

THE REMAINING STEREOISOMERS OF THE SPARTEINE GROUP

Sir:

We have found that the alkaloid *l*-spartalupine, C₁₅H₂₆N₂, 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, C₁₅H₂₄N₂O₂, 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 C₁₅H₂₆N₂: C, 76.86; H, 11.18; N, 11.96. Found: C, 76.99; H, 11.18; N, 12.02; [α]₂₅^D –15.4° (abs. alc.)). *Monoperchlorate*, m.p. 211.5–212° (calcd. for C₁₅H₂₆N₂·HClO₄: 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 C₁₅H₂₆N₂·2C₆H₂(NO₂)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 LiAlH₄.²

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, [α]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°, [α]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 Keil⁴ was repeated, except for reduction of the dioxo compound with LiAlH₄. Three dioxo compounds were isolated: A, m.p. 173–173.5° (calcd. for C₁₅H₂₂N₂O₂: 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 -isosparteine⁴). The infrared spectra of the natural *l*- and synthetic *dl* bases were superimposable. *dl*-Spartalupine dipicrate, m.p. 220.5–221° dec. (calcd. for C₁₅H₂₆N₂·2C₆H₂(NO₂)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.

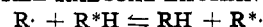
(5) Kindly supplied by Professor N. J. Leonard; cf. N. J. Leonard and R. E. Beyler, *THIS JOURNAL*, **72**, 1316 (1950).

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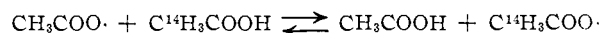
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MERCAPTAN CATALYSIS IN THERMONEUTRAL FREE RADICAL EXCHANGE:



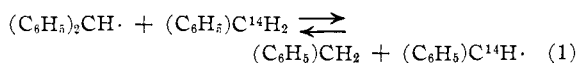
Sir:

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 CH₃COO· in solvent C¹⁴H₃COOH by decomposition of acetyl peroxide led to CH₄ containing about 1% of the radioactivity of the solvent,² indicating that the postulated exchange reaction

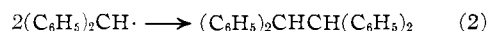


was slow compared to loss of CO₂ by the unstable acetate radical.

We have formed a more stable radical, (C₆H₅)₂CH· (I), in (C₆H₅)₂C¹⁴H₂ (II) by decomposition of (C₆H₅)₂CH—N=N—CH(C₆H₅)₂³ in 0.017 *m* solution in 3:1 (C₆H₅)C¹⁴H₂:C₆H₆ at 64° under CO₂. 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

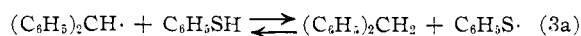


slower than the dimerization reaction



However, in the presence of 0.035 *m* C₆H₅SH (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.



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

(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. Kooymann, *Nature*, **170**, 211 (1952).

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

(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).