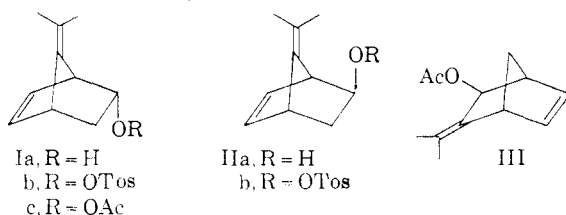
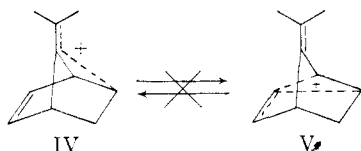


conjecture.¹ In particular it is not known how many types of non-classical ions might occur, *i.e.*, homoallylic, bi- and tricyclobutonium, *etc.*, nor what role classical ions might play in their reactions. We wish to report results which demonstrate, in a striking manner, the absence of classical cations in some homoallylic solvolyses, and which also place some important restrictions on the type of bonding involved in these cations.

We have reported recently the synthesis of *endo*-7-isopropylidenedehydronorborneol (Ia).² Base-catalyzed equilibration of Ia and gas chromatographic separation of the resultant mixture of dienols gave the *exo*-alcohol (IIa). Acetolysis of both *endo*- and *exo*-tosylates (Ib and IIb) proceeded readily at 30° ($k_{Ib} = 7 \times 10^{-6}$ sec.⁻¹, $k_{IIb} = 6 \times 10^{-5}$ sec.⁻¹) showing that both reactions are strongly anchimerically accelerated.^{3,4} Despite the fact that both solvolyses led to positive charge at



carbon 2, the reactions are completely stereospecific, *endo*-tosylate (Ib) leading exclusively to *endo*-acetate (Ic),⁵ *exo*-tosylate giving only rearranged acetate (III) as product. Clearly, the cationic center at carbon 2 does not have classical character, since otherwise some mixing of products would have been observed. More importantly, equilibrium between the two homoallylic ions (IV and V) is also ruled out. Similar results were obtained



in the solvolysis of the 5,6 dihydro compounds, *exo*- and *endo*-7-isopropylidene-norbornyltosylates,² where the same stereospecificity in solvolysis was observed, the *endo* tosylate ($k = 4 \times 10^{-5}$ sec.⁻¹) giving only *endo* acetate and the *exo* ($k = 2 \times 10^{-4}$ sec.⁻¹) giving only dihydro III.

The absence of common intermediates in the two solvolyses demands an activation energy for the interconversion of the homoallylic ions, and rules out a symmetrical structure in which both sides of the unsaturated center at C₂ are stabilized by interaction with the double bonds. It seems pos-

(1) For recent, comprehensive discussions of the problem see S. Winstein and E. M. Kosower, *THIS JOURNAL*, **81**, 4399 (1959), and R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(2) C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960).

(3) S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(4) Interaction between the 2 and 7 position of the type displayed in IV has been sought previously without success. See J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957), and E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

(5) As little as 1% of III could have been detected readily by gas phase chromatography.

sible that equilibration of the cations may become detectable in solvents in which they have longer lifetimes, and that cations from different sources (*e.g.*, from the amine-nitrous acid reaction) may react differently. Experiments designed to test these points are in progress.

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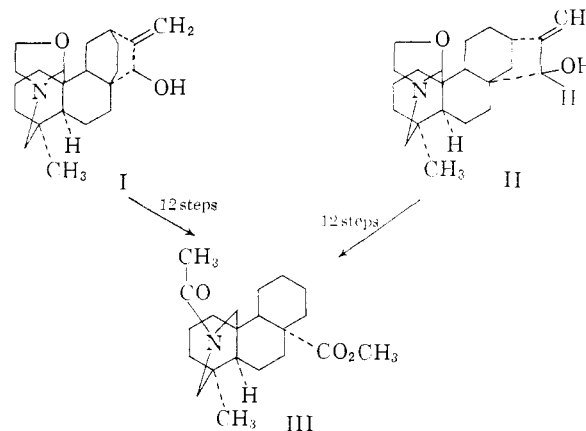
C. H. DEPUY
I. A. OGAWA
J. C. MCDANIELS

RECEIVED FEBRUARY 27, 1960

THE CORRELATION OF THE ATISINE AND VEATCHINE SERIES OF DITERPENE ALKALOIDS¹

Sir:

The presently accepted structures² of atisine (I)³⁻⁶ [*Aconitum heterophyllum*] and veatchine (II)^{3,7} [*Garrya veatchii*] differ only in the terminus of the hydroxyl-bearing ring. Because of the failure to interrelate the two series, the possibility has been suggested recently that the allylic alcohol group in atisine may be on the *cis*- (rather than the *trans*-) branch (with respect to nitrogen) of the 2,2,2-bicyclooctane system.⁸ As subsequent evidence from this⁶ and another laboratory⁵ was not compatible with this proposal, the direct correlation of these two important classes of diterpene alkaloids became imperative. This paper reports the successful correlation of atisine and veatchine *via* the degradation product III and provides the first unequivocal evidence for the common stereochemistry of their carbon skeletons.



