A Stereoselective Synthesis of *trans*-Chrysanthemic Acid

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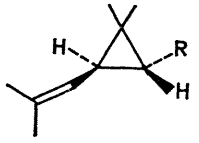
Summary (±) *trans*-Chrysanthemic acid has been synthesised by a route involving the stereoselective reduction of an intermediate allenic cyclopropane.

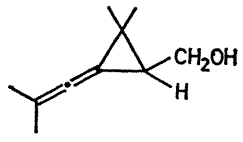
THE high insecticidal activity and low mammalian toxicity of the pyrethrins[1] have encouraged the development of synthetic routes[2] to a key parent acid, (+)-*trans*-chrysanthemic acid (**1a**). We report a synthesis of this racemic acid in which both the isoprenoid "halves" of the carbon skeleton 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,[3] the C_{10} allenic cyclopropane (**2**) containing the entire carbon skeleton of chrysanthemic acid. [*M* (mass spec.) **152**; ν_{max} 3615 (primary OH) and 2000 (allene) cm^{-1}; *p*-nitrobenzoate, m.p. 98—99°]. The n.m.r. spectrum (60 MHz; $CDCl_3$) showed resonances at τ 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[4] was highly regioselective and stereoselective and gave a high yield of (±)-*trans*-chrysanthemyl alcohol (**1b**) identified by comparison with an authentic sample. This result suggests the protonation of an intermediate cyclopropyl carbanion[5] 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 (±)-*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.



(1a) R=CO_2H
(1b) R=CH_2OH



(2)

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