pH 2 to 3.6, but very soon explode and set free within 1 or 2 sec hundreds of hemoglobin granules. The remaining membranes retain some of the hemoglobin and reveal several splits after the termination of the explosion. Judging from the splits, three layers of erythrocyte-membrane could be surmised. 0,5% tannic acid elicits a similar but less clear-cut phenomenon without a typical 'explosion'.

EDITH LITSCHEL und J. TOMCSIK

Hygiene Institut der Universität Basel (Schweiz), 4. Juli 1963.

The Alkaloids of *Aspidosperma discolor* A. DC[1, 2]

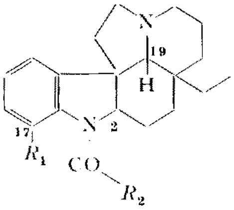
In a recent communication[3] DASTOOR and SCHMID reported the isolation from *Aspidosperma discolor* A. DC. of isoreserpiline, reserpiline, isoreserpiline-ψ-indoxyl, yohimbine, 10-methoxydihydrocorynantheol[4], and $\Delta^{19,20}$-dehydro-10-methoxydihydrocorynantheol[4]. Attention was drawn to the fact that no aspidospermine-type alkaloids were encountered and it was suggested that the presence of indolic and related alkaloids, as distinct from dihydroindolic compounds, might be characteristic of the subdivision *Nitida* of the genus *Aspidosperma*.

We have already reported earlier[5] on the isolation of isoreserpiline from this plant (trunk bark) and we should now like to record the presence of three alkaloids of the aspidospermine type, namely: demethylaspidospermine (I), demethoxyaspidospermine (II), and demethoxypalosine (III). This shows that the assumed[3] chemotaxonomic conclusions with regard to the supposed absence of such alkaloids is not justified. All three alkaloids were extracted by chloroform from a 10% acetic acid solution of the total bases, and subsequently separated by repeated chromatography on neutral alumina. The oily demethylaspidospermine (I)[6,7] was characterized as its crystalline perchlorate, $C_{21}H_{28}N_2O_2 \cdot HClO_4 \cdot MeOH$, m.p. 170° (dec.); $[\alpha]^{25}_{D} + 94°$ (c, 0.98 in methanol). The free base had ultraviolet absorption (λ_{max}^{EtOH} 220, 258 and 293 mμ, log ε 4.39, 3.52, 3.20; $\lambda_{max}^{EtOH-KOH}$ 307 mμ, log ε 3.97), and infrared absorption (λ_{max}^{KBr} 6.17, 6.29, 6.38 μ), characteristic of a 17-hydroxy-N_a-acyldihydroindole (aspidospermine numbering) while the n.m.r. spectrum[8] was entirely consistent[9] with structure I ($CH_2C\underline{H}_3$, 0.72 δ, triplet; C_{19}-H, 2.28 δ, singlet; N_a-$COCH_3$, 2.32 δ, singlet; C_{17}-OH, 10.83 δ, singlet; C_2-$\underline{H}$, 4.07 δ, quartet, J = 6 and 10 cps.; 3 aromatic protons, 6.9 δ, multiplet). This structure was fully confirmed by mass spectrometry[10] (molecular ion at *m/e* 340 as well as peaks at M-28 and *m/e* 124, typical[11] of the aspidospermine skeleton) and by methylation with dimethyl sulfate to (−)-aspidospermine, identical with the natural alkaloid (by mixture m.p., IR, UV and thin-layer chromatography).

The previously unknown amorphous demethoxyaspidospermine (II)[7] was isolated as its perchlorate, $C_{21}H_{28}N_2O \cdot HClO_4 \cdot 0.5H_2O$, $[\alpha]^{25}_{D} + 21°$ (c, 1.3 in methanol). The free base, $[\alpha]^{25}_{D} - 15°$ (c, 1.8 in chloroform), showed ultraviolet absorption (λ_{max}^{EtOH} 253, 280, 289 mμ, log ε 4.12, 3.58, 3.52) characteristic of an N-acyldihydroindole unsubstituted in the benzene ring. The NMR spectrum again showed the absorptions characteristic[9] of the aspidospermine skeleton ($CH_2C\underline{H}_3$, 0.73 δ, triplet; N_a-$COCH_3$, 2.27 δ, singlet; C_2-H, 4.08 δ, quartet, J = 6 and 10 cps.) the four aromatic protons absorbing as a one-proton multiplet at 8.13 δ (C_{17}-$\underline{H}$) and a three-proton multiplet at 7.17 δ.

