Two 2-ml aliquots of a solution of D,L-tryptophan (5.1 mg) in 1.8×10^{-3} M HCl (100 ml) were placed in culture tubes and each was treated with 5 mCi (200 μl) of aqueous $KH_2\,^{32}PO_4$ solution (NEN). A control for each sample was prepared by mixing 2 ml of the above tryptophan solution with 200 μl 0.042 M KH_2PO_4. The tubes were sealed and stored at −25 °C for 85 days, then thawed and opened. The irradiated samples were each divided into two equal portions and one portion was treated with 20 μl of a 1.3×10^{-2} M solution of D-tryptophan to allow estimation of the per cent degradation using GC and the enantiomeric marker technique[18]. Each solution was then warmed and evaporated in a nitrogen stream and the residues were treated with 1 ml 2-propanol saturated with HCl gas. The culture tubes were sealed and heated at 120 °C for 2.5 h, opened and the volatiles were again evaporated in a nitrogen stream. The residues were treated with 1 ml ethyl acetate and 50 μl heptafluorobutyric anhydride, then were maintained at 120°C for 45 min. The volatiles were again evaporated and each oily residue was dissolved in dichloromethane to give an $\sim 10^{-2}$ M solution for GC analysis. The samples were analysed as previously described[17] using a 46 m × 0.5 mm (i.d.) stainless steel capillary GC column coated with *N*-docosanoyl-D-valine-*tert*-butylamide phase[19]. At 160 °C (isothermal) and a N_2 flow rate of ~ 10 ml min^{-1}, baseline GC resolution of the enantiomeric tryptophan derivatives was achieved with the L-isomer eluting in 51.7 min and the D-isomer in 56.9 min. All samples were analysed in replicate, with the control samples interspersed 'back-to-back' with the irradiated samples. The results of these analyses are shown in Table 1, along with the analysis of a known mixture of D- and L-tryptophan which was included to see if an enantiomeric excess (e.e.) as small as ~6% could be reliably detected with such tryptophan derivatives by the GC technique used. A combined GC–mass spectra analysis of the above D,L-tryptophan derivative showed that each GC peak gave the same fragmentation pattern and corresponded to a tryptophan isopropyl ester having one heptafluorobutyryl residue on each nitrogen atom.

Table 1

Exp	1*	1C†	2*	2C†	Known mixture‡
% Degradation	48	—	39	—	—
s.d. (±)	9	—	9	—	—
% D-tryptophan	50.5	51.1	49.5	50.8	48.3
% L-tryptophan	49.5	48.9	50.5	49.2	51.7
s.d. (±)[4]	0.6	0.2	0.1	0.3	0.7

* Irradiated samples of D,L-tryptophan.
† Control samples of D,L-tryptophan.
‡ Containing 47.1% D- and 52.9% L-tryptophan.
s.d. Standard deviation.

Although the gross degradation which we observed (43.5% average, Table 1) was somewhat larger than that reported (33%) by Darge *et al.*[13], we found no evidence whatsoever for any asymmetric radiolysis. While the GC analyses in Table 1 do not seem to be quite as precise as those previously noted[17] for leucine enantiomers, it is nevertheless clear that the irradiated tryptophan residues have an enantiomeric composition not experimentally distinguishable from that of the D,L-tryptophan controls. Furthermore, the detection of a known 5.8% e.e. (as 3.4%) in the known mixture of Table 1 suggests that the ~19% e.e. (59.7% D-, 40.3% L-tryptophan) claimed by Darge *et al.*[13] could scarcely have been missed by the present GC technique. Unable to find an asymmetric effect after using an alternative analytical procedure (GC), we can only conclude that Darge's reported 19% asymmetric radiolysis of D,L-tryptophan with ^{32}P β radiation may have resulted from a systematic error in the very small polarimetric readings involved or from an artefact present in the crude solutions examined.

Received 20 November 1978; accepted 31 July 1979.

