according to the procedure defined by Welch,[17] deprotection,[16] and PCC oxidation provided ketone **11**. Desilylation with tetrabutylammonium fluoride[18] and bromo ether formation[19] were necessary to effect epoxidation of the exocyclic methylene group. Sodium borohydride reduction of the ketone was highly stereoselective since the exo face of the bicyclic [3,2,1] subunit is much more accessible. Epoxidation was accomplished with buffered trifluoroperacetic acid at 0 °C.[20] Regeneration of the trisubstituted olefin was effected with zinc–silver couple:[21] Other reagents such as zinc dust (DMF or THF or CH_3OH) or magnesium (ether, THF) were ineffective. Th acetylation with acetic anhydride and (4-dimethylamino)pyridine in CH_2Cl_2 provided calonectrin. Synthetic calonectrin was identical (^1H, ^{13}C NMR, IR, MS, TLC) with an authentic sample.

The synthetic route described above is efficient and highly stereoselective. We intend to synthesize anguidin and verrucarol using olefinic ketone **11**.

Acknowledgment. We thank the National Institutes of Health (CA23663) for generous financial support. We thank Professor J. R. Hanson for a generous sample of calonectrin.

Registry No. 3, 38818-51-8; **4b**-(α-OH), 80484-01-1; **4b**-(β-OH), 80484-02-2; **5**, 80513-95-7; **6**, 80484-03-3; **7**, 80484-04-4; **8a**, 80484-05-5; **8b**, 80484-06-6; **11**, 80484-07-7; (3α,9A,10β)-10-bromo-9,15-epoxy-12-methylenetrichothecane-3-ol, 80484-08-8.

(17) Welch, S. C.; Rao, A. S. C. P.; Gibbs, C. G.; Wong, R. Y. *J. Org. Chem.* **1980**, *45*, 4077.
(18) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(19) Corey, E. J.; Pearce, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 5843.
(20) Emmons, W. D.; Pagano, A. S. *J. Am. Chem. Soc.* **1955**, *77*, 89.
(21) Tokoroyama, T.; Matsuo, K.; Kanazawa, R. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3383.

Total Synthesis of Racemic Verrucarol

R. H. Schlessinger* and R. A. Nugent

Department of Chemistry, University of Rochester Rochester, New York 14627

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The molecular array, verrucarol (**1**),[1] is the sesquiterpene linchpin of a large family of macrocyclic di- and trilactones which possess novel and synthetically challenging structures together with significant antitumor activity.[2] As part of a larger program directed toward the synthesis of representatives of these macrocyclic systems,[3] the construction of verrucarol became desirable.[4] Herein, we describe a biomimetic formulation of racemic **1** by a route which will ultimately allow its preparation in the required optical form.

We chose as the starting material for construction of **1** the readily available ketonic substance **2**. This material contains two elements required by the structure **1**, namely, the oxygen residue on C_4 and the angular C_{14} methyl group.[5] Thus, our initial task was the transformation of this substance into the keto acid **3**. Degradation of the six-membered ring of **2** was commenced by kinetic deprotonation of the enone with lithium diisopropylamide in THF solution followed by trapping of the enolate with trimethylsilyl chloride. The resulting enol ether was subjected to oxidation with *m*-chloroperbenzoic acid in hexane/*tert*-butyl alcohol at 0 °C yield the α-trimethylsilyloxy enone **4**.[6] Ozonolysis of **4** in methanol at −78 °C followed by oxidation of the intermediate α-hydroxy acid with sodium metaperiodate/chromium trioxide in acetic acid at 22 °C afforded the keto acid **3** (mp 126–127 °C) in 53% yield from **2**.[7]

