Acknowledgments. We are grateful to Professor Paul D. Bartlett for his valuable discussions. We also express our thanks to Professors E. S. Huyser and J. W. Crump for their helpful discussions and encouragement.

* Address correspondence to this author.

Charles E. Reineke,* James R. McCarthy, Jr.
Halogens Research Laboratory, The Dow Chemical Company
Midland, Michigan 48640
Received August 16, 1970

Deidaclin: A Natural Glucoside of Cyclopentenone Cyanohydrin

Sir:

The classical cyanogenetic glycosides are nearly all derivatives of valine, isoleucine, leucine, phenylalanine, and hydroxylated phenylalanines.[1,2] An exception is gynocardin, recently proved[3,4] to be the β-D-glucopyranoside (**1**) of 3σ-cyano-3ρ,4σ,5ρ-trihydroxycyclopentene.[5] The original sources of gynocardin belong to the tribe Pangieae of the dicotyledon family Flacourtiaceae. The Pangieae and adjacent cyanogenetic tribe Oncobeae of Flacourtiaceae[6] are the producers of chaulmoogra fatty acids having structure **2**, where *n* runs over even numbers from 12 down apparently to as low[7] as 4 and the side chains are all σ oriented.[8,9] Chromatographic evidence[10] now indicates gynocardin to occur also in the closely related family Passifloraceae. Barterin, isolated[11] from a genus on the border between Flacourtiaceae and Passifloraceae, is the β-D-glucopyranoside of a 3-cyano-3,5σ-dihydroxycyclopentene.[11,12] Another new cyanogenetic glycoside was discovered by Hegnauer and coworkers[10] in *Deidamia clematoides* (Passifloraceae). They called the substance (mp 127–128°) deidamin, which we are altering to deidaclin with Professor Hegnauer's gracious consent in order to avoid the suggestion of basic properties. Enzymatic hydrolysis of deidaclin gave glucose, hydrogen cyanide, and a volatile carbonyl compound, isolated as a 2,4-dinitrophenylhydrazone.[10] In a color test[13] the hydrazone reacted like a conjugated unsaturated derivative. Having received deidaclin samples from Professor Hegnauer for additional study, we find it to be the β-D-glucopyranoside (**3**) of an enantiomer of 2-cyclopenten-1-one cyanohydrin.

The structure of deidaclin (*Anal.* Calcd for $C_{12}H_{17}NO_6$: C, 53.13; H, 6.32; N, 5.16. Found: C, 52.95; H, 6.03; N, 5.11) was revealed by its pmr spectrum [100 MHz, D_2O, external[14] $(CH_3)_4Si$]. The spectrum showed a multiplet representing four protons [$(CH_2)_2$] at δ 3.0 and an AB pair of doublets (each line apparently an unresolved triplet) at δ 6.40 and 6.87 (J = 6 Hz) for the two vinylic protons.[3] It also contained a doublet at δ 5.25 (J = 7.5 Hz) for the anomeric proton of a β-glucopyranoside[3,15] and signals from δ 3.6 to 4.5 for the six other unexchanged protons of the glucopyranosyl group. The 70-eV mass spectrum of deidaclin (probe temperature 130°) was consistent with the spectra of barterin and gynocardin (all had peaks at m/e = M − 49) and showed a strong doublet at m/e 92 and 93 ($ROC_6H_{11}O_5 \rightarrow R^+, RH^+$) corresponding to the barterin doublet[12] at m/e 108–109 and the single intense gynocardin peak[3] (R^+) at m/e 124.

Structure **3** was established for deidaclin by identification of the carbonyl compound formed on hydrolysis with gynocardase[10] as 2-cyclopenten-1-one. The 2,4-dinitrophenylhydrazone that we obtained in a Conway diffusion dish[10] or by treatment of a chloroform extract of the hydrolysis mixture with dinitrophenylhydrazine consisted of red needles, mp 167.5–169°, which were identical as judged by mixture melting point, ir spectrum, and tlc with the dinitrophenylhydrazone (lit.[16] mp 168–170°) of authentic 2-cyclopenten-1-one (Aldrich).

