Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.50; H, 9.68.

The 2,4-dinitrophenylhydrazone, mp 132–133°, was recrystallized from EtOH.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.04; H, 5.40; N, 18.25.

Registry No. 1, 2758-18-1; 2, 49664-66-6; 3, 49664-67-7; 4, 49664-68-8; 5, 49664-69-9; 6, 49664-70-2; 7, 49664-71-3; 8, 49664-72-4; 8 2,4-dinitrophenylhydrazone, 49664-73-5.

References and Notes

(1) J. B. Grutzner, M. Jautelate, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970), have described the ^{13}C nmr spectra of all methylnorcamphors except that of **8**. This paper provides references for syntheses of the other methylnorcamphors.

(2) G. H. Posner, *Org. React.*, **19**, 1 (1972).

(3) J. Hooz and R. B. Layton, *Can. J. Chem.*, **48**, 1626 (1970).

(4) J. L. Marshall, *Tetrahedron Lett.*, 753 (1971), showed that 3-(2′-tosyloxyethyl)cyclopentanone, obtained in 12% yield from norcamphor, could be cyclized with base to yield norcamphor.

(5) R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970); R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *ibid.*, **95**, 4346 (1973). The synthesis of **9** from **1** and ethylene and the spectra of **9** are described: R. L. Cargill and B. W. Wright, manuscript in preparation.

(6) Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., Alfred Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany, and S. T. Bella, the Rockefeller University. Boiling points and melting points are uncorrected. The ^{13}C spectra were obtained on a Varian XL-100-15 nmr spectrometer operating at 25.2 MHz in the Fourier transform mode. Carbon-13 chemical shifts were determined with respect to internal benzene-d_6 and then converted to a CS_2 scale by adding 64.8 ppm. Spectra were also determined in CCl_4 solution and no significant medium effects were noted.

(7) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

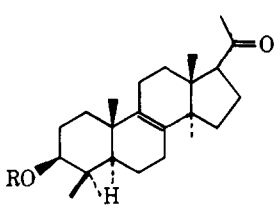
Improved Methods for the Side-Chain Degradation of Lanosterol. The Synthesis of 4,4,14α-Trimethyl-5α-pregn-8-en-20-one Derivatives

Bruce Ganem*[1] and Michael S. Kellogg

Department of Chemistry, Stanford University, Stanford, California 94350

Received October 16, 1973

Although descriptions of steroid side-chain degradations abound in the literature,[2] no such process for lanosterol has been reported which preserves the acid-sensitive Δ^8 olefin.[3] The present note discloses two facile side-chain degradations leading to the 20-keto lanostane derivatives **1** and **2** free of the Δ^7 isomer.

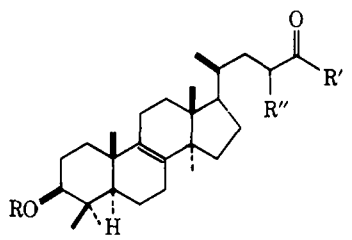


1, R = H
2, R = CH_3CO

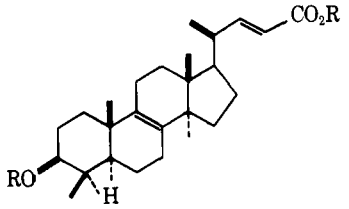
Reaction of lanosterol as its acetate[4] or benzoate[5] with 1 molar equiv of ozone followed by Jones reagent[4] produced the trisnor acids **3** and **6** in about 50% yield. Treatment of **6** with diazomethane gave the methyl ester **7**, which was added to lithium isopropylcyclohexylamide in tetrahydrofuran–hexamethylphosphoric triamide (THF–HMPA) solution at −78°, giving the enolate anion quantitatively after 45 min.[6] Addition of this solution to bromine in THF at −78° afforded the α-bromo ester **8**, which was smoothly dehydrobrominated in HMPA[7] at 120° to the α,β-unsaturated ester **9** in 72% overall yield from **7**. Hydrolysis of the benzoate and reesterification of the sparingly soluble α,β-unsaturated acid **10** by reaction of the sodium salt with ethyl iodide in HMPA[8] afforded an 80% yield of the ethyl ester **11**. Treatment with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) transformed **11** into the β,γ-unsaturated acid **12** (80% yield),[9] which on ozonolysis (as its methyl ester **13**) afforded the desired 3β-hydroxy-4,4,14α-trimethyl-5α-pregn-8-en-20-one (**1**).[10] None of the Δ^7 isomer could be detected.[11]