Two refractory reactions were then encountered during the elaboration of **3** into the α-methylene lactone **5**, a key synthetic intermediate in our route to **1**. The first of these difficulties was the conversion of **3** into the exocyclic olefin **6**—a reaction which was successful only if the ylide derived from methyltriphenylphosphonium bromide was generated with sodium *tert*-amylate in toluene and the reaction carried out at 110 °C for 12 h. under these conditions, **6** was readily obtained from **3**.[8] Oxidation of **6** with selenium dioxide and *tert*-butyl hydroperoxide in methylene chloride at 22 °C afforded a mixture of allylic alcohols in which the α-orientated isomer **7** predominated in a ratio of 5:1.[9] Treatment of this mixture with *p*-toluenesulfonic acid in methylene chloride at 22 °C for 24 h gave the lactone **8** in 55% yield from **3**.[10] Surprisingly, methylenation of **8** to obtain the lactone **5** proved to be the second difficulty encountered in the reaction scheme. A novel and unexpected solution to this problem was discovered, however, during the course of reacting the enolate derived from **8** with monomeric formaldehyde (generated at 160 °C in a flow system). The reactant and reagent were combined at −78 °C and then brought to 22 °C followed by stirring for 14 h; this afforded the α-methylene lactone **5** and not the expected hydroxymethyl lactone.[11] Compound **5** was obtained in 62% yield from *8*.

We next faced the problem of spiroannulating the lactone **5** to obtain **9**—a compound which we felt could be readily converted into the target natural product. The Diels–Alder reaction was the obvious choice for this annulation process, and after careful consideration of molecular models of **5**, we were able to convince ourselves that a [4 + 2] cycloaddition between 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene and the methylene lactone would result in addition of the diene from the β surface of the lactone to ultimately afford the unsaturated ketone **9**.[12] Indeed, our view of this reaction course was borne out upon thermal combination of **5** and the above cited butadiene derivative at 140 °C in toluene solvent containing a small amount of methylene blue as a stabilizer. After 48 h of heating followed by removal of the volatiles under vacuum and treatment of the residue with Amberlite IR-120 in methylene chloride for 30 min at 22 °C, we obtained **9** as the sole unsaturated ketone product in 76% yield from **5**.[13]

We had several divergent plans for conversion of **9** into verrucarol. Interestingly, two of these routes were successful, and

(1) Gutzwiller, J.; Mauli, R.; Sigg, H. P.; Tamm, Ch. *Helv. Chim. Acta* **1964**, *47*, 2234.
(2) For an excellent review, see: Tamm, Ch. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 63.
(3) In our laboratories the natural product vertisporin reported by Minato et al. (Minato, H.; Katayama, T.; Tori, K. *Tetrahedron Lett. 1975*, 2579) is the current object of our synthetic activities. Recently, we were informed by Professor W. C. Still of Columbia University that he had completed a total synthesis of the related natural product verrucarin A starting from naturally occurring verrucarol. We congratulate Professor Still on this very fine achievement. Still, W. C.; Ohmizu, H. *J. Org. Chem.* **1981**, *46*, 5242.
(4) For studies related to verrucarol, see: (a) Colvin, E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 658. (b) Trost, B. M.; Rigby, J. H. *J. Org. Chem.* **1978**, *43*, 2938. (c) Roush, W. R.; D'Ambra, T. E. *Ibid.* **1980**, *45*, 3927. (d) White, J. D.; Matsui, T.; Thomas, J. A. *Ibid.* **1981**, *46*, 3376. For syntheses of trichodermol, see: (a) Colvin, E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1989. (b) Still, W. C.; Tasi, M.-Y. *J. Am. Chem. Soc.* **1980**, *102*, 3654. For a synthesis of trichodiene, see: Welch, S. C.; Rao, A. S. C. P.; Gibbs, C. G.; Wong, R. Y. *J. Org. Chem.* **1980**, *45*, 4077.
(5) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615.
(6) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.
(7) Hase, T. A.; McCoy, K. *Synth. Commun.* **1979**, *9*, 63. Satisfactory spectral and physical data were obtained for all new compounds.
(8) Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3760.
(9) Unbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.
(10) The β-allylic alcohol could also be converted into the lactone **8** using a procedure described by: Mitsunobu, O *Synthesis* **1981**, 1.
(11) For excellent reviews on the methylenation of lactones, see: (a) Grieco, P. A. *Synthesis* **1975**, 67. (b) Gammill, R. B.; Wilson, C. A.; Bryson, T. A. *Synth. Commun.* **1975**, *5*, 245.
(12) The use of this diene in total synthesis has been dramatically championed by its originator. For the most recent example of this diene in a synthetic context, see: Danishefsky, S.; Vaughn, K.; Gadwood, R.; Tsuzuki, K. *J. Am. Chem. Soc.* **1981**, *103*, 4138. For the definitive series of papers describing the use of this diene, see: (a) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *Ibid.* **1979**, *101*, 6996. (b) Danishefsky, S.; Yan, C. F.; Singh, R. K.; Gammil, R. B.; McCurry, P. M.; Fritsch, N.; Clardy, J. *Ibid.* **1979**, *101*, 7001. (c) Danishefsky, S.; Harayama, T.; Singh, R. K. *Ibid.* **1979**, *101*, 7008.
(13) The usual reaction conditions, dilute HCl, that bring about conversion of these types of Diels–Alder adducts into enone systems gave mostly the β-methoxy ketone is this instance: see ref 12a.

