Revised Structures of the Triterpenes Q, T, and U from *Salacia prinoides* DC; *X*-Ray Crystal Structure of Triterpene T

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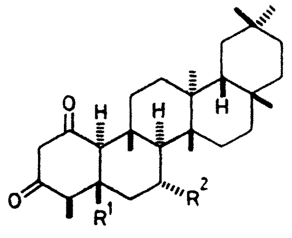
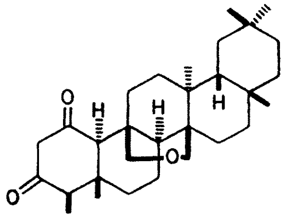
Summary. An *X*-ray study of triterpene T ($C_{30}H_{48}O_3$) has shown that the related compounds Q, T, and U which are derivatives of 1,3-diketofriedelane have their third oxygen function at C(26) intead of C(24) as previously proposed; rings D and E occur in a *cis*-fused boat–boat ('trimaran') conformation.

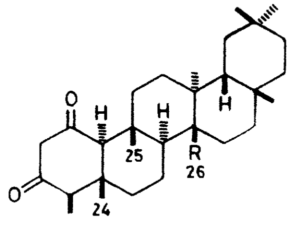
We have reported earlier the isolation of several friedelane-type triterpenes (P, Q, R, S, T, and U) from the root bark of *Salacia prinoides* DC.[1–3] Of these the structures of P and S have been proved to be (**1**) and (**2**) respectively by direct correlation with compounds of established structures. The structure of R was established as (**3**) by an *X*-ray study of its dibromo-derivative.[2]



(**1**) $R^1 = Me$, $R^2 = H$
(**2**) $R^1 = Me$, $R^2 = OH$
(**4**) $R^1 = CHO$, $R^2 = H$
(**5**) $R^1 = CH_2OH$, $R^2 = H$
(**6**) $R^1 = CO_2H$, $R^2 = H$



(**3**)



(**7**) R = CHO
(**8**) R = CH_2OH
(**9**) R = CO_2H

The remaining compounds, Q, T, and U, were mutually interrelated and formulated as (**4**), (**5**), and (**6**), respectively. The assignment of the hydroxy-group in T rested on mass spectral evidence and similarities in the melting points and optical rotations of the 1,3-bis-deoxo-derivative and its acetate with those of 24-hydroxy-friedelane and 24-acetoxy-friedelane respectively.[4] However we had commented on the significant difference in the melting points of the aldehyde from T and friedelan-24-al.[1] Rangaswami and co-workers have also reported the isolation of compound Q (designated by them as D)[5] and formulated it as (**4**) by conversion into the 1-deoxo-derivative and comparison of its melting point with that of the known 3-oxo-friedelan-24-al.[6] But no direct comparison appears to have been made.

Since the structure of R had been established as (**3**), it appeared possible that its congeners Q, T, and U could also have their oxygen substituents at C(25) or C(26) instead of C(24). To settle this point, an *X*-ray structure determination of compound T was undertaken.

Crystal data: monoclinic, space group $P2_1$, $a = 14.626(1)$, $b = 13.279(1)$, $c = 6.743(1)$ Å, $\beta = 101.00(1)°$, $Z = 2$. The structure was solved by direct methods and refined to $R = 0.054$ for 2469 observed reflexions.† The Figure shows that structures Q, T, and U must be revised to (**7**), (**8**), and (**9**) respectively. The only other friedelane derivatives reported as oxygenated at C(26) are friedelan-3-on-26-oic acid (trichadonic acid), friedelan-3α-ol-26-oic acid (trichadenic acid A), its acetate, and 3β-acetoxy-friedelan-26-oic acid (acetyl trichadenic acid B), all isolated from *Trichadenia zeylanica* Thw.[7]

