

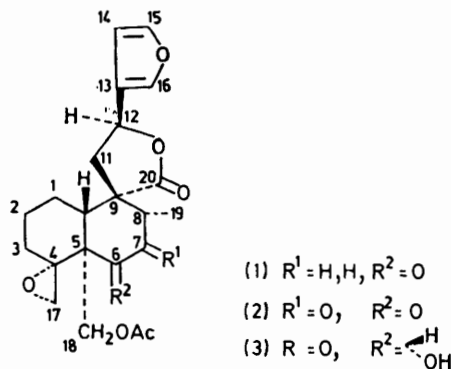
A New Clerodane Diterpene from *Teucrium polium* L.

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The structure of a clerodane-6,7-dione (2), isolated from *Teucrium polium* L., has been established, and related to that of the corresponding 7-hydroxy-6-ketone picropolin (3). The stereostructures of (2) and (3) are tentatively assigned.

THE diterpene content of *T. polium* has been investigated previously;¹ picropolin (3), a diterpene of the clerodane type, was reported as the main component. A re-investigation of this plant, collected at Arganda (Madrid), was undertaken with the primary aim of isolating this compound. Since the actual content of our plant material differs considerably from that reported, we now describe our results.

Three diterpenes were isolated. The ¹H n.m.r.



spectrum of the first compound (1) shows the characteristic signals of the β -substituted furan ring encountered in diterpenes of the clerodane type (Table). In addition there are signals for a primary acetylated hydroxy-group (an AB-quartet at δ 5.26) and the lactonic H-12 (a triplet at δ 5.46). This product was recently isolated from *T. gnaphalodes*;² the stereochemistry indicated was deduced from a single crystal X-ray diffraction study of the natural compound.²

¹H N.m.r. signals (δ values; solvent CDCl₃; internal standard Me₄Si)

Compound	H-15	H-16	H-14	H-12 ^a	H-18 ^b	H-19
(1)	7.48	6.40	5.46	5.26	1.10 ^c	
(2)	7.45	6.35	5.50	4.92	1.84	
(3)	7.46	6.38	5.46	4.52	1.10 ^c	

^a J 8 Hz. ^b J 12 Hz. ^c J 6 Hz.

The i.r. and ¹H n.m.r. spectra of the second component (2) showed a close relationship with the previous compound. The molecular formula, C₂₂H₂₄O₈, added to the observation of i.r. bands characteristic of a C:C(OH)•CO grouping (at 1 675 and 1 645 cm⁻¹), and together with

the appearance of a methyl singlet (δ 1.84 p.p.m.) in the ¹H n.m.r. spectrum, agrees with the assigned structure.

The ¹H n.m.r. spectrum of (3), as well as other data (i.r. absorption, $[\alpha]_D$, elemental analysis, etc.) corresponds with that published¹ for picropolin.

Reduction of (2) with sodium borohydride in methanol produces picropolin in high yield. This confirms the structure (2) and allows one to speculate about the stereochemistry at C-6 and C-8 in picropolin. As indicated above, the carbonyl system at C-7 of (2) is almost entirely in the enol form.

The stereochemistry of the AB ring junction, as well as other stereochemical aspects indicated in the formulae (1)–(3) are based on analogies with spectroscopic data and the common natural source of the three compounds.

EXPERIMENTAL

General experimental details have been described previously.³ ¹H N.m.r. spectra were determined at 100 MHz with a Varian XL-100 spectrometer.

Extraction of *Teucrium polium*.—*T. polium* was collected at Arganda (Madrid), in the summer of 1975, and identified at the Botany Department, University of Madrid. The whole plant was air-dried and powdered (300 g) and extracted with acetone (3 l) at room temperature for 72 h. The extract was concentrated *in vacuo* and the crude residue was chromatographed on a dry silica gel column. Elution with 80% ethyl acetate–n-hexane afforded material which, on crystallization from chloroform–ether, gave the diterpene (1) (600 mg), m.p. 227–228 °C; $[\alpha]_D +82.6$ (*c* 0.67 in CHCl₃) (Found: C, 65.35; H, 6.8. Calc. for C₂₂H₂₆O₇: C, 65.65; H, 6.5%), ν_{\max} 3 120, 1 735, 1 710, 880, and 770 cm⁻¹; *m/e* 402, 387, 360, 342, 330, 311, 301, 283, 236, 95, 94, and 81.

Further elution gave 18-acetoxy-4-epi,17:15,16-diepoxy-6,7-dioxocleroda-13(16),14-dieno-20,12-lactone (2) (400 mg), m.p. 218–219 °C (n-hexane–acetone); $[\alpha]_D +44.4$ (*c* 0.67 in CHCl₃) (Found: C, 63.15; H, 5.7. C₂₂H₂₄O₈ requires C, 63.45; H, 5.8%); ν_{\max} 3 460, 3 130, 1 750, 1 740, 1 675, 1 645, 880, and 750 cm⁻¹; λ_{\max} 280 nm (ϵ 6 500); *m/e* 416, 398, 388, 356, 343, 315, 250, 177, 95, 94, and 81.

A third component, eluted last, after preparative t.l.c. was identified as picropolin (3) (25 mg), m.p. 198–199 °C (chloroform–ether); $[\alpha]_D +42.1$ (*c* 0.67 in CHCl₃) (Found: C, 63.45; H, 6.2. Calc. for C₂₂H₂₆O₈: C, 63.15; H, 6.2%); ν_{\max} 3 450, 3 140, 1 750, 1 730, and 880 cm⁻¹; *m/e* 418, 400, 358, 343, 95, 94, and 81.

Conversion of the Dione (2) into Picropolin (3).—To a solution of (2) (50 mg) and boric acid (100 mg) in methanol (10 ml), an excess of sodium borohydride was added in

portions. The mixture was kept for 5 h at room temperature. The product (44 mg) was identical with (3).

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