CHEMISTRY LETTERS, pp. 769-772, 1973. Published by the Chemical Society of Japan

CHEMICAL PROOF OF ENANTIOMERIC (-)-LONGIBORNEOL[1]

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During the course of investigation on constituents of liverworts, four sesquiterpenoids showing opposite rotation, (-)-longiborneol, (-)-α-longipinene, (-)-longifolene and (+)-α-himachalene, were isolated from a Japanese liverwort. By preparation of derivatives and application of physical methods the absolute configuration of (-)-longiborneol, the main component, was elucidated as an optical antipode (I) of (+)-longiborneol isolated from higher plants.

The liverworts (Hepaticae) which form a unique group in the plant kingdom are constituted of haploidal plant bodies growing from the spores, and in the cells several oil bodies are contained. From liverworts, thus, several novel sesquiterpenoids, bazzanene,[2] chiloscyphone,[3] pinguison,[4] frullanolide,[5] bazzanenol,[6] myliol[7] and δ-cuparenol,[8] have been successively isolated up to date. We have now isolated, from a Japanese liverwort (Scapania undulata (L.) Dum.), four sesquiterpenoids, (-)-longiborneol (I), (-)-α-longipinene ($[\alpha]_D$ -33.4°), (-)-longifolene ($[\alpha]_D$ -46.9°) and (+)-α-himachalene ($[\alpha]_D$ +111.5°),[9] which showed respectively opposite signs in optical rotation compared with those isolated from higher plants (Gymmospermae).[10] Since a pair of enantiomorphs has hardly been isolated in the sesquiterpenoid field and also the co-occurrence of these compounds is an interesting support for a biogenetic hypothesis, in which they are produced from trans-farnesyl pyrophosphate, via a common eleven-membered ring carbonium ion, the detailed investigation was carried out on the absolute configuration of the main component, (-)-longiborneol.

(-)-Longiborneol (I), $C_{15}H_{26}O$ (M^{+} 222), mp 106-107°, which was isolated from a hexane extract of the liverwort by elution chromatography with a silica gel column, showed $[\alpha]_D$ -16.3° (0.66 %, $CHCl_3$) and afforded oily acetate (II), $C_{17}H_{28}O_2$

(M^+ 264), $[\alpha]_D$ -3.7° (0.27 %, $CHCl_3$), ν 1740, 1250 and 1035 cm^{-1}, and crystalline 3,5-DNB (III), mp 156-157°, $[\alpha]_D$ -27.1°. Melting points and the IR and NMR spectra of alcohol (I) and derivatives (II, III) were respectively in good agreement with those of (+)-longiborneol ($[\alpha]_D$ +16-21°)10) and its corresponding derivatives, but the signs of these optical rotations were opposite.

Alcohol (I), after being transformed into a hydrocarbon (IV), $C_{15}H_{24}$ (M^+ 204), $[\alpha]_D$ -51.6° (1.03 %, $CHCl_3$) by treatment with $POCl_3$ in pyridine, was subjected to ozonolysis in AcOH to be derived into (-)-longicamphenylone (V), $C_{14}H_{22}O$ (M^+ 206), mp 49-50°, $[\alpha]_D$ -25.5° (0.38 %, $CHCl_3$), ν 1745 cm^{-1}; alcohol (I) was oxidized with Jones reagent to be converted into (-)-longicamphor (VI), $C_{15}H_{22}O$ (M^+ 220), $[\alpha]_D$ -1.8° (1.18 %, $CHCl_3$), ν 1735 cm^{-1}. As to these reaction products (IV-VI), again the IR, NMR and MS spectra showed the coincidence with those of known compounds, (+)-longifolene, (+)-longicamphenylone and (+)-longicamphor, but the signs of the optical rotations were opposite.11) The above-mentioned evidences indicate that alcohol (I) may be characterized as (-)-longiborneol which is the optical antipode of the known compound.

