the corresponding CD curves in the first absorption region due to the vicinal and conformational effects of each *N*-glycoside ligand of opposite sense.

Supplementary Material Available: Final positional and thermal parameters and their estimated standard deviations (2 pages). Ordering information is given on any current masthead page.

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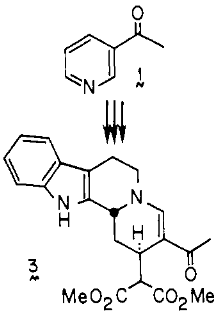
Short Syntheses of Hirsutine and Geissoschizine

Sir:

The recent introduction of a short, new scheme of construction of the indoloquinolizidine skeleton characteristic of the indole alkaloids of the heteroyohimboid, yohimboid, and corynantheioid types[1] has led the way to total syntheses of a variety of heteroyohimboid[2] and yohimboid[3] bases. Thus N-alkylation of β-acetylpyridine (**1**) and methyl β-(β-pyridyl)acrylate (**2**) with tryptophyl bromide, treatment of the salts with dimethyl sodiomalonate, and acid-induced cyclization of the resultant 1,4-dihydropyridines have afforded indoloquinolizidines **3** and **4** en route to the heteroyohimboid and yohimboid alkaloids, respectively. The following syntheses of hirsutine (**5**) and geissoschizine (**6a**) from the tetracyclic intermediates also illustrate the power of the new method of synthesis in the construction of members of the corynantheioid alkaloid family.



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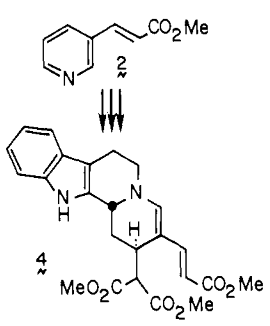

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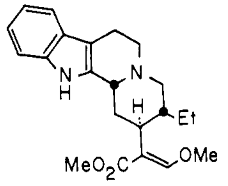

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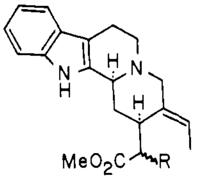
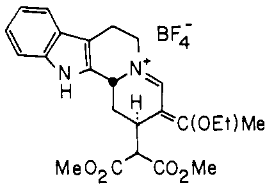
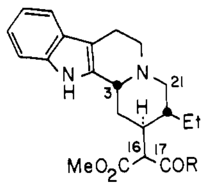


6a R = CHO
b R = H
c R = CH(OMe)$_2$

Exposure of tetracycle **3** to triethyloxonium tetrafluoroborate in methylene chloride solution gave salt **7**, whose immediate hydrogenation (20% Pd–C, MeOH, atmospheric pressure) yielded (74%) ester **8a** [mp 175–176 °C; IR (KBr) 3408, 1748, 1717 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.82 (t, 3, *J* = 6 Hz, Me), 3.73 [s, 6, (OMe)$_2$], 3.97 (m, 1, H-3), 6.6–7.2 (m, 4, aromatic Hs)]. Reduction of the latter [(*i*-Bu)$_2$AlH, CH$_2$Cl$_2$, −78 °C] afforded (61%) amorphous aldehydo ester **8b** [IR (CHCl$_3$) 3467, 1716, 1658 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.80 (m, 3, Me), 3.80 (s, 3, OMe), 4.53 (m, 1, H-3), 6.9–7.6 (m, 4, aromatic Hs), 8.00 (s, 1, H-17)], whose treatment with methanolic acid (1:1 aldehyde–MeOH, CH$_2$Cl$_2$ saturated with HCl gas, −20 °C, 3 days) yielded (56%) (±)-hirsutine (**5**) (mp 152–153 °C; IR and ^{1}H NMR spectra are identical with those of an authentic sample).

