equivalent[4] and $\sigma_I = 0.5$ for fluorine, we calculate that the inductive effect alone of a 9 fluorine would result in a rate increase of 10^5; hence, the π-conjugation effect actually results in a millionfold rate decrease.

By contrast, two α fluorines *increase* the LiCHA-catalyzed exchange of toluene by a factor of $>10^4$.[6] The relatively high primary isotope effects obtained for both systems ensure that the rates measured are those of hydrogen abstraction; that is, internal return is not important in either case. To explain these apparently divergent results we propose that the 9-fluorofluorenyl anion is *planar* whereas the α,α-difluorobenzyl anion is *pyramidal*. Estimates of the magnitude of the inductive stabilization of a nonconjugating pyramidal phenyldifluoromethyl anion are fully consistent with the observed reactivity of benzal fluoride. For this system the increased conjugation of a planar benzyl anion is countered by the corresponding increased conjugative destabilization of the two fluorines that are then also coplanar. However, the stability associated with a planar fluorenyl anion is much greater than for a phenyl anion and overcomes the destabilizing effect of a single conjugating fluorine.

These results may be generalized into the following working hypothesis: *a fluorine substituent stabilizes a pyramidal or nonconjugated anion but can destabilize a conjugated anion.* Such obvious corrolaries that trifluoromethyl anion is pyramidal and that nitrogen trifluoride should have a smaller bond angle than ammonia, etc., will be developed in the full paper. Similar considerations apply in a direct way to oxygen and nitrogen substituents.

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 59, reports that all four hydrogens of *m*-methylbenzal fluoride undergo hydrogen–deuterium exchange at comparable rates with potassium *t*-butoxide in *t*-butyl alcohol-*d*. This corresponds to a far slower relative rate for the difluoromethyl hydrogen than we have found, but this apparent discrepancy may very well be due to extensive internal return in the *t*-butyl alcohol system.

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Alkaloid Studies. LIX.[1] The Structure and Absolute Configuration of Vallesamidine

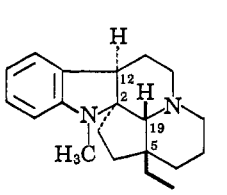
Sir:

In 1965 we reported[2] the isolation of 28 alkaloids from *Vallesia dichotoma* Ruiz *et* Pav. One of these appeared to be isomeric with N-methylaspidospermidine (II) on the basis of physical and chemical data, but no definite structure could be assigned in view of the very limited amount of material. We report now the determination of the molecular structure and absolute configuration of this new alkaloid, vallesamidine (I), by X-ray diffraction analysis. Formally, vallesamidine (I) differs from the usual aspidospermine skeleton (*e.g.*, III) only in that C-19 is attached to the indole nucleus at C-2 rather than at C-12.

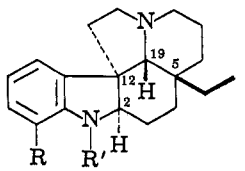
(1) For paper LVIII see R. R. Arndt, S. H. Brown, N. C. Ling, P. Roller, C. Djerassi, J. M. Ferreira, B. Gilbert, E. C. Miranda, S. E. Flores, A. P. Duarte, and E. P. Carrazzoni, *Phytochemistry*, **6**, 1653 (1967).

(2) A. Walser and C. Djerassi, *Helv. Chim. Acta*, **48**, 391 (1965).

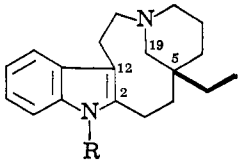
This is the first direct determination of the absolute configuration of a naturally occurring alkaloid related to aspidospermine (III). As such it lends support to the previous conclusions[3,4] regarding absolute configurations in the *Aspidosperma* alkaloid series. Alkaloids of this group isolated[2] in common with vallesamidine (I) include (+)-N-methylaspidospermidine (II), (−)-aspidospermine (III), (−)-vallesine (IV), (−)-N-methylquebrachamine (V), and (+)-haplocidine. By means of the optical rotatory dispersion technique[3] and chemical interconversions[2,4–6] these compounds have been shown to have the same absolute configurations at their respective equivalent asymmetric centers (carbons 2, 5, 12, and 19 in II). Stereochemically, vallesamidine (I) belongs to the same class, and it is particularly noteworthy that the absolute configuration at carbon 5 in I is the same as that at the equivalent carbon (5 in II–V) in all of the co-occurring aspidospermine-type bases for which the absolute configuration is known.



