acetone–methanol. The dimethyl derivative of Id separated as colorless, glistening prisms, mp 202°.

Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.5; H, 6.47; 3MeO, 21.3. Found: C, 71.7; H, 6.53; MeO, 21.3.

Salicylaldehyde–5,5-Dimethyl-1,3-cyclohexanedione Condensation Product (V or VI). A.—Condensation of salicylaldehyde (2.8 g) and II (3.5 g) in aqueous KOH as described by Chakravarti, *et al.*,[4] gave V or VI: mp 207–208°, λ_{max}^{EtOH} 268 mμ, λ_{max}^{NaOEt} 285 mμ.

B.—Salicylaldehyde (2.44 g) and II (5.6 g), warmed in acetic acid (30 ml) and water (40 ml) for 30 min, formed a crystalline product. Recrystallized from acetone–methanol, V or VI separated as colorless prisms, 5.8 g, mp and mmp 207–208°.

Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.4; H, 7.15. Found: C, 75.2; H, 7.13.

***o*-Vanillin–5,5-Dimethyl-1,3-cyclohexanedione Condensation Product.** A.—A mixture of *o*-vanillin (1.52 g) and II (2.80 g) condensed in acetic acid (10.0 ml) and water (20 ml) as described above gave a product (3.60 g, mp 226–228°) which crystallized from acetone–methanol as colorless needles: mp 228°, λ_{max}^{EtOH} 268 mμ, λ_{max}^{NaOEt} 284 mμ.

Anal. Calcd for $C_{24}H_{23}O_5$: C, 72.7; H, 7.12; 1MeO, 7.83. Found: C, 72.7; H, 7.17; MeO, 7.94.

B.—A solution of *o*-vanillin (1.52 g), II (1.40 g), and III (1.36 g), condensed similarly in hot aqueous acetic acid, gave only the above *o*-vanillin–II condensation product (1.86 g), mp and mmp 228°.

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Strictamine

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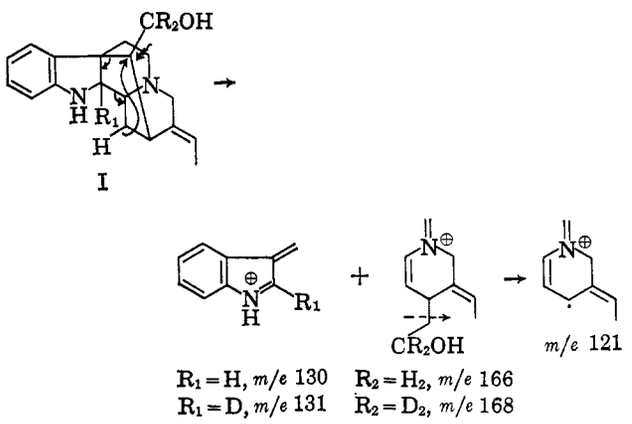
In continuation of earlier work[1,2] on the basic constituents of *Rhazya stricta* Decaisne we had isolated a new alkaloid, mp 110–112° (or 80–83°, hydrate), $[\alpha]^{24}D$ +103°, which was named strictamine. Later it was found that its mass spectrum was identical with that of vincamidine, an alkaloid isolated from *Vinca minor* L. and reported[3] to melt at 78–80° and to possess a composition $C_{20}H_{24}N_2O_3$.

This alkaloid (for which we prefer to retain the name strictamine, because of the similarity of the name vincamidine and vincamedine, an alkaloid of completely unrelated structure[4]) exhibits ultraviolet absorption of the indolenine type: λ_{max}^{EtOH} 213 mμ (log ε 4.37) and 262 mμ (log ε 3.80). Infrared bands at 1740,1630, and 1610 cm^{-1} (in $CHCl_3$) can be assigned to ester, C=N, and C=C groups. The nmr spectrum corroborated some of these conclusions: a complex series of signals between 7.1 and 7.8 ppm indicates four aromatic protons and a singlet at 3.78 ppm (3 H) a methoxy function, while an ethylidene side chain is indicated by the doublet (J = 7 cps, 3 H) at 1.56 ppm, further split (J = 1.5–2 cps) into a quartet (a phenomenon we observed also for other systems possessing an ethylidene side chain). The mass spectrum[5] of the alkaloid is fairly uncharacteristic: a strong molecular ion at m/e 322.1690 requiring the composition $C_{20}H_{22}N_2O_2$ (calcd 322.1681), and prominent peaks due to loss of H and CO_2CH_3 are its distinguishing (but uninformative) features. Most importantly, the spectrum revealed the correct elemental composition and that the two oxygens are present as a carbomethoxy group.

