

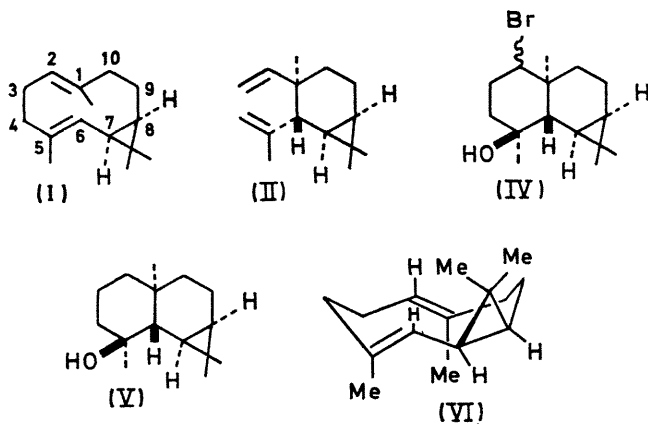
Absolute Configuration of Bicycloelemene and Conformation of Bicyclogermacrene

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Summary The absolute configuration of bicycloelemene (II) has been elucidated and from this result the stereostructure of bicyclogermacrene (I) has been clarified.

NISHIMURA *et al.*¹ have recently isolated bicyclogermacrene (I) from the cold-pressed peel oil of *Citrus junos*, and reported the structural elucidation and the Cope rearrangement of (I). When heated at 200° for 30 min, compound (I) gave a mixture of (I), bicycloelemene (II), and isobicyclogermacrene (III) in the ratio 5:4:1.



On the other hand, although bicycloelemene (II), a sesquiterpene, was isolated from peppermint oil by Herout *et al.*,² no information has so far been obtained on its stereochemistry.

We have recently reported³ that the stereochemistry of a Cope rearrangement product depends on the conformation of the original ten-membered ring and that a knowledge of the absolute configuration of the rearrangement product would provide evidence for the conformation of the ten-membered ring in the starting material. Therefore, establishing the absolute configuration of bicycloelemene (II) should clarify the stereochemistry of bicyclogermacrene (I).

When bicycloelemene (II) was treated with *N*-bromosuccinimide⁴ in aqueous Me₂CO, it gave an oily bromohydrin (IV). Compound (IV) afforded an alcohol (V), m.p. 103–104°, [α]_D + 18° by reduction with Li in liquid NH₃, followed by alumina chromatography and preparative t.l.c. on AgNO₃-silica gel. This alcohol was shown to be identical with maaliol,⁵ by comparison of the i.r. spectra and of the [α]_D values. The stereochemistry of bicycloelemene was thus established and its absolute configuration is therefore represented by the formula (II).

From this result and from our previous work,³ the following conclusions can be drawn: (a) the cyclopropane ring in bicyclogermacrene (I) has the β -configuration; (b) as the Cope rearrangement product, bicycloelemene (II) is a *trans*-1,2-divinyl-cyclohexane derivative, the double bonds at $\Delta^{1,2}$ and $\Delta^{5,6}$ in (I) both have a *trans*-configuration and have a crossed orientation; (c) as (II) is an antipodal elemene-type product, the methyl groups at C-1 and C-5 are located at the back of the molecule. It is therefore postulated that bicyclogermacrene has the stereostructure shown in (VI).

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¹ K. Nishimura, N. Shinoda, and Y. Hirose, *Tetrahedron Letters*, 1969, 3097; Abstracts, 7th International Symposium on Natural Products, Riga, 1970, p. 415.

² R. Vlahov, M. Holub, I. Ognjanov, and V. Herout, *Coll. Czech. Chem. Comm.*, 1967, **32**, 808.

³ K. Takeda, *Pure Appl. Chem.*, 1970, **21**, 181; K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. (C)*, 1970, 1142; K. Takeda, K. Tori, I. Horibe, M. Ohtsuru, and H. Minato, *ibid.*, 2697.

⁴ J. C. Jain, C. M. Banks, and J. E. McCloskey, *Tetrahedron Letters*, 1970, 2387.

⁵ G. Büchi, M. Schach v. Wittenau, and D. M. White, *J. Amer. Chem. Soc.*, 1959, **81**, 1968.