X-Ray Crystal and Molecular Structure of the Triterpenoid 24,25-Dibromokulactone

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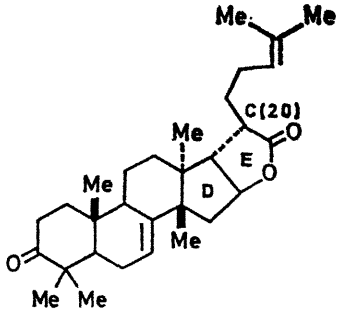
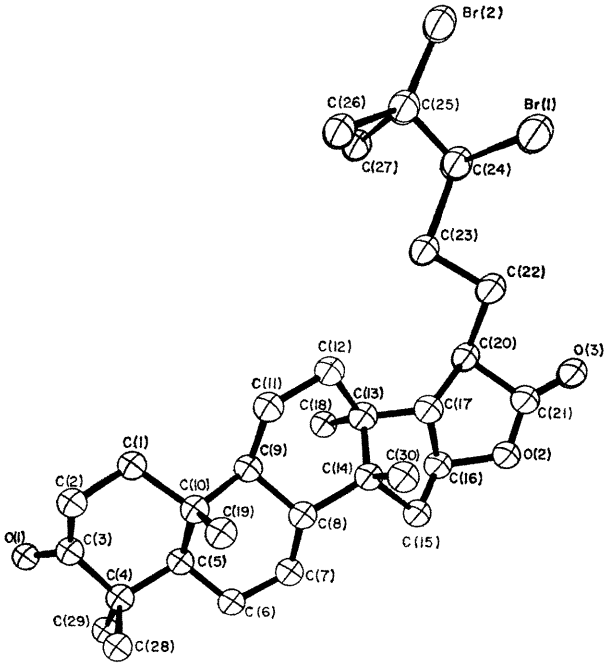
Summary The molecular structure of this novel tetracyclic triterpenoid has been unequivocally determined by single-crystal *X*-ray diffraction techniques.

RECENTLY kulactone (I) was isolated from the Asiatic plant, *Melia azedarach*, L., a plant long used in folk medicine.[1] Chemically kulactone is of interest because of its novel 2-oxa-*trans*-bicyclo[3,3,0]octan-3-one moiety (the D and E rings). A second point of interest involves the configuration of C-20. All compounds previously reported from Meliaceae have been derivatives of the triterpenoid hydrocarbon tirucallane, which has the α-H configuration at C-20. Kulactone is derived from euphane of the 20β-H series. To establish these points unequivocally we undertook a single-crystal *X*-ray diffraction study, of the 24,25-dibromo-derivative of (I) prepared from kulactone by controlled treatment with pyridinium hydrobromide perbromide in pyridine solution; M^+, 610, 612, 614; δ 8·17 and 7·98 p.p.m. and no olefin signal at 4·9 p.p.m. (Δ^{24}).



The dibromo-derivative crystallizes in the monoclinic space group $P2_1$; deduced from the systematic extinctions $0k0$ for $k = 2n + 1$ and the known optical activity. The cell constants determined from a least-squares fit of diffractometer-measured θ values are, $a = 14{\cdot}705$ (5), $b = 6{\cdot}562$ (8), $c = 15{\cdot}395$ (5) Å and $\beta = 78{\cdot}37(9)°$. This implies that there are two molecules per unit cell. Intensity data were collected on a fully-automated Hilger–Watts four-circle diffractometer using Ni-filtered Cu-K_α radiation (1·5418 Å). The unique reflections within a θ sphere of 55° were corrected for background and Lp factors and only 1270 reflections were judged observed.



FIGURE

A sharpened, three-dimensional Patterson synthesis unambiguously revealed one Br. A second full Br could not be found, but a disordered model with two half-Br's was consistent with the Patterson synthesis. An electron

density synthesis revealed all of the remaining 33 non-hydrogen atoms. Using full-matrix least-squares techniques all non-hydrogen atoms were refined anisotropically until the discrepancy index reached its present minimum of 0·11 for the observed reflections.

The Figure is a computer-generated drawing of the final *X*-ray model[2] with the presumed absolute configuration. Br(2) occupies two positions, *anti* and *gauche* to Br(1), approximately equally. Only one conformation is shown. The configuration at C-20 is α. The two five-membered rings [C(13)—C(17), C(20), C(21), and O(2)] are *trans*-fused. The configuration at C(24) is *S*. Rings A and B are in the chair conformation while ring C is in the boat conformation. All bond distances and angles, including those for the 2-oxa-*trans*-bicyclo[3,3,0]octan-3-one moiety, agree well with previously reported values.[3]

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[1] E. C. Chang and C.-K. Chiang, *Chem. Comm.*, 1968, 1156.
[2] C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge, Tennessee, 1965.
[3] "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.