Reduction of strictamine with lithium aluminum hydride and deuteride furnished the first important information on the carbon skeleton of the alkaloid. The product of the hydride reaction showed a molecular ion peak at m/e 296 (322 − 26) corresponding to transformation of an ester to the alcohol and saturation of the C–N double bond. Ultraviolet absorption at 242 and 289 mμ (ε 6040 and 2750) indicated a dihydroindole system; infrared bands at 3610 and 3380 cm^{-1} identified hydroxyl and amino functions, respectively. The mass spectral fragementation pattern was distinguished by strong peaks m/e 166, 144, 143, 136, 130, 122, and 121, which in the case of the deuteride reduction product appeared at m/e 168, 145, 144, 136, 131, 123, 122, and 121. The peaks at m/e 130, 143, and 144 represent indole fragments and their shift by 1 mass unit in the trideuterio derivative indicates incorporation of one deuterium atom into the indole moiety as required by reduction of the indolenine to an indoline. The remaining peaks are best rationalized in terms of the ψ-akuammigine[6,7] type structure I (Scheme I).

SCHEME I



R_1 = H, m/e 130 R_2 = H_2, m/e 166
R_1 = D, m/e 131 R_2 = D_2, m/e 168

(1) H. K. Schnoes, A. L. Burlingame, and K. Biemann, *Tetrahedron Letters*, **No. 22**, 993 (1962).

(2) (a) A. Chatterjee, C. R. Ghosal, N. Adityachaudhury, and S. Ghosal, *Chem. Ind.* (London), 1034 (1961); (b) G. Ganguli, N. Adityachaudhury, V. P. Arya, and A. Chatterjee, *ibid.*, 1623 (1962); (c) M. Spiteller-Friedmann, R. Kaschnitz, G. Spiteller, A. Chatterjee, N. Adityachaudhury, and G. Ganguli, *Monatsh. Chem.*, **95**, 1228 (1964).

(3) (a) Z. Cekan, J. Trojanek, O. Strouf, and K. Kavkova, *Pharm. Acta Helv.*, **35**, 96 (1960); (b) J. Trojanek, O. Strouf, K. Kavkova, and Z. Cekan, *Collection Czech. Chem. Commun.*, **25**, 2045 (1960).

(4) M.-M. Janot, J. LeMen, J. Gosset, and J. Levy, *Bull. Soc. Chim. France*, 1079 (1962).

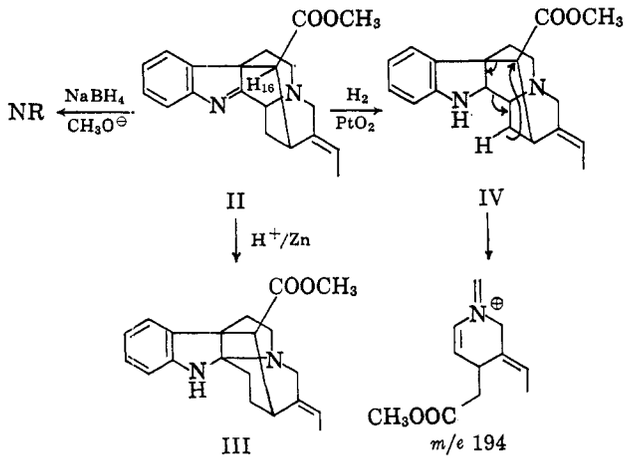
(5) All mass spectra were determined with a conventional, single focusing mass spectrometer (CEC 21-103C) with the exception of the spectrum of strictamine itself which was determined also with a double-focusing spectrometer (CEC 21-110).

(6) H. Budzikiewicz, C. Djerassi, and D. A. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. I, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 8.

(7) (a) A. Z. Britten, P. N. Edwards, J. A. Joule, G. F. Smith, and G. Spiteller, *Chem. Ind.* (London), 1120 (1963); (b) L. Olivier, J. Levy, J. LeMen, M.-M. Janot, C. Djerassi, H. Budzikiewicz, J. M. Wilson, and L. J. Durham, *Bull Soc. Chim. France*, 646 (1963).