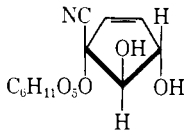
Although the enantiomers of cyclopentenone cyanohydrin should have substantial, predictable rotations,[9] the molecular rotation of deidaclin [$[\alpha]^{27}D$ −20.4° (c 1, H_2O)] is near values for β-D-glucopyranosides of achiral aglucones. The configuration of deidaclin next to the cyano group, like that of barterin, stands unknown at present. Nevertheless, deidaclin can be regarded as a structural prototype of the series comprising barterin, gynocardin, and possible isomers[10] of these, linking them to the cyclopentenoid fatty acids. A logical biosynthetic precursor[1,2] of deidaclin is a 2-cyclopentene-1-glycine. The hydroxylation step of the biosynthesis may be expected to proceed with retention of configuration.[17,18] A plausible though not a necessary conjecture is that the cyano groups of deidaclin and barterin are σ oriented like their counterpart in gynocardin and the side chains of the chaulmoogra acids and that the precursor of the whole cyanogenetic series is L-2-cyclopentene-1σ-glycine (**4**).

Fowden has emphasized steric analogies between protein and nonprotein plant amino acids.[19] Mixed stereoisomers of 2-cyclopentene-1-glycine form a metabolic antagonist of both valine and isoleucine toward *Escherichia coli*, owing to steric likeness.[20] The im-

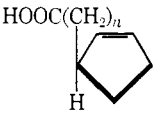
(1) E. E. Conn and G. W. Butler in "Recent Advances in Phytochemistry," J. B. Harborne and T. Swain, Ed., Academic Press, New York, N. Y., 1969, Chapter 2.
(2) E. E. Conn, *J. Agr. Food Chem.*, 17, 519 (1969).
(3) R. A. Coburn and L. Long, Jr., *J. Org. Chem.*, **31**, 4312 (1966).
(4) H. S. Kim, G. A. Jeffrey, D. Panke, R. C. Clapp, R. A. Coburn, and L. Long, Jr., *Chem. Commun.*, 381 (1970).
(5) In cyclopentenes bearing directly attached carbon atoms at only one allylic position, consider the specified allylic carbon atom of the ring (imagined planar) to be replaced by oxygen, and disregard substituents elsewhere. Call the face of the cyclopentene corresponding to the *re–re* face [K. R. Hanson, *J. Amer. Chem. Soc.*, **88**, 2731 (1966); D. Arigoni and E. L. Eliel, *Top. Stereochem.*, 4, 127 (1969)] of the double bond in the resulting molecule of 2,3-dihydrofuran ρ, and the other face σ.
(6) R. Hegnauer, "Chemotaxonomie der Pflanzen," Vol. 4, Birkhäuser Verlag, Basel and Stuttgart, 1966, pp 157–163.
(7) H. I. Cole and H. T. Cardoso, *J. Amer. Chem. Soc.*, 61, 2349, 2351 (1939); I. Zeman and J. Pokorný, *J. Chromatogr.*, 10, 15 (1963).
(8) K. Mislow and I. V. Steinberg, *J. Amer. Chem. Soc.*, 77, 3807 (1955).
(9) J. H. Brewster, *ibid.*, **81**, 5493 (1959).
(10) B. Tantisewie, H. W. L. Ruijgrok, and R. Hegnauer, *Pharm. Weekblad*, 104, 1341 (1969).
(11) M. Paris, A. Bouquet, and R.-R. Paris, *C. R. Acad. Sci., Paris, Ser. D*, 268, 2804 (1969).
(12) M. G. Ettlinger and R.-R. Paris, in preparation.
(13) A. Mehlitz, K. Gierschner, and T. Minas, *Chem.-Ztg., Chem. App.*, **87**, 573 (1963).
(14) The standard signal fell *ca.* 0.4 ppm higher in field than that of internal $(CH_3)_4Si$.
(15) R. C. Clapp, F. H. Bissett, R. A. Coburn, and L. Long, Jr., *Phytochemistry*, **5**, 1323 (1966).
(16) H. Koch, J. Kotlan, and H. Mohar, *Monatsh. Chem.*, **95**, 1257 (1964).
(17) F. H. Bissett, R. C. Clapp, R. A. Coburn, M. G. Ettlinger, and L. Long, Jr., *Phytochemistry*, **8**, 2235 (1969).
(18) L. J. Morris and C. Hitchcock, *Eur. J. Biochem.*, 4, 146 (1968).
(19) L. Fowden, I. K. Smith, and P. M. Dunnill in "Recent Aspects of Nitrogen Metabolism in Plants," E. J. Hewitt and C. V. Cutting, Ed., Academic Press, New York, N. Y., 1968, pp 165–177.

