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SESQUISABINENE DERIVATIVES FROM *HAPLOCARPHA* SPECIES*

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Key Word Index—*Haplocarpha scaposa*; *H. lyrata*; Compositae; Arctoteae; sesquiterpenes; sesquisabinene derivatives.

Abstract—The roots of two *Haplocarpha* species afforded, in addition to sesquisabinene itself, three of its derivatives.

The genus *Haplocarpha* (Compositae, tribe Arctoteae) is widespread in the southern countries of Africa and extends as far as northern Ethiopia. So far little is known of the chemistry of this genus, which is closely related to *Arctotheca* and *Arctotis*[1]. The roots of *H. lanata* contain the widespread pentaynene and entetraynene[2] only. We have now investigated two further species, *H. scaposa* and *H. lyrata*. The roots of both species afforded, in addition to known compounds, several sesquisabinene derivatives, two of which have not been isolated before.

The roots of *Haplocarpha scaposa* Harv. afforded in addition to **1**, β-farnesene and sesquisabinene (**2**) [3], the derivatives of the latter, the acetates **3** and **4** as well as the aldehyde **5**. **4** has been isolated before from *Arctotis grandis*[4]. The isolation of both isomers allowed the confirmation of the proposed stereochemistry of the 10,11-double bond since $LiAlH_4$ reduction and oxidation of **4** afforded **7**, its stereochemistry clearly following from the downfield shift of the H-13 signal in the ^1H NMR spectrum of **5** (Table 1). By spin decoupling all signals could be assigned. The presence of a *W*-coupling in one of the

Table 1. ^1H NMR spectral data of compounds **3**–**7** (400 MHz, $CDCl_3$, TMS as int. standard)

	3	**4**	**5**	**6**	**7**
H-1α	0.73*dd*	0.73*dd*	0.73*dd*	0.73*dd*	0.76*dd*
H-1β	0.63*ddd*	0.63*ddd*	0.64*ddd*	0.63*ddd*	0.63*ddd*
H-2	1.52*dd*	1.53*dd*	1.53*dd*	1.53*dd*	1.53*dd*
H-4α	2.15*br dd*	2.15*br dd*	2.16*br dd*	2.15*br dd*	2.15*br dd*
H-4β	2.01*m*	2.00*m*	2.02*m*	2.00*m*	2.02*m*
H-5α	1.60*br dd*	1.61*br dd*	1.65*br dd*	1.60*br dd*	1.63*br dd*
H-5β	1.78*br dd*	1.75*m*	1.78*br dd*	1.77*br dd*	1.78*br dd*
H-7	1.18*tq*	1.19*tq*	1.25*m*	1.19*tq*	1.25*m*
H-8	1.43*ddt*	1.43*ddt*	1.43*ddt*	1.43*ddt*	1.43*ddt*
H-8′	1.26*ddt*	1.28*ddt*	1.25*m*	1.25*m*	1.25*m*
H-9	2.11*br t*	2.11*br t*	2.41*dt*	2.10*br t*	2.62*dt*
H-10	5.39*br t*	5.44*br t*	6.47*br t*	5.24*br t*	6.51*br t*
H-12	1.74*dt*	1.65*br s*	9.39*s*	1.79*dt*	1.77*dt*
H-13	4.57*br s*	4.44*br s*	1.75*br s*	4.14*br s*	10.16*s*
H-14	0.93*d*	0.94*d*	0.98*d*	0.93*d*	0.97*d*
H-15	4.80*br s*	4.80*br s*	4.82*br s*	4.80*br s*	4.82*br s*
H-15′	4.61*br s*	4.62*br s*	4.64*br s*	4.61*br s*	4.64*br s*

J (Hz): 1α,1β = 1α,2 = 4; 1β,2 = 8; 1β,5β = 1; 4α,4β = 15; 4α,5α = 8.5; 4α,5β = 1.5; 4β,5β = 10; 5α,5β = 12; 7,8 = 7,14 = 7; 8,8′ = 14; 8,9 = 7.5; 9,10 = 7; 9,12(13) = 10,12(13) ~ 1.

