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REFERENCES

1. D'Arcy, W. G. and Hunziker, A. T. (1979) in *The Biology and Taxonomy of the Solanaceae* (Hawkes, J. G., Lester, R. N. and Skelding, A. D., eds.) p. 3, 49. Linnean Society Symposium, Series No. 7. Academic Press, London.
2. Walters, D. (1969) Ph.D. Thesis, Indiana University.
3. Sudzuki, F. (1944) Thesis, Universidad de Chile.
4. San Martín, A., Rovirosa, J., Gambaro, V. and Castillo, M. (1980) *Phytochémistry*, **19**, 1007.
5. Ripperger, H. (1979) *Phytochemistry* **18**, 717.
6. McGaw, B. A. and Woolley, J. G. (1978) *Phytochemistry* **17**, 257.
7. Evans, W. C. (1979) in *The Biology and Chemistry of the Solanaceae* (Hawkes, J. G., Lester, R. N. and Skelding, A. D., eds.) p. 241. Linean Society Symposium Series No. 7. Academic Press, London.
8. Bassey, K. and Woolley, J. G. (1973) *Phytochemistry* **12**, 2883.
9. Achari, R., Evans, W. C. and Newcombe, F. (1969) *Naturwissenchaften* **56**, 88.
10. Fodor, G. and Kovacs, O. (1973) *J. Chem. Soc.* 2341.
11. Evans, W. C. and Griffin, W. J. (1963) *J. Chem. Soc.* 4348.

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# METABOLISM OF [METHYL-$^{14}C_2$]HORDENINE IN *HORDEUM VULGARE* PLANTS

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**Key Word Index**—*Hordeum vulgare*; Gramineae; barley; metabolism; [methyl-$^{14}C_2$]hordenine.

**Abstract**—Intact plants of *Hordeum vulgare* quantitatively degrade [methyl-$^{14}C_2$]hordenine to $^{14}CO_2$.

We have recently reported [1] that homogenates from root tissue of *Hordeum vulgare* seedlings degrade [methyl-$^{13}C_2$]hordenine to *N*-methyltyramine and probably tyramine. The uncertainty regarding the fate of the *N*-methyl groups came from the fact that in the sequence of $^{13}C$ NMR spectra there appeared no signal indicating the fate of the [$^{13}C$]methyl groups. This result suggested either a dispersion of the labelled methyl groups or their elimination as $^{13}CO_2$ whose resonance signal is very difficult to observe because of its long $T_1$ value.

In order to solve this problem, we fed 8-day-old *H. vulgare* plants with [methyl-$^{14}C_2$]hordenine under similar conditions to those previously described [2] and the carbon dioxide expelled by the plants was collected. The results (Table 1) indicated that, considering the amount of alkaloid not metabolized, the methyl groups were almost completely eliminated as $^{14}CO_2$.

This degradation pathway is in agreement with that reported by Frank and Marion [3] and also with our earlier results [1, 2, 4] and explains the lack of a third signal in the experiment with [$^{13}C$]hordenine [2].

## EXPERIMENTAL

*Plant material.* Similar to that previously described [2, 4].

*Synthesis of* [*methyl-*$^{14}C_2$]*hordenine.* To a soln of tyramine hydrochloride (108 mg) in MeOH (15 ml), [$^{14}C$]formaldehyde (2%, 38.4 μl, 500 μCi) (Amersham, U.K.) and formaldehyde (32.7%, 40 μl) were added and the mixture was hydrogenated over 10% Pd–C (20 mg) at room temp. and atmospheric pres. for 4 hr. Then, formaldehyde (32.7%, 90 μl) was added and the hydrogenation was continued for 12 hr. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was taken-up in MeOH (2 ml) and evaporated again; this procedure was repeated twice more. The residue was taken-up in $NH_4OH$ (1 ml) and evaporated. Sublimation (0.001 torr, 110°) of the residue afforded pure (IR) hordenine (103 mg) with a sp. act. of 0.68 mCi/mmol.

*Feeding experiment and collection of the expelled* $CO_2$. The development of the seedlings, the administration of the tracer, the collection of $CO_2$ as $BaCO_3$ and the assays for radioactivity were performed as previously described [2, 4, 5]. The results are shown in Table 1.

Table 1. Formation of $^{14}CO_2$ in 50 intact *H. vulgare* plants after administration of [methyl-$^{14}C_2$]hordenine (18.2 mg; 0.68 mCi/mmol)

| Total time (hr) | $BaCO_3$ mg | $BaCO_3$ dpm/mg | Total activity (dpm) | Total $^{14}CO_2$* ($\mu$mol) | Formation of $^{14}CO_2$* ($\mu$mol/hr) | Total activity recovered (%) |
|---|---|---|---|---|---|---|
| 2.5 | 150 | $2.32 \times 10^3$ | $3.49 \times 10^5$ | 0.2 | 0.1 | 0.2 |
| 5.0 | 57 | $6.41 \times 10^3$ | $3.65 \times 10^5$ | 0.5 | 0.1 | 0.4 |
| 22.8 | 1070 | $1.52 \times 10^4$ | $1.63 \times 10^7$ | 11.2 | 0.6 | 10.2 |
| 26.0 | 118 | $2.70 \times 10^4$ | $3.19 \times 10^6$ | 13.4 | 0.7 | 12.1 |
| 28.5 | 70 | $2.80 \times 10^4$ | $1.96 \times 10^6$ | 14.7 | 0.5 | 13.3 |
| 46.8 | 507 | $4.68 \times 10^4$ | $2.37 \times 10^7$ | 30.4 | 0.9 | 27.6 |
| 50.5 | 99 | $5.72 \times 10^4$ | $5.66 \times 10^6$ | 34.1 | 1.0 | 31.0 |
| 72.0 | 587 | $5.85 \times 10^4$ | $3.43 \times 10^7$ | 56.9 | 1.1 | 51.7 |
| 143.0 | 1855 | $3.84 \times 10^4$ | $7.12 \times 10^7$ | 104.0 | 0.7 | 94.6 |

Radioactivity remaining in the feeding solution after 6 days: $5.7 \times 10^6$ dpm (3.4% of the labelled hordenine).

* Calculated values.

*Extraction of roots and aerial parts.* After 143 hr, roots, aerial parts and feeding soln were separated. Radioactivity of the feeding soln was measured by LSC. Roots and aerial parts were extracted separately with MeOH (200 ml each) and the respective methanolic extracts were assayed for radioactivity by LSC. The roots extract had $2.8 \times 10^6$ dpm (1.7% of the total act.) while the radioactivity of the aerial parts extract was negligible. The recovery of radioactivity amounted to 99.7% of the labelled hordenine.

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## REFERENCES

1. Russo, C. A., Burton, G. and Gros, E. G. (1983) *Phytochemistry* **22**, 71.
2. Russo, C. A. and Gros, E. G. (1981) *Phytochemistry* **20**, 1763.
3. Frank, A. W. and Marion, L. (1956) *Can. J. Chem.* **34**, 1641.
4. Russo, C. A. and Gros, E. G. (1982) *Phytochemistry* **21**, 609.
5. Ghini, A. A., Burton, G. and Gros, E. G. (1982) *Phytochemistry* **21**, 605.