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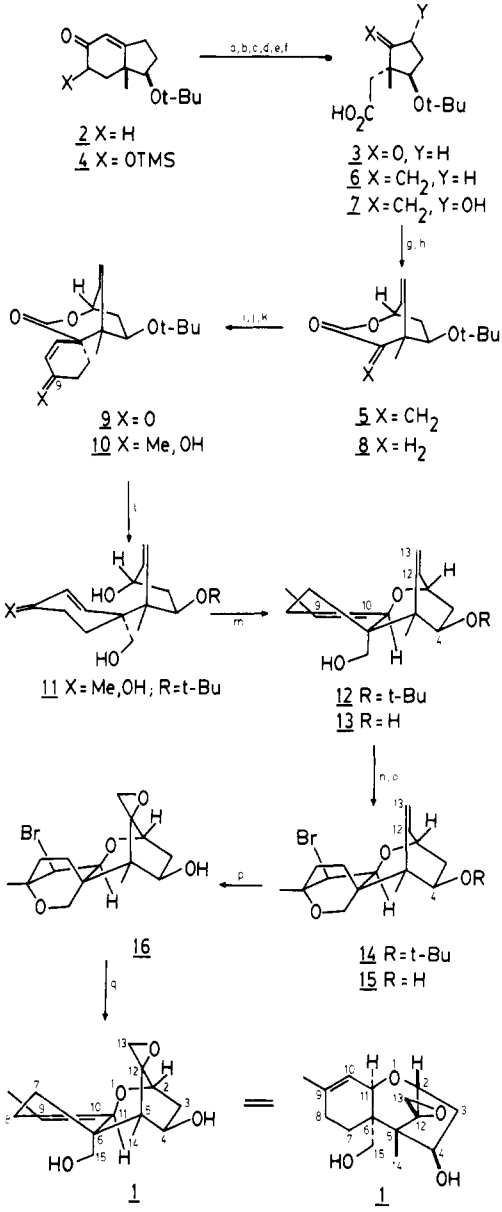
Scheme I