Subsequent experiments (Scheme II) bore out these assumptions and permitted assignment of structure II for strictamine. Treatment of strictamine (II) with sodium borohydride in methanol–methoxide solution left the compound unchanged, providing a strong argument against the possibility of an akuammicine[6,8,9]–aspidospermatidine[9,10] skeleton, since indolenines of this skeleton are known[8b] to undergo ring opening to the corresponding indole under such conditions. The remarkable inertness of the C=N double bond points to much greater steric hindrance around this group in II, as compared with akummicine (VII).

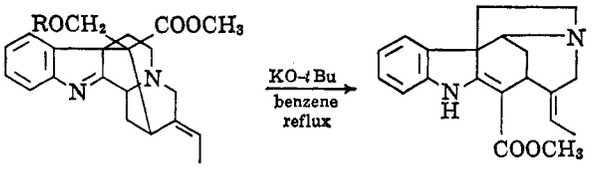
SCHEME II



Reduction of II with zinc in methanolic sulfuric acid resulted in the dihydro derivative III (mp 190–193°) which features a rearranged α-aminoindoline skeleton. The ultraviolet chromophore of this compound [λ_{max}^{EtOH} 244, 298 mμ (ϵ 7900, 3250)] suffers a hypsochromic shift in acid solution [$\lambda_{max}^{EtOH \cdot HCl}$ 235, 290 mμ (unchanged extinction)], a behavior characteristic for systems containing a Ph–N–C–N grouping.[11] Further proof that III possessed indeed a rearranged skeleton was furnished by the catalytic reduction of II to a quite different dihydroproduct, IV. The latter shows the ultraviolet bands of an indoline and its mass spectrum is quite similar to that of alcohol I [peaks at *m/e* 324 (M^+), 309 (M − 15), 251 (M − 73), 194 (166 + 28), 144, 143, 130, 122, and 121], and the interpretation of these ions is readily accommodated by the mechanism sketched above for strictaminol (I). Furthermore, reduction of IV with lithium aluminum hydride furnished the corresponding alcohol (mol wt = 296) whose mass spectrum was identical with that of I, whereas the alcohol obtained by hydride reduction of the α-aminoindoline system III showed a quite different fragmentation pattern.

It should be noted that recently the alkaloid akuammiline[12] was shown to possess structure V featuring the skeleton we propose for strictamine. Unfortunately, the published data do not permit a very meaningful comparison and correlation of our results. An important piece of evidence, cited by the French-American workers,[12] is the rearrangement (Scheme III) of deacetylakuammiline (VI) to (−)-akuammicine (VII) under treatment with strong base.

SCHEME III



V, R = Ac
VI, R = H

VII

We have been unable, as yet, to firmly duplicate this transformation with strictamine (II) itself. Reflux (1–2 hr) in benzene and potassium *t*-butoxide led to a mixture (representing about one-half of the original material) which consisted mainly of starting material and trace amounts of a compound with the same R_f value (tlc) as natural akuammicine.

It may be that equilibrium concentration of the anion derived from II by removal of the hydrogen at C-16 is very low, while during the deformylation of VI a full negative charge is developed at that position.

The representation of the stereochemistry of the carbomethoxy grouping as shown in II is based primarily upon the nmr spectrum of the compound which shows a doublet (J = 7 cps, 1 H) at 4.78 ppm which we assign to the hydrogen atom at C-16; the shielding of the indolenine nucleus would seem sufficient cause for the abnormal chemical shift.

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(9) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 8.

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(11) H. F. Hodson and G. F. Smith, *J. Chem. Soc.*, 1877 (1957).

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The Geometry of Bisamide–Glyoxal Adducts

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The formation of vicinal dihydroxyimidazolidines and -piperazines by the addition of alkylenebisamides (I) to glyoxal has been reported,[3] but the geometry of these adducts was not established. In a similar system, N,N′-dimethylurea was shown[4] to add nonstereospecifically to glyoxal to form equimolar amounts of *cis*- and *trans*-4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone, but, under the conditions of this reaction, the less stable *cis* isomer was converted to the *trans* configuration. Rates for the formation of the *cis*- and *trans*-imidazolidones and for the conversion of the pure isomers into equilibrium mixtures at various pH values

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(2) The mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

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