Treatment of IV,⁹ available from atisine hydrochloride in six steps,¹⁰ with sodium metaperiodate

(1) This investigation was supported in part by Grants RG 5807 and RG 5807 (CI) from the National Institutes of Health, United States Public Health Service.

(2) The indicated structures assume the *trans-anti* fusion of rings A and B which is common to most diterpenes.

(3) K. Wiesner, *et al.*, *Chemistry and Industry*, 132, (1954); *Experientia* **11**, 255 (1955).

(4) S. W. Pelletier and W. A. Jacobs, *THIS JOURNAL*, **76**, 4496 (1954).

(5) D. Dvornik and O. E. Edwards, *Chemistry and Industry*, 633 (1958).

(6) S. W. Pelletier, *ibid.*, 1118 (1958).

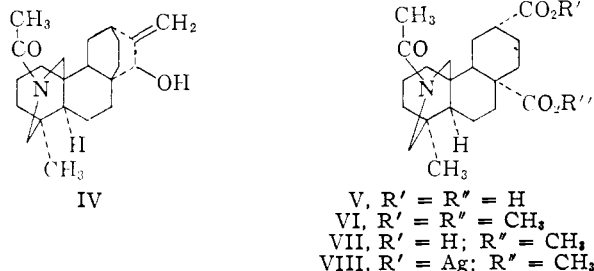
(7) K. Wiesner, *et al.*, *THIS JOURNAL*, **76**, 6068 (1954).

(8) K. Wiesner and Z. Valenta, *Progress in the Chemistry of Organic Natural Products*, **XVI**, 52 (1958).

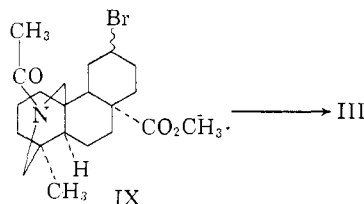
(9) S. W. Pelletier and W. A. Jacobs, *THIS JOURNAL*, **78**, 4144 (1956).

(10) The intermediate azomethine acetate was prepared by the method of Dvornik and Edwards, *Canad. J. Chem.*, **35**, 860 (1957).

and potassium permanganate¹¹ gave directly the dicarboxylic acid V,¹² m.p. 285–289°; $[\alpha]^{29D} + 11.0^\circ$; ν^{Nujol} (CO₂H) 1727, 1692 cm.⁻¹; (N-Ac) 1610 cm.⁻¹. Conversion of V to the dimethyl ester (VI), m.p. 196–198.5°; $[\alpha]^{29D} + 13^\circ$; ν^{Nujol} (CO₂Me) 1724 cm.⁻¹; (N-Ac) 1639 cm.⁻¹ and selective saponification afforded the monoester-acid, VII, m.p. 248–250°; $[\alpha]^{29D} + 15^\circ$; ν^{Nujol} (CO₂H, CO₂Me) 1712 cm.⁻¹; (N-Ac) 1603 cm.⁻¹. Rearrangement of the silver salt (VIII) with bro-



mine in carbon tetrachloride gave IX as an amorphous resin; ν^{film} (CO₂Me) 1730 cm.⁻¹; (N-Ac) 1647 cm.⁻¹. Reductive debromination of IX with zinc in acetic acid and extensive chromatography, gave III, m.p. 156–157°; $[\alpha]^{27D} - 18.9^\circ$.



Application of a parallel series of reactions to veatchine gave these compounds: veatchine diacetate chloride (X), m.p. 254–257°; ν^{Nujol} (OAc) 1739 cm.⁻¹, 1238 cm.⁻¹; ($>C=N<$) 1669 cm.⁻¹; azomethine acetate (XI), m.p. 122.5–124°; $[\alpha]^{26D} - 87^\circ$; γ^{Nujol} (OAc) 1730, 1233 cm.⁻¹; ($>C=N-$) 1647 cm.⁻¹; azomethine alcohol (XII)¹³, m.p. 186–188°; $[\alpha]^{29D} - 109^\circ$; ν^{Nujol} (OH) 3300 cm.⁻¹; ($>C=N-$) 1656 cm.⁻¹; ($>C=CH_2$) 897 cm.⁻¹; XIII,¹³ m.p. 165.5–167.5°; $[\alpha]^{27D} - 99^\circ$; XIV,⁷ resin, (OH) 3571 cm.⁻¹; (N-Ac) 1653 cm.⁻¹; ($>C=CH_2$) 905 cm.⁻¹; dicarboxylic acid (XV), 254–256°; $[\alpha]^{27D} + 20^\circ$ (EtOH); ν^{Nujol} (CO₂H) 1757 cm.⁻¹; (N-Ac) 1650 cm.⁻¹; methyl ester XVI, m.p. 182–185°; $[\alpha]^{28D} + 17.5^\circ$; ν^{Nujol} (CO₂H, CO₂Me) 1730, 1709 cm.⁻¹, (N-Ac) 1597 cm.⁻¹. Reduction of bromide XVII (resin) gave a product with the same melting point (155–156.5°, no depression), rotation (-17°), and infrared spectrum in both Nujol and chloroform as that of III obtained from atisine.

