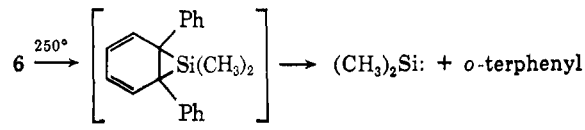
acid in benzene with azeotropic removal of water (recirculating Dean-Stark trap filled with Linde 4A molecular sieves). Chromatography of the reaction mixture on silica gel provided (hexane elution) a mixture of *m*-terphenyl (24%),[15] *o*-terphenyl (*ca.* 3%), and 1,1-dimethyl-2,7-diphenyl-1-silacyclohepta-2,4,6-triene (**6**) (*ca.* 11%). Further elution with 1:1 hexane–ether removed 1,1-dimethyl-*cis*-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (**7**) (colorless oil; 12.2%; nmr[15] (CCl_4) δ 9.44 (m, 1 H), 6.80–7.40 (m, 10 H), 6.21 (d of d, 1 H, J = 7 and 3 Hz), 6.00 (d of d, 1 H, J = 7 and 2 Hz), 3.24 (br s, 1 H), 3.04 (d of d, 1 H, J = 18 and 2 Hz), 2.51 (d of d, 1 H, J = 18 and 3 Hz), 0.26 Os, 3 H), −0.78 (s, 3 H); ir $\nu_{C=O}$ (neat) 1727 cm^{-1}; mass spectrum (70 eV) *m/e* 304 (M^+)).[16] Aldehyde **7** was found to be quantitatively formed from **5a** in a 300° flow pyrolysis.

In our hands the silepin (**6**) could not be completely purified from the terphenyls with gc, tlc, or fractional crystallization. However liquid chromatography (4 ft × 3/8 in. Bondapak C_{18}/Porasil B column with MeCN–H_2O as carrier solvent) allowed clean separation of **6** (mp 60–61°).

The question of the geometry of **6** is a crucial one as ring planarity would imply significant cyclic (p-d-p)π delocalization[12] providing a neutral analog of the tropylium cation. The methyl protons of **6** appear as one singlet (δ 0.10)[17] in the nmr spectrum which can be accounted for by a rapidly inverting boat geometry, a planar geometry, or a noninverting boat with fortuitous nmr equivalence.[10] The latter possibility may be discounted as even with no cyclic delocalization a very low barrier for inversion of boat forms would be predicted from the calculations of Allinger[18] for benzo- and dibenzosilepins. To distinguish between inverting boat and planar geometry, spectral comparison of **6** and a model compound of reasonably certain geometry was employed. An excellent model compound for **6** is 1,6,7-triphenyltropilidene (**8**) which was prepared from Diels–Alder addition of α-pyrone to 1,2,3-triphenylcyclopropene followed by thermal extrusion of CO_2. The vinyl protons of **8** appear as an AA′BB′ eight-line spectrum (lower field protons exhibit slight allylic coupling) with centers at δ 6.40 and 6.71, J apparent = 3.0, 4.5 Hz. This is remarkably similar to the olefinic spectrum of **6** which is also an AA′BB′ eight-line pattern with centers at δ 6.51 and 6.80, J apparent = 3.0, 4.5 Hz. This would imply that **6** possesses the same geometry as **8** which can be assumed to be *inverting boat*. The uv spectrum of **6** ($\lambda_{max}^{MeCl_2}$ (log ϵ) 234 (4.29), 320 (4.04)) is rather similar to that of **8** (λ_{max}^{MeCN} (log ϵ) 259 (4.38), 330 (3.99)). Thus it would appear that cyclic conjugation through silicon does not control the geometry of **6**. If indeed such bonding is present, the only effect may be a possible lowering of the inversion barrier through stabilization of the planar form.

Pyrolysis of **6** (sealed tube, 250°, 15 min) cleanly afforded *o*-terphenyl. This was expected from the reported thermal conversion of benzo[*d*]silepins to naphthalene.[4,5] This is of considerable interest as the elimination presumably takes place through the intermediacy of the silanorcardiene (**9**)[19] and thus would involve the until recently unknown[20] silacyclopropane.



9

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(17) No splitting of this peak is observed with lower temperatures although broadening is seen at −95° in CS_2.

(18) N. L. Allinger, R. A. Greengard, and C. J. Finder, *Tetrahedron Lett.*, 3095 (1973).

(19) Such a mechanism is most commonly used to explain conversion of thiepins to benzenes through sulfur extrusion: B. P. Stark and A. J. Duke, "Extrusion Reactions," Permagon Press, Oxford, 1967.

(20) R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972).

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(22) NASA Predoctoral Fellow, 1969–1972.

