

violet.¹¹ As an indication of the conformational information which can be obtained the following two examples can be cited. The fact that L-idose exhibits a curve nearly superimposable on that for D-glucose suggests that the predominant conformer for this sugar in aqueous solutions is C-1, since other L-sugars which have been examined show curves which are mirror images of their corresponding D-isomers. Secondly, we have recently observed that α -L-idose pentaacetate, indicated by nuclear magnetic resonance spectroscopy to be in the 1-C conformation, gave a Cotton effect curve opposite to that of β -D-glucose pentaacetate, thus confirming the n.m.r. results. Since these results were obtained on less than 1 mg. of material, the advantages are obvious.

All compounds giving plain dispersion curves followed a simple Drude equation with λ_c varying between 130 and 175 $m\mu$ in agreement with previously reported values.^{1,10}

(11) T. H. Harris, E. L. Hirst, and C. E. Wood, *J. Chem. Soc.*, 2108 (1932).

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The Biosynthesis of Azetidine-2-carboxylic acid

Sir:

Azetidine-2-carboxylic acid (II) was first isolated from *Convallaria majalis* (lily of the valley)^{1,2} and is fairly widely distributed in the *Liliaceae*. Attempts to determine the precursors of this unusual imino acid have so far failed. The azetidine-2-carboxylic acid isolated from *C. majalis* leaves which were fed aspartic acid or α,γ -diaminobutyric acid, uniformly labeled with C¹⁴, had negligible activity.^{3,4} Since spermidine has been shown to arise by the nucleophilic attack of 1,4-diaminobutane on S-adenosylmethionine,⁵ it was considered that azetidine-2-carboxylic acid may be formed by the intramolecular displacement of thiomethyladenosine by the α -amino group of S-adenosylmethionine (I) as illustrated in Fig. 1.

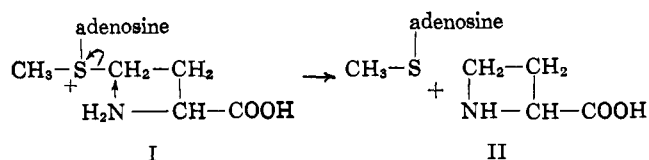


Fig. 1.—Hypothetical biosynthetic scheme for azetidine-2-carboxylic acid.

Experiments have now been carried out to test this hypothesis. DL-Methionine-carboxyl-C¹⁴ (9.32 mg., 0.2 mc.) dissolved in 20 ml. of water was administered to 20 *C. majalis* plants growing in soil out of doors

(1) L. Fowden, *Nature*, **176**, 347 (1955); *Biochem. J.*, **64**, 323 (1956).

(2) A. I. Virtanen and P. Linko, *Acta Chem. Scand.*, **9**, 551 (1955); A. I. Virtanen, *Nature*, **176**, 989 (1955).

(3) L. Fowden and M. Bryant, *Biochem. J.*, **71**, 210 (1959).

(4) P. Linko, *Acta Chem. Scand.*, **12**, 101 (1958).

(5) H. Tabor, S. M. Rosenthal, and C. W. Tabor, *J. Biol. Chem.*, **233**, 907 (1958)

(May) by means of cotton wicks inserted through the leaves near to ground level. One week after feeding the tracer, the leaves and roots (fresh weight 2.4 kg.) were harvested and azetidine-2-carboxylic acid (1.45 g., 5.0×10^5 d.p.m./mmole), aspartic acid (0.303 g., 2.0×10^4 d.p.m./mmole), and glutamic acid (0.491 g., 1.2×10^4 d.p.m./mmole) were isolated from the amino acid fraction by ion-exchange chromatography as previously described.¹ The radioactive azetidine-2-carboxylic acid was decarboxylated by heating with ninhydrin,⁶ the evolved carbon dioxide being collected and assayed as barium carbonate (4.7×10^5 d.p.m./mmole). This result indicates that essentially all the activity of the azetidine-2-carboxylic acid was located on the carboxyl group and strongly supports the new hypothesis. It is of course conceivable that the methionine is metabolized *via* homoserine to aspartic- β -semialdehyde, and then to the imino acid, as suggested by Fowden.¹ However, the low incorporation of tracer into aspartic acid (0.010%), compared with the incorporation into azetidine-2-carboxylic acid (1.67%), is not consistent with this metabolic sequence.

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(6) S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Vol. IV, Academic Press, Inc., New York, N. Y., 1957, p. 711.

(7) Alfred P. Sloan Fellow, 1962-1965.

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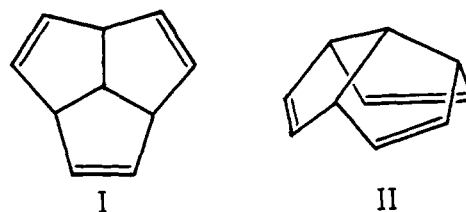
EDWARD LEETE⁷

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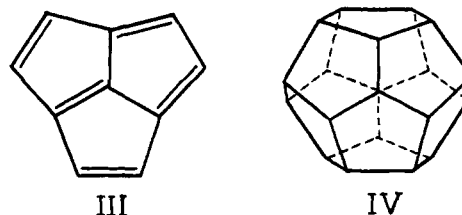
Triquinacene

Sir:

The hitherto unknown hydrocarbon, tricyclo[5.2.1-0^{4,10}]deca-2,5,8-triene (I \equiv II), here designated triquinacene, possesses three double bonds so situated in



fixed positions as to provide valuable information about the postulated phenomenon of homoaromaticity¹ and about the nature and extent of homoallylic participation in olefinic reactivity. A study of the capacity of triquinacene to form metal complexes would also be of special interest, and its possible roles as a precursor of acepentylene (III)² and of dodecahe-



(1) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); cf. also P. Radlick and S. Winstein, *ibid.*, **85**, 343 (1963), and K. G. Untch, *ibid.*, **85**, 345 (1963).

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 90, 290.