

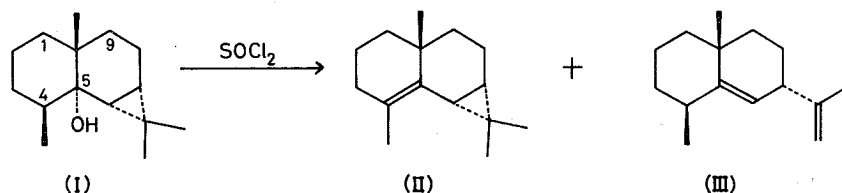
(-)-Maalian-5-ol, a new enantiomeric sesquiterpenoid from the liverwort *Plagiochila ovalifolia*A. Matsuo, H. Nozaki, H. Kataoka, M. Nakayama and S. Hayashi¹*Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, 730 Hiroshima (Japan), 16 January 1979***Summary.** A new enantiomeric sesquiterpene alcohol named (-)-maalian-5-ol was isolated from the liverwort, and the structure and absolute configuration was determined to be the stereostructure **I** by chemical and spectral evidence.

In the course of our investigation on terpenoids from the liverworts (Hepaticae), which form a unique group in the plant kingdom, several enantiomeric sesquiterpenoids² being antipodes to the normal ones from vascular plants were isolated along with several novel carbon skeletal sesquiterpenoids³. The present communication deals with the isolation and the structure determination of an additional new enantiomeric sesquiterpene alcohol, named (-)-maalian-5-ol, from the leafy liverwort, *Plagiochila ovalifolia* Mitt. belonging to the Plagiochilaceae in the Jungermannineae.

The liverwort (860 g), collected at Kuju in Kyushu and dried in the shade for a few days, was digested with methanol. The methanol solution, after being concentrated in vacuo, was then extracted with ether and the solvent was distilled out at reduced pressure to afford a viscous matter (10.2 g). Part of the extract (6.8 g) was chromatographed over silica gel with a mixed solvent of chloroform and ether (v/v, 5:1) to isolate the new sesquiterpene alcohol (150 mg) as a major constituent. Spectroscopic evidence showed that the compound, C₁₅H₂₄O (M⁺ 222.1990), [α]_D +106° (c 2.5, CHCl₃), was a saturated tricyclic sesquiterpene alcohol containing a cyclopropane ring [δ_{CDCl₃} 0.4–0.8 (2H, com-

hexane as a solvent. The spectral properties of the former (**II**), C₁₅H₂₄ (M⁺ 204); ν_{CCl₄} 1230, 1140, 1070, 973 and 953 cm⁻¹; δ_{CDCl₃} 0.83, 0.99 and 1.09 (each 3H, s), 1.57 (3H, br.s), coincided with those of (-)-β-maaliene reported by Büchi et al.⁴, and the latter (**III**), C₁₅H₂₄ (M⁺ 204); ν_{CCl₄} 3060, 1650, 1210, 985, 955, 900 and 885 cm⁻¹; δ_{CDCl₃} 1.15 (3H, d, J=8.0), 1.14 (3H, s), 4.65 and 4.78 (each 1H, br.s), 5.20 (1H, d, J=4.0), did with those of (+)-selina-5,11-diene⁴. However, the optical rotations of both the sesquiterpene hydrocarbons (**II**, [α]_D +129° and **III**, [α]_D -145°) derived from (-)-maalian-5-ol (**I**) gave opposite sign compared with the values ([α]_D -138° and [α]_D +149°) of the known compounds⁴.

Accordingly, it was certain that the alcohol consists of the structure and absolute configuration, excluding the tertiary hydroxyl group on C-5, as shown in the stereostructure **I**. Next, the configuration of the hydroxyl group was elucidated by examination of the solvent effect on ¹H-NMR spectra to be trans to both the methyls on C-4 and C-10: when the ¹H-NMR spectra of the alcohol (**I**) were measured in CDCl₃ and C₂D₂N solutions, the C-4 secondary methyl (Δ 0.04) and the C-10 tertiary methyl (Δ 0.02)



plex)] together with a tertiary hydroxyl group [ν_{CCl₄} 3625 and 3500 cm⁻¹; no signal between δ 3.0 and 4.5], a secondary methyl [δ 0.93 (3H, d, J=7.5)] and 3 tertiary methyls [δ 1.00, 1.05 and 1.10 (each 3H, s)]. This structure was supported by the off-resonance ¹³C-NMR spectrum which showed 3 singlets (δ 17.6, 36.4 and 75.0), 3 doublets (δ 20.4, 32.9 and 34.1), 5 triplets (δ 16.9, 21.6, 30.0, 31.0 and 37.0) and 4 quartets (δ 16.5, 16.5, 23.4 and 31.0). The alcohol (120 mg) was dehydrated with SOCl₂ in pyridine to yield 2 kinds of hydrocarbons, which were, respectively, isolated as a less polar (40 mg) and a more polar (40 mg) product by means of preparative TLC over silica gel using

exhibited no solvent shift due to vicinal deshielding of the C-5 hydroxyl group⁵.

On the basis of the above chemical and spectroscopic evidence, the structure and absolute configuration of the sesquiterpene alcohol, (-)-maalian-5-ol, was determined to be shown by the stereostructure **I**. This may be biosynthesized from trans-farnesyl pyrophosphate via (-)-bicyclogermacrene which has been isolated as a common component in the liverworts⁶. We were interested in such occurrence of the enantiomeric sesquiterpenoids in the liverworts with respect to a chemotaxonomy of the plants and a biogenesis of the compounds.

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- At our laboratory (-)-bicyclogermacrene were isolated from the following liverworts, *Porrella densifolia*, *Plagiochila semidecurrens*, *Lepidozia vitrea*, *Riccardia jackii*, etc. (unpublished data).