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TETRALUDIN A, B AND C, THREE NEW MELAMPOLIDES FROM *TETRAGONOTHECA LUDOVICIANA*

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Key Word Index—*Tetragonotheca ludoviciana*; Compositae; melampolides; sesquiterpene lactones; C-17 acetylenes.

Abstract—The investigation of the roots of the four *Tetragonotheca* species, *T. ludoviciana*, *T. repanda*, *T. texana* and *T. helianthoides*, resulted in the isolation of the known heptadeca-2-(*Z*)-8,10-(*E*)-16-tetraene-4,6-diin-1-ol and its aldehyde derivative from all four species. Aerial parts of *T. ludoviciana* also contained the acetate of the latter compound as a minor constituent and provided three new melampolide-type sesquiterpene lactones, tetraludin A, B and C.

INTRODUCTION

In continuation of our search for anti-neoplastic constituents in members of the family Compositae, we have investigated *Tetragonotheca ludoviciana* of the subtribe Heliantheneae. Besides two known C-17 acetylenic compounds (**4** and **5**) [1] from low polarity fractions, more polar chromatographic fractions provided three new melampolide-type sesquiterpene lactones which we named tetraludin A, B and C. Their structures were established by chemical transformations and spectroscopic methods, mainly NMR and MS.

RESULTS AND DISCUSSION

Tetraludin A (**1a**), $C_{23}H_{30}O_{10}$, was a gum with IR absorptions at 3500 cm^{-1} (hydroxyl) and carbonyl bands at 1760, 1740 and 1715 cm^{-1} which correspond to an α-methylene γ-lactone, a saturated ester and an α,β-unsaturated ester, respectively. Further bands at 1665 and 1615 cm^{-1} indicated double bonds. The ^1H NMR spectrum of **1a** exhibited two doublets at δ 6.25 (J = 3.5 Hz) and 5.76 (J = 3.2 Hz) typical of exocyclic methylene protons in a γ-lactone. The ^1H NMR spectral patterns of tetraludin A showed in major parts of the spectrum signals similar to those of uvedalin, a melampolide which had previously been isolated from *Polymnia uvedalia* [2], the absolute configuration of which is known from correlation with enhydrin [3]. Based on inspection and detailed double resonance experiments of tetraludin A and its derivatives (Table 1), this new compound must represent a melampolide-type sesquiterpene lactone with a *cis*-1 (10), *trans*-4,5-germacradiene skeleton bearing ester side chains at C-8 and C-9. The NMR spectral parameters of the three tetraludins differed only for those signals which were assigned to the ester side chain at C-8 or C-9. Instead of the signals due to epoxyangelate at C-8 in uvedalin, tetraludin A exhibited, besides an acetate singlet at δ 1.98, a three-proton doublet at 1.16 (J = 6.0 Hz), a singlet (3H) at 1.20 and a one-proton quartet at 3.85 (J = 6.5 Hz), suggesting an oxidation pattern in the

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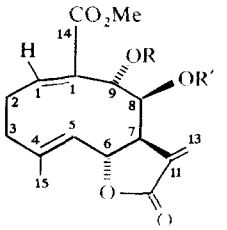
Table 1. ^1H NMR data of tetraludin A and derivatives*

