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A NEW SECO-LABDANE DERIVATIVE FROM *ATHRIXIA ELATA**

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Key Word Index—*Athrixia elata*; Compositae; diterpenes; seco-labdane derivative; triterpenes; 2β-hydroxyerythrodiol.

Abstract—*Athrixia elata* afforded, in addition to known compounds, a new seco-labdane derivative and a new triterpene.

From the mainly South African genus *Athrixia* (tribe Inuleae, subtribe Athrixiinae) some species have been investigated chemically [1]. In addition to triterpenes and thymol derivatives some diterpenes related to kaurene were present. We have now studied the constituents of *A. elata* Sond. The roots afforded the thymol derivatives **1–3**, friedelin, dammadienone and the corresponding acetate, *ent*-kaurenic acid (**6**) and the 9, 11-dehydro derivative **7** and 4-formylathrixinone (**8**) [1]. The aerial parts gave squalene, germacrene D, caryophyllene, α-humulene, the cinnamates **4** and **5** [2], the triterpene **9** and the seco-labdane derivative **10**. The structure of **9** followed from the molecular formula and the ^{1}H NMR spectrum (Table 1), which was close to that of erythrodiol [3]. The position and the stereochemistry of the additional hydroxyl group followed from the couplings of H-2 and from double resonance experiments. Ac-

Table 1. ^{1}H NMR spectral data of compound **9** (400 MHz, $CDCl_3$, TMS as int. standard)

H-1	2.07 *dd*	H-23′	3.56 *d*
H-1′	2.14 *dd*	H-24	1.01 *s*
H-2	4.09 *ddd*	H-25	1.03 *s*
H-3	3.23 *d*	H-26	0.96 *s*
H-9	1.49 *ddd*	H-27	1.16 *s*
H-11	1.87 *ddd*	H-28	1.26 *s*
H-11′	1.99 *ddd*	H-29	0.87 *s*
H-12	5.21 *dd*	H-30	0.89 *s*
H-23	3.21 *d*		

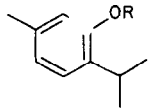
J(Hz): 1, 1′ = 12.5; 1′, 2 = 2.5; 2, 3 = 5; 9, 11 = 6.5; 9, 11′ = 12; 11, 11′ = 17; 11, 12 = 11′, 12 = 3; 12, 12′ = 11.

Table 2. ^{1}H NMR spectral data of compound **10** (400 MHz, TMS as int. standard)

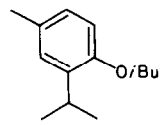
	$CDCl_3$	C_6H_6
H-5	2.03 *t*	2.06 *t*
H-6	2.43 *d*	2.33 *d*
H-9	2.66 *dd*	2.63 *dd*
H-11	2.39 *ddd*	2.46 *ddd*
H-11′	2.61 *ddd*	2.75 *ddd*
H-12	5.23 *dd*(*br*)	5.51 *dd*(*br*)
H-14	6.30 *dd*	6.51 *dd*
H-15	4.94 *d*	5.01 *d*
H-15′	5.09 *d*	5.17 *d*
H-16	1.72 *s*(*br*)	1.84 *s*(*br*)
H-17	2.12 *s*	1.90 *s*
H-18	0.98 *s*	0.74 *s*
H-19	0.99 *s*	0.73 *s*
H-20	0.95 *s*	0.92 *s*

J (Hz): 5, 6 = 4.5; 9, 11 = 2; 9, 11′ = 11.5; 11, 11′ = 13; 11, 12 = 5; 11′, 12 = 8.5; 14, 15 = 11; 14, 15′ = 17.

*Part 435 in the series "Naturally Occurring Terpene Derivatives". For Part 434 see Bohlmann, F. and Gupta, R. K. (1982) *Phytochemistry* **21** (in press).