1. Vester, F. seminar, Yale Univ., 7 Feb. (1957).
2. Lee, T. D. & Yang, C. N. *Phys. Rev.* **104**, 254 (1956).
3. Wu, C. S. *et al. Phys. Rev.* **105**, 1413 (1957).
4. Vester, F., Ulbricht, T. L. V. & Krauch, H. *Naturwissenschaften*, **46**, 68 (1959).
5. Ulbricht, T. L. V. & Vester, F. *Tetrahedron* **18**, 629 (1962).
6. Garay, A. S., *Nature* **219**, 338 (1968).
7. Goldanskii, V. I. & Khrapov, V. V. *Sov. Phys. JETP* **16**(3), 582 (1963).
8. Bonner, W. A. *J. molec. Evolut.*, **4**, 23 (1974).
9. Bonner, W. A. & Flores, J. J. *Origins of Life* **6**, 187 (1975).
10. Bernstein, W. J., Lemmon, R. M. & Calvin, M. in *Molecular Evolution: Prebiological and Biological* (eds Rolfing, D. L. & Oparin, A. I.) 151 (Plenum, New York, 1972).
11. Noyes, H. P., Bonner, W. A. & Tomlin, J. A. *Origins of Life* **8**, 21 (1977).
12. Bonner, W. A., Lemmon, R. M. & Noyes, H. P. *J. org. Chem.* **43**, 522 (1978).
13. Darge, W., Laczko, I. & Thiemann, W. *Nature* **261**, 522 (1976).
14. Bonner, W. A., Van Dort, M. A. & Yearian, M. R. *Nature* **258**, 419 (1975); **264**, 198 (1976).
15. Bonner, W. A., Van Dort, M. A., Yearian, M. R., Zeman, H. D. & Li, G. C. *Israel J. Chem.* **15**, 89 (1976/77).
16. Keszthelyi, L. *Origins of Life* **8**, 299 (1977).
17. Bonner, W. A., Van Dort, M. A. & Flores, J. J. *Analyt. Chem.* **46**, 2104 (1974).
18. Bonner, W. A. *J. Chromat. Sci.* **11**, 101 (1973).
19. Bonner, W. A. & Blair, N. E. *J. Chromat.* **169**, 153 (1979).

W. Darge*, I. Laczko† and W. Thiemann‡ reply: Bonner *et al.* criticise the reproducibility of our earlier results[1] and claim to have reproduced the original experiment. In fact they have applied a very different analytical technique based on gas-chromatographic analysis of the irradiation residue. There is also the difference that Bonner *et al.* have been able to analyse exclusively the enantiomeric composition of the partially destructed residual tryptophan only, while in our earlier optical rotatory dispersion (ORD) measurements we were able to detect the effect of the sum of all potential chiral products (be they residual tryptophan, intermediate or final irradiation products such as any oxyacids, ketonic, or even peptidic substances commonly encountered in similar experiments). There are possibilities that any such intermediate products exhibit quite specifically large optical rotations and thus contribute to the overall effect in spite of their possibly small concentration in the investigated solution. We believe that this is exactly the advantage of a carefully performed ORD measurement over GC or other analytical methods. Having eliminated 'physical artefacts' as far as possible according to available techiques[2], one is left with any 'chemical artefacts' in the above defined sense, namely the existence of hitherto unidentified chiral intermediate irradiation products in the chain of the decomposition process of D,L-tryptophan. We never had claimed that any 'stereoselective effect' would manifest itself necessarily in the destruction of racemics but included the equally probable chance of stereoselective synthesis as a source of optical activity.

We wonder why Bonner *et al.* declare out earlier results as 'the most striking positive result': Garay in his original paper[3] and Merwitz[4] had both published much larger 'striking' stereoselective effects as a result of irradiation. Bonner *et al.* themselves confirm the basic hypothesis with their polarised electron bombardment of D,L-leucine[5]. What then is the essential difference between accelerated polarised electrons and β^- particles emitted from radionuclides in this context of 'helicity transferred from the classically physical level to the chemical level'?

1. Darge, W., Laczko, I. & Thiemann, W. *Nature* **261**, 522 (1976).
2. Thiemann, W. & Darge, W. *Origins of Life* **5**, 263 (1974).
3. Garay, A. J. Nature **219**, 338 (1968).
4. Merwitz, *Radiat. Envir. Biophys.* **13**, 73 (1976).
5. Bonner, W. A., Van Dort, M. A. & Yearian, M. R. *Nature* **258**, 419 (1975); **264**, 198 (1976).

* Fachhochschule Aachen, FRG. † Biological Research Center Szeged, Hungary. ‡ Fachbereich Chemie, Universität Bremen, Postfach 330 440, D-2800 Bremen 33, FRG.