	1a	**1b**	**1c**	**1d**	**1e**	Multiplicity	J
H-1	7.00 (6.75)	7.00 (6.75)	7.02	7.00 (6.70)	7.00 (7.03)	*dd*	10; 8
H-5	4.93 (4.60)	4.91 (4.58)	4.94	4.91 (4.51)	4.91 (4.54)	*brd*	10
H-6	5.13 (5.20)	5.08 (5.20)	5.17	5.18 (5.16)	5.24 (5.17)	*t*	10
H-8	6.62 (6.85)	6.62 (6.87)	6.65	6.58 (6.92)	5.18 (5.0–5.3)	*dd*	8.5; 1.5
H-9	5.42 (5.48)	5.36 (5.42)	5.42	5.35 (5.41)	5.18 (5.0–5.3)	*d*	8.5
H-13a	6.25 (6.31)	6.22 (6.20)	6.25	6.24 (6.21)	6.33 (6.24)	*d*	3.5
H-13b	5.76 (5.81)	5.81 (5.82)	5.73	5.71 (5.66)	5.60 (5.19)	*d*	3.2
C-4-Me	1.98 (1.81)	2.00 (1.80)	2.00	1.97 (1.76)	1.95 (1.69)	*d*/*brs*	1.2
C-2′-Me	1.20 (1.21)	1.23 (1.18)	2.39	1.48 (1.40)	— —	*s*	
C-3′-Me	1.16 (1.11)	1.22 (1.11)	—	2.16 (1.90)	— —	*d*/*s*	6.5
H-3′	3.85 (3.88)	5.15 (5.26)	—	— —	— —	*q*	6.5
OMe	3.80 (3.48)	3.79 (3.45)	3.80	3.79 (3.41)	3.76 (3.41)	*s*	
OAc	1.98 (1.68)	1.91 (1.76) 1.97 (1.55)	1.94	1.97 (1.61)	2.07 (1.69)	*s*	

* Run at 100 MHz in $CDCl_3$ (C_6D_6) with TMS as internal standard. Values are in ppm (δ).



1a R = Ac, R′ = **A**
1b R = Ac, R′ = **A**, 3′-OAc
1c R = Ac, R′ = **D**
1d R = Ac, R′ = **B**
1e R = Ac, R′ = H
2a R = **C**, R′ = **A**
2b R = **C**, 3′-OAc, R′ = **A**, 3′-OAc
2c R = **C**, R′ = **D**
2d R = —C(=O)—CH(Me)—C(=O)—Me, R′ = **D**
2e R = —C(=O)—CH(Me)—C(=O)—Me, R′ = **B**
2f R = **C**, R′ = H
3a R = **C**, R′ = **A**
3b R = **C**, 3′-OAc, R′ = **A**
3c R = **C**, R′ = **D**
3d R = **C**, R′ = H

