Gymnomitrol, A Novel Tricyclic Sesquiterpenoid from *Gymnomitrion obtusum* (Lindb) Pears (Hepaticae)

By J. D. CONNOLLY,* A. E. HARDING, and (in part) I. M. S. THORNTON
(*Department of Chemistry, University of Glasgow, Glasgow,* G12 8QQ)

Summary Gymnomitrol, a novel tricyclic sesquiterpenoid alcohol from the liverwort *Gymnomitrion obtusum* (Lindb) Pears, is formulated as (**1**) on chemical and spectroscopic evidence; several related compounds have been isolated and the novel carbon skeleton is shown to be derivable biogenetically from γ-bisabolene *via* a trichodiene intermediate.

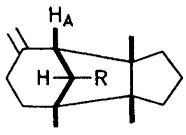
FROM the liverwort *Gymnomitrion obtusum* (Lindb.) Pears we have isolated a number of related sesquiterpenoids with a new tricyclic skeleton. These include the alcohol gymnomitrol (**1**), the corresponding acetate (**2**), epoxygymnomitrol acetate (**7**), the epoxide diacetate (**10**) and the hydrocarbon (**15**).

The major component, gymnomitrol (**1**), $C_{15}H_{24}O$, m.p. 114—116°, $[\alpha]_D + 7°$, had, in its n.m.r. spectrum, three tertiary methyls, an exomethylene, and a secondary alcohol (δ 3·69 p.p.m., sharp s) and is therefore tricyclic. Additionally there was a sharp singlet (H_A) at δ 2·31 p.p.m. which had a small coupling to the carbinol proton and was also allylic since it was clearly coupled to the new carbinol proton in hydroxy-acetate (**3**) obtained by ozonolysis and sodium borohydride reduction of gymnomitrol acetate (**2**) m.p. 65—66°, $[\alpha]_D + 19°$.

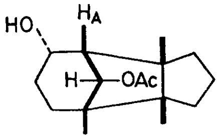
Oxidation of gymnomitrol afforded a cyclopentanone in which H_A was deshielded (δ 2·58 p.p.m.) and had lost its coupling to the original carbinol proton. This evidence leads to the part structure (**4**). The lack of further coupling of H_A and the original carbinol proton requires the adjacent carbon atoms to be fully substituted. Reduction of the ketone (**4**) gave back only the original alcohol (**1**).

Ozonolysis of the ketone (**4**) yielded a diketone (ν_{max} 1710 and 1745 cm^{-1}) in which H_A was further deshielded (δ 2·91 p.p.m.). This β-diketone was not enolisable and in view of the above evidence must form part of a bicyclo[3,2,1]-octane system [as (**5**)].

The presence of two adjacent methylene groups in the six membered ring was established thus: (a) gymnomitrol (**1**), with acid, gave the isomer (**6**) whose n.m.r. spectrum clearly indicated the presence of a vinyl methyl, vinyl proton, and an allylic methylene adjacent to a fully substituted carbon atom as in (**6**), (b) epoxygymnomitrol acetate (**7**), m.p. 149—150°, $[\alpha]_D$ $-27°$ was identical to the major epoxide formed in the reaction of gymnomitrol acetate with peracid. Since attack by peracid would be expected to occur largely from the *exo*-face, the resultant epoxide is β. Compound (**7**) rearranged in acid to (**8**) whose diacetate underwent oxidation to the enone (**9**) (λ_{max} 240 nm).



(1) R = OH
(2) R = OAc
(15) R = H



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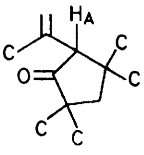

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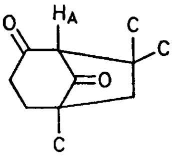

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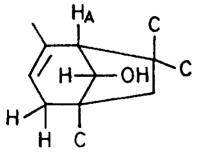
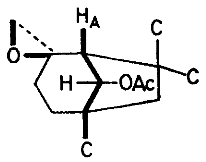


(6)



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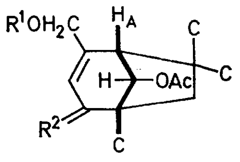
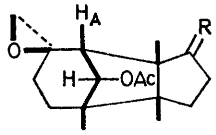
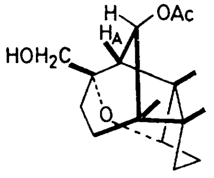


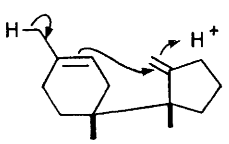
(8) $R^1 = H$; $R^2 = H_2$
(9) $R^1 = Ac$; $R^2 = O$



(10) R = H , βOAc
(11) R = H , βOH
(12) R = O



(13)



(14)

The three tertiary methyls and the remaining ring were accommodated as follows. In the Eu(dpm)$_3$-shifted spectrum of gymnomitrol (**1**), H_A and all three methyls moved downfield by approximately 2 p.p.m. suggesting that all three methyls were near to and approximately equidistant from the hydroxy group. This leads to the stereochemical situation depicted in (**1**).† The remaining carbon atoms must form a second five-membered ring.

The chemical and spectroscopic properties of (**10**), m.p. 155—156°, $[\alpha]_D$ $-60°$, showed that there was an acetate group attached to this second five membered ring. The

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† C.d. results indicate the absolute configuration shown in (**1**).

position and configuration (β) of this acetate [as in (**10**)] was decided on the basis of the $Eu(dpm)_3$ induced shifts of the corresponding hydroxy-acetate (**11**). Oxidation of (**11**) afforded (**12**) which, with borohydride, yielded the ether (**13**) [n.m.r. supports $-\overset{|}{\underset{|}{C}}-CH_2OH$, $-CH_2\overset{|}{C}H-O-$, loss of epoxide] and not the expected epimeric alcohol. The formation of (**13**) provides valuable confirmatory evidence for the constitution and stereochemistry of gymnomitrol (**1**) and its congeners.

A plausible biogenetic derivation of this new skeletal type can be drawn from γ-bisabolene *via* the trichodiene intermediate (**14**)[1-3] which can undergo further cyclisation to the hydrocarbon (**15**). The hydrocarbon (**15**) $[\alpha]_D$ $-26°$ has been isolated from the extract.

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