portance of steric resemblance in the biosynthesis of cyanohydrin glucosides is shown in the prevalent simultaneous synthesis from valine and isoleucine[2,17] and by the fact that *O*-methylthreonine, an isoleucine analog, inhibits the conversion in flax of valine to linamarin.[1,21] Since isobutyraldoxime accumulates in the blocked system and *O*-methyllactaldoxime also is inhibitory, *O*-methylthreonine probably is carried at least to the aldoxime stage. We suggest that if a group of plants has the quirk of producing an L-2-cyclopentene-1-glycine, the passage to deidaclin and its additionally hydroxylated congeners involves little change in enzymatic specificities from the widespread synthesis of linamarin and methyllinamarin[17] (lotaustralin).

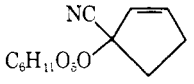
The Passifloraceae, related tribes of Flacourtiaceae, and perhaps other, neighboring families (*e.g.*, Turneraceae[10]) promise to be a nest of cyclopentenes bearing a single, straight carbon chain in the 3 position. To understand the taxonomic limits of and biosynthetic pathways within this group of plants is a challenge.



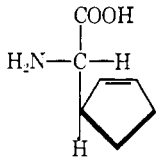
1



2



3



4

Acknowledgment. We thank Professor R. Hegnauer for generously enabling us to work on this problem by supplying us with deidaclin (and gynocardase), Dr. G. O. Dudek, Harvard University, Cambridge, Mass., for the mass spectra, and F. H. Bissett for pmr spectra.

(20) R. L. Dennis, W. J. Plant, C. G. Skinner, G. L. Sutherland, and W. Shive, *J. Amer. Chem. Soc.*, 77, 2362 (1955); R. M. Gipson, C. G. Skinner, and W. Shive, *Arch. Biochem. Biophys.*, **111**, 264 (1965).

(21) G. W. Butler, *Proc. Roy. Aust. Chem. Inst.*, **36**, 65 (1969).

(22) National Research Council Senior Visiting Research Associate.

* Address correspondence to this author.

R. C. Clapp, M. G. Ettlinger,[22] L. Long, Jr.*

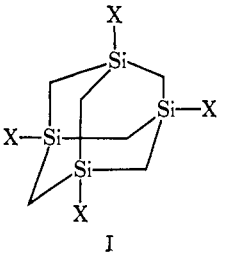
Pioneering Research Laboratory, U. S. Army Natick Laboratories
Natick, Massachusetts 01760

Received August 5, 1970

1,3,5,7-Tetrasilaadamantanes. A Facile Synthesis *via* Catalyzed Ligand Redistribution

Sir:

The novel, highly symmetrical 1,3,5,7-tetrachloro-1,3,5,7-tetrasilaadamantane (*i.e.*, I, X = Cl) was prepared in very low yield (<0.1%) several years ago[1] when an $AlCl_3$-catalyzed redistribution reaction of Me_3SiCl and $SiCl_4$ was inadvertently overheated to 500°. Fritz and coworkers[2] subsequently isolated the tetramethyl analog (I, X = Me) in the complex mixture of products arising from the pyrolysis of Me_4Si at 650°. Whereas the arrangement of carbon atoms in



