X-Ray Structure and Absolute Configuration of (+)-Edunol

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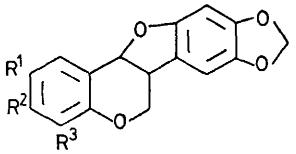
Summary The *X*-ray structure of (+)-edunol (as its 4-bromo-3-methoxy derivative) confirms its conformation and absolute configuration.

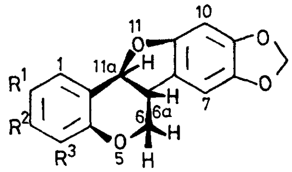
THE phytoalexin (−)-edunol [(**1**), (6a*R*,11a*R*)] was first isolated from *Neorautanenia edulis*[1] while the enantiomeric (+)-edunol [(**1**), (6a*S*,11a*S*)] was recently isolated from *N. amboensis*. Our interest in pterocarpan phytoalexins has been stimulated by a report[2] that antitumour activity is shown by several members of this group. (+)-Edunol is of special interest in that dextrorotatory isomers (*e.g.* trifolirhizin) showed superior antitumour activity to laevorotatory forms.[2]



(1) $R^1 = CH_2CH{=}CMe_2$; $R^2{=}OH$; $R^3{=}H$

(2) $R^1 = R^3{=}H$; $R^2{=}O$-glucose

(3) $R^1 = CH_2CH{=}CMe_2$; $R^2{=}OMe$; $R^3{=}Br$



(4) $R^1 = CH_2CH{=}CMe$; $R^2{=}OMe$; $R^3{=}Br$

Relative and absolute configuration assignments of pterocarpans have hitherto been based mainly on optical rotation and o.r.d.[3] data. Absolute configuration assignments in solution of all dextrorotatory (6a*S*,11a*S*) and laevorotatory (6a*R*,11a*R*) pterocarpans followed from the establishment of the absolute configuration at C-11a of trifolirhizin[4] (**2**) as *R* and on the indication that the heterocyclic rings are *cis*-fused[5] as is evident from n.m.r. studies.[5] Since this has become an important method for determining the absolute configuration of pterocarpans, it seemed imperative to verify this assignment unambiguously by *X*-ray analysis.

The bromo-derivative (**3**) was formed by stirring a mixture of (+)-edunol (1 mmol), *N*-bromosuccinimide (1 mmol), and benzoyl peroxide (1 mg) in CCl_4 for 30 min at 50 °C under N_2. The resulting product, after methylation with CH_2N_2, gave (**3**), $C_{22}H_{21}BrO_5$, as orthorhombic crystals ($P2_12_12_1$) with $a = 21{\cdot}486$, $b = 11{\cdot}348$, $c = 8{\cdot}357$ Å, $D_m = 1{\cdot}42$, $D_c = 1{\cdot}44$ g cm^{-3} for $Z = 4$. Intensities of 1136 independent reflections were measured by an automatic Philips diffractometer (Mo-K_α radiation, graphite monochromator).†

The structure was solved by the heavy-atom technique and refined by the anisotropic least-squares procedure to $R = 0{\cdot}059$. At this stage the enantiomeric structure was refined under identical conditions. It converged at $R = 0{\cdot}067$, which shows that this structure may be rejected[6] in favour of the former.

The solid-state conformation, therefore, confirms the initial assignment of absolute configuration to (+)-edunol (**4**) (6a*S*,11a*S*) and hence the absolute configuration assignments of all other pterocarpans.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should accompanied by the full literature citation for this communication.

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