An alternative degradation was accomplished by converting the acetoxy acid **3** to its acid chloride **4** and treating this substance with lithium diphenylcopper[12] to produce the phenyl ketone **5** in 50% yield after chromatography. When irradiated at 350 nm in *tert*-butyl alcohol using a Rayonet reactor, this ketone underwent facile Norrish Type II cleavage[13] to afford the 20-methylene derivative **14** in 53% yield. Ozonolysis in this instance generated 3β-acetoxy-4,4,14α-trimethyl-5α-pregn-8-en-20-one (**2**, 47% yield) free of the Δ^7 isomer, and having melting point, ir, and nmr characteristics in full accord with reported values for this compound.[10] Moreover, this substance could be saponified to the hydroxy ketone **1**.

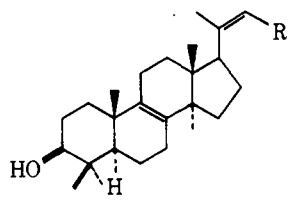
The yield of the final ozonolysis step in both series was disappointing, and could not be improved even by using a slight deficiency of ozone. This is apparently due to a competing, allylic oxidation known to occur in the Δ^8 lanostane system with a variety of oxidizing agents.[14] A comparison of the two degradation schemes reveals that overall yields were somewhat higher for the first route (9.0–9.2%) than for the second (6–6.5%); however, the latter, photochemical sequence may be faster and more convenient.



3, R = CH_3CO; R′ = OH; R″ = H
4, R = CH_3CO; R′ = Cl; R″ = H
5, R = CH_3CO; R′ = C_6H_5; R″ = H
6, R = C_6H_5CO; R′ = OH; R″ = H
7, R = C_6H_5CO; R′ = OCH_3; R″ = H
8, R = C_6H_5CO; R′ = OCH_3; R″ = Br



9, R = C_6H_5CO; R′ = CH_3
10, R = H; R′ = H
11, R = H; R′ = CH_3CH_2



12, R = CH_2CO_2H
13, R = $CH_2CO_2CH_3$
14, R = H (3β-Ac derivative)

Experimental Section

Melting points were determined using a Kofler hot stage microscope. Nmr spectra of deuteriochloroform solutions were recorded on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Ir spectra of chloroform solutions were determined on a Perkin-Elmer 137 spectrophotometer. Gas–liquid chromatographic analyses were carried out on a Hewlett-Packard HP-402 gas chromatograph using 3% XE-60 in 80–100 gas chromatograph Q packed in a 6-ft glass column with a helium flow rate of 40–50 ml/min, unless otherwise stated. Mass spectral measurements

were determined on an Atlas CH-4 spectrometer. Samples were dissolved in $CHCl_3$ for measurement of specific rotations. Microanalyses were performed by the Stanford microanalytical laboratory.

3β-Benzoyloxy-25,26,27-trisnorlanost-8-en-24-oic Acid Methyl Ester (7). This procedure was adapted directly from a published method.[4] A methylene chloride solution of 3β-benzoyloxylanosta-8,24-diene (21 g, 47 mmol, *ca.* 50% pure lanosterol from Aldrich Chemical Co.) and pyridine (1.5 ml) was treated with ozone (23 mmol) from a Welsbach generator at room temperature. The intermediate ozonide was diluted with an equal volume of acetone and treated with excess Jones reagent and the acidic material was collected by base extraction. Acidification, extraction into ether, and recrystallization from chloroform–methanol gave pure benzoate acid **6**, mp 234–235°. Diazomethane esterification of the crude acid in chloroform afforded 6.5 g (52% yield) of **7**: mp 159–161°; nmr δ 8.28–7.41 (m, 5 H), 4.82 (m, 1 H), 3.65 (s, 3 H), 1.03 (s, 6 H), 0.99 (s), 0.94 (s, total 9 H), 0.74 (s, 3 H, C-18); ir 5.81, 5.85 μ.