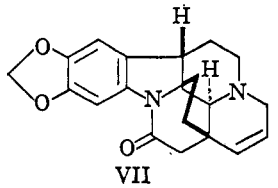
I



II, R = H; R′ = CH_3
III, R = OCH_3; R′ = CH_3CO
IV, R = OCH_3; R′ = CHO



V, R = CH_3
VI, R = H



VII

Camerman, *et al.*,[4] have shown that the aspidospermine skeleton (II–IV), with correct relative stereochemistry, can be generated by the intramolecular cyclization of quebrachamine (VI), the stereochemistry at carbon 5 determining the configuration at the other three asymmetric centers formed. This observation supports the earlier suggestion[7] that the path to the *Aspidosperma* alkaloids (II–IV) *in vivo* proceeds *via* quebrachamine-like intermediates (V, VI). Vallesamidine (I) might be regarded as the product of an "abnormal" cyclization which, however, generates the same stereochemistry at carbons 2, 12, and 19 as in the "normal" case. Such a biosynthetic route

(3) W. Klyne, R. J. Swan, B. W. Bycroft, D. Schumann, and H. Schmid, *Helv. Chim. Acta*, **48**, 443 (1965).

(4) A. Camerman, N. Camerman, J. P. Kutney, E. Piers, and J. Trotter, *Tetrahedron Letters*, 637 (1965); J. P. Kutney and E. Piers, *J. Am. Chem. Soc.*, **86**, 953 (1964).

(5) K. Biemann and G. Spiteller, *Tetrahedron Letters*, 299 (1961); K. Biemann, M. Spiteller-Friedmann, and G. Spiteller, *J. Am. Chem. Soc.*, **85**, 631 (1963).

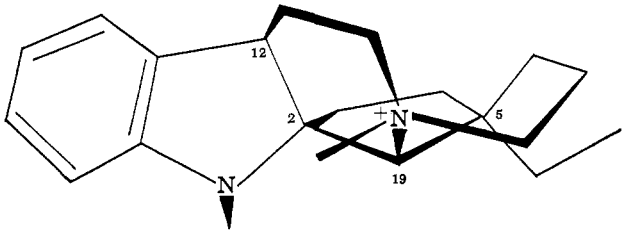
(6) G. F. Smith and M. A. Wahid, *J. Chem. Soc.*, 4002 (1963).

(7) C. Djerassi, A. A. P. G. Archer, T. George, B. Gilbert, and L. D. Antonaccio, *Tetrahedron*, **16**, 212 (1961); E. Wenkert, *J. Am. Chem. Soc.* **84**, 98 (1962); K. Biemann, M. Spiteller-Friedmann, and G. Spiteller, *Tetrahedron Letters*, 485 (1961).

might also apply to the *Schizozygia* alkaloids[8] (*e.g.*, schizozygine (VII)[9]), the only other reported compounds having the vallesamidine (I) skeleton. Vallesamidine is formally a completely reduced member of this series, and it should be noted that both genera belong to the same family, *Apocynaceae*. Whereas *Schizozygia* has yielded[8] alkaloids based on only one structural type, *Vallesia* contains[2] a remarkable variety of skeletons, making this plant a prime candidate for biochemical tracer studies.

Vallesamidine N(b)-methiodide (Chart I)[2] was crystallized from acetone to give monoclinic prisms or needles elongated along the unique axis. The space group is $P2_1$. The unit cell dimensions are: a = 11.977 ± 0.005, b = 12.009 ± 0.006, c = 9.4224 ± 0.0008 Å; γ = 115.95 ± 0.20°; V = 1218.4 Å^3. The density measured by flotation accounts for two alkaloid molecules and two molecules of acetone per unit cell (calcd: 1.353 g/cc; found: 1.347 ± 0.020 g/cc).

