The Biosynthesis of Terrein

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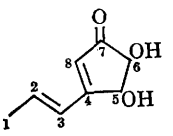
INSPECTION of the formula (I) of terrein, from *Aspergillus terreus* Thom, suggests that it arises at least partly by the polyketide–fatty acid route. It is unusual in containing a five-membered ring since polyketides normally contain six-membered ones if any, because they are connected with

closures at the β-positions of the original chain.[1] Incorporation of polyketide precursors (see Table) as Schmidt degradations of fatty acids. Counting results have a statistical error of $\pm 3\%$.

Position	[1-^{14}C]acetate r.m.a. labels		[2-^{14}C]acetate r.m.a. labels		[2-^{14}C]malonate r.m.a. labels	
1	0	0	10·1	1	4·7	1
2	4·6	1	0	0	0	0
3	0	0	9·7	0·96	4·9	1·04
4	5·0	1·08	0	0	0	0
5	0	0	9·5	0·95	4·7	1
6	4·9	1·05	0	0	0·5	0·1
7	5·6	1·18	0·2	0·2	0·45	0·09
8	0	0	10·3	1·02	4·8	1·02

r.m.a. are 10^{-4}. Labels are calculated on a value of 1 for the first in the side-chain.

demonstrates clearly a polyketide origin with the unusual feature of two linked "carboxyl" carbons at the 6,7-positions. Mechanistically, this distribution is probably best explained by contraction of a six-membered precursor. The slight activity of the 6,7-carbons using two precursors could be due to a small degree of randomisation during ring contraction. The degradations were based on the original literature[2] or were obvious extensions such



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[1] A. J. Birch and F. W. Donovan, *Austral. J. Chem.*, 1953, **6**, 360; A. J. Birch, *Proc. Chem. Soc.*, 1961, 3.
[2] P. W. Clutterbuck, H. Raistrick, and F. Reuter, *Biochem. J.*, 1937, **31**, 987.