Anal. Calcd for $C_{35}H_{50}O_4$: C, 78.6; H, 9.4. Found: C, 78.45; H, 9.35.

3β-Benzoyloxy-25,26,27-trisnorlanosta-8,22-dien-24-oic Acid Methyl Ester (9). Lithium isopropylcyclohexylamide, prepared in dry THF (40 ml) from isopropylcyclohexylamine (5 mmol) and *n*-butyllithium (4.4 mmol, Alfa Corp.), was cooled to −78°; then a solution of the ester **7** (1.19 g, 2.22 mmol) and HMPA (8.8 mmol, 1.58 ml distilled from Na) in THF (10 ml) was added dropwise. The mixture was allowed to stir at −78° for 45 min, then transferred by Dry Ice cooled syringe to a freshly prepared mixture of bromine (0.8 ml) in THF (10 ml) at −78°. After 2 min, saturated sodium bisulfite solution (5 ml) and 5% HCl (5 ml) were added, then the mixture was diluted with ether (100 ml). The colorless ether layer was washed once with 5% HCl, five times with water, and once with brine, dried ($MgSO_4$), and concentrated to yield 1.78 g of crude α-bromo ester, nmr δ 4.28 (m, 1 H), 3.75 (s, 3 H), ir 5.73, 5.84 μ.

This crude bromo ester was heated in pure HMPA (10 ml) for 12 hr at 120° under nitrogen; then water and ether were added. The ether layer was washed copiously with water, dried ($MgSO_4$), and concentrated. Chromatography on silica gel gave, on elution with chloroform, 0.845 g (72% yield from **7**) of crystalline α,β-unsaturated ester **9**: mp 157–159°; nmr δ 6.97, 5.82 (ABX, J_{AB} = 16, J_{AX} = 8 Hz), 3.75 (s, 3 H); ir 5.85 μ (broad); mass spectrum (70 eV) *m/e* 532 (M^+), 395 (base).

Anal. Calcd for $C_{35}H_{48}O_4$: C, 78.9; H, 9.1. Found: C, 78.9; H, 8.9.

3β-Hydroxy-25,26,27-trisnorlanosta-8,22-dien-24-oic Acid Ethyl Ester (11). A solution of **9** (0.58 g) in THF (8 ml), ethanol (20 ml), and 10% aqueous KOH (10 ml) was refluxed for 2.5 hr under nitrogen. Acidification (5% HCl) and extraction into $CHCl_3$ afforded 0.44 g (97% yield) of **10**, mp 233–237° (from $CHCl_3$).

Anal. Calcd for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.05; H, 10.0.

This hydroxy acid was dissolved in HMPA (10 ml) and stirred for 2.5 hr at room temperature with ethyl iodide (1 ml) and 30% aqueous NaOH solution (1 ml). Ether was added and after five water washings the organic layer was dried ($MgSO_4$) and concentrated. Chromatography of the crude product on silica gel using $CHCl_3$ afforded 0.380 g (81% yield) of ethyl ester: mp 159°; nmr δ 6.97, 5.82 (ABX, J_{AB} = 16, J_{AX} = 8 Hz), 4.15 (q, 2 H, J = 7 Hz), 0.71 (s, 3 H, C-18); ir 5.83 μ (broad). This material appeared as a single spot by the analysis.

