Isolation and Structure Elucidation of Abruslactone A: a New Oleanene-type Triterpene from the Roots and Vines of *Abrus precatorius* L.

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Abruslactone A, a new triterpenoid sapogenin isolated from the roots and vines of *Abrus precatorius* L., has been characterized by spectral and *X*-ray analysis as the γ-lactone of 3β,22α-dihydroxy-olean-12-en-29α-oic acid, with ring E in an unusual boat conformation.

Abrus precatorius L. (Leguminosae), Xiang-si-zi in Chinese, is well known for its beautiful but toxic red and black seeds (rosary peas, jequirity beans).[1,2] Cultivated widely in South China and South East Asia, its seeds, roots, vines, and leaves have all been used as folk medicines in China and in India since ancient times.[3,4] Hitherto most attention has been given to the seeds,[3,5,6] whereas few studies have been reported on the roots[7,8] and other parts of the plant.[3] These facts prompted us to conduct further chemical investigations of the roots and vines of *A. precatorius* L.[9]

Extraction of the dried roots and vines of the plant with methanol afforded a considerable quantity of saponins. On acid hydrolysis with dilute sulphuric acid in aqueous methanol, the crude saponins gave a complex mixture of sapogenins. Its t.l.c. analysis showed at least five spots, the major one yielding a new triterpene here named as abruslactone A (**1**).

Abruslactone A (**1**) crystallized from chloroform–methanol as well-formed prisms, m.p. 329—330 °C. The empirical formula was established as $C_{30}H_{46}O_3$ by elemental analysis. The i.r. spectrum showed a hydroxy-band at 3502 cm^{-1} and a band at 1753 cm^{-1} attributable to a lactone carbonyl group. The nature of the three oxygen functions in the molecule was thus established. The ^{1}H n.m.r. spectrum showed signals corresponding to one vinyl proton and seven methyl groups bonded to quaternary carbon atoms, the latter indicating that (**1**) has a β-amyrin skeleton. The mass spectrum of (**1**) clearly revealed that it belongs to the olean-12-ene type. From the fragmentation pattern in the mass spectrum [*m*/*z* 246 (base peak) and 207, typical of the *retro*-Diels–Alder breakdown[10]] it was evident that the lactone group is located in ring D and/or E, and that the hydroxy-group is attached to ring A or B, most likely at the usual 3β-position. In order to establish the structure and stereochemistry unequivocally, we have investigated (**1**) (see Figure 1) by single crystal *X*-ray structure analysis.

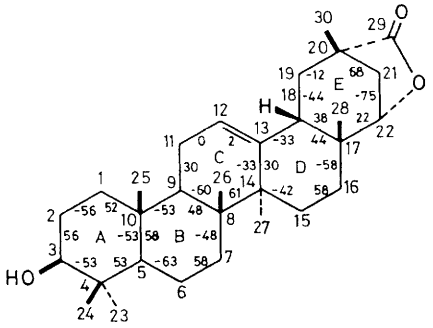

Figure 1. Molecular formula of abruslactone (**1**) showing numbering of the atoms and selected torsion angles (°) in the ring skeleton.

Crystal data: abruslactone A (**1**), $C_{30}H_{46}O_3$, prisms elongated along *a*, M = 454.69, orthorhombic, space group $P2_12_12_1$, a = 7.321(1), b = 12.820(3), c = 26.864(5) Å, U = 2521(1) Å^3, D_m = 1.12 g cm^{-3}, Z = 4, D_c = 1.198 g cm^{-3}, $F(000)$ = 1000, μ(Mo-K_α) = 0.70 cm^{-1}. The unit-cell parameters were obtained from least-squares refinement of 20 high-angle reflections measured on a Nicolet R3m automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Intensities were recorded using the ω–2θ variable scan technique in the bisecting mode for 2θ < 50°. Structure solution by direct phasing was accomplished after many trials with different reflections in the starting set. All C atoms were refined isotropically, the three O atoms anisotropically, and all H atoms except that of the hydroxy-group were introduced at their calculated positions and allowed to ride on their respective parent C atoms with fixed C–H bond distances (0.96 Å) and the same isotropic thermal parameter (0.06 Å^2). Refinement of 1564 observed reflections [|F| >

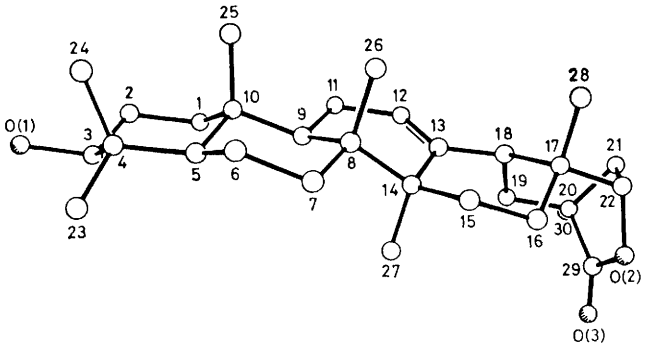

Figure 2. A perspective view of the molecular structure of abruslactone A (**1**). The O atoms are represented by shaded spheres, and all H atoms have been omitted for clarity.