A = —C(=O)(1′)—C(Me)(OH)(2′)—CH(OH)(3′)—Me

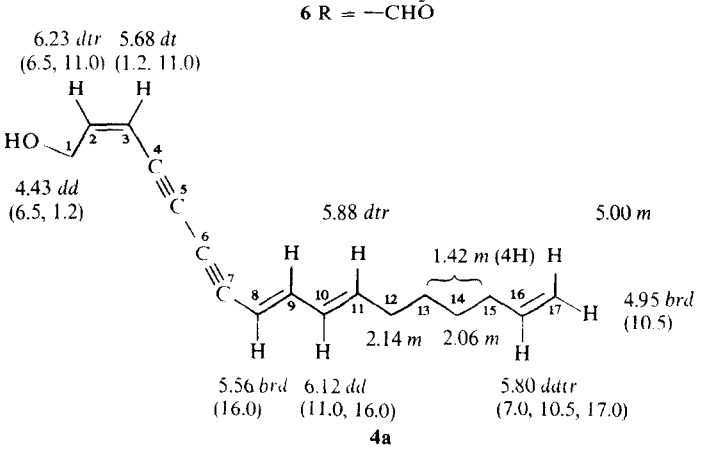
C = —C(=O)(1″)—CH(Me)(2″)—CH(OH)(3″)—Me

B = —C(=O)(1′)—C(Me)(OH)(2′)—C(=O)(3′)—Me

D = —C(=O)(1′)—C(=O)(2′)—Me

$=(CH_2)_4\overset{E,E}{=\!=}{}_2\equiv{}_2\overset{Z}{=} - R$

4 R = —CH_2OH
5 R = —CH_2OAc
6 R = —CHO



4a

side chain of **1a** analogous to the one in uvedalin. Evidence for the presence of a five-carbon dihydroxy ester was provided by diagnostic MS peaks at *m/e* 350 ($M - C_5H_8O_3$), 332 ($M - C_5H_{10}O_4$) and 45 ($Me—\overset{+}{C}H=OH$), suggesting the attachment of a 2-methyl-2,3-dihydroxybutyrate (**A**) to C-8 or C-9 in **1a**. This assumption was verified by several chemical transformations. Acetylation of tetraludin A afforded acetate **1b** which gave an OH absorption at 3500 cm^{-1} indicating the presence of a tertiary OH group in **1a**. The ^1H NMR spectrum of **1b** exhibited two acetate singlets at δ 1.91 and 1.97 and instead of a quartet at 3.85 in **1a**, a quartet at 5.15 (H-3′) was observed in **1b**. Further support for the presence of a 2-methyl-2,3-dihydroxybutyrate side chain in **1a** was provided by periodic acid oxidation resulting in the pyruvate derivative **1c** whose ^1H NMR spectrum showed a methyl signal at δ 2.39 characteristic of the pyruvate methyl absorption. The attachment of the 2-methyl-2,3-dihydroxybutyrate side chain to C-8 was determined by hydrolysis of the pyruvate **1c**. Treatment of **1c** with sodium bicarbonate in ethanol resulted in an alcohol (**1e**), the ^1H NMR spectrum of which showed an acetate signal at 2.07 but had lost the pyruvate methyl signal. Most importantly, the H-8 signal in **1e** appeared at a higher field at 5.18 indicating that the pyruvate group in **1c** and therefore the 2-methyl-2,3-dihydroxybutyrate moiety in tetraludin A must be attached to C-8. Oxidation of tetraludin A (**1a**) with Jones' reagent provided product

Table 2. ^{1}H NMR data of tetraludin B, C and derivatives*

	2a	2b	2c	2d	2e	2f	3a	3b	Multiplicity	*J*
H-1	6.98 (6.74)	6.97 (6.67)	7.04 (6.75)	7.04	7.00	6.97	6.99 (6.75)	6.96 (6.69)	*dd*	10; 8
H-5	4.93 (4.59)	4.92 (4.51)	4.96 (4.59)	4.94	4.8–5.2	4.90	4.93 (4.58)	4.90 (4.56)	*brd*	10
H-6	5.06 (5.04)	5.16 (5.14)	5.18 (5.16)	5.12	4.8–5.2	5.21	5.16 (5.23)	5.10 (5.17)	*t*	10
H-8	6.65 (6.83)	6.63 (6.79)	6.66 (6.89)	6.63	6.56	5.10	6.61 (6.87)	6.62 (6.71)	*dd*	8.5; 1.5
H-9	5.36 (5.38)	5.28 (5.31)	5.45 (5.51)	5.37	5.28	5.28	5.37 (5.45)	5.32 (5.36)	*d*	8.5
H-13a	6.30 (6.26)	6.24 (6.16)	6.23 (6.21)	6.24	6.26	6.29	6.25 (6.34)	6.19 (6.17)	*d*	3.5
H-13b	5.83 (5.77)	5.68 (5.56)	5.75 (5.72)	5.73	5.72	5.60	5.75 (5.82)	5.76 (5.74)	*d*	3.2
C-4-Me	2.00 (1.76)	2.00 (1.80)	2.04 (1.80)	2.02	1.97	1.95	2.00 (1.79)	1.99 (1.79)	*d/brs*	1.2
C-2′-Me	1.18 (1.09)	1.25 (1.13)	2.39 (2.14)	2.48	1.51	—	1.21 (1.26)	1.26 (1.28)	*s*	
C-3′-Me	1.16 (1.10)	1.16 (1.15)	— —	—	2.16	—	1.17 (1.12)	1.21 (1.15)	*d/s*	6.5
H-3′	3.82 (3.83)	5.09 (5.17)	— —	—	—	—	3.87 (3.90)	5.09 (5.21)	*q*	6.5
C-2″-Me	0.99 (0.85)	1.09 (0.94)	1.00 (0.78)	1.25	1.25	1.07	1.03 (0.88)	1.07 (0.89)	*d*	7
C-3″-Me	1.16 (1.01)	1.20 (0.96)	1.12 (0.82)	2.18	2.16	1.26	1.14 (0.97)	1.16 (0.97)	*d/s*	6.5
H-3″	3.86 (3.84)	4.96 (5.02)	3.77	—	—	—	3.81 (3.75)	4.95 (4.99)	*m*	
H-2″	2.39 (2.36)	2.46 (2.46)	—	3.49	3.47	3.85	2.35 (2.27)	(2.32)	*m*	
OMe	3.79 (3.50)	3.80 (3.57)	3.80 (3.49)	3.80	3.80	3.75	3.80 (3.49)	3.79 (3.57)	*s*	
OAc	— —	2.00 (1.80)	— —	—	—	—	— —	1.92 (1.76)	*s*	
		1.90 (1.67)						1.90 (1.68)		