[a] LDA, 1.1 equiv in THF, 1.0 M; add **2**, 1.0 equiv, −78 °C, 1 h; warm to 0 °C; Me_3SiCl, 3.0 equiv, 2.0 M, in THF with Et_3N; 45 min, 0 °C; workup with $NaHCO_3$ and hexane. (b) Preceding material 1.0 equiv, 1.1 M in hexane, $NaHCO_3$, 2.1 equiv; 0 °C; *m*-CPBA (85%) 2.0 equiv in hexane 1.1 M, with *t*-BuOH added until peracid soluble; stir until complete (TLC); standard workup. (c) **4**, 1.0 equiv in MeOH, 0.1 M; −78 °C; O_3 until solution blue; evaporated in vacuum; standard acid/base workup. (d) Preceding material 1.0 equiv in HOAc; add to $NaIO_4$, 1.0 equiv and CrO_3, 2.0 equiv in 5:1 HOAc/H_2O, 0.3 M; 22 °C, 3 h; standard workup. (e) $(Ph)_3PCH_3Br$, 2.0 equiv in toluene, 1.0 M; NaO-*t*-Am, 3.15 equiv in toluene, 2.0 M; add **3**, 1.0 equiv; 110 °C, 8 h; standard acid base workup. (f) **6**, 1.0 equiv in methylene chloride, 1.0 M; SeO_2, 0.1 equiv, *t*-BuOOH (90%), 4.0 equiv; 22 °C, 24 h; standard workup. (g) **7**, 1.0 equiv in methylene chloride, 1.0 M; *p*-TSA, 0.1 equiv; 22 °C, 24 h; standard workup; filtration chromatography (silica gel, hexane/ether, 2/1). (h) LDA, 1.1 equiv, in THF 1.0 M; add **8**, 1.0 equiv; −78 °C, 30 min; warmed to 0 °C; CH_2O in N_2 stream carried over reaction surface for 25 min [CH_2O generated at 160 °C, 5.0 equiv of $(CH_2O)_x$]; diluted I vol with THF; 22 °C, 14 h; standard workup. (i) **5**, 1.0 equiv in toluene 0.1 M; methylene blue 0.01 equiv; 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene, 3.0 equiv; 3 freeze-thaw cycles; sealed under vacuum, −100 °C; 140 °C, 48 h; volatiles removed under vacuum. (j) Preceding material 1.0 equiv in methylene chloride 1.0 M, Amberlite IR-120, 3.0 equiv; 22 °C, 30 min; filtered; crystallized (methylene chloride/ether). (k) **9**, 1.0 equiv, 0.5 M in THF; 1.1 equiv, MeLi, −78 °C, until complete by TLC; standard workup, 93% yield. (l) **10**, 1.0 equiv, 0.1 M in DME; 4.0 equiv, LAH, reflux 10 h; standard workup. (m) crude **11** ca. 1.0 equiv, in CH_2Cl_2, 0.25 M; catalytic *p*-TSA, 5 min, 22 °C; standard workup; filtration chromatography (silica gel, EtOAc/hexane, 2:3) 73% yeidl from **10**. (n) **12**, 1.0 equiv, in acetone 0.5 M; NBS, 1.5 equiv, 5 min, 22 °C; standard workup 100% yield one spot on TLC. (o) **14**, 1.0 equiv, in CH_2Cl_2 0.25 M, 0 °C; $TiCl_4$, 1.5 equiv, 0 °C, 1 min; standard workup; 85% yield. (p) **15**, 1.0 equiv, in CH_2Cl_2 0.10 M; 1.5 equiv, *m*-CPBA; 4 h, 22 °C; standard workup, 70% yield. (q) **16**, 1.0 equiv, 0.5 M in THF; 15.0 equiv, sodium metal, 0.01 M $EtNH_2$; 12 h, 0 °C; quenched with MeOH; standard workup; crystallization from Et_2O; 62% yield.

the most efficient and, in our view, the most interesting is detailed below. Reaction of **9** with methyllithium in THF afforded a 93% yield of a single alcohol, **10**.[14] The lactone portion of **10** was then reduced with LAH in refluxing DME to afford the triol **11**. Without purification, **11** was treated with a catalytic amount of *p*-toluenesulfonic acid in methylene chloride to produce **12** isolated in 73% yield from **10**.[15]

Initially, we had hoped to remove the C_4 *tert*-butyl ether protecting group from **12** and then to selectively epoxidize the exocyclic olefin (12–13) to complete the synthesis of verrucarol. While we were successful in removing the either protecting group to obtain the diene-diol **13**, we had no success in selectively epoxidizing the exocyclic olefin due to concomitant oxidation of the trisubstituted olefin (9–10).[16] To circumvent this problem, we converted **12** into the bromo ether **14** by reaction of the former with *N*-bromosuccinimide in acetone. We then removed the *tert*-butyl ether protecting group of **14** with titanium tetrachloride to obtain the alcohol **15** in 85% yield from **12**. Stereospecific epoxidation of **15** into **16** in 70% yield was then realized by using *m*-chloroperbenzoic acid.[17] Finally, regeneration of the trisubstituted olefin and formation of verrucarol was brought about by treatment of **16** with sodium metal in the presence of ethylamine and THF. Standard workup of this reaction followed by simple crystallization of the crude reaction mixture from ether afforded pure racemic verrucarol (**1**) (mp 159–161 °C, lit.[18] 159.5–161 °C) in 62% yield from **16** and 3.4% yield from *2* (17 steps).