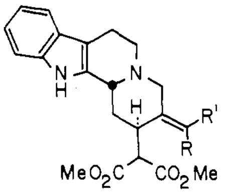


7

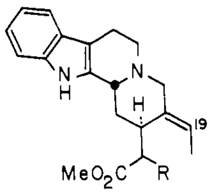


8a R = OMe
b R = H

By the utilization of both intermediates **3** and **4**, there emerged three routes of geissoschizine synthesis of which the first two to be described constitute formal total syntheses of the alkaloid by virtue of a connection with an earlier synthesis. Reduction (NaBH$_4$, MeOH, 0 °C) of salt **7** yielded (65%) a ca. 5:4:1 mixture of enol ether **9a** [mp 178–180 °C; IR (CHCl$_3$) 3480, 3400, 1752, 1730, 1673 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.18 (t, 3, *J* = 7 Hz, OEt Me), 1.87 (s, 3, Me), 3.3–4.3 (m, 6, H-3, H-16, H$_2$-21, OCH$_2$), 3.61, 3.80 [s, 3 each, (OMe)$_2$], 6.8–7.4 (m, 4, aromatic Hs)], diester **9b** [mp 99–101 °C; IR (CHCl$_3$) 3478, 1751, 1732 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.60 (d, 3, *J* = 6 Hz, Me), 3.18 (s, 2, H$_2$-21), 3.64, 3.80 [s, 3 each, (OMe)$_2$], 5.52 (q, 1, *J* = 6 Hz, H-19), 6.9–7.5 (m, 4, aromatic Hs)], and diester **9c**,[4] respectively. Sequential alkaline hydrolysis, acid-catalyzed thermal decarboxylation, and esterification in methanolic acid converted (87%) malonic ester **9b** into monoester **10a** [mp 134–136 °C (lit.[5] mp 134–136 °C); IR (CHCl$_3$) 3495, 1736 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.58 (d, 3, *J* = 6 Hz, Me), 3.13 (s, 2, H$_2$-21), 3.3–3.6 (m, 1, H-3), 3.67 (s, 3, OMe), 5.42 (q, 1, *J* = 6 Hz, H-19), 6.9–7.5 (m, 4, aromatic Hs)].



9a R = Me (or OEt), R' = OEt (or Me)
b R = Me, R' = H
c R = H, R' = Me



10a R = H
b R = CHO
c R = CH(OMe)$_2$

Ester **10a** also was the product (69%) of hydrolysis and didecarboxylation of tetracycle **4** (4 N HCl, 100 °C, 5 h), esterification (HCl, MeOH, ambient temperature, 18 h), and reduction (NaBH$_4$, MeOH, 0 °C, 1 h) of the resultant immonium salt 21-dehydro-**10a**.[6] Racemic deformyl-3-isogeissoschizine (**10a**) has been transformed previously into (±)-geissoschizine (**6a**)[5] by sequential mercuric acetate oxidation, zinc–acetic acid reduction,

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[1] E. Wenkert, *Recent Chem. Nat. Prod., Incl. Tob., Proc Phillip Morris Sci. Symp., 2nd*, 15–28 (1975).

[2] E. Wenkert, C.-J. Chang, H. P. S. Chawla, D. W. Cochran, E. W. Hagaman, J. C. King, and K. Orito, *J. Am. Chem. Soc.*, **98**, 3645 (1976).

[3] E. Wenkert, T. D. J. Halls, G. Kunesch, K. Orito, R. L. Stephens, W. A. Temple, and J. S. Yadav, *ibid.*, **101**, 5370 (1979).

[4] In view of the difficulty of isolation of **9c** from a mixture of the isomers **9b** and **9c**, diester **9c** was not obtained in a pure state. It could be identified, however, by ^{1}H and ^{13}C NMR analyses of the mixture and by the characterization of the acetic ester equivalent of malonate **9c** after decarbomethoxylation of the **9b**–**9c** mixture and separation of the resultant acetic esters.

[5] K. Yamada, K. Aoki, T. Kato, D. Uemura, and E. E. van Tamelen, *J. Chem. Soc., Chem. Commun.* 908 (1974).

[6] The hydrolysis and decarboxylation of the 5-amino-2,4-pentadienoic ester moiety of the doubly vinylogous urethane **4** are based on earlier experience: E. Wenkert, K. G. Dave, and F. Haglid, *J. Am. Chem. Soc.*, **87**, 5461 (1965). For a recent example see R. Besselièvre, B.-P. Cosson, B. C. Das, and H.-P. Husson, *Tetrahedron Lett.*, 63 (1980).

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and formylation of the resultant racemic deformylgeissoschizine (**6b**).[7]

