THE REMAINING STEREOISOMERS OF THE SPARTEINE GROUP

Sir:

We have found that the alkaloid *l*-spartalupine, $C_{15}H_{26}N_2$, which we have isolated for the first time from specimens of *Lupinus sericeus* Pursh collected in Utah, is one of the enantiomorphs of the third and remaining racemic pair stereoisomeric with *dl*-sparteine and *dl*-α-isosparteine. Our structure proof consists of epimerization to *d*-sparteine and to *d*-α-isosparteine and the direct comparison of the natural base with *dl*-spartalupine, which we have synthesized along with its diastereoisomers. The only other naturally occurring alkaloid thus far isolated having the same stereochemical configuration as spartalupine is lupanoline, $C_{15}H_{24}N_2O_2$, a hydroxy-lactam.[1]

Isolation.—Alcoholic extraction of the dried plant yielded 1–2% of total alkaloid, which gave directly upon distillation mostly *l-spartalupine base*, b.p. 110° (0.03 mm.), m.p. 32.2–32.4° (calcd. for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18; N, 11.96. Found: C, 76.99; H, 11.18; N, 12.02; $[\alpha]^{25}D$ $-15.4°$ (abs. alc.)) *Monoperchlorate*, m.p. 211.5–212° (calcd. for $C_{15}H_{26}N_2 \cdot HClO_4$: C, 53.80; H, 8.13; N, 8.37; Cl, 10.59. Found: C, 53.82; H, 8.20; N, 8.06; Cl, 10.53). *Dipicrate*, m.p. 133–133.5° (calcd. for $C_{15}H_{26}N_2 \cdot 2C_6H_2(NO_2)_3OH$: C, 46.82; H, 4.66; N, 16.18. Found: C, 47.03; H, 4.43; N, 16.40). The infrared spectrum of the base was very similar to that of the base obtained from lupanoline with $LiAlH_4$.[2]

Structure Proof.—*l*-Spartalupine was treated with mercuric acetate by the method of Winterfeld and Rauch.[3] Under mild conditions, a dehydro base was formed which was hydrogenated over platinum to *d*-sparteine, $[\alpha]^{28}D$ $+19.5°$ (ethanol). Under more drastic conditions, a didehydro base was obtained which was rehydrogenated to *d*-α-isosparteine monohydrate, m.p. 110–115°, $[\alpha]^{28}D$ $+48.4°$ (methanol). The infrared spectra of the products were identical with those of their respective authentic *l*-isomers.

Synthesis.—The synthesis of Šorm and Keil[4] was repeated, except for reduction of the dioxo compound with $LiAlH_4$. Three dioxo compounds were isolated: A, m.p. 173–173.5° (calcd. for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.83; H, 8.59; N, 10.63). Reduction of A yielded *dl*-spartalupine (and not *dl*-α-isosparteine[4]). The infrared spectra of the natural *l*- and synthetic *dl* bases were superimposable. *dl*-Spartalupine dipicrate, m.p. 220.5–221° dec. (calcd. for $C_{15}H_{26}N_2 \cdot 2C_6H_2(NO_2)_3OH$: C, 46.82; H, 4.66; N, 16.18. Found: C, 46.64; H, 4.64; N, 16.19). The dioxo compound B, m.p. 132–133.5°, reduced to *dl*-sparteine, and a third dioxo compound C, isolated as a monohydrate, m.p. 159–160°, reduced to *dl*-α-isosparteine monohydrate. The two latter bases were identified by direct comparison of the bases with their optically active forms and with the picrates of authentic synthetic *dl*-bases,[5] using infrared spectra and melting points where applicable.

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[1] L. Marion, N. J. Leonard, and B. P. Moore, *Can. J. Chem.*, **31**, 181 (1953); *cf.* J. F. Couch, THIS JOURNAL, **62**, 554 (1940).

[2] B. P. Moore and L. Marion, *Can. J. Chem.*, **31**, 187 (1953).

[3] K. Winterfeld and C. Rauch, *Arch. Pharm.*, **272**, 273 (1934).

[4] F. Šorm and B. Keil, *Coll. Czech. Chem. Comm.*, **13**, 544 (1948).

[5] Kindly supplied by Professor N. J. Leonard; *cf.* N. J. Leonard and R. E. Beyler, THIS JOURNAL, **72**, 1316 (1950).

CHEMISTRY DEPARTMENT
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA
MARVIN CARMACK
BRYCE DOUGLAS
ERIC W. MARTIN
HANNA SUSS

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MERCAPTAN CATALYSIS IN THERMONEUTRAL FREE RADICAL EXCHANGE: $R\cdot + R^*H \rightleftharpoons RH + R^*\cdot$

Sir:

It has been proposed that when a free radical is generated in a solvent from which it may be thought of as being derived by removal of one atom, the radical will be continually regenerated in type by exchange with the solvent.[1] However, the formation of acetate radical $CH_3COO\cdot$ in solvent $C^{14}H_3COOH$ by decomposition of acetyl peroxide led to CH_4 containing about 1% of the radioactivity of the solvent,[2] indicating that the postulated exchange reaction

$$CH_3COO\cdot + C^{14}H_3COOH \rightleftharpoons CH_3COOH + C^{14}H_3COO\cdot$$

was slow compared to loss of CO_2 by the unstable acetate radical.

We have formed a more stable radical, $(C_6H_5)_2CH\cdot$[3] (I), in $(C_6H_5)_2C^{14}H_2$ (II) by decomposition of $(C_6H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2$[3] in 0.017 *m* solution in 3:1 $(C_6H_5)C^{14}H_2:C_6H_6$ at 64° under CO_2. 1,1,2,2-Tetraphenylethane (III) was obtained in 95% yield, and its radioactivity was only 1.1% of that of the solvent. The exchange was far

$$(C_6H_5)_2CH\cdot + (C_6H_5)C^{14}H_2 \rightleftharpoons (C_6H_5)CH_2 + (C_6H_5)C^{14}H\cdot \quad (1)$$

slower than the dimerization reaction

$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \quad (2)$$

However, in the presence of 0.035 *m* C_6H_5SH (IV) the yield of nitrogen remained nearly quantitative, and the yield of III fell to 59%, but its radioactivity was 17% of that of the solvent, the exchange reaction (1) having effectively occurred to this extent in the presence of the mercaptan.

This may be accounted for by a sequence of two reactions[4,5] of lower activation energy than reaction (1) which tend to equilibrate diphenylmethyl, diphenylmethane, thiophenol and phenylthio radical.

$$(C_6H_5)_2CH\cdot + C_6H_5SH \rightleftharpoons (C_6H_5)_2CH_2 + C_6H_5S\cdot \quad (3a)$$

$$C_6H_5S\cdot + (C_6H_5)_2C^{14}H_2 \rightleftharpoons C_6H_5SH + (C_6H_5)_2C^{14}CH\cdot \quad (3b)$$

Reaction (3a) leads to diminished yield of III since

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[1] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., second edition, 1948, p. 19, 139, 231.

[2] A. J. Fry, B. M. Tolbert and M. Calvin, *Trans. Faraday Soc.*, **49**, 1444 (1953).

[3] S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457 (1955).

[4] A. F. Bickel and E. C. Kooyman, *Nature*, **170**, 211 (1952).

[5] K. E. J. Barrett and W. A. Waters, *Disc. Faraday Soc.*, **14**, 221 (1953).