$3\sigma(|F|)$] converged at $R = \Sigma\Delta/\Sigma|F_o| = 0.063$ and $R_w = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.064$, where $\Delta = ||F_o| - |F_c||$ and $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$.† All computations were performed on a DGC Nova 3 minicomputer with the SHELXTL package of crystallographic programs.[11] Analytic expressions of complex atomic scattering factors were employed.[12] The final difference map was virtually flat, with residual maxima and minima lying between 0.25 and -0.25 e Å^{-3}.

The measured molecular dimensions of (**1**) are normal, and molecules related by the 2_1 screw axis parallel to *a* are linked by O(1)–H . . . O(3′) hydrogen bonds (2.872 Å) to form infinite zigzag chains in the crystal lattice. A perspective view of the stereochemistry of (**1**) is illustrated in Figure 2. The six-membered rings A, B, and D are in the chair form, and C assumes a twist conformation owing to the presence of the ethylenic double bond at C-12 (see torsion angles displayed in the molecular formula). The most notable feature is that ring E adopts a boat conformation, which differs markedly from the usual chair conformation observed in the basic olean-12-ene skeletons of hederagenin,[13] 3β-acetoxy-olean-12-en-28-oic acid,[14] sophoradiol,[15] cantoniensistriol,[15] and soyasapogenol B.[16] Examination of a molecular model shows that formation of the γ-lactone ring is facilitated by manipulating ring E into the observed boat conformation.

In the light of the conditions used for its isolation, the new triterpene abruslactone A (**1**) is shown to be present as such in the corresponding naturally occurring saponin rather than derived from the hitherto unknown 3β,22α-dihydroxy-olean-12-en-29α-oic acid, which we have subsequently prepared from the alkali hydrolysis of (**1**) with dilute NaOH in MeOH–EtOH.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23448 (11 pp) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

References

1 J. W. Hardin and J. W. Arena, 'Human Poisoning from Native and Cultivated Plants,' 2nd edn., Duke University Press, Durham, 1974, pp. 81–83.
2 W. H. Lewis and M. P. F. Elvin-Lewis, 'Medical Botany,' Wiley, New York, 1977, p. 42.
3 'Dictionary of Chinese Drugs,' ed. Kiangsu Hsin Yi Medical College, Shanghai People's Press, Shanghai, 1977, pp. 1503–1504 (in Chinese).
4 K. M. Nadkarni, 'Indian Materia Medica,' Popular Prakashan, Bombay, 1976, Vol. 1, pp. 5–7.
5 N. C. Gupta, B. Singh, and D. S. Bhakuni, *Phytochemistry*, 1969, **8**, 791.
6 D. K. Bhardwaj, M. S. Bisht, and C. K. Mehta, *Phytochemistry*, 1980, **19**, 2040.
7 A. Khaleque, Md. Aminuddin, and S. Azim-Ul-Mulk, *Sci. Res. (Dacca, Bangladesh)*, 1966, **3**, 203; through *Chem. Abs.*, 1967, **67**, 90987n.
8 A. Lupi, F. D. Monache, G. B. Marini-Bettolo, D. L. B. Costa, and I. L. D'Albuquerque, *Gazz. Chim. Ital.*, 1977, **9**, 109.
9 H.-M. Chang and T.-C. Chiang, unpublished work.
10 H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, 1963, **85**, 3688.
11 G. M. Sheldrick, SHELXTL User Manual, Revision 3, Nicolet XRD Corporation, Cupertino, 1981.
12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, Vol. 4, pp. 99, 149.
13 R. Roques, D. Druet, and L. Comeau, *Acta Crystallogr., Sect. B*, 1978, **34**, 1634.
14 R. Roques, J. P. Declercq, and G. Germain, *Acta Crystallogr., Sect. B*, 1978, **34**, 2367.
15 T. C. W. Mak, T.-C. Chiang, and H.-M. Chang, *J. Chem. Soc., Chem. Commun.*, 1982, 785.
16 I. Kitagawa, M. Yoshikawa, H. K. Wang, M. Saito, V. Tosirisuk, T. Fujiwara, and K. Tomita, *Chem. Pharm. Bull.*, 1982, **30**, 2294.