

$\text{CHMe}_2^+$  (14), 159  $[202 - \text{CHMe}_2]^+$  (30), 119 (41), 109 (62), 91 (51), 69 (80), 55 (100); CI (iso-butane): 237  $[\text{M} + 1]^+$  (7), 219  $[237 - \text{H}_2\text{O}]^+$  (3), 203  $[237 - \text{H}_2\text{O}_2]^+$  (100).

$$[\alpha]_{\text{D}}^{25} = \frac{589}{-38} \frac{578}{-40} \frac{546}{-46} \frac{436 \text{ nm}}{-80} (\text{CHCl}_3; c 0.1).$$

To 3 mg **6** in 0.5 ml  $\text{CDCl}_3$ , 10 mg triphenylphosphine was added. After 5 min the  $^1\text{H}$  NMR spectrum was identical with that of **7**.

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#### REFERENCES

1. Bohlmann, F., Suwita, A. and Zdero, C. (1978) *Phytochemistry* **17**, 1763.
2. Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* **17**, 1337.
3. Bohlmann, F., Singh, P. and Jakupovic, J. (1981) *Phytochemistry* **21**, 157.

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## TEUPOLIN III, A FURANOID DITERPENE FROM *TEUCRIUM POLIUM*

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**Key Word Index**—*Teucrium polium* var. *polium*; Lamiaceae; teupolin III; furanoid diterpene; clerodane.

**Abstract**—A new clerodane derivative was isolated from *Teucrium polium* var. *polium*. The structure and stereochemistry have been established by detailed studies of the  $^1\text{H}$  NMR spectra.

We have previously described some clerodane and nor-clerodane derivatives from *Teucrium polium* var. *polium* [1]. In a continuation of this work we have isolated from the same plant a new clerodane diterpene, teupolin III (**1**). The IR spectrum of **1** contained two strong bands for a primary and a tertiary alcohol (1050, 1150, 3420  $\text{cm}^{-1}$ ), a furan ring (3130, 1600, 1505, 870  $\text{cm}^{-1}$ ), and a strong band for a carbonyl group (1700  $\text{cm}^{-1}$ ).

The  $^1\text{H}$  NMR spectrum (Table 1) showed two ABq ( $\delta$  3.70, 3.78 and 3.90, 4.60) which we have assigned to H-19 and H-18. The double doublet at  $\delta$  5.13 and the singlet at 5.20 were assigned to H-12 and H-20, respectively. The proton of the hydroxyl group at C-4 appeared as a singlet at  $\delta$  3.88 (hydrogen bond of OH-4 with 6-keto).

$^1\text{H}$  NMR spin decoupling studies were particularly informative. A double doublet ( $\delta$  3.70) which we have assigned to H-19 $\beta$ , was coupled to a single-proton resonance at  $\delta$  1.97 ( $^4J_{10\beta,19\alpha} = 1 \text{ Hz}$ ). A double dou-

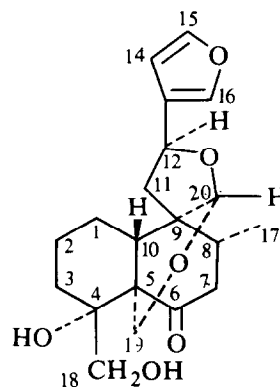


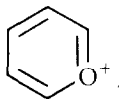
Table 1.  $^1\text{H}$  NMR spectral data of teupolin III (400 MHz, TMS as internal standard)

	$\text{CDCl}_3$	$\text{CDCl}_3\text{-C}_6\text{D}_6$
H-1 $\alpha$	2.21 dddd	1.99 dddd
H-1' $\beta$	2.02 dddd	1.63 dddd
H-2 $\alpha$	1.81 ddddd	1.56 ddddd
H-2' $\beta$	1.30 ddddd	1.06 ddddd
H-3 $\alpha$	1.52 dddd	1.41 dddd
H-3' $\beta$	2.26 br d	2.10 br d
H-7 $\alpha$	2.72 dd	2.38 dd
H-7' $\beta$	2.39 dd	2.13 dd
H-8 $\beta$	2.18 m	1.75 ddq
H-10 $\beta$	1.97 br dd	1.51 br dd
H-11 $\alpha$	2.28 dd	1.94 dd
H-11' $\beta$	2.14 dd	1.88 dd
H-12	5.13 dd	4.95 dd
H-14	6.37 dd	4.26 dd
H-15 }	7.41 d	7.29 dd
H-16 }		6.74 s
H-17	1.03 d	0.76 d
H-18 $\alpha$	4.60 d	4.49 d
H-18' $\beta$	3.90 dd	3.79 dd
H-19 $\alpha$	3.78 d	3.58 dd
H-19' $\beta$	3.70 dd	3.52 d
H-20	5.20 s	5.03 s
OH	3.88 s	3.85 s

$J$  (Hz): 1, 1' = 1, 2' = 2, 2' = 2', 3 = 3, 3' = 14; 1, 2 = 1', 2 = 1', 2' = 1', 10 = 2, 3 = 2, 3' = 2', 3' = 4; 1, 10 = 13; 3, 18 = 0.5; 7, 7' = 19; 7, 8 = 8; 7, 8' = 10; 8, 17 = 6.5; 10, 19 = 1; 11, 11' = 19; 11, 12 = 11', 12 = 8; 18, 18' = 19, 19' = 12.

blet ( $\delta$  3.90), which was assigned to H-18 $\beta$ , was coupled to H-3 $\alpha$  ( $^4J_{3\alpha,18\beta} = 0.5$  Hz). All assignments were established by spin decoupling.

The structure assigned to teupolin III was also supported by the mass spectrum. The fragmentation of the molecular ion ( $m/z$  362) gave an ion at 344 [ $\text{M} - \text{H}_2\text{O}$ ] $^+$ . The base peak at  $m/z$  94 was assigned to the ion  $\text{C}_6\text{H}_6\text{O}^+$  and the peak at  $m/z$  81 to the ion:



## EXPERIMENTAL

Dried areal plant parts (5 kg) were extracted with  $\text{Me}_2\text{CO}$  and after evaporation the residue was treated as in ref. [2]. The  $\text{CHCl}_3$  extract (40 g) was passed through a Si gel column. Elution with petrol- $\text{CHCl}_3$  (9:1) gave crude crystals (48 mg), which were recrystallized from  $\text{Et}_2\text{O-Me}_2\text{CO}$  to yield pure teupolin III, mp 178–180°,  $[\alpha]_D^{28} - 57.1^\circ$  ( $\text{Me}_2\text{CO}$ ;  $c$  0.154). IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1700 (ketone), 1600, 1500 and 872 (furan ring), 3420, 1150 and 1050 (hydroxyl groups). MS (70 eV)  $m/z$  (rel. int.): 362 [ $\text{M}$ ] $^+$  (5),  $\text{C}_{20}\text{H}_{26}\text{O}_6$ ; 344 [ $\text{M} - \text{H}_2\text{O}$ ] $^+$  (15), 94 (100), 81 (40), 91 (30).

## REFERENCES

1. Malakov, P. Y., Papanov, G. Y. and Mollov, N. M. (1979) *Z. Naturforsch. Teil B* **34**, 1570.
2. Popa, D. P. and Reinbol'd, A. M. (1972) *Khim. Priir. Soedin.* **1**, 57.