

Reissantioloxide: A Novel Epoxytriterpenoid from *Reissantia indica*; X-Ray Crystal Structure¹

Chandra B. Gamlath,^a A. A. Leslie Gunatilaka,^{*a} and Elmer O. Schlemper^b

^a Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

^b Department of Chemistry, University of Missouri, Columbia, Missouri, 65211, U.S.A.

The structure and stereochemistry of reissantioloxide, a triterpene epoxide with a novel (24*S*)-24,25-epoxy-19(10 → 9) *abeo*-8 α ,9 β ,10 α -euph-5-en-3 β -ol skeleton isolated from *Reissantia indica*, have been established from spectral data and single-crystal X-ray analysis.

Continuing our interest in terpenoids and steroids of Sri Lankan plants, we have undertaken a detailed investigation of the triterpenoids of Celastraceae and in this communication we report the structure of the first natural (24*S*)-24,25-epoxy-19(10 → 9) *abeo*-8 α ,9 β ,10 α -euph-5-en-3 β -ol reissantioloxide (**1**), one of the major triterpenes of *Reissantia indica* (Hallee) Ding Hou.[†] Previous studies on this plant had revealed the presence of only quinone methide triterpenoids.²

Reissantioloxide was isolated in 0.02% yield from the neutral fraction of the methanol soluble portion[‡] of the hot

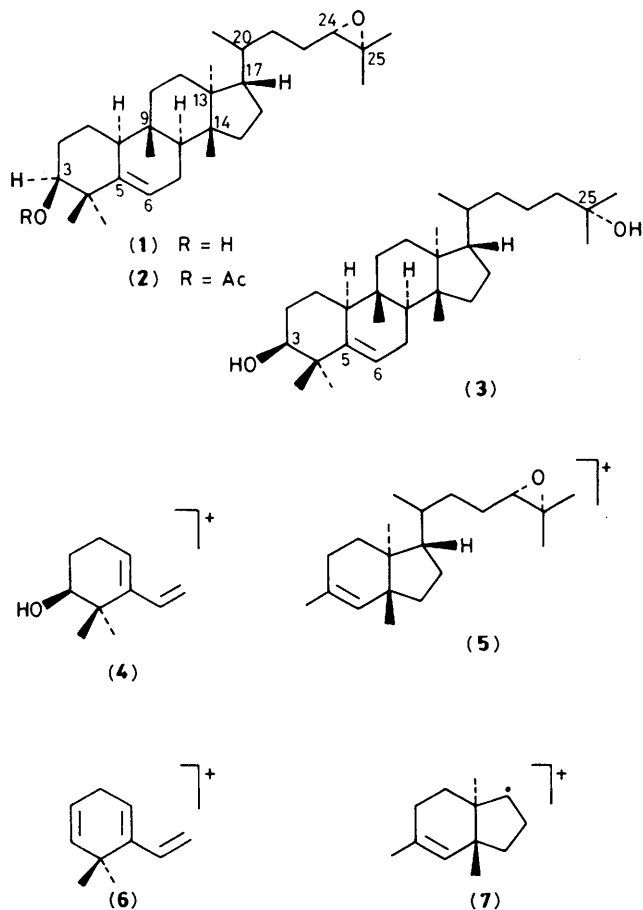
hexane extract of the root bark of *R. indica*. Reissantioloxide (**1**) {C₃₀H₅₀O₂, *m/z* 442.3807 (*M*⁺), m.p. 175–177 °C, [α]_D²⁷ + 34.4° (*c* 1.2, CHCl₃)} showed i.r. bands (KBr) at 3475(OH), 2900(CH), 1455, 1380, 1110, 970(C–O–C), and 890 cm⁻¹. The ¹H n.m.r. spectrum (400 MHz, CDCl₃) indicated the presence of seven tertiary methyl groups (δ 0.83, 0.84, 0.88, 1.06, 1.15, 1.27, and 1.31), one secondary methyl group [δ 0.87(d, *J* 6.6 Hz)], an olefinic proton [δ 5.64 (d, *J* 6.1 Hz)], and two protons attached to carbon atoms bearing oxygen functions [δ 2.69 (1H, t, *J* 6.1 Hz, 24-H) and 3.47(1H, dd, *J* 6.9 and 3.0 Hz, 3-H)].

