

## A Stereoselective Synthesis of *trans*-Chrysanthemic Acid

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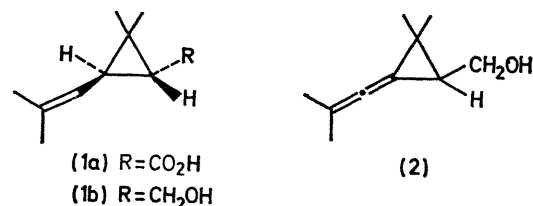
**Summary** ( $\pm$ ) *trans*-Chrysanthemic acid has been synthesised by a route involving the stereoselective reduction of an intermediate allenic cyclopropane.

THE high insecticidal activity and low mammalian toxicity of the pyrethrins<sup>1</sup> have encouraged the development of synthetic routes<sup>2</sup> to a key parent acid, (+)-*trans*-chrysanthemic acid (**1a**). We report a synthesis of this racemic acid in which both the isoprenoid "halves" of the carbon skeleton are derived essentially from the same starting material, 2-methylbut-3-yn-2-ol.

Treatment of a mixture of 2-chloro-2-methylbut-3-yne and 3-methylbut-2-en-1-ol with potassium *t*-butoxide gave, *via* the intermediate dimethylallenecarbene,<sup>3</sup> the C<sub>10</sub> allenic cyclopropane (**2**) containing the entire carbon skeleton of chrysanthemic acid. [*M* (mass spec.) 152;  $\nu_{\max}$  3615 (primary OH) and 2000 (allene) cm<sup>-1</sup>; *p*-nitrobenzoate, m.p. 98–99°]. The n.m.r. spectrum (60 MHz; CDCl<sub>3</sub>) showed resonances at  $\tau$  8.73 and 8.72 (each 3H, s; geminal tertiary Me), 8.25 (6H, s; vinylic Me), 8.15 (1H, t, *J* 7 Hz) and 6.24 (2H, dd, *J* 7 and 2 Hz). Reduction of the allene with sodium in liquid ammonia<sup>4</sup> was highly regioselective and stereoselective and gave a high yield of ( $\pm$ )-*trans*-chrysanthemyl alcohol (**1b**) identified by comparison

with an authentic sample. This result suggests the protonation of an intermediate cyclopropyl carbanion<sup>5</sup> by intramolecular delivery from the pendant hydroxy-group. This was supported by the finding that the tetrahydropyranyl ether of the allene (**2**) gave, after reduction and hydrolysis, an equimolecular mixture of *cis*- and *trans*-chrysanthemyl alcohols. The alcohol (**1b**) was oxidised to ( $\pm$ )-*trans*-chrysanthemic acid by chromium trioxide-pyridine without loss of stereochemical integrity.

This synthesis can produce various analogues of chrysanthemic acid and its scope is now being explored.



We thank Professor L. Crombie for providing samples of ( $\pm$ )-*trans*-chrysanthemic acid and ( $\pm$ )-*cis*- and ( $\pm$ )-*trans*-chrysanthemyl alcohols, and the S.R.C. for a studentship (to R.W.M.).

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