current machine using 2 *M* acetate buffer *p*H 5.5 and benzene. The known triester, neogermitrine,[3] was obtained by crystallizing the material recovered from tubes 6–10 from acetone–water.

The hypotensive activity[4,5] of germanitrine, germanidine, and germanitrine was found to be 0.12 μg. [0.11–0.14], 0.77 μg. [0.46–2.3], and 0.41 μg. [0.36–0.49], respectively.

(3) J. Fried, P. Nimerof and N. H. Coy, THIS JOURNAL, **74**, 3041 (1952).

(4) Edward D. Swiss and George L. Maison, Federation Proceedings, Vol. II, No. 1, March, 1952.

(5) Expressed as micrograms per kilogram of anesthetized dog per minute required for a ten-minute intravenous infusion to lower the mean arterial blood pressure 30% when administered according to the method of G. L. Maison and J. W. Stutzman. The bracketed numbers express the 95% confidence limits.

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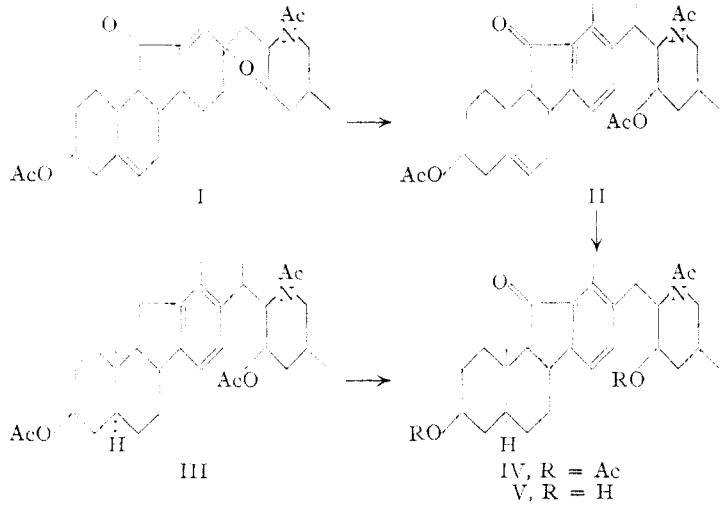
THE STRUCTURAL CORRELATION OF JERVINE AND VERATRAMINE

Sir:

As reported in preliminary communications from this Laboratory,[1] O,N-diacetyljervine (I) on acetolysis with acetic anhydride–acetic acid containing a catalytic amount of sulfuric acid gave rise to a triacetate, $C_{33}H_{43}O_6N$, (m.p. 239–240°, $[\alpha]^{24}D$ −29°[2]), which on the basis of its ultraviolet and infrared characteristics (λ_{max}^{alc} 251 mμ, log ε 4.08; 300 mμ, log ε 3.30; IR: intense bands at 5.75, 5.88 and 6.09 μ, indicative, respectively, of O-acetyl, ketonic carbonyl and N-acetyl) and other evidence was assigned the indanone structure II. On the other hand, there has been obtained by chromic acid oxidation of triacetyldihydroveratramine ($C_{33}H_{47}O_6N$, now assigned structure III[3]) a compound $C_{33}H_{45}O_6N$ (m.p. 241–245°, $[\alpha]^{21}D$ +59°) which likewise exhibited the above spectral properties, and the new keto group of which, like that of II, was unreactive to ketone reagents.[3] We have now reduced II catalytically with palladium–calcium carbonate in ethanol to its 5,6-dihydro derivative IV,[4] and found the latter identical in all respects, inclusive of the infrared characteristics over the whole measurable range, with the oxidation product from triacetyldihydroveratramine (m.p. 242–245°, $[\alpha]^{23}D$ +57.5°; *Anal.* Calcd. for $C_{33}H_{45}O_6N$: C, 71.83; H, 8.22. Found: C, 71.94; H, 8.26). The respective N-acetates (V), prepared by hydrolysis with methanolic potassium hydroxide, were likewise identical (m.p. 264–266.5°, $[\alpha]^{23.5}D$ +71.7°, +68.8°; *Anal.* Calcd. for $C_{29}H_{41}O_4N$: C, 74.46; H, 8.84. Found: C, 74.57; H, 8.64). The vicinal effect of the indanone grouping on the contribution to molecular rotation of C_5 is evident in the abnormally high $\Delta[M]_D$ for the saturation of the double bond (+484° for II → IV, +495° for O-desacetylated II → V) as compared with the values +399° for triacetylveratramine → triacetyldihydroveratramine, +404° for N-acetylveratramine → N-acetyldihydroveratramine, and +243° for normal Δ^5-stenyl acetates.[5]

The significance of this result lies in the fact that it renders extremely remote the possibility of a rearrangement of the carbon skeleton in the formation of the acetolysis product II from diacetyljervine, since (1) the presence in veratramine of a preformed benzenoid ring has been assured not only by ultraviolet spectrophotometry[6] but also by chemical means,[3] (2) the conversion of triacetyldihydroveratramine to IV obviously cannot involve a change in the skeleton, and (3) it is reasonable on biogenetic grounds to accord also to jervine the abnormal ring structure which has now been shown to pre-exist in veratramine.



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(1) J. Fried, O. Wiutersteiner, A. Klingsberg, M. Moore and B. M. Iselin, THIS JOURNAL, **73**, 2970 (1951); O. Wintersteiner and M. Moore, Abstracts, XIIth Internat. Congress of Chemistry, New York, Sept. 10–13, 1951, p. 292.

(2) All melting points corrected; all rotations in chloroform.

(3) Ch. Tamm and O. Wintersteiner, THIS JOURNAL, **74**, 3842 (1952).

(4) The catalytic hydrogenation of II presented unexpected difficulties in that it did not proceed smoothly under any of the conditions tried, and invariably gave rise to mixtures. Thus, with PtO_2 in acetic acid the indanone carbonyl was partly reduced, and the product obtained by reoxidation with chromic acid, (m.p. 214–217°, $[\alpha]D$ +57.5°) was obviously not pure IV. On the other haud, hydrogen uptake in the reaction catalyzed with palladium was very sluggish, and the crude product was contaminated with less dextrorotatory impurities (apparently for the most part unchanged starting material), which could not always be completely removed by recrystallization or eliminated by rehydrogenation, so that the yield of pure dihydro product was always low.

(5) D. H. R. Barton, *J. Chem. Soc.*, 512 (1946).

(6) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **160**, 555 (1945).

(7) This paper is part of the dissertation to be presented by Norman Hosansky in partial fulfillment of the requirements for the Ph.D. degree in the Graduate School of Rutgers University.