3β-Hydroxy-25,26,27-trisnorlanosta-8,22-dien-24-oic Acid Methyl Ester (13). A solution under nitrogen of α,β-unsaturated ester **11** (0.164 g) in DMSO (8 ml) containing *tert*-butyl alcohol (0.5 ml) and potassium *tert*-butoxide (0.160 g) was heated in a 70° oil bath for 3 hr, then acidified (5% HCl) and extracted with ether. After four water washings, the ether layer was washed with brine, treated with diazomethane solution, and then concentrated under reduced pressure to yield 0.131 g (80%) of β,γ-unsaturated ester **13**: mp 100–101°; nmr δ 5.38 (broad m, 1 H, vinyl), 3.65 (s, 3 H), 1.61 (broad s, 3 H), 0.50 (s, 3 H, C-18); ir 5.78 μ. A small amount of the α,β isomer was also present in this material.

3β-Hydroxy-4,4,14α-trimethyl-5α-pregn-8-en-20-one (1). Using a 10-ml Rubin ozonizer,[15] a sample of β,γ-unsaturated ester **13** (44 mg, 0.1 mmol) in methylene chloride (3 ml) was treated at −78° with a saturated solution (3.6 ml) of ozone in methylene chloride (0.145 mmol of O_3) containing pyridine (3 drops). The characteristic blue solution rapidly decolorized, and, after addition of dimethyl sulfide (0.3 ml) and methanol (0.3 ml), the solution was stirred at room temperature for 2 hr. After the solvents were evaporated, the residue was partitioned between ether and water, and the organic layer was dried ($MgSO_4$) and concentrated. Chromatography of the crude product on silica gel using 5:95 ether–$CHCl_3$ gave 20 mg of white solid, mp 235–240°. One crystallization from MeOH returned 14 mg (40% yield) of white needles, mp 247–250°. Glc analysis demonstrated this material to be greater than 95% pure (one peak, retention time 15.0 min at 230°). Two more recrystallizations afforded an analytical sample: mp 252–253° (reported[10] mp 255–256°); $[\alpha]^{20}D$ +116° (*c* 0.046); nmr δ 2.14 (s, 3 H, acetyl), 1.00 (s, 3 H), 0.98 (s, 6 H), 0.83 (s, 3 H), 0.60 (s, 3 H, C-18); ir 5.85 μ.

3β-Acetoxy-24-phenyl-25,26,27-trisnorlanost-8-en-24-one (5). To a solution of 0.916 g (2 mmol) of the acid **3** in benzene (15 ml) under nitrogen was added 2 drops of dimethylformamide followed by 0.2 ml (2.34 mmol) of oxalyl chloride. The resulting solution was stirred for 1.5 hr at room temperature, concentrated *in vacuo* to give a yellow solid, and stirred in dry THF (5 ml) for treatment with lithium diphenylcopper.[12]

The cuprate was prepared by the addition of 13.3 ml (12 mmol) of 0.9 *M* phenyllithium in THF to a suspension of 1.142 g (6 mmol) of purified cuprous iodide in dry ether (25 ml) at −5° with stirring for 1 hr under argon. The resulting black liquid was cooled to −20°, the acid chloride in THF was added, and the mixture was stirred for 20 min at that temperature. Methanol was added, and the reaction mixture was poured into ether–water (200 ml) and then filtered through Celite. The aqueous layer was extracted twice with ethyl acetate (50 ml), and then combined organic layers were dried ($MgSO_4$) and concentrated to give 1.4 g of dark, viscous oil. Chromatography on silica gel gave, on elution with $CHCl_3$, 0.525 g (50% yield) of the phenyl ketone **5** as a white, crystalline solid: mp 174–77° (MeOH); nmr δ 7.97 (m, 2 H), 7.50 (m, 3 H), 4.53 (t, 1 H, J = 6.5 Hz), 2.95 (t, 2 H, J = 8 Hz), 2.01 (s, 3 H), 0.87 (s, 9 H), 0.70 (s, 3 H); ir 5.80, 5.95 μ; mass spectrum *m/e* 518 (M^+), 443 (base).

Anal. Calcd for $C_{35}H_{50}O_3$: C, 81.0; H, 9.7. Found: C, 80.9; H, 9.5.

