chlorides are obtained and with the bis-(trichloromethyl) compounds, diacid chlorides such as terephthalyl or isophthalyl chloride are obtained.

The reaction is carried out by heating a stoichiometric mixture of the reactants to 200–300°. A vigorous reaction occurs and the volatile metal chloride or oxychloride is distilled from the reaction mixture. Vacuum distillation of the residue gives an excellent yield of the acid chloride. For example, 313 g. (1 mole) or 1,3-bis-(trichloromethyl)-benzene and 82 g. of TiO_2 (1.02 mole) are added to a suitable reaction vessel equipped with an efficient stirrer and a fractionating column. The reactants are heated rapidly to about 270° with continuous agitation. During this heating period, there is a slight evolution of HCl gas. When the reaction vessel reaches 220°, $TiCl_4$ begins to distill indicating that the reaction has begun. The distillation of $TiCl_4$ becomes quite rapid when the temperature of the reaction mixture reaches 270°. Completion of the reaction is indicated by a marked rise in the temperature of the charge and a rise of the vapor temperature in the column At this point, the pressure in the system is reduced and isophthalyl chloride is distilled at a pressure of 15 mm. and a temperature of 145°. The distilled isophthalyl chloride solidifies to a crystalline solid melting in the range 39–40° (reported[1] m.p. 41°). The yield of $TiCl_4$, which on redistillation boiled at 135–136°, (reported[2] b.p. 135–136°) is 95% and the yield of isophthalyl chloride is 85%.

Acknowledgment.—The assistance of Dr. R. B. Hand of the Pigments Department of E. I. du Pont de Nemours & Co. is gratefully acknowledged.

[1] J. Schreder, *Ber.*, **7**, 708 (1874).

[2] Georg Brauer, "Handbuch der präparativen anorganischer Chemie," Ferdinand Enke, Stuttgart, Germany, 1954, pp. 894–897.

POLYCHEMICALS DEPARTMENT
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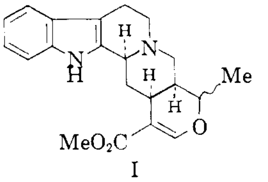
WILMINGTON, DELAWARE

RECEIVED MAY 28, 1958

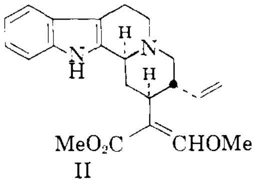
THE ABSOLUTE CONFIGURATION OF SOME INDOLE ALKALOIDS[1]

Sir:

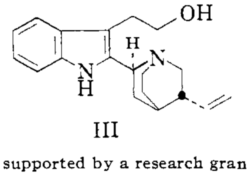
We wish to report the first chemical determination of the absolute configuration of non-cinchona indole alkaloids. It was accomplished by the conversion of ajmalicine (I), corynantheine (II) and cinchonamine (III) into common intermediates.



I

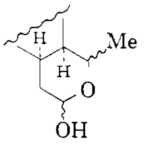


II

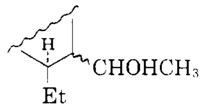


III

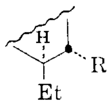
An alcoholic alkali treatment of ajmalicine[2] (I), followed by short heating with aqueous acid, led to the hemiacetal IV, m.p. 226–228° (Found for $C_{19}H_{24}O_2N_2$: C, 72.65; H, 7.85; N, 8.95), which on Wolff–Kishner reduction yielded the alcohol V, m.p. 200–201° (Found for $C_{19}H_{26}ON_2$: C, 76.62; H, 9.12; N, 9.82). Oppenauer oxidation of the latter gave the ketone VIa, m.p. 225–227° (found for $C_{19}H_{24}ON_2$: C, 76.98; H, 8.35), which could be converted by Wolff–Kishner reduction to dihydrocorynantheane[3] (VIb), identical in m.p. 189°, m.m.p. 188–189°, $[\alpha]_D$ −94° (pyridine) and infrared spectrum with an authentic specimen.



IV

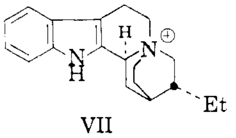


V



VIa, R = $COCH_3$
b, R = Et

Tosylation of dihydrocinchonamine[4] in pyridine solution led to the quaternary chloride VII, m.p. 320–321°. Silver tosylate treatment of the latter yielded the quaternary tosylate VII, identical in m.p. 313–315° (dec.), m.m.p. 315° (dec.), $[\alpha]_D$ −69.5 (90% methanol) and infrared spectrum with the compound obtained from the tosylation and dimethylformamide refluxing of dihydrocorynantheol.[5]



VII

In view of the recent conversion of dihydrocinchonidine into dihydrocinchonamine[6] and the known absolute configuration of the cinchona bases,[7] *the above data constitute the first chemical tie-up between the two great classes of alkaloids, the cinchona and yohimbé bases, they prove the absolute configuration of ajmalicine and corynantheine to be as indicated in I and II, respectively, and they point up again the unique C(15)-H α-orientation of the indole bases.*[8] The biogenetic significance of these results will be reported in the full publication.[9,10]

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE ERNEST WENKERT
AMES, IOWA N. V. BRINGI

RECEIVED MAY 21, 1958

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[1] This work was supported by a research grant from the National Institutes of Health, Public Health Service, Department of Health, Education and Welfare (M 1301).

[2] E. Wenkert and D. K. Roychaudhuri, THIS JOURNAL, **80**, 1613 (1958).

[3] M.-M. Janot, R. Goutarel and V. Prelog, *Helv. Chim. Acta*, **34**, 1207 (1951).

[4] R. Goutarel, M.-M. Janot, V. Prelog and W. I. Taylor, *ibid.*, **33**, 150 (1950).

[5] C. Vamvacas, W. v. Philipsborn, E. Schlittler, H. Schmid and P. Karrer, *ibid.*, **40**, 1793 (1957).

[6] E. Ochiai and M. Ishikawa, *Pharm. Bull.* (Japan), **5**, 498 (1957).

[7] V. Prelog and E. Zalán, *Helv. Chim. Acta*, **27**, 545 (1944).

[8] *Cf.* E. Wenkert, E. W. Robb and N. V. Bringi, THIS JOURNAL, **79**, 6570 (1957).

[9] A novel theory of alkaloid biogenesis, able to interpret the above and other yet puzzling structural features of alkaloids, was first enunciated by the senior author in lectures before a chemistry colloquium at Northwestern University and the Organic Discussion Group, New York Section, A.C.S., on February 14 and 17, 1958, respectively.

[10] The authors are most grateful to Drs. Hochstein, Lucas, Raymond-Hamet and Schlittler for generous gifts of alkaloids and to the Institute of Atomic Research, Ames, Iowa, and Dr. Kniseley for the infrared spectra.