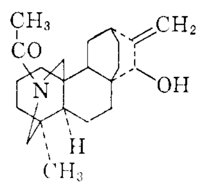
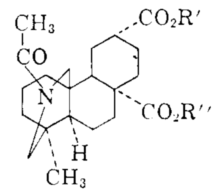
and potassium permanganate[11] gave directly the dicarboxylic acid V,[12] m.p. 285–289°; $[\alpha]^{29}D$ $+11.0°$; ν^{Nujol} (CO_2H) 1727, 1692 cm.$^{-1}$; (N–Ac) 1610 cm.$^{-1}$. Conversion of V to the dimethyl ester (VI), m.p. 196–198.5°; $[\alpha]^{29}D+13°$; ν^{Nujol} (CO_2Me) 1724 cm.$^{-1}$; (N–Ac) 1639 cm.$^{-1}$ and selective saponification afforded the monoester-acid, VII, m.p. 248–250°; $[\alpha]^{29}D+15°$; ν^{Nujol} (CO_2H,CO_2Me) 1712 cm.$^{-1}$; (N–Ac) 1603 cm.$^{-1}$. Rearrangement of the silver salt (VIII) with bro-

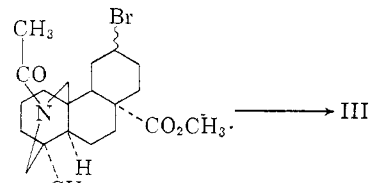


IV



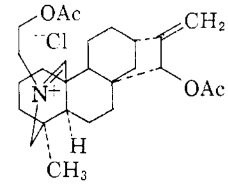
V, R′ = R″ = H
VI, R′ = R″ = CH_3
VII, R′ = H; R″ = CH_3
VIII, R′ = Ag; R″ = CH_3

mine in carbon tetrachloride gave IX as an amorphous resin; ν^{film} (CO_2Me) 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°; $[\alpha]^{27}D-18.9°$.

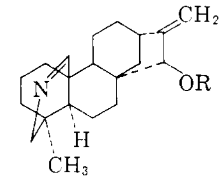


IX

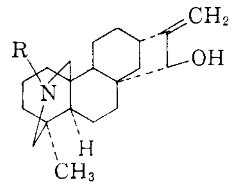
Application of a parallel series of reactions to veatchine gave these compounds: veatchine diacetate chloride (X), m.p. 254–257°; ν^{Nujol} (OAc) 1739 cm.$^{-1}$, 1238 cm.$^{-1}$; ($>C{=}\overset{+}{N}<$) 1669 cm.$^{-1}$; azomethine acetate (XI), m.p. 122.5–124°; $[\alpha]^{26}D$ $-87°$; γ^{Nujol} (OAc) 1730, 1233 cm.$^{-1}$; ($>C{=}N{-}$) 1647 cm.$^{-1}$; azomethine alcohol (XII)[13], m.p. 186–188°; $[\alpha]^{29}D-109°$; 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°; $[\alpha]^{27}D-99°$; XIV,[7] resin, (OH) 3571 cm.$^{-1}$; (N-Ac) 1653 cm.$^{-1}$; ($>C{=}CH_2$) 905 cm^{-1}; dicarboxylic acid (XV), 254–256°, $[\alpha]^{27}D+20°$ (EtOH); ν^{Nujol} (CO_2H) 1757 cm.$^{-1}$; (N-Ac) 1650 cm.$^{-1}$; methyl ester XVI, m.p. 182–185°; $[\alpha]^{28}D+17.5°$; ν^{Nujol} (CO_2H, CO_2-Me) 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.



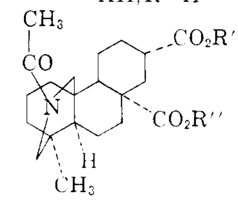
X



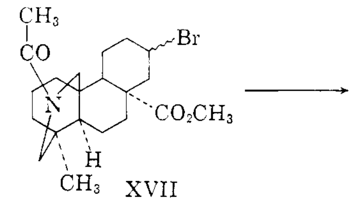
XI, R = Ac
XII, R = H



XIII, R = H
XIV, R = Ac



XV, R′ = R″ = H
XVI, R′ = H; R″ = CH_3



XVII

Since garryfoline[14,15] (*Garrya laurifolia*) has been shown to be 19-epiveatchine,[15,16] this correlation interrelates the three series of biogenetically important diterpene alkaloids, atisine, veatchine and garryfoline.

(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.

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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°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).

by Wood, Sweeney and Derbes are in good agreement with the above equation when the heat of transition is taken to be 1.55 kcal./mole. This value may be compared with data from the literature for the heat of transition of cesium chloride. Wagner and Lippert estimated the heat of transition to be 1.8 kcal./mole from lattice energies.[3] Cooling curves by Zemczuzny and Rambach give an estimated heat of transition equal to 1.2 kcal./mole.[4] It therefore seems reasonable to believe that the correct value for the heat of transition is close to 1.5 kcal./mole, with the cations statistically distributed over all cation positions in the solid solution.

NOTE ADDED IN PROOF.—After this paper was written, a calorimetric measurement of ΔH_{tr} equal to 0.581 kcal./mole has been published.[5] If the heat content equations given in that work are considered, one obtains $\Delta H_{tr} = 0.76$ kcal./mole, one half the value suggested in this paper. A pairing of the rubidium atoms in the solid solution thus seems to be indicated, if there is no solid solution of rubidium chloride in low cesium chloride.