3β-Acetoxy-4,4,14α-trimethyl-17β-isopropenylandrost-8-ene (14). A solution of 85 mg (0.16 mmol) of phenyl ketone **5** in *tert*-butyl alcohol (50 ml) was deaerated in a Pyrex vessel by argon purge, then irradiated for 90 min with RPR 350-nm lamps in a Rayonet reactor. The solution was concentrated *in vacuo* to give 85 mg of a light yellow oil. Preparative thin layer chromatography (silica gel–benzene) afforded 34 mg (53% yield) of white crystalline solid **14**: mp 164–168°; nmr δ 4.78 (d, 2 H, J = 6 Hz), 4.53 (t, 1 H, J = 6.5 Hz), 2.03 (s, 3 H), 1.75 (broad s, 3 H, vinyl methyl), 1.00 (s, 3 H), 0.93 (s, 3 H), 0.87 (s, 6 H), 0.60 (s, 3 H); ir 5.80, 11.2 μ; mass spectrum *m/e* 398 (M^+), 149 (base).

3β-Acetoxy-4,4,14α-trimethyl-5α-pregn-8-en-20-one (2). Using the Rubin ozonizer described above, 34 mg (0.085 mmol) of **14** in methylene chloride (2 ml) was treated with a saturated solution of ozone in methylene chloride (2.1 ml, 0.095 mmol of ozone) at −78°. After addition of methanol (2 ml) and dimethyl sulfide (several drops), the vessel was allowed to reach room temperature and its contents were stirred for 1 hr. The work-up as described for **1** afforded 34 mg of a light yellow, viscous oil. Preparative thin layer chromatography on silica gel using 90:10 benzene–ethyl acetate gave 16 mg (47% yield) of a white, crystalline solid which was greater than 85% pure by glc analysis (200°, retention time 19.5 min) and contaminated by a single impurity (retention time 17.5 min). Recrystallization from MeOH afforded white needles of **2** (5 mg): mp 169–173° (reported[2,10] mp 169°, 169–170°); $[\alpha]^{20}D$ +110° (*c* 0.059); nmr δ 4.53 (t, 1 H, J = 6.5 Hz), 2.10 (s, 3 H), 2.01 (s, 3 H), 1.00 (s, 3 H), 0.97 (s, 3 H), 0.87 (s, 6 H), 0.60 (s, 3 H); ir 5.80, 5.85 μ; mass spectrum *m/e* 400 (M^+), 325 (base). This material was homogeneous by glc analysis.

Saponification of the mother liquors (from recrystallization, 11 mg) using aqueous ethanolic KOH followed by chromatography afforded a sample of hydroxy ketone (7 mg) identical with pure **1**.

Acknowledgment. We thank Professor William S. Johnson for his guidance and encouragement, and acknowledge helpful discussions with Dr. R. N. Woodhouse. We are also grateful to the National Institutes of Health and the National Science Foundation for grants (to W. S. J.) in support of this work.

Registry No. **1**, 5217-14-1; **2**, 27868-09-3; **3**, 30655-15-3; **5**, 22415-21-0; **7**, 49810-32-4; **8**, 49810-33-5; **9**, 49810-34-6; **10**, 49810-35-7; **11**, 49810-36-8; **13**, 49810-37-9; **14**, 49810-38-0.

