

SHORT COMMUNICATION

FLUOROCITRATE IN PLANTS AND FOOD STUFFS

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Abstract—Monofluorocarbon acids can be formed from inorganic fluoride by single cell cultures of *Acacia georginae* and tea. Fluorocitrate is also present in small amounts in commercial specimens of tea and oatmeal. The significance of these observations is discussed, especially in relation to the toxic plants.

INTRODUCTION

UNTIL RECENTLY there was no evidence that inorganic fluoride was metabolized by plants. The only exceptions were those poisonous plants which synthesized fluoroacetate and which are found in Africa, Australia and S. America.¹ A first indication that other plants can convert fluoride to an organically combined form, partly volatile,² was followed by the interesting discovery that some forage plants could synthesize fluoroacetate and fluorocitrate;³ and that lettuces could form fluorocitrate from fluoroacetate.⁴

We have shown recently⁵ that single cell cultures of soya bean (*Glycine max*) can convert fluoride to fluoroacetate and fluorocitrate. We here add some further observations in this field.

RESULTS

Single cell cultures of *Acacia georginae* F. M. Bailey when grown in the presence of 10^{-3} M sodium fluoride for 8 weeks, synthesized both fluoroacetate and fluorocitrate, in the approximate ratio of 2:1. This observation of the synthesis of fluoroacetate confirms the report of Preuss *et al.*⁶

Single cell cultures of tea (*Thea sinensis*), which had been grown in the presence of fluoride for 8 weeks were also shown to contain fluorocitrate, in amounts of 5–10 $\mu\text{g/g}$ tissue. Using GLC, we have now found small amounts of fluorocitrate in a commercial sample of tea, which had previously been missed⁷ using less sensitive methods. It confirms an unpublished observation that tea extracts are inhibitory to a soluble aconitase from pig heart. The amount of fluorocitrate does not exceed 30 $\mu\text{g/g}$ and is too small to be of toxic significance; an average person drinking 8 cups of tea per day would only be taking 3.4 $\mu\text{g/k}$, which is far from a toxic dose taken orally.⁸

¹ *Ciba Symposium on Carbon Fluorine Compounds* (in Press).

² R. A. PETERS and M. SHORTHOUSE, *Nature, Lond.* **216**, 80 (1967).

³ C. J. LOVELACE, G. W. MILLER and G. W. WELKIE, *Atmosph. Environ.* **2**, 187 (1968).

⁴ P. F. V. WARD and H. S. HUSKISSON, *Biochem. J.* **113**, 9P (1969).

⁵ R. A. PETERS and M. SHORTHOUSE, *Phytochem.* (in press).

⁶ P. PREUSS, R. BIRKHAHN and E. D. BERGMAN, *Israel J. Bot.* **19**, 609 (1970).

⁷ R. A. PETERS and M. SHORTHOUSE, *Nature, Lond.* **202**, 21 (1964).

⁸ R. A. PETERS and M. SHORTHOUSE, *J. Physiol.* **216**, 40P (1971).

We have also found fluorocitrate not exceeding 62 $\mu\text{g/g}$ in a commercial specimen of oatmeal. A small amount of fluoroacetate was also detected.

DISCUSSION

The proof that inorganic fluoride, in small amounts, can be incorporated into fluoroacetate leading to fluorocitrate in plants demonstrates that there can be a metabolism of fluoride. Hence the F^- ion does not always enter and leave a plant in the inorganic form. Some edible plants can make monofluorocarbon compounds; but normally the amounts of these formed appear to be too low to be toxic by the mouth.

Nevertheless, it appears now that the toxic plants exaggerate a normal reaction to fluoride, and the question is raised whether such plants make fluoroacetate more quickly or whether they degrade it more slowly. Their toxicity is known to vary considerably.⁹ It has been shown that lettuces can split F^- from fluoroacetate,⁴ and it has been found that the African plants accumulate much inorganic fluoride.¹⁰ It is also known that the formation of some monofluorocarbon acids such as fluoroaspartate¹¹ leads to instability and inorganic fluoride is readily liberated from such compounds in mammalian *in vitro* systems. So plants showing high toxicity may vary from normal plants in the absence of certain important compounds, such as glutathione. Fluorocitrate also appears to vary in its inhibition to aconitate hydratase; it was 2000 times less toxic in one instance.¹² Fluoride can also be converted to monofluoroacetone by homogenates of *A. georginae*.¹³

EXPERIMENTAL

The technique for single cell cultures and their extraction was identical with that described in.⁵ For GLC a column (1.5 m \times 6 mm) of PEG 20 M was used, except in one case (oatmeal) where a 2.7 m \times 6 mm was needed for satisfactory separation of the products from long chain fatty acids. The GLC estimations are considered to be accurate to $\pm 10\%$, but the efficiency of extraction is difficult to assess accurately.

⁹ L. R. MURRAY and D. R. WOOLEY, *Australian J. Soil Res.* **6**, 203.

¹⁰ R. J. HALL, M.Sc. Thesis. Newcastle-upon-Tyne, 1969.

¹¹ E. KUN, D. W. FANSHIER and D. R. GRASSETI, *J. Biol. Chem.* **235**, 416 (1960).

¹² D. H. TREBLE, D. T. A. LAMPORT and R. A. PETERS, *Biochem. J.* **85**, 113 (1962).

¹³ R. A. PETERS and M. SHORTHOUSE, *Nature, Lond.* **231**, 123 (1971).

Key Word Index—*Acacia georginae*; Leguminosae; *Thea sinensis*; Theaceae; tea; oatmeal; fluoroacetate; fluorocitrate.