Acknowledgment. We thank the National Institutes of Health for support of this work. R.A.N. gratefully acknowledge receipt of a Sherman-Clarke Fellowship from the University of Rochester.

(14) The configurational assignment of the C_9 position in compound **10** is not known with certainty. However, from its-400 MHz ^1H spectrum it is obvious that **10** is a single substance.

(15) For biomimetic ring-closure reactions similar to that described in this manuscript, see: (a) Masuoka, N.; Kamikawa, T. *Tetrahedron Lett.* **1976**, 1691. (b) Reference 4c (verrucarol).

(16) This type of selective epoxidation reaction has been reported in systems which possess a methyl group at C_{15} instead of the hdyroxymethyl group present in compound **13**. The latter residue is undoubtly the culprit responsible for this disappointing result; see ref 4a,b (trichodermol).

(17) Similar stereochemical results have been obtained in the trichodermol series; see ref 4a,b.

(18) See ref 3 as well as: Tulshian, D. B.; Fraser-Reid, B. *Tetrahedron Lett.* **1980**, 4549. Spectra (including ^1H NMR at 400 MHz) of synthetic verrucarol and verrucarol diacetate were identical with spectra obtained from naturally occurring verrucarol and its diacetate derivative. After submission of this manuscript, it came to our attention that Professor G. Kraus (Iowa State University) had completed a total synthesis of a related substance, calonectrin. We congratulate Professor Kraus on thiss very fine synthetic effort.

Registry No. (±)-**1**, 80514-49-4; (±)-**2**, 39765-89-4; (±)-**3**, 80502-13-2; (±)-**4**, 80514-50-7; (±)-**5**, 80502-14-3; (±)-**6**, 80502-15-4; (±)-**7**-(α-OH), 80502-16-5; (±)-**7**-(β-OH), 80558-53-8; (±)-**8**, 80502-17-6; (±)-**9**, 80514-55-2; **10**, 80502-18-7; **11**, 80502-19-8; (±)-**12**, 80514-51-8; (±)-**14**, 80514-52-9; (±)-**15**, 80514-53-0; (±)-**16**, 80514-54-1; 1-methoxy-3-trimethylsilyloxy-1,3-butadiene, 80502-20-1; (±)-**13**, 80531-97-1.

Total Synthesis of (±)-Limaspermine Derivatives Using Organoiron Chemistry

Anthony J. Pearson* and David C. Rees

University Chemical Laboratory
Cambridge, CB2 1EW, Great Britain

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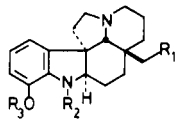
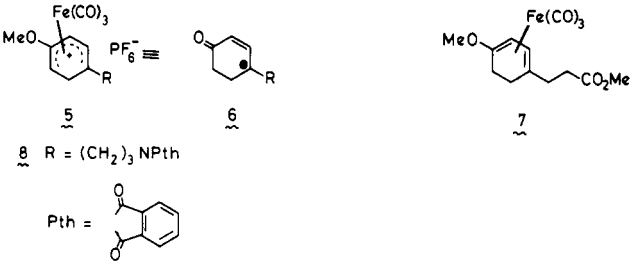
The aspidosperma alkaloids, a group of compounds typified by the simple derivative Aspidospermine (**1**), are now a well-known class of natural products.[1] A number of alkaloids possessing a functionalized C-20 angular grouping have been characterized in recent years,[2] some examples being cylindrocarpinol (**2**), cylindrocarine (**3**), and limaspermine (**4**), among others. Aspi-