References and Notes

(1) National Institutes of Health Postdoctoral Fellow, 1973–1974.
(2) For some pertinent examples, see L. H. Briggs, J. P. Bartley, and P. S. Rutledge, *J. Chem. Soc., Perkin Trans. 1*, 806 (1973), and references cited therein.
(3) R. E. Marker, L. W. Mixon, and E. L. Wittle, *J. Amer. Chem. Soc.*, **79**, 1368 (1957).
(4) M. Lu, F. Kohen, and R. E. Counsell, *J. Med. Chem.*, **14**, 136 (1971).
(5) H. Wieland, H. Pasedach, and A. Ballauf, *Justus Liebigs Ann. Chem.*, **529**, 68 (1937).
(6) M. W. Rathke and A. Lindert, *Tetrahedron Lett.*, 3995 (1971).
(7) R. Hanna, *Tetrahedron Lett.*, 2105 (1968).
(8) J. E. Shaw, D. C. Kunerth, and J. J. Sherry, *Tetrahedron Lett.*, 689 (1973).
(9) Since ester cleavage competes with isomerization, and the acid **7** was not isomerized by these conditions, use of a more hindered ester might further improve this transformation.
(10) D. Rosenthal, P. Grabowich, E. F. Sabo, and J. Fried, *J. Amer. Chem. Soc.*, **85**, 3971 (1963).
(11) The C-7 vinyl hydrogen has been reported to appear in the nmr spectrum of this isomer at δ 5.18 (see ref 1).
(12) To our knowledge this represents the first phenyl ketone synthesis by this method. See G. H. Posner and C. E. Witten, *Tetrahedron Lett.*, 4647 (1970).
(13) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).
(14) See, for example, E. V. Lassak, J. T. Pinhey, and J. J. H. Simes, *Aust. J. Chem.*, **26**, 1051 (1973), and references cited therein.
(15) M. B. Rubin, *J. Chem. Educ.*, **41**, 388 (1964).

A Total Synthesis of Cassamedine

Michael P. Cava* and Susan S. Libsch

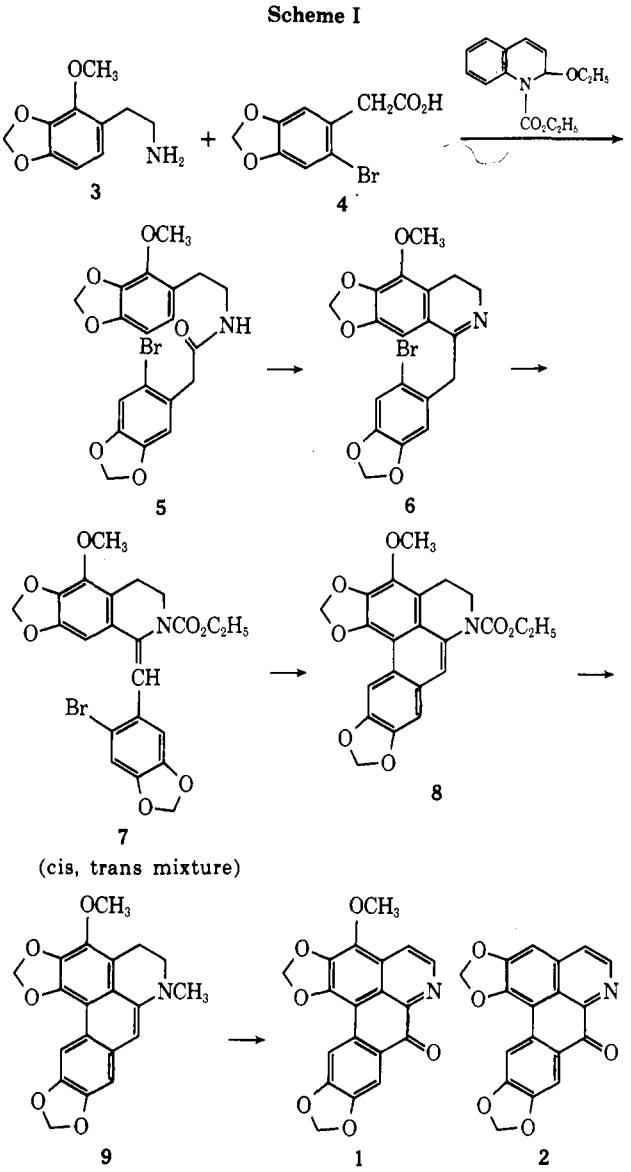
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Received October 1, 1973

The orange alkaloid cassamedine, which was isolated from *Cassytha americana*, has been assigned structure **1**, solely on the basis of its spectral properties.[1] We now report a total synthesis of cassamedine which unambiguously confirms structure **1** for the alkaloid.