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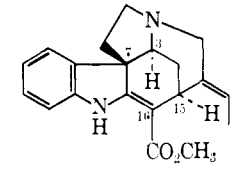
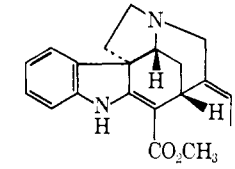
A Laboratory Model for the Biogenesis of the "Antipodal" Strychnos Alkaloids

Sir:

The discovery of enantiomeric forms[1] of the *Strychnos* alkaloid akuammicine (**1**) and the diastereoisomers (−)-lochneridine (**2**) and (+)-20-epilochneridine[2] (**3**) has


(−)-1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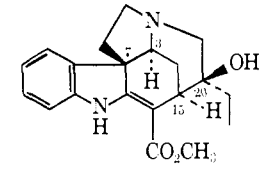
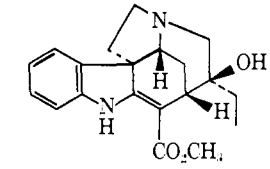

2


3

presented a long standing problem[3] in terms of the absolute stereochemistry of the biogenetic pathway to (+)-**1** and **3**. Thus a nonstereospecific step involving C_{15} has been invoked[1] to account for the difficulty in arriving at a plausible mechanism for the inversion of stereochemistry at C_3, C_7, and C_{15} in **1** and **2** which would surely involve rupture of the C_3–C_7 and C_{15}–C_{16} bonds. Biosynthetic experiments[4] have revealed that

(1) P. N. Edwards and G. F. Smith, *Proc. Chem. Soc., London*, 215 (1960).

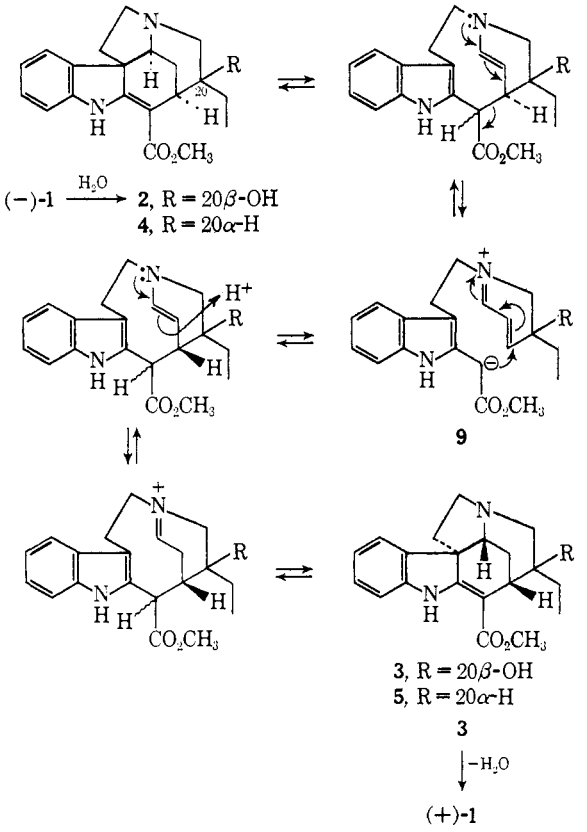
(2) P. Lathulliere, L. Olivier, J. Lévy and J. Le Men, *Ann. Pharm. Fr.*, 24, 547 (1966).

(3) J. E. Saxton in "The Alkaloids," Vol. VIII, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1965, Chapter 7; Vol. X, 1968, Chapter 11.

(4) A. I. Scott, P. C. Cherry, and A. A. Qureshi, *J. Amer. Chem. Soc.*, **91**, 4932 (1969); A. R. Battersby and E. S. Hall, *Chem. Commun.*, 793 (1969).

the *Corynanthé* alkaloid geissoschizine is a good precursor of both (−)-akuammicine (**1**) and strychnine,[5] the absolute stereochemistry at C_{15} being preserved in this process.[6] In the absence of a racemization mechanism for (**1**) the logical conclusion is that the biosynthesis of (+)-(**1**) and (**3**) involves a set of *Corynanthé* alkaloids bearing antipodal C_{15} stereochemistry. Inspection of the stereochemistry of (**3**) suggests a possible