1 R_1 = Me, R_2 = Ac, R_3 = Me
2 R_1 = CH_2OH, R_2 = H, R_3 = Me
3 R_1 = CO_2Me, R_2 = H, R_3 = Me
4 R_1 = CH_2OH, R_2 = CO·Et, R_3 = H
19 R_1 = CH_2OMe, R_2 = H, R_3 = Me
20 R_1 = CH_2OMe, R_2 = CO·Et, R_3 = Me
21 R_1 = CH_2OH, R_2 = CO·Et, R_3 = Me

dospermine itself was synthesized by Stork and Dolfini[3] in 1963, while construction of the functionalized derivatives has been reported by Ban et al.[4] and Saxton's group.[5] Our interest in total synthesis of these compounds was stimulated as part of a program aimed at the synthetic utilization of tricarbonylcyclohexadienyliumiron complexes of general structure **5**, which we[6] and others[7] have shown to be synthetic equivalents of the cyclohexenone γ-cation **6**. We were interested in applying suitably functionalized complexes to the synthesis of relatively complex natural products, and in this respect we recently described the conversion of the tricarbonyl(cyclohexadiene)iron complex **7**, readily obtained from *p*-methoxycinnamic acid,[9] to the protected amino derivative **8** in 77% overall yield. We present here the results of our further investigation into the synthetic utility of **8**, culminating in a total synthesis of (±)-limaspermine.

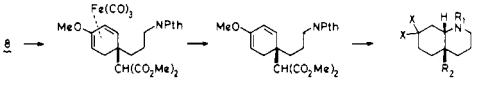


5 **6** **7**

8 R = $(CH_2)_3$NPth

Pth =

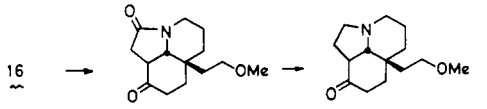
Reaction of **8** with dimethyl potassiomalonate[10] (THF, 20 °C, 15 min), followed by crystallization, afforded the complex **9** in 68% yield; mp 155.5–156.5 °C; ν_{max} 2055, 1950, 1771, 1755, 1732, 1713, 1490 cm^{-1}. We noted that it would be necessary at some



9 **10**

11 X,X = O, R_1 = H, R_2 = $CH(CO_2Me)_2$
12 X,X = OCH_2CH_2O, R_1 = Ac, R_2 = $CH(CO_2Me)_2$
13 X,X = OCH_2CH_2O, R_1 = Ac, R_2 = CH_2CO_2Me
14 X,X = OCH_2CH_2O, R_1 = Ac, R_2 = $(CH_2)_2OMe$
15 X,X = OCH_2CH_2O, R_1 = H, R_2 = $(CH_2)_2OMe$
16 X,X = O, R_1 = $CO·CH_2Cl$, R_2 = $(CH_2)_2OMe$
22 X,X = O, R_1 = H, R_2 = Et