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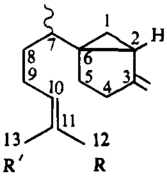
*Part 392 in the series "Naturally Occurring Terpene Derivatives". For Part 391 see Bohlmann, F., Singh, P., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21**, 456.

$Me(C\equiv C)_5CH=CH_2$



	2	3	4	5	6	7
R	Me	Me	CH_2OAc	CHO	Me	Me
R'	Me	CH_2OAc	Me	Me	CH_2OH	CHO

H-1 signals only was in agreement with the β-position of this proton, which also followed from the couplings 1,2. The signals of H-4 and H-5 in part were multiplets. As, however, the H-5β was the coupling partner of H-1β the signals could be assigned. H-2 and the side-chain at C-6 have to be *cis*-orientated. Therefore two racemates only are possible. The structures therefore are presented arbitrarily in one of these possibilities. The relative stereochemistry at C-7, however, could not be determined.

The aerial parts gave no characteristic compounds. The roots of *Haplocarpha lyrata* Harv. also afforded **1**, sesquisabinene and its derivatives **3** and **4**, while the aerial parts gave the triterpenes sitosterol, stigmasterol, lupeol and its acetate as well as taraxasteryl acetate. The chemistry of these two *Haplocarpha* species showed close relationships to *Arctotis*.

EXPERIMENTAL

The air dried plant material, collected during February 1981 in Transvaal, was extracted with Et_2O–petrol (1 : 1) and the resulting extracts separated by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. Vouchers are deposited in the National Botanic Research Institute, Pretoria.

Haplocarpha scaposa (*voucher* 81/10). The aerial parts (450 g) gave no characteristic compounds, while the roots (200 g) afforded 5 mg **1**, 3 mg β-farnesene, 40 mg **2**, 15 mg **3** (Et_2O–petrol, 1 : 20), 15 mg **4** and 6 mg **5** (Et_2O–petrol, 1 : 20).

Haplocarpha lyrata (*voucher* 81/241). The roots (100 g) gave 5 mg **1**, 30 mg **2**, 50 mg **3** and 10 mg **4**, while the aerial parts (85 g) afforded 3 mg sitosterol, 3 mg stigmasterol, 3 mg lupeol, 15 mg of its acetate and 10 mg taraxasteryl acetate.

13-Acetoxysesquisabinene (**3**). Colourless oil, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 1740, 1235 (OAc), 3080, 1660, 870 ($C=CH_2$); MS *m/z* (rel. int.): 262.193 $[M]^+$ (3) ($C_{17}H_{26}O_2$), 220 $[M-\text{ketene}]^+$ (0.5), 202 $[M-HOAc]^+$ (7), 187 $[202-Me]^+$ (14), 93 $[M-CH_2CH_2CH{=}C(Me)CH_2OAc]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{-39.5}\quad\frac{578}{-40}\quad\frac{546}{-46}\quad\frac{436\ \text{nm}}{-71.5}\ (\text{CHCl}_3;\ c\ 0.2).$$

Sesquisabinen-12-al (**5**). Colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3080, 1660, 880 ($C=CH_2$), 2720, 1700 ($C=CCHO$); MS *m/z* (rel. int.): 218 $[M]^+$ (0.1), 203 $[M-Me]^+$ (0.3), 93 $[C_7H_9]^+$ (100); CI (*iso*-butane): 219 $[M+1]^+$ (100).

Preparation of **7**. 15 mg **4** were reduced in 2 ml Et_2O with 20 ml $LiAlH_4$ affording 10 mg **6**, which on oxidation with MnO_2 in Et_2O gave 7 mg **7**, colourless oil. ^1H NMR see Table 1.

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