1 R = H
2 R = *i*Bu



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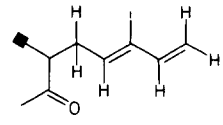
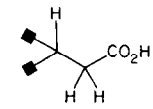


A



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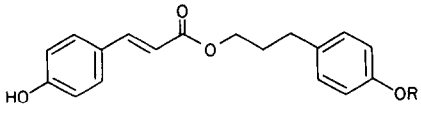
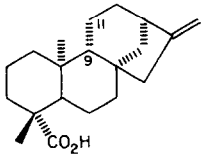
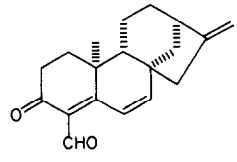


4 R = H
5 R = Me



6
7 Δ 9, 11



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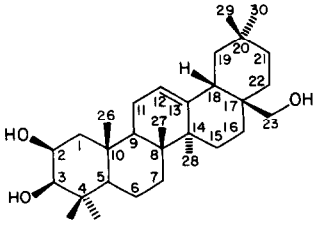
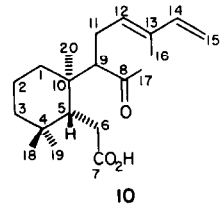


9



10

cordingly, **9** was 2β-hydroxyerythrodiol. The MS supported the structure with a 12, 13-double bond by a typical RDA fragment. The structure of **10**, which was isolated only in minute amounts, also followed from the molecular formula and the ^{1}H NMR spectral data (Table 2). A singlet at δ 2.12 indicated the presence of a methyl ketone. Spin decoupling, starting with the signals of a vinyl group, led to the sequence **A**.

Further, irradiation of a two-proton doublet at δ 2.43 collapsed a triplet to a singlet. The chemical shift of the doublet required a neighbouring carbonyl group, which could only be a carboxyl group, the presence of which followed from the IR spectrum. Accordingly, sequence **B** should be present. Three methyl signals and overlapped multiplets, corresponding to three additional methylene groups, finally led to the structure **10**. Obviously this keto acid was formed by degradation of a labdane. As *ent*-kaurane derivatives were present, **10** was derived most likely from an *ent*-labdane. We have named this acid seco-athrixic acid. This structure, however, could not be established unequivocally due to the small amounts of material. The renewed isolation of thymol derivatives and compounds derived from kaurene, especially **8**, show that these compounds may be typical for *Athrixia*.

EXPERIMENTAL

The air-dried plant material, collected in Feb. 1981 in Transvaal, voucher 81–21 (deposited in the Botanic Research Institute, Pretoria), was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. The roots (85 g) gave 20 mg dammadienyl acetate, 10 mg dammadienone, 10 mg friedelin, 10 mg **1**, 15 mg **2**, 5 mg **3**, 12 mg **6**, 25 mg **7** and 9 mg **8**, while the aerial parts (150 g) afforded 10 mg germacrene D, 20 mg caryophyllene, 20 mg α-humulene, 20 mg squalene, 1 mg **4**, 1 mg **5**, 9 mg **9** (Et_2O) and 1 mg **10** (Et_2O–petrol, 3:1).

2-β-Hydroxyerythrodiol (**9**). Colourless crystals, mp ~220°, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 458.376 $[M]^+$ (2) ($C_{30}H_{50}O_3$), 440 $[M-H_2O]^+$ (1), 427 $[M-CH_2OH]^+$ (2.5), 409 $[427-H_2O]^+$ (1.5), 234 $[C_{16}H_{26}O]^+$ (18) (RDA), 203 $[234-CH_2OH]^+$ (100).

Seco-athrixic acid (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3500–2700, 1700 (CO_2H), 1700 (C=O); MS *m/z* (rel. int.); 320.235 $[M]^+$ (0.5) ($C_{20}H_{32}O_3$), 302 $[M-H_2O]^+$ (0.5), 287 $[302-Me]^+$ (0.5), 259 $[287-CO]^+$ (1), 137 $[C_{10}H_{17}]^+$ (100), 69 $[C_5H_9]^+$ (97).

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