Structure of Rhuslactone, an Unusual Dammarane-type Triterpene Lactone with a 17α-Side Chain from *Rhus javanica* L.

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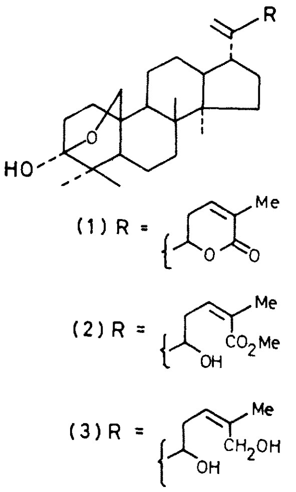
Summary The structure of rhuslactone (**1**), a new triterpene with a novel dammarane-type skeletal structure, having a 17α-oriented side chain, isolated from the bark of *Rhus javanica* L., has been established from spectral data and by single crystal *X*-ray analysis of its corresponding triol (**3**).

The bark extract of *Rhus javanica* L. (Anacardiaceae) has been used in Korea as a folk medicine in the treatment of liver diseases, but no chemical studies have been described. We report here the isolation and structure-elucidation of a novel, modified dammarane-type triterpene, for which we suggest the name rhuslactone (**1**).



The methanol extract of the bark was separated by partition methods, and column chromatography of the neutral fraction on silica gel afforded rhuslactone as colourless needles, m p 199—200 °C, $[\alpha]_D^{20}$ +54 1° (*c* 0 51, $CHCl_3$), i r (KBr) 3520 (OH) and 1715 (C=O) cm^{-1}, u v (EtOH) end absorption only The molecular formula, $C_{30}H_{44}O_4$, was indicated by a combination of elemental analysis, mass spectrometry (M^+, 468), and ^{13}C n m r spectroscopy The 100 MHz ^1H n m r spectrum ($CDCl_3$) showed four methyl singlets at δ 0 84, 0 87, 0 96, and 1 00, one vinyl methyl singlet at δ 1 90, one exo methylene group at δ 5·20 (d, *J* 4 Hz) and one CH_2O group at δ 3 7 (*J* 9 Hz) and 4 2 (J_1 9, J_2 3 Hz) (AB part of ABX type), in addition to a vinyl multiplet at δ 6 58 and a lactone >CHO– double doublet at δ 4 70 (J_1 11 Hz, J_2 5 Hz) The ^{13}C n m r spectrum (25 05 MHz, $CDCl_3$) showed a signal at 98 0 (s) p p m due to the hemi-acetal carbon atom in addition to the expected signals† These data suggest that (**1**) is a tetracyclic triterpene possessing a six-membered lactone ring in a side chain

Treatment of (**1**) with alkali, followed by methylation using diazomethane gave a product (**2**) with a u v spectrum typical of a conjugated ester (λ_{max} 220 nm, ε 9800) indicating that (**1**) possesses an $\alpha\beta$-unsaturated lactone $LiAlH_4$ reduction of (**1**) gave the corresponding triol (**3**), crystals of which, grown from EtOH, were suitable for a single-crystal *X*-ray analysis

Crystal data $C_{30}H_{48}O_4$, $M = 472$, monoclinic, space group $P2_1$, $a = 7\ 457(4)$, $b = 29\ 111(15)$, $c = 6\ 280(3)$ Å, $\beta = 111\ 8(1)°$, $Z = 2$ A total of 2351 reflections were recorded in the 2θ–ω scan mode using a Philips four-circle diffractometer with graphite-monochromated Cu-K_α radiation The structure was solved by direct methods with the aid of the multisolution technique[1] All hydrogen atoms except those of the terminal methyl group of the side chain and the 3α-hydroxy-group were eventually located on a difference electron-density synthesis map and included in subsequent calculations Block-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms, and isotropic temperature factors for hydrogen atoms converged to a conventional *R*-value of 0 048 ‡ Since the molecule contains only a small proportion of oxygen atoms, we did not attempt to determine the absolute configuration by *X*-ray methods using oxygen as an anomalous scatterer The Figure shows a computer-generated perspective drawing of (**3**)[2] The absolute configuration follows from the known configuration of dammarane-type triterpenes All bond distances and angles agree well with accepted values for given bond types and there are no abnormal, short, intermolecular contacts Ring A adopts a boat conformation and the configuration of the substituent at C(22) is (*S*), based on the assumed absolute configuration of the parent skeleton The ^1H and ^{13}C n m r spectra are consistent with structure (**3**) Based on the above results, the structure of rhuslactone should be represented by the structure (**1**) To the best of our knowledge, rhuslactone is the first example of a naturally occurring dammarane-type triterpene, having a 17α-oriented side chain

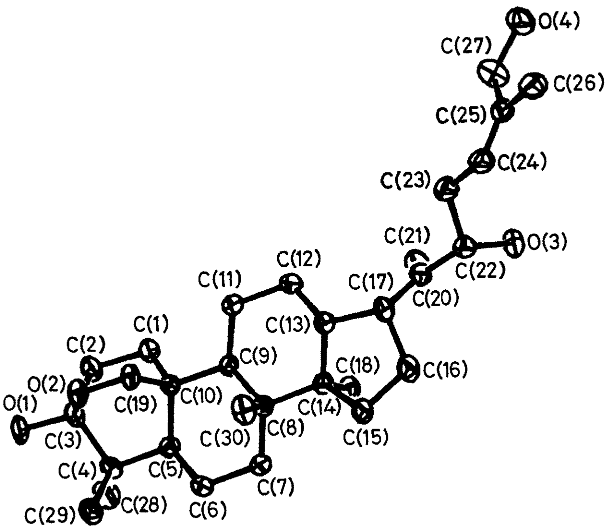


FIGURE The molecular structure of (**3**) Hydrogen atoms are omitted for clarity and no absolute configuration is implied

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† ^{13}C N m r data for (**1**), chemical shift (p p m) and multiplicity 15 4 (q), 16 5 (q), 16 9 (q), 18 5 (q), 19 8 (t), 23 1 (t), 25 3 (t), 26 7 (q), 28 9 (t), 29 5 (d), 30 1 (t), 33 0 (t), 33 0 (t), 35 4 (s), 35 5 (t), 39 6 (s), 40 0 (d), 40 3 (s), 44 9 (t), 45 3 (t), 49 2 (s), 49 8 (d), 67 7 (t), 80 6 (d), 113 4 (t), 128 0 (s), 138 9 (d), 148 9 (s), and 165 6 (s)

‡ 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 requests should be accompanied by the full literature citation for this communication

[1] P Main, M M Woolfson, L Lessinger, G Germain and J P Declercq, MULTAN 74, 'A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-ray Diffraction Data,' Universities of York, and Louvain-la-Neuve, Belgium, 1974
[2] C K Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965