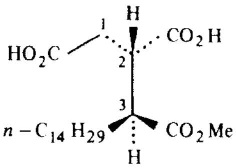

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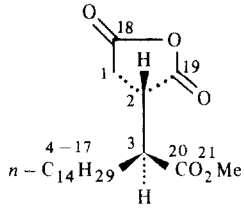

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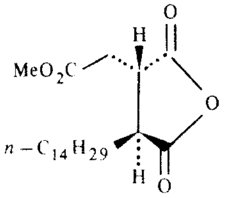

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4–C-14: 26.50–30.37; C-15: 31.90; C-16: 22.65; C-17: 14.05; C-18: 172.39*; C-19: 172.32*; C-20: 170.66; C-21: 52.40 (values marked with * can be exchanged). MS m/z (rel. int.): 368 $[M]^+$ (7), 350 (5), 337 (7), 322 (18), 308 (9), 294 (9), 290 (16), 223 (9), 214 (11), 210 (11), 200 (11), 196 (29), 182 (39), 168 (25), 154 (23), 140 (18), 126 (16), 109 (20), 95 (32), 81 (39), 74 (27), 69 (50), 55 (82), 43 (100). ORD (MeOH): $[\alpha]_{350} - 975°$, $[\alpha]_{300} - 1544°$, $[\alpha]_{250} - 3577°$, $[\alpha]_{244} - 4146°$, $[\alpha]_{230} - 1382°$.

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A FURTHER BITHIENYL DERIVATIVE FROM *BERKHEYA ZEYHERI*

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Key Word Index—*Berkheya zeyheri*; Compositae; thiophene derivative; acetylenic compound.

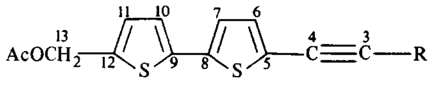
Abstract—The roots of *Berkheya zeyheri* afforded 2-acetoxymethyl-5-[but-1-in-1-yl]-bithienyl-(2',5) while the aerial parts gave onopordopicrin.

In continuation of our investigations of representatives of the large genus *Berkheya* (Compositae tribe Arctotheae) [1] we have studied the constituents of *B. zeyheri* (Sond. et Harv.) Oliv. et Hiern. subsp. *zeyheri*. The roots afforded lupeol and its Δ^{12} isomer, taraxasterol, 2-[thienyl(2)-ethinyl]-5-[prop-1-in-1-yl]-thiophen [2], the bithienyl derivatives **1** [3] and its dihydro derivative **2**. The structure of the latter followed from the molecular formula and the ^1H NMR spectrum (Table 1). In deuteriobenzene all signals of the thiophene protons could be assigned while these were overlapping in deuteriochloroform. The nature of the end groups could easily be deduced from the characteristic ^1H NMR signals while the relative position of these groups could be assigned by comparing the chemical shifts of the CH_2OAc signal with that of similar compounds which showed that the magnitude of the deshielding effect of a thiophene ring is larger

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

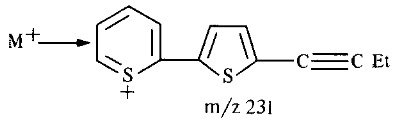
	$CDCl_3$	C_6D_6
H-1	1.29 *t*	0.97 *t*
H-2	2.46 *q*	2.13 *q*
H-6	7.00 *m*	6.62 *d*
H-7		6.73 *d*
H-10		6.74 *br d*
H-11		6.93 *br d*
H-13	5.21 *br s*	4.96 *br s*
OAc	2.12 *s*	1.64 *s*

J (Hz): 1, 2 = 7; 6, 7 = 10, 11 = 3.5; 10, 13 = 11, 13 ~ 0.5.



1 R = CH = CH$_2$

2 $R = \overset{2}{C}H_2\overset{1}{Me}$



3

than that of an acetylenic bond [4]. Furthermore the base peak (m/z 231) in the mass of **2** supported these proposals as the formation of a thiapyrrylium ion (**3**) is more favoured than a propargylium ion [5]. The co-occurrence of **1** and **2** is of interest as so far only very few pairs of acetylenic compounds with a vinyl and an ethyl end group have been isolated [4]. The co-occurrence of **1** and **2** indicated that **2** most likely was formed by enzymatic hydrogenation of **1**. The aerial parts afforded the germacrolide onopordopicrin [6]. The presence of the latter indicated a relationship of the tribe Arctotheae to Cynareae.

EXPERIMENTAL

The air dried plant material (voucher 81/14 and 81/116, collected in February 1981 in Transvaal) was extracted with Et_2O-petrol (1:2) and the extract obtained was worked-up in the usual fashion. The fractions from the roots (450 g) were as follows: 1–3 (petrol), 4–6 (Et_2O-petrol, 1:10), 7–9 (Et_2O-petrol, 1:3), 10–12 (Et_2O-petrol, 1:1), 13–15 (Et_2O) and 16–17 (Et_2O–MeOH, 20:1). Fractions 1–3 on TLC (petrol) gave 25 mg 2-[thienyl(2)-ethinyl]-5-[prop-1-in-1-yl]-thiophene [identical with authentic material (^{1}H NMR and TLC)] and fractions 4–6 on repeated TLC (Et_2O-petrol, 1:20) 8 mg **1** (identified by comparing all spectral data with those of authentic material) and 18 mg **2**. The fractions 7–9 on TLC (Et_2O-petrol, 1:3) afforded 14 mg taraxasterol and 20 mg of a mixture of lupeol and its Δ^{12} isomer (*ca* 2:1). The ^{1}H NMR spectra of these triterpene were identical with those of authentic material. The polar fractions of the extract from 220 g aerial parts (Et_2O–MeOH, 20:1) afforded on TLC (Et_2O–C_6H_6–CH_2Cl_2, 1:1:1) 50 mg onopordopicrin, identical with authentic material (^{1}H NMR, TLC).

2-*Acetoxymethyl*-5′-[*but*-1-*in*-1-*yl*]-*bithienyl*(2′,5). Yellow coloured oil which showed no impurities in the 400 MHz ^{1}H NMR spectrum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc); MS m/z (rel. int.): 290.044 $[M]^+$ (74) ($C_{15}H_{14}O_2S_2$), 275 $[M - Me]^+$ (2), 231 $[M - OAc]^+$ (100), 216 $[231 - Me]^+$ (18).

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