A direct synthesis of (±)-geissoschizine (**6a**) from tetracycle **3** without loss of any nuclear carbon was executed by the following reaction sequence. Reduction of diester **9b** [$(i\text{-}Bu)_2AlH$, CH_2Cl_2, −78 °C] yielded (60%) amorphous (±)-3-isogeissoschizine (**10b**) [IR ($CHCl_3$) 3470, 1717, 1662, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50, 1.61 (d, 3, J = 6 Hz, Me of two isomers), 3.13, 3.18 (s, 2, H_2-21 of two isomers), 3.65, 3.71 (s, 3, OMe of two isomers), 5.36, 5.55 (q, 1, J = 6 Hz, H-19 of two isomers), 6.9–7.6 (m, 4, aromatic Hs), 8.00 (s, 1, H-17)], which could be converted (HCl, MeOH, ambient temperature, 18 h) (91%) into amorphous acetal **10c** [IR ($CHCl_3$) 3395, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58, 1.68 (s, 3, Me of two isomers), 3.18 (s, 2, H_2-21), 3.30, 3.35, 3.40, 3.49, 3.58, 3.78 [s, 9, $(OMe)_3$ of two isomers], 4.36 (d, 1, J = 6 Hz, H-17), 5.46, 5.57 (q, 1, J = 6 Hz, H-19 of two isomers), 6.8–7.5 (m, 4, aromatic Hs)]. Carbon-3 epimerization of the latter [$m\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, 0–25 °C, 5 h; $(CF_3CO)_2O$, CH_2Cl_2, −78–0 °C, 4 h; $NaBH_4$, THF, 0 °C, 1 h] yielded (21%) (±)-geissoschizine dimethyl acetal (**6c**) [mp 129–131 °C; IR ($CHCl_3$) 3472, 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60, 1.70 (d, 3, J = 6 Hz, Me of two isomers), 3.19 (s, 2, H_2-21), 3.25, 3.31, 3.40, 3.45, 3.58, 3.80 [s, 9, $(OMe)_3$ of two isomers], 5.52, 5.60 (q, 1, J = 6 Hz, H-19 of two isomers), 6.9–7.5 (m, 4, aromatic Hs)], whose partial hydrolysis (4.5 N HCl, acetone, ambient temperature, 24 h) gave (31%) (±)-geissoschizine (**6a**) [mp 186–188 °C (lit.[5] mp 187–189 °C); IR and ^1H and ^{13}C NMR spectra are identical with those of an authentic sample].[8]

Acknowledgment. We are indebted to the U.S. Public Health Service for support of this work, Professor S. Sakai for the gift of a sample of hirsutine, and Drs. R. Goutarel and M. Pais for the present of a geissoschizine specimen.

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[7] The oxidation–reduction sequence has been reported[5] to produce an 8% (25%, based on actual **10a** utilization) yield of **6b**. This now has been improved to 40% (51%, based on actual **10a** utilization) by the following reaction alteration. Ester **10a** was oxidized ($m\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, 0 °C, 1 h), the N_b-oxide was dehydrated [$(CF_3CO)_2O$, CH_2Cl_2, −78 to 0 °C, 4 h], and the resultant immonium salts were reduced ($NaBH_4$, THF, 0 °C, 1 h).

[8] For previous syntheses of (±)-geissoschizine (**6a**) see ref 5 and B. Hachmeister, D. Thielke, and E. Winterfeldt, *Chem. Ber.*, **109**, 3825 (1976).

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A New Geometrical Form of Germanium. Synthesis and Structure of Tetraethylammonium 2-Chloro-2,2′-spirobis(1,3,2-benzodioxagermole)

Sir:

Although pentacoordinated Ge(IV) species[1] having a trigonal bipyramidal structure have been characterized by X-ray crystallography, no reports are available concerning the structure of a spirocyclic pentacoordinate Ge(IV) compound.

We report herein the preparation and X-ray crystal structure of the first pentacoordinated Ge(IV) compound having a square pyramidal conformation. The compound, tetraethylammonium 2-chloro-2,2′-spirobis(1,3,2-benzodioxagermole) (**2**), mp 223-224 °C, was prepared by the reaction of (**1**)[2,3] with 1 equiv of $Et_4N^+Cl^-$ in methyl cyanide at room temperature (yield 90%). The bromo and fluoro analogues, **3** and **4**, were also prepared. Colorless crystals of **2** suitable for X-ray diffraction analysis were grown from methyl cyanide at 25 °C.