Structure II was confirmed by the mass spectrum[10] which differed from that of aspidospermine[11] only in the appearance of those peaks which contain the benzene ring at mass numbers thirty units lower.

Demethoxypalosine (III) was similarly identified by its mass spectrum and by direct comparison with a specimen isolated[12] from *A. limae* Woodson.



I	R_1	OH,	R_2	CH_3
II	R_1	H,	R_2	CH_3
III	R_1	H,	R_2	CH_2CH_3

Preliminary investigation has shown the presence of several other alkaloids in *A. discolor*, and these are the subject of continuing studies in our laboratories.

Zusammenfassung. Von *Aspidosperma discolor* A. DC. wurden drei Alkaloide (I, II, III) der Aspidospermin-Art isoliert, deren Struktur durch massenspektroskopische und Kernresonanzmessungen bewiesen wurde.

J. M. FERREIRA[13], B. GILBERT,
R. J. OWELLEN, and C. DJERASSI

Department of Chemistry, Stanford University, Stanford (California, U.S.A.) and Instituto de Quimica Agricola, Rio de Janeiro (Brazil), August 19, 1963.

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[1] Paper XLIII in the series *Alkaloid Studies*. For paper XLII see K. S. BROWN, H. BUDZIKIEWICZ, and C. DJERASSI, Tetrahedron Letters, in press.

[2] Financial assistance in support of the joint research effort on Brazilian plants between Stanford University, the Instituto de Quimica Agricola and the Universidade do Brazil was provided by the Rockefeller Foundation. Additional financial aid from the National Institutes of Health (grant No. 5 T1 GM-682) is gratefully acknowledged. We also thank Dr. D. DA ANDRADE LIMA and Mr. A. SARMENTO for assistance in collection and identification of the plant material.

[3] N. DASTOOR and H. SCHMID, Exper. *19*, 297 (1963).

[4] These two alkaloids have been encountered by us in other *Aspidosperma* species.

[5] B. GILBERT, J. AGUAYO BRISSOLESE, N. FINCH, W. I. TAYLOR, H. BUDZIKIEWICZ, J. M. WILSON, and C. DJERASSI, J. Amer. chem. Soc. *85*, 1523 (1963). See also footnote 5 in [3]. *A. discolor* was collected in the Dois Irmãos forest, Recife (Brazil).

[6] B. WITKOP and J. B. PATRICK, J. Amer. chem. Soc. *76*, 5603 (1954).

[7] Also isolated by us from *Aspidosperma eburneum* Fr. All.

[8] Measured by Dr. LOIS DURHAM in $CDCl_3$ solution (chemical shift reported in δ units with tetramethylsilane = 0.0 δ) using a Varian A-60 spectrometer.

[9] C. DJERASSI, A. A. P. G. ARCHER, T. GEORGE, B. GILBERT, J. N. SHOOLERY, and L. F. JOHNSON, Exper. *16*, 532 (1960). – C. DJERASSI, H. W. BREWER, H. BUDZIKIEWICZ, O. O. ORAZI, and R. A. CORRAL, J. Amer. chem. Soc. *84*, 3480 (1962).

[10] We are indebted to Drs. H. BUDZIKIEWICZ and J. M. WILSON for these measurements.

[11] K. BIEMANN, M. FRIEDMANN-SPITELLER, and G. SPITELLER, J. Amer. chem. Soc. *85*, 631 (1963).

[12] J. AGUAYO BRISSOLESE, C. DJERASSI, and B. GILBERT, Chem. and Ind. *1962*, 1949.

[13] Recipient of a fellowship from the International Cooperation Administration under a program administered by the U.S. National Academy of Sciences.