Acetylation (Ac₂O–pyridine) gave the monoacetate (**2**) [C₃₂H₅₂O₃, *m/z* 484 (*M*⁺); ν_{\max} (KBr) 2865(CH) and 1735(OAc) cm⁻¹; ¹H n.m.r. (60 MHz, CDCl₃) δ 0.83(6H, s, 2 × CH₃), 0.87(3H, d, *J* 7 Hz, 20-CH₃), 0.90(3H, s, CH₃), 1.03(3H, s, CH₃), 1.08(3H, s, CH₃), 1.26(3H, s, CH₃), 1.30(3H, s, CH₃), 2.00(3H, s, COCH₃), 2.70(1H, t, *J* 6 Hz, 24-H), 4.71(1H, m, 3-H), and 5.66(1H, d, *J* 6 Hz, 10-H)]. LiAlH₄ reduction afforded the diol (**3**) [C₃₀H₅₂O₂, *m/z* 444 (*M*⁺); the ¹H n.m.r. spectrum was similar to that of (**1**) except that the signal due to 24-H was shifted to high field] indicating the terminal nature of the epoxide ring. The hydroxy group in reissantioloxide was placed at C-3 on biogenetic grounds. Assignment of the double bond at C-5(6) was based on the observation of diagnostically important mass peaks at *m/z* 152 (61%) (**4**) and *m/z* 290 (71%) (**5**) associated with *retro* Diels–Alder cleavage of ring *b* typical of triterpenoids and steroids with C-5(6) unsaturation.³ The presence of significant peaks at *m/z* 134(100%) due to (**6**) [arising from (**4**) by the loss of a molecule of H₂O] and at *m/z* 163 (95%) due to (**7**) [arising from (**5**) by the loss of the side chain] further supported the proposed structure (**1**) for reissantioloxide.

The complete structure and stereochemistry of (**1**) were established unequivocally by single-crystal X-ray analysis.[§] A view of the structure of reissantioloxide (**1**) is shown in Figure 1. The major features of note are the C-5(6) double bond and the disposition of the C-18 and C-30 methyl groups.

The co-occurrence of reissantioloxide and 25(10 → 9) *abeo*, 26(8 → 15) *abeo*-9 β , 14 β , 15 α -olean-5-ene-3 β , 29-diol in *R. indica* suggests the occurrence of common post-cyclisation biogenetic changes in the A, B, and C rings of these triterpenoids.

[§] Crystal data for (**1**): C₃₀H₅₀O₂, *M* = 442.7, orthorhombic, space group *P*2₁2₁2₁, *a* = 10.736(3), *b* = 11.171(3), *c* = 22.358(6) Å, *U* = 2681 Å³, *Z* = 4, *D*_c = 1.097 g cm⁻³. 1780 independent reflections [1530 with *I*_o > 2 σ (*I*_o)] (2 θ ≤ 42°) were measured on an Enraf-Nonius CAD-4 diffractometer (Mo-K α radiation, incident beam graphite monochromator) using θ –2 θ scans. The structure was resolved by direct methods and the hydrogen atoms were included in fixed position to give *R* = 0.040 and *R*_w = 0.053 in the full-matrix least-squares refinement (C and O atoms anisotropic). Calculations were performed on a PDP 11/34 computer using the Enraf-Nonius SDP programmes. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



[†] This plant, which is also known as *Hippocratea indica* Willd. or *Pristimera indica* (Willd.) A.C. Sm., was collected at Wilpattu, Sri Lanka. Plant material was procured and identified by Professor S. Balasubramaniam of the Department of Botany, University of Peradeniya, Sri Lanka.

[‡] Treatment with methanol was necessary to remove gutta percha from the hot hexane extract.

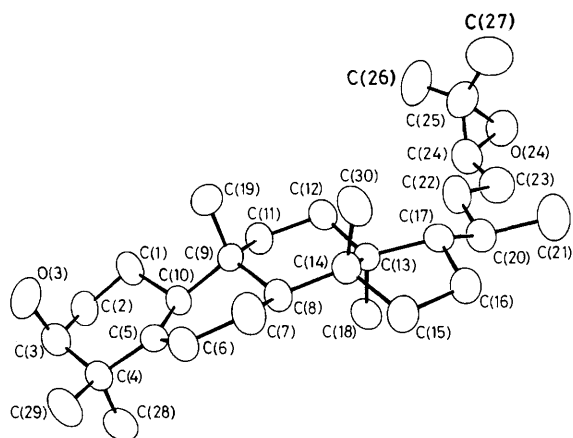


Figure 1. Structure and solid-state conformation of reissantioloxide (**1**); hydrogen atoms have been omitted for clarity.

We thank the International Foundation for Science (Sweden) and the Natural Resources, Energy and Science Authority of Sri Lanka for financial support, Dr. Akio Sonoda (Otsuka Pharmaceutical Co., Japan) for some n.m.r. data, and Professor J. D. Connolly (University of Glasgow, Scotland) for helpful suggestions.

Received, 21st August 1987; Com. 1231

References

- 1 For Part 12 in the series, 'Studies on Terpenoids and Steroids,' see C. B. Gamlath, A. A. L. Gunatilaka, and S. Balasubramaniam, *Phytochemistry*, submitted for publication.
- 2 R. Bruning and H. Wagner, *Phytochemistry*, 1978, **17**, 1821.
- 3 H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, 1963, **85**, 3688.