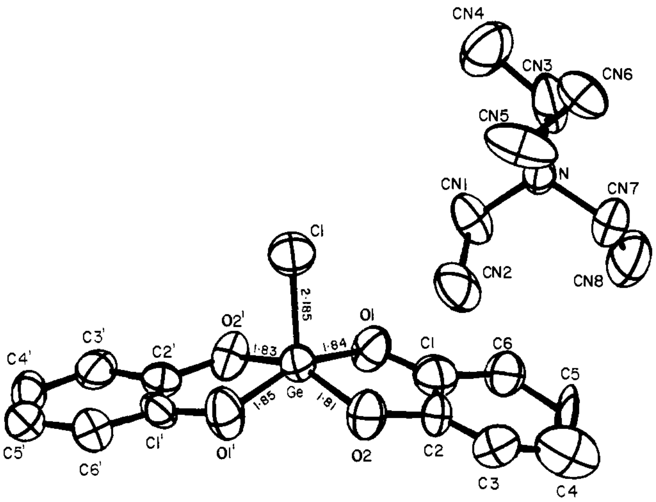
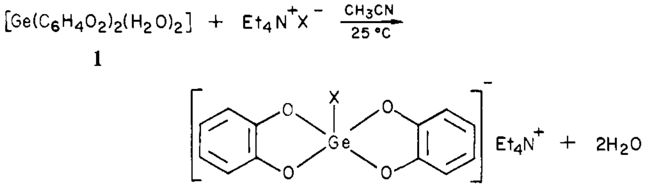


Figure 1. ORTEP plot of $[(C_6H_4O_2)_2GeCl]^-NEt_4^+$ (**2**) with thermal ellipsoids shown at the 50% probability level. Bond lengths: Ge–O1 = 1.842 (11), Ge–O1′ = 1.852 (14), Ge–O2 = 1.811 (12), Ge–O2′ = 1.828 (13), Ge-Cl = 2.185 (4) Å. Bond angles: O1–Ge–O1′ = 157.5 (6)°, O2–Ge–O2′ = 151.6 (6)°, O1–Ge–O2 = 88.0 (4)°, O1′–Ge–O2′ = 87.4 (5)°, O1–Ge–O2′ = 86.5 (6)°, O1′–Ge–O2 = 87.1 (6)°, Cl–Ge–O1 = 102.7 (4)°, Cl–Ge–O2 = 105.3 (5)°, Cl–Ge–O1′ = 99.8 (5)°, Cl–Ge–O2′ = 103.1 (4)°.


$[Ge(C_6H_4O_2)_2(H_2O)_2] + Et_4N^+X^- \xrightarrow[25\ °C]{CH_3CN}$ ... $Et_4N^+ + 2H_2O$

1

2, X = Cl, mp 223–224 °C
3, X = Br, mp 210 °C dec
4, X = F, mp 203 °C dec

Crystal Data. $C_{20}H_{28}O_4NClGe$, space group $Pbc2_1$ (alternate setting of $Pca2_1$, C_{2v}^5, No. 29),[4] with a = 12.244 (4), b = 16.366 (5), c = 10.662 (8) Å, and Z = 4. Independent reflections (1986) were measured on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode, to a maximum $2\theta_{MoK\bar{\alpha}}$ of 50°. The structure was solved by using heavy-atom techniques. Anisotropic full-matrix least-squares refinement[5a] based on the 27 independent nonhydrogen atoms led to a conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.059[5b] for the 1428 reflections having $I \geq 2\sigma(I)$.

The molecular geometry of **2** is shown in the ORTEP plot of Figure 1. It is evident, from the bond parameter data given in

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[1] (a) M. S. Bilton and M. Webster, *J. Chem. Soc., Dalton Trans.*, 722 (1972); (b) L. O. Atovmjan, Ja. Ja. Bleidelis, A. A. Kemme, and R. P. Shibaeva, *J. Struct. Chem.*, **11**, 295 (1970); (c) A. A. Kemme, Ja. Ja. Bleidelis, R. P. Shibaeva, and L. O. Atovmjan, *ibid.*, **14**, 90 (1973); (d) M. Dräger, *Chem. Ber.*, **108**, 1723 (1975); (e) M. Dräger, *Z. Anorg. Allg. Chem.*, **423**, 53 (1976).

[2] G. I. Kurnevich and V. B. Vishnevskii, *J. Appl. Spectros.*, **13**, 1201 (1970).

[3] Compound **1** was prepared by the slow addition (2 h) of a mixture of 2 equiv of catechol and 4 equiv of triethylamine in benzene to 1 equiv of germanium tetrachloride in benzene at room temperature. Evaporation of solvent from the reaction mixture and treatment of the residue with water gave a light-brown flocculent amorphous precipitate. Further purification of the sample of **1** was achieved by dissolving the crude product in a solution of $Et_4N^+Br^-$ in CH_3CN at 25 °C to form $[Ge(C_6H_4O_2)Br]^-Et_4N^+$ (**3**). Hydrolysis of **3** at 25 °C afforded pure **1** (65% yield).

[4] "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 115.

[5] (a) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 4, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Ge, Cl, and O were taken from the same source, pp 149–150; (b) this value is for the configuration having the lowest R_w.

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