Scheme I



solution to this enigma in that the absolute stereochemistry at C_{20} in **3** coincides with that of its diastereoisomer **2**. We suggest that the *Strychnos* alkaloids can suffer inversion at C_3, C_7, and C_{15} at the dihydropyridine level as indicated in Scheme I by a mechanism which is reminiscent of the theory developed for the biogenesis of antipodal versions of the pentacyclic *Aspidosperma* alkaloids.[7] The formation of **3** from **2** is thus rationalized while dehydration of **3** leads to (+)-**1**. A simple model to illustrate this hypothesis has been provided by the following experiment.[8] (−)-19,20-Dihydroakuammicine (**4**) was heated in degassed absolute methanol solution at 95° for 50 hr in a sealed tube. A steady decrease of the optical rotation of the solution was noted by ORD spectrum during this period and analysis of the products was achieved on EM silica gel F-254 analytical plate with 10% MeOH in $CHCl_3$ as developer. The diastereoisomer **5** was observed on the

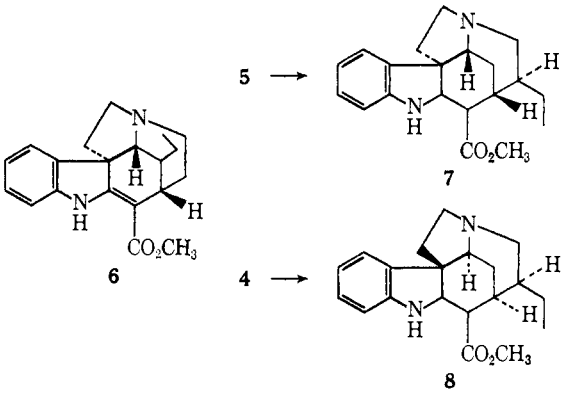


plate with R_f = 0.16 which was very close to the starting material (R_f ≈ 0.19). Preparative tlc with subsequent rechromatography afforded good separation of optically pure starting material (65%) (ORD[9] (CH_3OH) [Φ] (nm) −42,000 (340), +89,000 (295), +82,000 (245); λ_{max}^{MeOH} 325, 294, 233 nm) and its diastereoisomer (**5**) (15%) (ORD[9] (CH_3OH) [Φ] (nm) +24,000 (340), −81,000 (295), −78,000 (245); λ_{max}^{MeOH} 325, 294, 233 nm; *m/e* 324 (M^+; 65%), 293, 265 (10%), 225 (100%), 208 (18%), 194 (25%), 180 (30%), 167 (35%), 125 (55%), 94 (25%); nmr ($CDCl_3$), δ 8.70 (N*H*), 7.0 (ArH), 4.15 (C_3H), 3.78 (CO_2CH_3), 1.02 (CH_2CH_3). Diastereoisomer (**5**) was further characterized by its nonidentity with 19,20-dihydrocondylocarpine[10,11] (**6**), and by reduction (Zn–H_2SO_4) to (+)-20-epi-2,16,19,20-tetrahydroakuammicine (**7**) whose characteristic mass spectrum[10] was virtually identical with that of its diastereoisomer (**8**). The equilibration was also conducted in the reverse direction to give the same mixture (**4**:**5**; 4:1) starting with (**5**) in high yield (90%). The facility of this intriguing "racemase" model suggests that pseudoakuammicine [(±)-**1**] could be formed in *Picralima* species by the inversion mechanism operating either on the 20-hydroxy series (as **2**) or at the 19,20-dihydro level (as in **5** ⇄ **4**) followed by dehydration or oxidation, respectively, the former step having been demonstrated *in vitro*.[12]

These experiments are also suggestive for the design of a short stereospecific synthesis of the *Strychnos* alkaloids *via* the *seco* system (**9**).

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(5) A. I. Scott and S. I. Heimberger, *J. Chem. Soc., Chem. Commun.*, 217 (1973).

(6) *Cf.* the results of feeding 4R and 4S 4^3H, labeled mevalonates to the main classes of alkaloid where the $4R^3H$ label is retained at C_{15} in every case; A. R. Battersby, *Chem. Soc., Spec. Period. Rep.*, **1**, 31 (1971), and references cited therein.

(7) Reviewed by A. I. Scott, *Accounts Chem. Res.*, **3**, 151 (1970).

(8) *Cf.* P. N. Edwards and G. F. Smith, *J. Chem. Soc.*, 1458 (1961).

(9) W. Klyne, R. J. Swan, B. W. Bycroft, D. Schuman, and H. Schmid, *Helv. Chim. Acta*, **48**, 443 (1965); W. Klyne, R. J. Swan, B. W. Bycroft, and H. Schmid, *ibid.*, **49**, 832 (1966), and references cited by A. A. Gorman, M. Hesse, and H. Schmid, *Chem. Soc., Spec. Period. Rep.*, **1**, 325, (1971).

(10) H. Budzikiewicz, J. M. Wilson, C. Djerassi, J. Lévy, J. LeMen, and M.-M. Janot, *Tetrahedron*, **19**, 1265 (1963); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectrometry," Vol. I, Holden-Day, San Francisco, Calif., 1964, p 133.

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