The synthetic methodology employed was generally similar to that used in our synthesis of the companion alkaloid cassameridine (**2**).[1,2] The reaction of β-(2-methoxy-3,4-methylenedioxyphenyl)ethylamine (**3**)[3] with 6-bromohomopiperonylic acid (**4**) in the presence of EEDQ (*N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline)[4] gave the amide **5**, which was converted smoothly by phosphorus oxychloride in acetonitrile into the dihydroisoquinoline **6**. Reaction of **6** with triethylamine and ethyl chloroformate gave the benzylidine urethane **7** as a mixture of cis and trans isomers. Direct irradiation of crude **7** in benzene–*tert*-butyl alcohol containing potassium *tert*-butoxide afforded *N*-carbethoxy-6a,7-dehydrocassythidine (**8**). Reduction of **8** by lithium aluminum hydride–aluminum chloride in ether gave *N*-methyl-6a,7-dehydrocassythidine (**9**). Peracetic acid oxidation of **9** afforded, in 28% yield, orange needles of **1**, identical in all respects with cassamedine from natural sources (Scheme I).

Scheme I



Experimental Section

Melting points are uncorrected. Elemental analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind. Ultraviolet spectra were determined in ethanol with a Perkin-Elmer Model 202 spectrophotometer. Nmr spectra were recorded with Varian A-60A and HA-100 instruments.

β-(2-Methoxy-3,4-methylenedioxyphenyl)ethylamine (3) was prepared according to Govindachari, *et al.*[3] The oily amine was characterized and stored in the form of its acid oxalate salt, mp 173–175°, prepared by addition of an equimolar quantity of ethanolic oxalic acid.

Anal. Calcd for $C_{12}H_{15}NO_7$: C, 50.53; H, 5.30; N, 4.91. Found: C, 50.31; H, 5.16; N, 5.00.

***N*-(2′-Methoxy-3′,4′-methylenedioxyphenylethyl)-2-bromo-4,5-methylenedioxyphenylacetamide (5).** Amine **3** was liberated from its acid oxalate (2.00 g, 7.0 mmol) by treatment with ammonium hydroxide and extraction with benzene. The dried benzene extract (70 ml) was added to 6-bromohomopiperonylic acid[5] (**4**, 1.81 g, 7.0 mmol) and *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (1.91 g, 7.7 mmol). The solution was stirred at room temperature for 2 hr, and the precipitated amide **5** (2.32 g, 76%) was removed by filtration. Recrystallization from CH_2Cl_2 gave microneedles, mp 185°.

Anal. Calcd for $C_{19}H_{18}NO_6Br$: C, 52.31; H, 4.13; N, 3.21. Found: C, 52.22; H, 4.18; N, 3.18.

Hydrochloride of 1-(2′-Bromo-4′,5′-methylenedioxybenzyl)-3,4-dihydro-5-methoxy-6,7-methylenedioxyisoquinoline (6). A mixture of acetonitrile (60 ml), amide **5** (2.72 g, 6.2 mmol), and phosphorus oxychloride (4.9 ml, 53 mmol) was warmed on the steam bath until the amide dissolved. The solution was then stirred at room temperature for 20 hr. Absolute ethanol (5.5 ml) was then added dropwise. Addition of a large volume of ether gave the hydrochloride of **6** (2.62 g, 90%) as a yellow powder. Recrystallization from acetic acid–ether afforded the pure salt as yellow cubes, mp 243° dec.

Anal. Calcd for $C_{19}H_{17}NO_5BrCl$: C, 50.19; H, 3.77; N, 3.08. Found: C, 49.97; H, 3.82, N, 3.01.

1-(2′-Bromo-4′,5′-methylenedioxybenzylidine)-2-carbethoxy-1,2,3,4-tetrahydro-5-methoxy-6,7-methylenedioxyisoquinoline (7). A solution of ethyl chloroformate (0.72 ml, 7.5 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a mixture of the hydrochloride of **6** (1.374 g, 3.02 mmol), triethylamine (1.26 ml, 9.05 mmol), and CH_2Cl_2 (15 ml) with ice bath cooling. The mixture