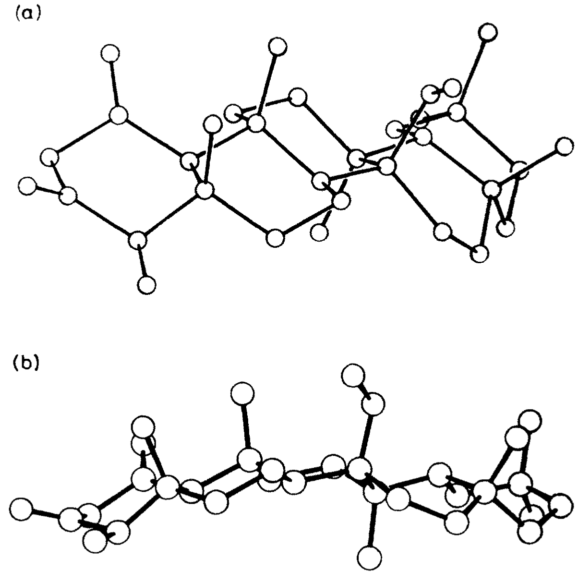


Figure. Two views of the molecular structure of compound (**8**).

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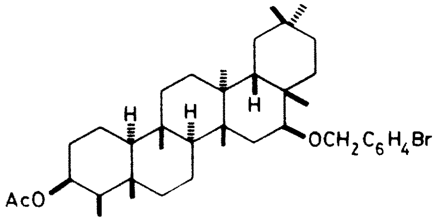
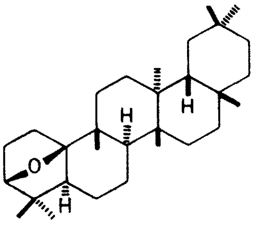
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Rings D and E have the *cis*-fused boat–boat (S, stretched)[8] conformation (resembling a capsized trimaran) previously found in compound R (**3**),[2] in 3-*O*-acetyl-16*β*-*O*-*p*-bromobenzoylpachysandiol B (**10**),[8] and in 3*β*-friedelanol.[9] Here, as in those three molecules, ring E is quite regular, but D is less so. In contrast, the *cis*-decalin chair–chair (F, folded)[8] conformation has been found in campanulin (**11**),[10] and possibly in 3α-friedelanol chloroacetate,[11] though this latter conclusion was based on a poorly resolved two-dimensional map. In T the opening of the ether bridge that exists in R allows the pentacyclic system to become more distinctly bowed (convex on the *β* side) as a result of the numerous *β*-substituent interactions [see Figure (b)], and the geometry and torsion angles (especially in rings C, D, and E) correspond quite well with those found in 3*β*-friedelanol. The similarities are consistent with the fact that there are no intra- or inter-molecular hydrogen bonds in the present crystal structure, and that calculations and stereopictures of the packing reveal no significant constraints that would dictate the shapes of rings D and E. The principal directing factor appears to be a C(27)–C(30) separation which, for a chair–chair conformation, becomes uncomfortably tight when bowing occurs. We believe the bowing to be the major driving force in the extraordinary, concerted series of four methyl and two hydrogen shifts which convert friedel-3-ene into olean-12-ene.[11,12]



(10)



(11)

The molecule of campanulin (**11**) does not exhibit bowing of rings A, B, C, and D, and this appears to be owing to the absence of methyl C(24), to a reversed *trans*-fusion of rings A and B, and to the presence of the 3*β*–10*β* epoxide: it is in fact partway toward the oleanane stereochemistry. In the absence of bowing, its D and E rings manage with the aid of some torsional strain to achieve the chair–chair conformation and a C(27)–C(30) separation of 3·31 Å. We are inclined, therefore, to regard campanulin as exceptional and not a true guide to the conformational preference of the D/E rings in the friedelins, which is known to be sensitive to strain imposed by substitution, for Kikuchi *et al.*[8] report that n.m.r. spectroscopy reveals it to be chair–chair for bulky 16α-substituents and boat–boat for 16*β*. This makes the original conclusion of a chair–chair in 3α-friedelanol chloroacetate[11] the more interesting and unlikely, and we think that that compound should be re-examined.

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