X-Ray Crystal and Molecular Structure of the *p*-Bromobenzoate of (−)-Myliol, a Novel Tetracyclic Sesquiterpene Alcohol from *Mylia taylorii* (Liverwort) Containing Two Conjugated Cyclopropane Rings. Revision of a Proposed Structure

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Summary The structure and absolute configuration of (−)-myliol (II) was determined by *X*-ray diffraction analysis of the *p*-bromobenzoate (III); the results lead to a revision of the previously proposed structure (I).

THE gross structure (I) was proposed for myliol on the basis of extensive degradation experiments and spectral analysis.[1] We now report *X*-ray measurements on the *p*-bromobenzoate of (−)-myliol, $C_{15}H_{22}O$, m.p. 111—112 °C, $[\alpha]_D$ −20·0°, which lead to the revised structure (II).

The *p*-bromobenzoate (III), $C_{22}H_{25}BrO_2$, m.p. 148—149 °C, $[\alpha]_D$ +23·7°, crystallized with two molecules per asymmetric unit in the triclinic space group, $P\bar{1}$; a = 10·37-

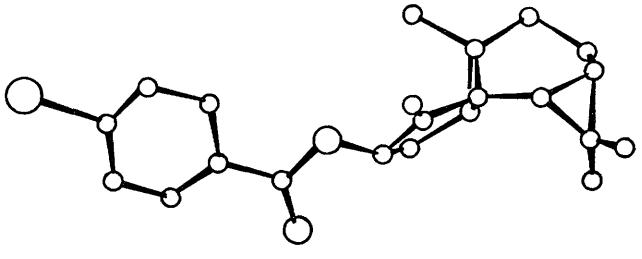
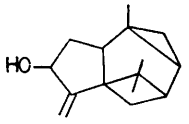
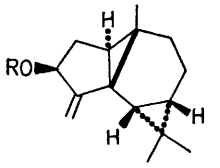


FIGURE. A perspective drawing of the *X*-ray model of the *p*-bromobenzoate (III).

(1), $b = 10{\cdot}20(1)$, $c = 10{\cdot}40(1)$ Å; $\alpha = 107{\cdot}8(1)$, $\beta = 71{\cdot}6(1)$, $\gamma = 110{\cdot}2(1)°$; $D_m = 1{\cdot}38$ g cm^{-3} (in $ZnCl_2$); $D_c = 1{\cdot}39$ g cm^{-3}. The intensity data ($2\theta \leqslant 100°$) were collected on a



(I)



(II) R = H
(III) R = COC_6H_4Br

fully automated diffractometer using Mo–K_α radiation (0·7107 Å). In the refinement of the structure, 2988 reflections having $I > 3\sigma$ (I) were used. The bromine atoms were easily located in a Patterson synthesis.† The subsequent electron density syntheses, which were complicated by a pseudo-inversion centre, finally gave the non-hydrogen atom skeleton of both molecules. 16 hydrogen atoms (except those of the three methyl groups) were placed at calculated positions. Block-diagonal least-squares refinements with anomalous scattering factor corrections for the bromine atoms converged to an R factor of 0·110 for the configuration shown in the Figure and 0·123 for its enantiomorph.[2] The Figure shows a perspective drawing of the X-ray model. Both molecules in the asymmetric unit have the same configuration and identical bond lengths and angles within experimental error (0·02 Å and 0·3°), and they agreed with the accepted values.[3]

The structure and absolute configuration of (—)-myliol should thus be represented by formula (II), containing a novel fused 5,3,6,3-tetracyclic ring system, with the two cyclopropane rings in conjugation. This unique sesquiterpene alcohol is enantiomeric to sesquiterpenoids of higher plants as well as those isolated from the liverworts.[4]

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† All the computations were carried out by means of the HITAC 8700 computer at Hiroshima University. The computer programs used were 'UNICS, Crystallographic Society of Japan (1965)' and slightly modified forms.

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