(3) S. Zemczuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 403 (1910).
(4) G. Wagner and L. Lippert, *Z. physik. Chem.*, **B31**, 263 (1936).
(5) C. E. Kaylor, G. E. Walden and D. F. Smith, *J. Phys. Chem.*, **64**, 276 (1960).

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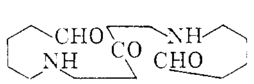
RECEIVED FEBRUARY 22, 1960

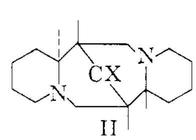
THE BIOGENETIC-TYPE SYNTHESIS OF *dl*-SPARTEINE

Sir:

An integral step in the proposed[1] biosynthesis of the alkaloid sparteine (II, X = H_2) is the formation of 8-ketosparteine (II, X = O) by cyclization of the diaminoketodialdehyde I, presumed to arise in nature by decarboxylation, deamination



I



II

and coupling of γ-keto-α,α'-diaminopimelic acid and two molecules of lysine.[2] In a laboratory synthesis designed to proceed through I, or a similar structure, the tetracyclic system of sparteine with the correct orientation of the four asymmetric centers, can be constructed in two simple operations starting from acetone, formaldehyde and piperidine.[3]

β,β'-Di-(N-piperidino)-diethyl ketone (III)[4] was prepared from the aforementioned starting materials by a Mannich reaction carried out in acetic acid.[5] Mercuric acetate dehydrogenation[6] of III to give I[7] (or the monocyclization product) is followed by stereoselective ring closure *in situ* to II (X = O), m.p. 71–72.5° (Found: C, 72.55; H, 9.79; N, 11.08). The constitution of this intermediate was proved by Wolff–Kishner reduction to *dl*-sparteine,[8] which was identified by comparison, through melting points of salts, with authentic *dl*-sparteine,[9] as well as by infrared spectral identity (chloroform solution) with *l*-sparteine free base.[10]

Biogenetic and mechanistic facets of this synthesis will be examined in a full publication.

(1) R. Robinson, "The Structural Relations of Natural Products," Oxford University Press, London, 1955, p. 75.
(2) The recent discovery (personal communication from Prof. M. Carmack, University of Indiana) of 8-oxygenated tetracyclic lupin alkaloids lends further credence to this biogenetic scheme.
(3) A reported physiological-type synthesis of 8-ketosparteine involving Δ^1-piperideine, formaldehyde and acetonedicarboxylic acid (E. Anet, G. K. Hughes and E. Ritchie, *Nature*, **165**, 35 (1950), has been discredited (C. Schöpf, G. Benz, F. Braun, H. Hinkel and R. Rokohl, *Angew. Chem.*, **65**, 161 (1953)). For utilization of the abnormal spiro compound actually produced, see abstract of lecture, C. Schöpf, GDCh-Ortsverband Frankfurt/M., *ibid.*, **69**, 69 (1957).
(4) First prepared by another method by S. M. McElvain and W. B. Thomas, THIS JOURNAL, **56**, 1806 (1934).
(5) See F. F. Blicke and F. J. McCarty, *J. Org. Chem.*, **24**, 1376 (1959).
(6) N. J. Leonard and F. P. Hauck, Jr., THIS JOURNAL, **79**, 5279 (1957).
(7) The aminoaldehyde, alkanolamine, enamine and iminium salt are regarded as equivalent structures for the present purpose.
(8) For prior syntheses of sparteine, see the references cited by N. J. Leonard in Manske and Holmes, "The Alkaloids," Vol. III, Academic Press, Inc., New York, N. Y., p. 163–166.
(9) N. J. Leonard and R. E. Beyler, THIS JOURNAL, **71**, 757 (1949); **72**, 1316 (1950).
(10) This investigation was supported by RG-3892, National Institutes of Health.

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RECEIVED MARCH 30, 1960

CHLORODIFLUOROAMINE[1]

Sir:

The anticipated behavior of difluoroamine,[2,3] HNF_2, as a Lewis base prompted an investigation of its interaction with boron trichloride. Equimolar quantities of the two gases condensed *in vacuo* at −130° to form a white solid, stable at −80°. Warming toward room temperature resulted in decomposition to hydrogen chloride, chlorine, a non-volatile solid, and the new compound chlorodifluoroamine, NF_2Cl. Purification was accomplished by vacuum fractionation through traps maintained at −142° and −196°. The −196° fraction was passed through an Ascarite tower to remove hydrogen chloride and refractionated. The yield of chlorodifluoroamine after purification was 50%.

Chlorodifluoroamine is a colorless, air-stable gas. Its vapor pressure curve is given by the equation

$$\log P_{mm.} = -(950/T) + 7.478$$

The extrapolated boiling point is −67°. The heat of vaporization calculated from the above equation is 4350 cal./mole with a Trouton constant of 21.0. The melting point of chlorodifluoroamine was not obtained but lies between −183° and −196°. A molecular weight determination by the vapor density method gave a value of 87.8 (theoretical 87.5).

The mass spectrum of chlorodifluoroamine, obtained on a Consolidated Electrodynamics Model 620 Mass Spectrometer, is given in Table I. Peaks attributed to Cl_2^+ may result from partial disproportionation of the sample to Cl_2 and N_2F_4 in the metal inlet system of the mass spectrometer.

(1) This work was conducted under Army Ordnance Contract, DA-01-021-ORD 5135.
(2) A. Kennedy and C. B. Colburn, THIS JOURNAL, **81**, 2906 (1959).
(3) E. A. Lawton and J. Q. Weber, *ibid.*, **81**, 4755 (1959).