D- and L-Filifolones, Monoterpenoid Cyclobutanones with the Bicyclo[3,2,0]heptane Ring System

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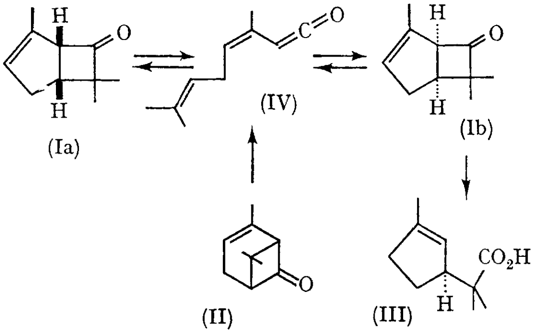
THE racemic mixture of (Ia) and (Ib) was first characterized by Beereboom,[1] who prepared it by heating a mixture of geranic acids with acetic anhydride and sodium acetate. We have now found (Ia), which we term D-filifolone, in the Australian plant *Zieria smithii* Andrews, and its enantiomer, L-filifolone (Ib), in the Arizonan sage *Artemisia filifolia* Torrey. These are the first monoterpenoids reported to have the bicyclo[3,2,0]-heptane ring system. We also record the racemization of the filifolones and the conversion of chrysanthenone (II) into (±)-filifolone on vapour-phase chromatography (v.p.c.).

On v.p.c. using a Triton on chromosorb column, Simonsen's sample of "Δ^3-carene-1 : 2-epoxide" from *Zieria smithii*[2] showed three major components: the expected chrysanthenone (II, 70%),[3] linalool (10%), and D-filifolone (Ia, 20%, $[\alpha]^{24}$ + 307°). The structure of (Ia) (except for absolute configuration) was established by i.r., n.m.r., and mass spectral comparison with the racemate.[1],† This substance is conceivably an artifact from chrysanthenone (II), but since it is difficult to imagine a mechanism by which (II) would yield optically active (I), we believe (Ia) to be a natural substance.

The absolute configuration of (Ia) was not known until larger amounts of its mirror image, (Ib), $[\alpha]^{25}$ −270°, became available from *Artemisia filifolia*; (Ib) constitutes 11% of the essential oil of this common Arizona plant. After spectral comparisons of (Ib) with (Ia) and the racemate had shown them to differ only in absolute configuration, L-filifolone was shown to be enantiomer (Ib) in two ways. First, circular dichroism showed L-filifolone to have a negative Cotton effect curve, which from the octant rule and analogy with some closely related cyclobutanones studied by Conia and Gore[4] implies structure (Ib).‡ Finally, L-filifolone was cleaved with base[1] to L-α-fencholenic acid (III, $[\alpha]_D^{25}$ −17°); D-α-fencholenic acid ($[\alpha]_D$ +30·7°) was reported by Cockburn[5] to be derived



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† We thank J. J. Beereboom for a generous sample of the racemate.

‡ We are grateful to Miss A.-M. Henry for measuring this circular dichroism curve and to Prof. G. Ourisson for interpreting it.

from D-fenchone, whose absolute configuration was established much later.[6]

The lower rotation of the L-filifolone (Ib) is probably due to partial racemization [possibly *via* the keten (IV)] on the Carbowax on firebrick v.p.c. column used in the purification of (Ib). This view is supported by the much lower rotations observed for (Ib) and (III) in some early experiments in which the same v.p.c. column was employed at a higher experiments in which the same v.p.c. column was employed at a higher temperature. Another reaction yielding (±)-(I) which could proceed *via* (IV) occurred when chrysanthenone (II, optically active) was passed through a v.p.c. column containing tricresyl phosphate on firebrick. The mechanisms of these reactions are at present obscure; it should be noted that Beereboom studied the pyrolysis of (±)-(I) at 340°, and found three monocyclic products, all of which might have been formed *via* (IV).[1]

We thank the U.S. Public Health Service for financial assistance.

(*Received, August* 14*th*, 1967; *Com.* 870.)

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