

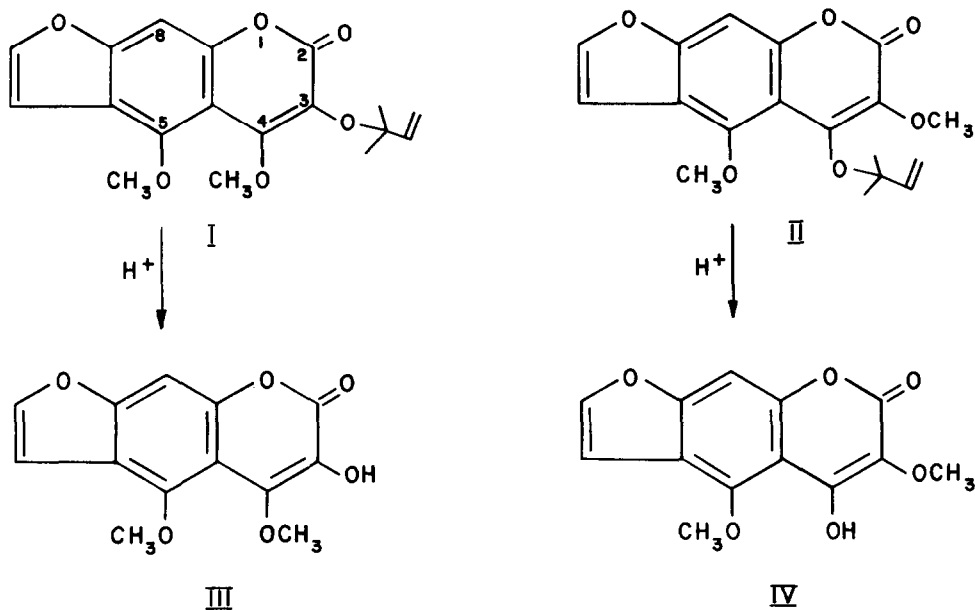
HALFORDININ - A REVISED STRUCTURE

J.K. MacLeod

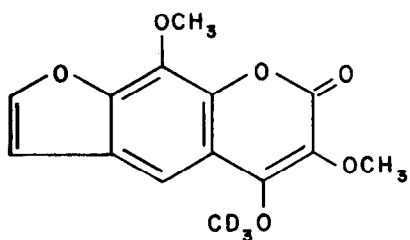
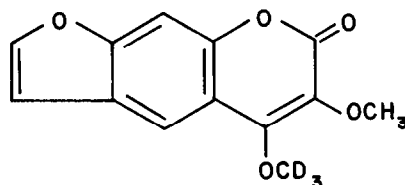
Research School of Chemistry, Australian National University,
P.O. Box 4, Canberra, A.C.T., Australia

(Received in UK 28 July 1970; accepted for publication 5 August 1970)

Since the recent publication¹ of the structure of halfordinin as (I), new evidence has come to hand which necessitates a reappraisal of the original structure. The change is a relatively minor one involving transposition of the methyl and α,α -dimethylallyl ether groupings on the 3- and 4-positions giving (II) as the correct structure for halfordinin.



The original assignment¹ of the unusual α,α -dimethylallyl ether grouping to the 3-position on the coumarin nucleus was based on quantitative conversion of halfordinin to norhalfordinin with acid. Hegarty and Lahey² had earlier produced evidence based on colour tests which indicated that norhalfordinin and norisohalfordinin had a free 3-OH group and the assignment of structure (III) for norhalfordinin and hence of structure (I) for halfordinin followed from this.

VVI

It seems, however, that the conclusion drawn from the observations of these original workers was erroneous. Samples of synthetic isohalfordin (V)³ and halkendin (VI)⁴ specifically deuterated in the 4-methoxyl grouping⁵ were subjected to similar acid-catalysed ether-cleavage treatment and the mass spectra of the starting compounds and nor-derivatives compared. In both cases, the molecular ion was decreased by 17 mass units (m/e 279 to 262 for (V), m/e 249 to 232 for (VI)), indicating that the 4-methyl, not the 3-methyl moiety was lost on acid treatment. Although the similarly deuterated halfordin has not been synthesised, there is no doubt that the same conclusion holds as found in the two other closely related 3,4-dimethoxylated furanocoumarins, viz., that halfordin also loses the 4-methyl group on acid treatment and therefore that norhalfordin has structure (IV). This result requires that the structure of halfordinin be revised to structure (II).

REFERENCES

1. J.K. MacLeod, *Tetrahedron Letters*, 1319 (1970)
2. M.P. Hegarty and F.N. Lahey, *Aust. J. Chem.* 9, 120 (1956)
3. K. Fukui, M. Nakayama, S. Fujimoto, and O. Fukuda, *Experientia* 25, 354 (1969)
4. J.K. MacLeod, K. Fukui, M. Nakayama, and S. Fujimoto, *Aust. J. Chem.*, submitted for publication.
5. M. Nakayama, *J. Sci. Hiroshima Univ., Ser. A-II*, 33, 213 (1969). The author would like to thank Dr Nakayama for generously providing samples of the two deuterated furanocoumarins.