Journal of

The Chemical Society,

Chemical Communications

NUMBER 11/1973 6 JUNE

Structure of the Triterpenoid Oxide from *Rhododendron macrophyllum*

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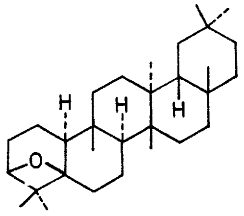
Summary The structure of the triterpenoid oxide from *Rhododendron macrophyllum* has been determined by single crystal *X*-ray analysis.

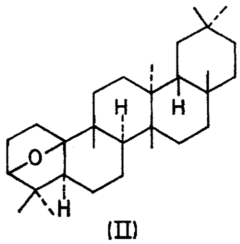
The triterpenoid oxide, variously known as dendropanoxide, epoxyglutinane, and campanulin has been assigned both the structure (I)[1,2] and the structure (II).[3] A related structural study of this compound failed to differentiate between these alternatives.[4] A key piece of evidence in the structural elucidation was the rearrangement of the oxide to a mixture (III and IV respectively) with boron trifluoride etherate or with zinc in acetate acid containing sodium acetate. It was shown that, whereas (III) readily rearranges to (IV),[4] the reverse isomerization does not occur under these conditions and, hence, (IV) does not intervene in the conversion of the natural product into (III).

In an initial investigation of this triterpene, isolated from *Rhododendron macrophyllum*, one of us suggested that the available chemical evidence was better accommodated by (I).[2] However, a subsequent reinvestigation with high resolution n.m.r. data at hand revealed that proton chemical shifts of 3α-H (3·70 p.p.m.) and 4α, 4β, and 9β methyl groups (1·14, 1·17, and 1·19 p.p.m.) were more compatible with (II).[5]

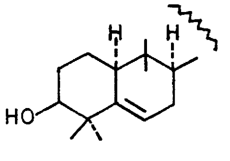
The single crystal *X*-ray structure determination now confirms the structure of this triterpene as (II).



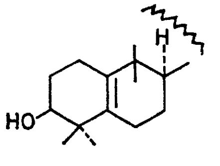
(I)



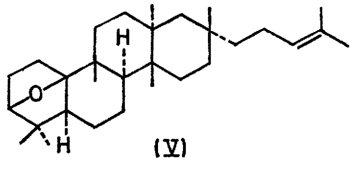
(II)



(III)

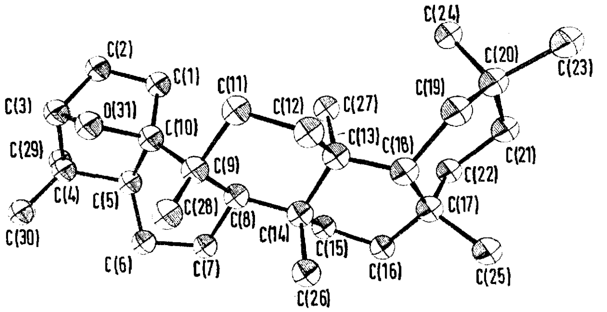


(IV)



(V)

Crystals of campanulin belong to the common orthorhombic space group $P2_12_12_1$ with $a = 6{\cdot}294(6)$, $b = 28{\cdot}89(3)$, $c = 13{\cdot}93(1)$ Å, D_c 1·12 g cm^{-3}, $Z = 4$ was interpreted to mean one molecule of $C_{30}H_{50}O$ per asymmetric unit. A total of 1888 independent reflections were measured on a fully automated Hilger-Watts diffractometer using Ni-filtered Cu-K_α (1·5418 Å) radiation. A total of 1078 were judged to be observed after data work-up. The structure was solved by a multisolution tangent formula approach followed by recycling a plausible chemical fragment through the tangent formula.[6] Full-matrix least-squares refinements smoothly converged to the present minimum of 0·11 for the conventional crystallographic discrepancy index.[7] The most significant aspect of the structure (Figure) is the C(3)–O(31)–C(10) oxide bridge.



FIGURE

Thus, the structure of dendropanoxide and epoxyglutinane, with which the extractive of *Rhododendron macrophyllum* is identical, must be corrected to (II). Formation of (III) from this material can be explained by invoking a 1,2-shift of 5α-H, concerted with oxide ring opening, to give a C(5) carbonium ion intermediate, from which proton elimination yields the two olefins (III) and (IV).[5] Assignment of the 3,10-oxide structure (II) is in accord with the recently revised structure (V) for baccharis oxide.[8]

J. D. W. thanks the National Science Foundation for support and J. C. thanks the Camille and Henry Dreyfus Foundation.

(*Received*, 16*th February* 1973; *Com.* 214.)

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