Chart I. Three-Dimensional Projection of Vallesamidine N(b)-Methiodide, Showing Correct Absolute Configuration



A total of 6375 diffraction intensities was collected using Mo Kα radiation. Averaging according to Friedel's law gave 3040 unique reflections, of which 2507 were nonzero. The unique iodine position was determined from a sharpened three-dimensional Patterson function. Refined iodine parameters were used to calculate a three-dimensional electron density function, which revealed all of the alkaloid atoms (except hydrogen). After full-matrix least-squares refinement with all of the data the discrepancy factor ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) was 0.098.

The partial structure which includes only the iodine atoms is centrosymmetric, giving rise to a false mirror plane at z = 0.25. Eight of the light atoms were determined to lie in or near this plane; the rest had a twofold ambiguity in z, so that both mirror images of the structure were obtained concomitantly. A probable single image was derived from consideration of bond distances and angles. This was confirmed independently to be the statistically most probable set of atom positions, as determined by a superposition analysis of the sharpened Patterson function in which the interatomic vectors involving an iodine atom and those between symmetry-related C, N, and O atoms were approximately removed. This objective method of sorting out atoms related by pseudo-symmetry was very useful in this case and will be described in a subsequent publication.

For the determination of the absolute configuration the raw data were re-averaged to take into account anomalous dispersion. Of 5744 unique reflections, 4595 were nonzero, including 1925 anomalous dispersion pairs. One cycle of refinement was run with each enantiomer using the nonzero data. The imaginary component of the iodine anomalous dispersion was included in the structure factor calculations. The enantiomer with carbon 5 in the R configuration (shown in I) had a significantly lower R factor and is clearly the correct one. A three-dimensional projection is shown in Chart I.

Attention should be called to the mass spectrum (see ref 2) of vallesamidine (I), which displays m/e 124 as the base peak, as well as a significant M − 28 peak, two features which are considered[5,10] to be characteristic of the aspidospermine (III) skeleton and which led us originally[2] to the working hypothesis that vallesamidine was simply a stereoisomer of II. A rationalization of these data will be provided in our detailed manuscript.

Acknowledgment. We wish to thank Dr. Ted E. Hopkins for assistance in collecting the diffraction data. We gratefully acknowledge research support from the Advanced Research Projects Agency through the Stanford Center for Materials Research (Grant SD-87), the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grants 407-G and 3068-A5), and the National Institutes of Health (Grant GM-11309).

(8) U. Renner and P. Kernweisz, *Experientia*, **19**, 244 (1963); U. Renner, *Lloydia*, **27**, 406 (1964); U. Renner and H. Fritz, *Helv. Chim. Acta*, **48**, 308 (1965).

(9) In contrast to structures I–IV, no absolute configuration is implied in VII.

(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 1, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 7.

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Homogeneous 1,4 Addition of Hydrogen Catalyzed by Tricarbonyl(arene)chromium Complexes

Sir:

Tayim and Bailar[1] elucidated the mechanism of homogeneous hydrogenation of polyolefins catalyzed by platinum- and palladium–$SnCl_3$ complexes. Among the various mechanisms discussed by Halpern[2] for the activation of hydrogen, formation of dihydride intermediates has been recognized in the catalytic reactions of soluble triphenylphosphine complexes of iridium[3] and rhodium.[4] We recently discovered that tricarbonyl(arene)chromium complexes catalyze the selective hydrogenation of methyl sorbate (*trans*-2,*trans*-4-hexadienoate) to methyl 3-hexenoate.[5] We now have evidence, based on deuterium tracer studies, that this reduction proceeds by 1,4 addition. A dihydride complex is implicated as an intermediate. Additional ob-

(1) H. A. Tayim and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 3420 (1967); **89**, 4330 (1967).

(2) J. Halpern in "Proceedings of the 3rd International Congress on Catalysis," Amsterdam, 1964, Vol. 1, W. M. H. Sachtler, G. C. A. Schuit, and P. Zweiteriug, Ed., North-Holland Publishing Co., Amsterdam, 1965, p 146; *Chem. Eng. News*, **44**, 68 (Oct 31, 1966).

(3) L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.*, **87**, 4970 (1965); G. G. Eberhardt and L. Vaska, *J. Catal.*, **8**, 183 (1967).

(4) (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966); (b) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid.*, 1574 (1967).

(5) E. N. Frankel and M. Cais, unpublished.