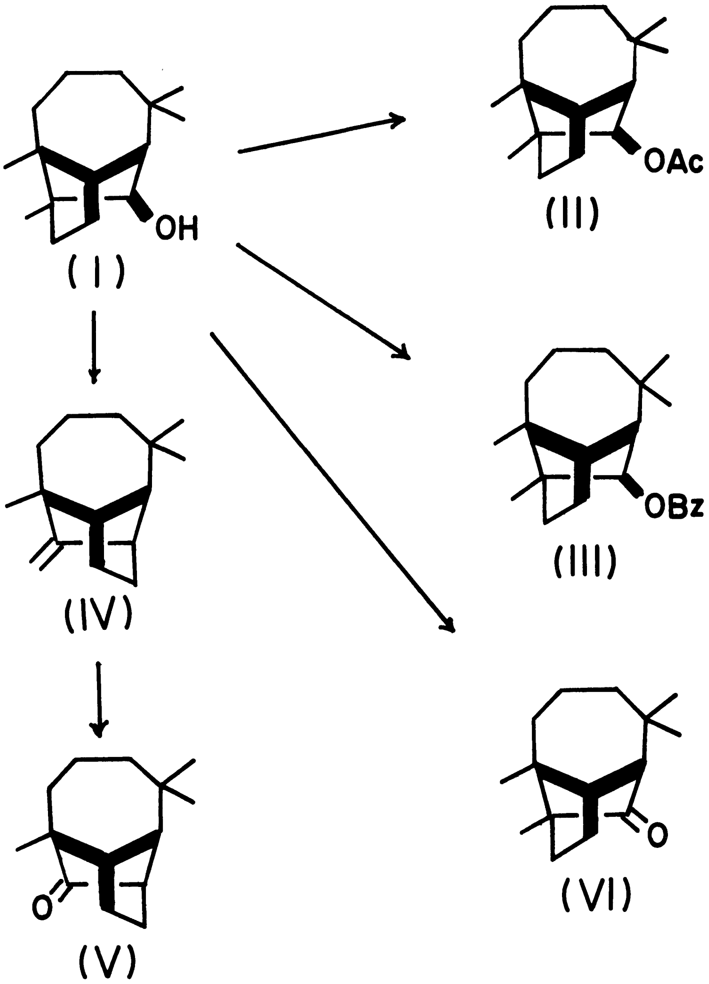
For the confirmation of this deduction, besides the examination of ORD and CD curves was carried out on (-)-longicamphenylone (V) and (-)-longicamphor (VI): (-)-longicamphenylone exhibited a positive Cotton effect ($[\phi]_{315}$ +1740, $[\phi]_{288}$ -2680, a= +44.2; $[\theta]_{304}$ +3750 in MeOH), and (-)-longicamphor a negative one ($[\phi]_{324}$ -1030, $[\phi]_{293}$ +1620, a= -26.5°; $[\theta]_{309}$ -1430 in MeOH). When this result was compared with that reported by Jacob11) on (+)-longicamphenylone ($[\phi]_{320}$ -760, $[\phi]_{292}$ +1750) and (+)-longicamphor ($[\phi]_{325}$ +650, $[\phi]_{295}$ -1530), the absolute configuration of (-)-longicamphenylone should be represented by stereostructure (V) and that of (-)-longicamphor by (VI). Therefore, the absolute configuration of (-)-longiborneol (I), the main alcohol isolated from the liverwort, was determined to be stereostructure (I), except the configuration of the hydroxyl group.

On the other hand, (-)-longiborneol showed $[\alpha]_D$ -16.3° as mentioned above, and its 3,5-DNB $[\alpha]_D$ -27.1°. This fact indicates the hydroxyl group of (-)-longiborneol to have the R configuration according to the benzoate rule.12) The absolute configuration of (-)-longiborneol (I) thus deduced corresponds to the enantiomorph of (+)-longiborneol.

We have isolated (-)-cuparene13) from Bazzania pompeana (Lac.) Mitt., (-)-manool14) from Jungermannia torticalyx Steph., and (+)-maalioxide and (-)-cyclocolorenone15) from Plagiochila acanthophylla Gott. subsp. japonica (Lac.) Inoue.

All these components were optical antipodes of those from higher plant. Thus, it may be said such occurrence of enantiomeric terpenoids of those from higher plants to be a common feature in liverworts. Biogenetic investigation of this alcohol is in progress.

We are grateful to the Ministry of Education of Japan for financial support of this work.



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(Received April 26, 1973)