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BIOSYNTHESIS OF SECURININE
INCORPORATION OF RADIOACTIVE TYROSINE, LYSINE AND CADAVERINE

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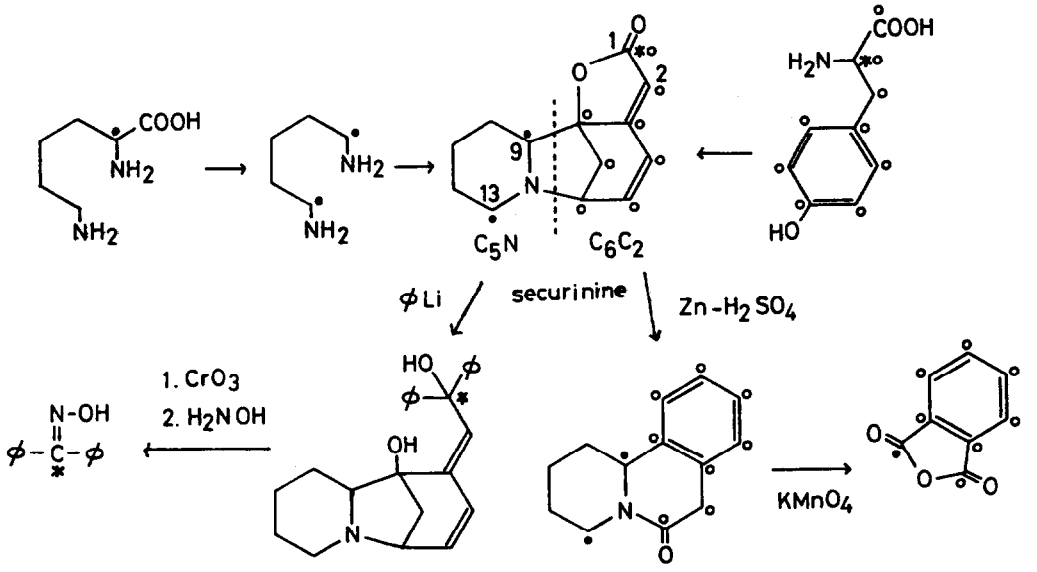
A recent report on the specific incorporation of radioactive tyrosine into securinine[1] prompted us to report our results on the biosynthesis of securinine. The labelled compounds listed in the Table were fed to Securinega suffruticosa Rehd.[2] by the conventional wick method. The leaves, harvested after 1 week cultivation, were extracted to isolate alkaloids. Higher incorporation ratios were observed when radioactive lysine, cadaverine and tyrosine had been administered. Securinine labelled by cadaverine (1,5-^{14}C) was degradated to phthalic anhydride, which showed approximately 50% of the total radioactivity of securinine.

Labelled Compounds	Incorp. Ratio%	Benzophenone Oxime	Phthalic Anhydride	Theoretical
DL-Lysine(2-^{14}C)	0.11	-	-	-
L-Lysine(U-^{14}C)	0.026	-	-	-
Cadaverine(1,5-^{14}C)				
securinine	0.020	-	49.6	50.0
allosecurinine		-	52.2	50.0
DL-Tyrosine(2-^{14}C)	0.028	106.0	-	100.0
L-Tyrosine(U-^{14}C)	0.038	-	86.3	87.5
Homogentisic Acid (carboxyl-^{14}C)	0.0063	3.8	-	-
DL-Dopa(2-^{14}C)	0.0011	-	-	-
Tyramine(1-^{14}C)	0.0047	-	-	-
L-Phenylalanine (arom.-^{14}C)	0.00027	-	-	-
Na-acetate(1-^{14}C)	0.0053	-	-	-

Allosecurinine (an epimer of securinine), obtained from the same feeding experiment, showed a similar result. The results indicate an equal distribution of labelling between C-9 and C-13 of securinine, and it was evident that the piperidine ring of securinine is derived from lysine via cadaverine. All the radioactivity in securinine labelled by tyrosine (2-^{14}C) was found in benzophenone oxime representing C-1 of securinine. Phthalic anhydride obtained from securinine labelled by tyrosine (U-^{14}C) showed 86.3% of the total radioactivity of securinine, whose theotheoretical value is 87.5% (7/8). Labelling experiments with tyrosine-^{14}C clearly demonstrated that the C_6-C_2 part of securinine is derived from the aromatic ring, C-2 and C-3 of tyrosine.

Further experiments were carried out with tyramine(1-^{14}C), homogentisic acid (carboxyl-^{14}C) and dopa(2-^{14}C), which are known as the intermediates of various natural products derived from tyrosine. However, the incorporation ratios of the above labelled compounds were definitely lower than those of established precursors such as tyrosine and cadaverine. Degradation reaction clarified that the labelling from homogentisic acid (carboxyl-^{14}C) was randomly distributed by extensive catabolism. By the experimental results so far obtained, p-hydroxyphenylpyruvic acid seems to be a possible intermediate.



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