I

adamantane[3] is based on the diamond structure, silicon carbide is the structural parallel for the 1,3,5,7-tetrasilaadamantanes.[4]

The unprecedented resistance to solvolysis[1] of cages such as I (X = Cl) is believed to derive from (a) their bridgehead structure which precludes backside attack, and (b) their markedly lessened strain which renders them much less susceptible to flank attack than earlier, highly strain-activated, bridgehead silicon derivatives.[5] Regarding this latter point, examination of molecular models reveals that any distortion of the bond angles between a silicon and its three adjacent carbon atoms distorts the atomic arrangement throughout the whole cage, and would require the addition of substantial amounts of energy to the system. Thus the enhanced solvolytic stability of the tetrasilaadamantane system is consistent with earlier inferences that flank attack at silicon involves a transition state with appreciably altered bond angles between the silicon center and the three nonleaving substituents. In order to facilitate further studies of the unique chemistry of this novel heterocyclic system, we have devised a markedly improved synthesis based on the catalyzed ligand redistribution reaction of appropriate tetraorganosilicon substrates, such as 1,3,5-hexamethyl-1,3,5-trisilacyclohexane; *i.e.*

$$2(Me_2SiCH_2)_3 \xrightarrow{AlBr_3} [MeSi(CH_2)_{3/2}]_4 + 2Me_4Si$$
(*i.e.*, I, X = Me)

A ligand redistribution approach to this problem was selected because (a) simple tetraalkylsilanes are known to undergo random exchange of alkyls in the presence of aluminum halides (thus $BuSiMe_3$ affords Bu_2SiMe_2, Bu_3SiMe, Bu_4Si, and Me_4Si),[6,7] (b) the best route to adamantane itself is *via* the $AlBr_3$-catalyzed rearrangement of hydrocarbon precursors,[3] and (c) appropriate

(1) A. L. Smith and H. A. Clark, *J. Amer. Chem. Soc.*, **83**, 3345 (1961).

(2) (a) For a summary of Fritz's work, see G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, 7, 349 (1965); (b) G. Fritz, F. Diem, H. Köhler, D. Kummer, and H. Scheer, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970).

(3) For details concerning the nomenclature, synthesis, and chemistry of adamantanes, see R. C. Fort and P. von R. Schleyer, *Chem Rev.*, **64**, 277 (1964).

(4) Based on this analogy, Fritz[2b] has referred to the various silcarbane cage structures (including Si_4, Si_7, Si_9, and Si_{10} examples) arising from Me_4Si pyrolysis as carborundanes. We suggest that use of the trivial name *carborundane* be reserved for the parent tetrameric silsesquimethylene structure (*i.e.*, I, X = H).

(5) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **79**, 1008 (1957); **81**, 251 (1959).

(6) (a) G. Calingaert, H. Soroos, and V. Hnizda, *ibid.*, **62**, 1107 (1940); (b) G. A. Russell, *ibid.*, 81, 4185 (1959); (c) P. D. George, L. H. Sommer, and F. C. Whitmore, *ibid.*, 77, 1677 (1955); (d) see also, A. J. Barry and J. W. Gilkey, U. S. Patent 2,647,912 (1953).

(7) The literature also contains a few examples of simple heterocyclic synthesis *via* the AlX_3-catalyzed redistribution of appropriate substrates. Thus, $Me_3Si(CH_2)_4SiMe_3$ afforded 1,1-dimethyl-1-silacyclopentane[8] and $Me_3SiCH_2CH_2SiMe_3$ yielded $Me_2Si(CH_2CH_2)_2SiMe_2$.[9]

(8) N. S. Nametkin, V. M. Vdovin, and K. S. Pushchevaya, *Dokl. Akad. Nauk SSSR*, **150** (3), 562 (1963).

(9) Yu. P. Egorov, K. S. Pushchevaya, E. D. Lubuzh, V. M. Vdovin, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 822 (1963).