Crystallographic Structure Determination of a Triterpene Dimethyl Ester ε-Lactone from Dammar Resin

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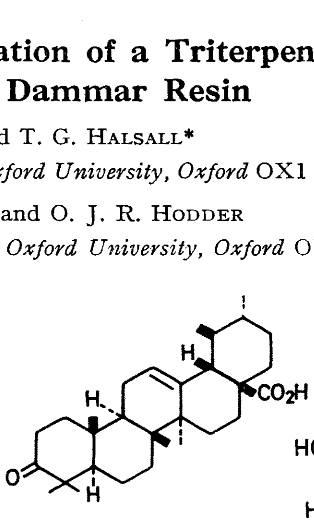
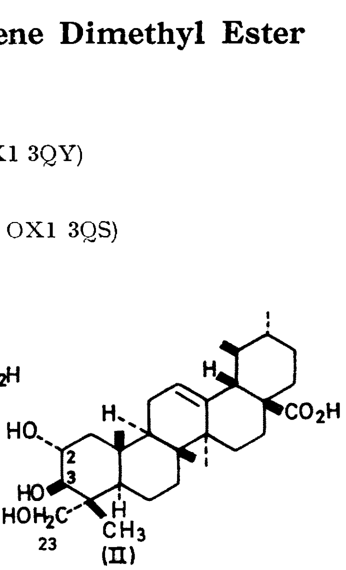
Summary A triterpenoid dimethyl ester ε-lactone isolated from dammar resin has been shown by *X*-ray crystallographic examination to be 23-hydroxy-2,3-secours-12-ene-2,3,28-trioic acid (2 → 23)-lactone 3,28-dimethyl ester (IV): it is probably formed biogenetically by oxidation of asiatic acid (II).

SOME years ago a triterpenoid unsaturated dimethyl ester lactone ("compound B"), m.p. 234—236°, $[\alpha]_D + 117°$ was isolated[1] from dammar resin in small quantity along with ursonic acid (I) and asiatic acid (II).[2] The elemental analysis and i.r. spectrum of "compound B" indicated a molecular formula of $C_{32}H_{50-52}O_6$ and the presence of two methoxycarbonyl groups and a δ-lactone. Its u.v. spectrum suggested that it might be an ursane derivative. Lack of material has prevented further chemical work on this compound but the recent developments in *X*-ray crystallography have now enabled the structure to be determined on one of the few remaining crystals.

"Compound B" forms triclinic crystals in the non-centrosymmetric space group $P1$, with $Z = 1$, and $a = 7{\cdot}01$, $b = 9{\cdot}16$, $c = 11{\cdot}72$ Å, $\alpha = 90{\cdot}62$, $\beta = 92{\cdot}03$, and $\gamma = 100{\cdot}42°$. 3180 reflections out to a Bragg angle of 80° were collected on a computer-controlled, four-circle diffractometer using Ni-filtered Cu-K_α radiation. The structure was solved with a computer programme based on the tangent formula[3] applied in a manner similar to that suggested by Germain and Woolfson.[4] The molecular structure is the dimethyl ester ε-lactone (IV) with the molecular formula $C_{32}H_{48}O_6$: the original analysis is correct for this formula. So far 47 of the 48 hydrogen atoms have been placed with difference-Fourier syntheses, and R is 0·05. All bond lengths and angles are as expected except for some longer bonds (1·58—1·59 Å) between highly substituted carbon atoms (*e.g.* C-9 and C-14). The presence of the ε-lactone group is novel in the pentacyclic triterpene field.


(I)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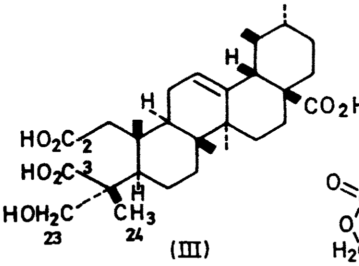
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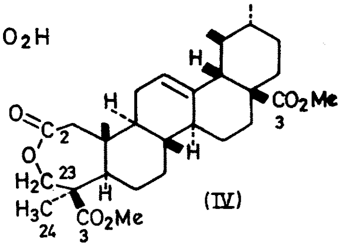
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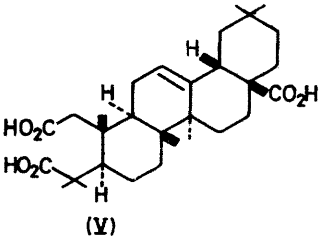
(V)

The biogenetic origin of "compound B" can be explained by assuming that it originates from asiatic acid (II) with which it occurs in dammar resin. Oxidation of the 2α,3β-diol grouping in asiatic acid could lead to the 2,3-seco-trioic acid (III). Lactonisation of the C-2 carboxy-group with the C-23 hydroxy-group and esterification of the free carboxyl groups would then afford "compound B." A naturally occurring 2,3-seco-dioic acid (V)[5] is already known.

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