Since garryfoline^{14,15} (*Garrya laurifolia*) has been shown to be 19-epiveatchine,^{15,16} this cor-

(11) R. U. Lemieux and E. von Rudloff, *Canad. J. Chem.*, **33**, 1701, 1710 (1955); E. von Rudloff, *ibid.*, **33**, 1714 (1955).

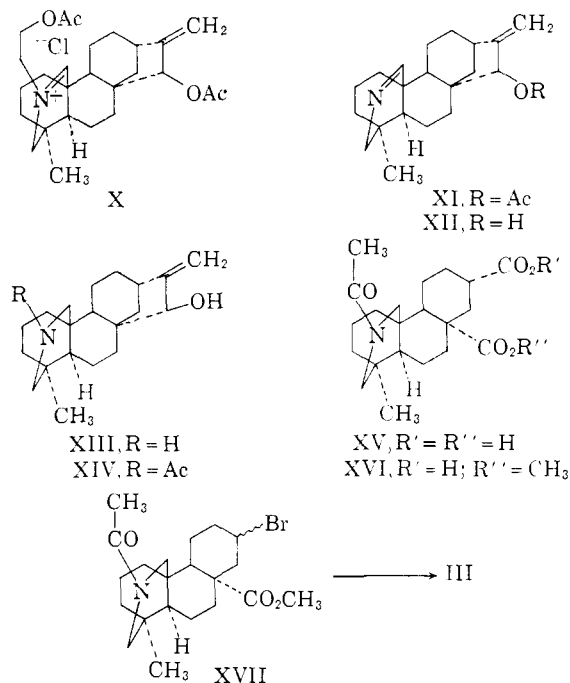
(12) Satisfactory analytical data were obtained for all new compounds. Rotations are in chloroform unless otherwise specified.

(13) Cf. M. F. Bartlett, W. I. Taylor and K. Wiesner, *Chemistry and Industry*, 173 (1953); K. Wiesner, *et al.*, *Ber.*, **86**, 800 (1953).

(14) C. Djerassi, *et al.*, *THIS JOURNAL*, **76**, 5889 (1954).

(15) C. Djerassi, *et al.*, *ibid.*, **77**, 4801 (1955); **77**, 6633 (1955).

(16) Reference 8, page 41.



relation interrelates the three series of biogenetically important diterpene alkaloids, atisine, veatchine and garryfoline.

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RECEIVED MARCH 2, 1960

THE TRANSITION OF CESIUM CHLORIDE

Sir:

At 472° cesium chloride has a well-known transition point, where the primitive cubic cell transforms to a face-centered cubic cell. A recent paper by Wood, Sweeney and Derbes establishes that rubidium chloride goes in solid solution in the high temperature face-centered cubic modification, but not in the low temperature modification.¹ Moreover rubidium chloride is found to depress the transition point substantially. Experimental values for this depression are reported.¹

It has been shown recently by Förland and Krogh-Moe that systems with this kind of transition point depression readily lend themselves to a thermodynamic interpretation.² Assuming that the rubidium atoms are statistically distributed over all cation positions, we have

$$-R \ln N_{Cs} = \Delta H_{tr} \left(\frac{1}{T} - \frac{1}{T_{tr}} \right)$$

Here N_{Cs} is the mole fraction of cesium chloride in the solid solution, ΔH_{tr} the heat of transition of cesium chloride and $T_{tr} = 745^\circ K$, and T the transition temperatures of pure cesium chloride and the solid solution, respectively. A plot of the reciprocal of the transition temperature against the logarithm of the mole fraction of cesium chloride shows that the experimental points obtained

(1) L. J. Wood, C. Sweeney and M. T. Derbes, *THIS JOURNAL*, **81**, 6148 (1959).

(2) T. Förland and J. Krogh-Moe, *Acta Chem. Scand.*, **13**, 1051 (1959).