stage to effect decarbomethoxylation of the gem diester, and the following strategy is the one which proved to be least problematical Removal of the metal from **9** (anhydrous Me_3NO, benzene, 50 °C, 1.5 h) gave the hydrolytically unstable dienol ether **10** in 87% yield as an analytically pure white solid which did not give a sharp melting point. Liberation of the primary amine (N_2H_4, MeOH, 40 °C, 1 h) proceeded smoothly, and the resulting dienol ether was hydrolyzed ($[CO_2H]_2$, MeOH, H_2O, 20 °C, 60 min) and cyclized ($NaHCO_3$, MeOH, H_2O, 20 °C, 45 min, 74% overall) to give the *cis*-decahydroquinoline derivative **11**; ν_{max} (CCl_4) 1760, 1740, 1730 cm^{-1}. A number of attempts to decarbomethoxylate **11** resulted in very low yields of the corresponding monoester, and it was necessary to fully protect this compound ((i) Ac_2O, C_5H_5N, 20 °C, 18 h; (ii) $[CH_2OH]_2$, benzene, *p*-TsOH, reflux, 24 h) to give **12** in order to achieve this conversion satisfactorily, at the expense of lengthening the sequence. Decarbomethoxylation of **12** (2 equiv of NaCN, wet Me_2SO, 118 °C, 13 h) afforded the monoester **13** as an analytically pure white solid in 79% overall yield from **11**; mp 71–82 °C (amide resonance shown in 400-MHz NMR spectrum); ν_{max} (CCl_4) 1738, 1650 cm^{-1}. Selective reduction of the ester ($LiBH_4$, THF, 20 °C, 3.5 days, 38 °C, 8 h) followed by protection of the resulting alcohol (NaH, MeI, THF, 20 °C, 15 h) produced the methyl ether **14** (77%); mp 88–93 °C (amide resonance); ν_{max} (CCl_4) 1643 cm^{-1}; 90-MHz NMR ($CDCl_3$) δ 4.6 (1 H, m), 3.97 (4 H, s), 3.43 (2 H, t, J = 7 Hz), 3.33 (3 H, s), 3.65 (2 H, m), 2.09 (3 H, s), 2.3–1.2 (12 H). Deprotection of the amino functionality of **14** proved to be impossible under standard conditions (KOH, aqueous MeOH, reflux) but was readily effected in 96% yield by metal reduction[11] (Ca, liquid NH_3, DME, EtOH, 4 h) to give **15** as a colorless oil, which was converted to the intermediate **16** in the normal way ((i) $ClCH_2COCl$, C_5H_5N, benzene, 10 °C, 4 h, 84%, (ii) ethanolic HCl, 76 °C, 2 h, 95%); ν_{max} ($CHCl_3$) 1720, 1648 cm^{-1}. The remaining steps of the synthesis are unexceptional, following exactly the methodology already used in other syntheses.[3-5] Thus, treatment of **16** with base (1.1 equiv. KOBu-*t*, *t*-BuOH, benzene, 20 °C, 4.5 h) afforded the crystalline tricyclic amido ketone **17** (mp 123–124.5 °C) in 95% yield [ν_{max}($CHCl_3$) 1712, 1687 cm^{-1}] which was converted to the oily tricyclic amino ketone **18** [ν_{max} ($CHCl_3$) 2810, 2735, 2690 (Bohlmann bands), 1705 cm^{-1}] in three steps ((i) $[CH_2OH]_2$, *p*-TsOH, benzene, reflux, 20 h, (ii) $LiAlH_4$, THF, 20 °C, 1 h, (iii) 9% ethanolic HCl, 90 °C, 1 h; 33% overall). This inter-



16 → **17** → **18**

mediate was converted in 39% yield to *O*-methylcylindrocarpinol **19** by Fischer indole cyclization ((i) 2-methoxyphenylhydrazine, HCl, EtOH, reflux, 1 h, (ii) AcOH, 95 °C, 1 h, (iii) $LiAlH_4$, Et_2O); ν_{max} ($CHCl_3$) 3380, 2810, 2735, 1619, 1597 cm^{-1}; 90-MHz

(1) Cordell, G. A. *Alkaloids* **1979**, *17*, 200.
(2) Pinar, M.; von Philipsborn, W.; Vetter, W.; Schmid, H. *Helv. Chim. Acta* **1962**, *45*, 2260. Milborrow, B. V.; Djerassi, C. *J. Chem. Soc. C* **1969**, 417.
(3) Stork, G.; Dolfini, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 2872.
(4) Inoue, I.; Ban, Y. *J. Chem. Soc. C* **1970**, 602. Ban, Y.; Ohnuma, T.; Seki, K.; Oishi, T. *Tetrahedron Lett.* **1975**, 727. Ohnuma, T.; Oishi, T.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 301.
(5) Saxton, J. E.; Smith, A. J.; Lawton, G. *Tetrahedron Lett.* **1975**, 4161. Lawton, G.; Saxton, J. E.; Smith, A. J. *Tetrahedron* **1977**, *33*, 1641.
(6) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 67.
(7) Birch, A. J.; Stephenson, G. R. *Tetrahedron Lett.* **1981**, 779.
(8) Pearson, A. J.; Rees, D. C. *Tetrahedren Lett.* **1980**, 3937.
(9) Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1255.
(10) We have found that the potassium salt gives more favorable regioselectivity than sodium or lithium salts: Pearson, A. J.; Perrior, T. R.; Rees, D. C., submitted for publication.
(11) Stork, G.; Darling, S. D.; Harrison, I. T.; Wharton, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 2018.

0002-7863/82/1504-1118$01.25/0