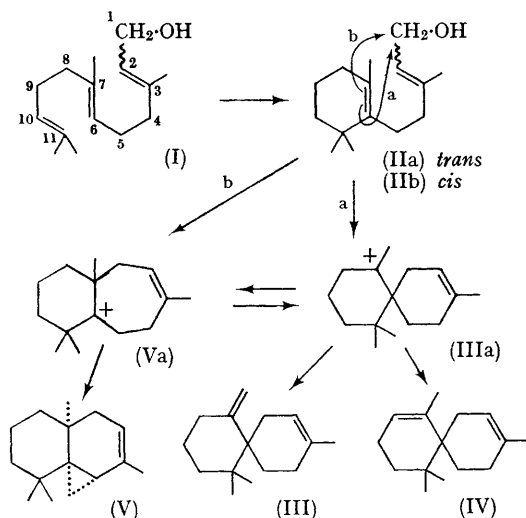


Biogenetic-type Synthesis of (\pm)- α -Chamigrene

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ONE of the possible biogenetic pathways¹ from farnesol (I) to chamigrene² (III), α -chamigrene† (IV), and thujopsene³ (V) might be the cyclization of *cis*-monocyclofarnesol (IIb), as shown in the scheme, without specifying the *cis-trans*-isomerization stage of the alcohols that are involved.



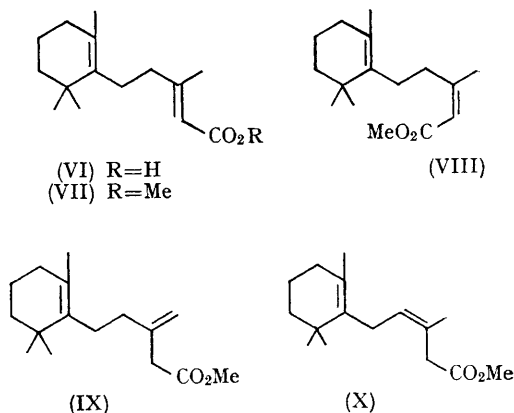
Cyclizations, in which C(1) of (IIb) joins with C(6) (path a) and C(7) (path b), lead to the formation of (III), (IV), and (V) through the intermediates (IIIa) and (Va), respectively.

Although chamigrene has already been synthesized,⁴ our interest in a biogenetic-type synthesis of the chamigrene skeleton prompted us to examine the cyclization of *cis*- and *trans*-monocyclofarnesols (IIa and IIb) which were prepared in relatively high yield by the following reactions (these and their related compounds have been prepared by other methods,⁵ especially by the acid-catalyzed cyclization⁶ of farnesic acid).

Condensation of dihydro- β -ionone with triethyl phosphono-acetate, followed by hydrolysis afforded *trans*-monocyclofarnesic acid (VI) in 30% yield.

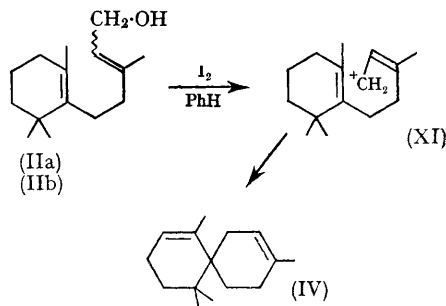
After removal of (VI) and esterification of the remaining acids with diazomethane, the mixture of esters was separated by chromatography on AgNO_3 - SiO_2 to give (VII), (VIII), (IX), and (X) in

relative yields of 25, 22, 33, and 20%, respectively. Their structures were assigned on the basis of the physical data.



Compound (VII) was also transformed into a mixture of (VIII) and (X) by irradiation with a 400 w mercury lamp. Reduction of (VII) and (VIII) with lithium aluminum hydride afforded the corresponding alcohols, (IIa) and (IIb), respectively. The n.m.r. spectra[‡] of these alcohols were consistent with the assigned structure:⁷ (IIa): δ 1.69 (C_3 -Me, d, $J = 1$), 5.34 (C_2 -H, bt, $J_1 = 6.5$), 4.05 (C_1 -H, d, $J = 6.5$), (IIb): δ 1.78 (C_3 -Me, d, $J = 1.5$), 5.34 (C_2 -H, bt, $J = 7$), 4.03 (C_1 -H, dd, $J = 7, 1.5$). Dehydration and simultaneous cyclization of (IIa) and (IIb) were carried out by treatment of these alcohols with iodine in benzene solution at room temperature.

Interestingly, both (IIa) and (IIb) gave the same



† Isolated from the essential oil of *Schisandra chinensis* by Dr. Y. Hirose (private communication).

‡ Measured in CCl_4 with reference to Me_4Si as internal standard.

three hydrocarbons, although the relative rates of dehydration of these alcohols were different. These three components were separated by chromatography on $\text{AgNO}_3\text{-SiO}_2$ in relative yields of 23, 25 and 26%, respectively. One of the components (25%) was identical with authentic α -chamigrene (IV), by comparison of the i.r. and

n.m.r. spectra, and might be formed through the intermediate (XI). Structure elucidation of two other components is the subject of further study.

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