ml) was added dropwise (2 min) to a stirred solution of 0.40 (2.0 mmol) of *cis*-5-tetradec-3-yn-1-ol (XIa) in 10 ml of acetone at 15°. Stirring was continued under nitrogen for 10 min, and 25 ml of pentane was added. The pentane solution was decanted, washed twice with water, and extracted twice with sodium carbonate solution. The sodium carbonate solution was acidified with 1 *N* hydrochloric acid and extracted with ethyl ether. The ether solution was washed twice with water, dried over magnesium sulfate, and concentrated to give 0.30 g of *cis*-5-tetradecen-3-yn-oic acid (XIIa). Ir (λ^{film}, μ) 2.9 to 4.1 (characteristic COOH pattern), 4.5 and 4.6 (weak doublet, C≡C), 5.8 (C=O), 6.15 (weak, C=C), 10.7 (COOH dimer), and 13.6 (*cis* -CH=CH-).

A solution of diazomethane (4 mmol) in 10 ml of ethyl ether was added to a cold solution of 0.3 g (1.5 mmol) of XIIa in 5 ml of ethyl ether. After 5 min at 0°, the solution was concentrated to give 0.3 g of product. A portion of this was fractionated (Carbowax 20 M, 10% on Gas Chrom Q, 60–80 mesh, 0.6 m × 8 mm i.d. Pyrex, 170°, 100 cm³ He/min), and the major peak (30 to 40 min) was collected. Ir (λ^{film}, μ) 3.33 (C=CH), 4.5 (very weak, C≡C), 5.83 (C=O), 9.85, 13.5 (broad, *cis* -CH=CH-).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.2; H, 10.2. Found: C, 76.3; H, 10.7.

Methyl *trans*-5-Tetradecen-3-ynoate (XIIIb).—This was prepared from XIb using the same procedure used to prepare XIIIa. Compound XIIIb had ir (λ^{film} μ) 2.9–4.1 (characteristic COOH pattern), 4.5 and 4.6 (weak doublet, C≡C), 5.81 (C=O), 6.15 (weak, C=C), 10.45 (*trans*-CH=CH-), 10.7 (shoulder, COOH dimer). XIIIb: ir (λ^{film}, μ) 3.33 (C=CH), 4.5 (very weak, C≡C), 5.83 (C=O), 9.85, 10.4 (*trans* -CH=CH-).

Methyl *cis*-3,*cis*- and -*trans*-5-Tetradecadienoate (IXa and XIV).—These dienoic esters were prepared from their corresponding enyne compounds (XIIIa and XIIIb) using the procedure for the preparation of IXa and IXb. Spectra for IXa synthesized by both sequences were congruent.

The data obtained on the *cis*-3,*trans*-5 isomer (XIV) were very similar to those obtained on the *trans*-3,*cis*-5 isomer (IXb). Subtle differences in the nmr and ir spectra were observed. The main distinguishing feature was the 9.8 μ ir band, which was very weak in IXb and moderate in XIV where it is as strong as the 10.5 μ band. The uv spectra were indistinguishable as were the retention times on 3 m × 3 mm columns with the following substrates: Carbowax 20 M, Versamid 900, STAP, EGSS-X, CHDMS, PDEAS, HI-EFF-IBP, ECNSS-S.

Methyl *trans*-3,*trans*-5-Tetradecadienoate (XV).—A solution of 10 mg of methyl *cis*-3,*trans*-5-tetradecadienoate in 0.3 ml of carbon tetrachloride containing ~1 μmol of iodine in a sealed Pyrex tube was irradiated with a 250-W lamp for 16 hr. The solvent and iodine were removed under reduced pressure, and the residue was tube-distilled at 100° and 0.02 mm pressure to give 7 mg of distillate. Ir (λ^{film}, μ) 3.32, 5.73, 8.0, 8.35, 8.60, 10.1 (*trans*, *trans* -CH=CHCH=CH-); uv (λ_{max}^{hexane}, mμ) 229 (ϵ 28,000).

Glc data on the 4 isomeric esters (Carbowax 20 M, 4% on Chromosorb G 60–80 mesh, 3 m × 3 mm aluminum tubing, 160°, 20 cm³ He min), IXb, XIV, IXa, XV, showed retention times of 28.5, 28.5, 30.2, and 34 min, respectively.

Synthesis of Megatomoic Acid Isomers (II, III, and IV).—In each case, 1-mg samples of the ester (a glc fraction, 98 to 99% pure) was hydrolysed as described for megatomoic acid. The products showed the following uv data (λ_{max}^{hexane}, mμ): II, 235; III, 233; IV, 229. A portion of each acid solution was reesterified and analyzed by glc (conditions described above).

Registry No.—I, 23400-52-4; II, 25091-12-7; III, 17022-64-9; IV, 25091-14-9; V, 25091-15-0; *cis*-VI, 25091-16-1; *trans*-VI, 25091-17-2; *cis*-VII, 25091-18-3; *trans*-VII, 25091-19-4; *cis*-VIII, 25091-20-7; *trans*-VIII, 25091-21-8; IXa, 25091-22-9; IXb, 25091-23-0; Xa, 25091-24-1; Xb, 25091-25-2; XIa, 25091-26-3; XIb, 25091-27-4; XIIIa, 25091-28-5; XIIIb, 25091-29-6; XV, 25091-30-9.

(5) L. F. Fieser and M. Fieser," Reagents for Organic Synthesis," Wiley, New York, N. Y., p 142.

Studies on Resin Acids. VI. Synthesis of (+)-4-Epidehydroabietic Acid[1]

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(+)-4-Epidehydroabietic acid (callitrisic acid, abieta-8,11,13-trien-19-oic acid) (1) has recently been isolated as a natural product by several workers[2] and its synthesis from agathic acid has been reported.[3] In addition, the total synthesis of racemic 1 has been reported by several groups.[3a,4]

An obvious synthetic approach to 4-epidehydroabietic is its preparation from podocarpic acid (2) *via* methyl 12-methoxy abieta-8,11,13-trien-19-oate (3).[5] This general approach was attempted by Chuah and

(1) Part V: J. W. Huffman, *J. Org. Chem.*, **35**, 478 (1970). This work was supported in part by Career Development Award GM-5433 from the National Institutes of Health.

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(3) (a) R. M. Carman, H. C. Deeth, R. A. Marty, K. Mori, and M. Matsui, *Tetrahedron Lett.*, 3359 (1968); (b) R. C. Carman and R. A. Marty, *Aust. J. Chem.*, **22**, 2696 (1969).

(4) (a) R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939); (b) M. Sharma, U. R. Ghatak, and P. C. Dutta, *Tetrahedron*, **19**, 985 (1963).

(5) W. P. Campbell and D. Todd, *J. Amer. Chem. Soc.*, **62**, 1287 (1940).