* Conditions the same as for Table 1.

1d, the ^{1}H NMR spectral parameters of which were identical with those reported for polydalin [2].

Tetraludin B (**2a**), $C_{26}H_{36}O_{11}$, mp 164–5° and tetraludin A (**1a**) exhibited very similar ^{1}H NMR spectra, except that in **2a** the acetate methyl signal was missing and instead two methyl doublets appeared at δ 0.99 (J = 7 Hz) and 1.16 (J = 6.5 Hz). Since the IR spectrum of the acetate (**2b**) showed an OH absorption at 3480 cm^{-1}, and in the ^{1}H NMR spectrum two acetate methyls at δ 1.9 and 2.0 were present, tetraludin B must contain two secondary and one tertiary hydroxyl group. Based on the empirical formula, two five-carbon ester side chains must be present in **2a**. From ^{1}H NMR and MS data, one of the side chains had to be the 2-methyl-2,3-dihydroxybutanoate moiety (**A**) as in **1a**. MS peaks at *m/e* 406 (M − $C_5H_{10}O_3$) and 101 ($C_5H_9O_2$) together with the above ^{1}H NMR signals suggested a 2-methyl-3-hydroxybutanoate (**C**) as the second ester group in **2a**. Oxidation of tetraludin B with periodic acid and subsequent hydrolysis of the pyruvate (**2c**) provided the alcohol **2f**, which in the ^{1}H NMR spectrum showed a distinct upfield shift of the H-8 signal from 6.66 in **2a** to 5.1 in **2f**, thus establishing a C-8 attachment of **A** in **2a**. Oxidation of **2a** with Jones' reagent provided a mixture of products which were, after PLC, identified by ^{1}H NMR as **2c**, **2d** and **2e**. The ^{1}H NMR parameters of these oxidation products further verified the correctness of the above spectral assignments of the side chains.

Tetraludin C (**3a**), $C_{26}H_{36}O_{11}$, mp 172–3° (ether) showed IR and ^{1}H NMR spectra nearly superimposable with those of tetraludin B (**2a**). ^{1}H NMR spectra exhibited nearly identical signal shifts for the medium ring proton absorptions with very slight differences only observed for the methyl signals of the ester side chains.

Acetylation of tetraludin C gave the diacetate (**3b**). When compared with **2b**, the ^{1}H NMR spectrum of **3b** in $CDCl_3$ showed only slight chemical shift differences for one of the acetate signals and the ester side chain methyls. The shift differences became rather clear when the ^{1}H NMR spectrum of the diacetates **2b** and **3b** were determined in C_6D_6. The ^{1}H NMR spectrum of tetraludin C diacetate (**3b**) showed three doublets with chemical shifts at δ 0.89, 0.97, 1.15 and a singlet at 1.28 compared with signals at 0.94, 0.96, 1.15 and 1.13, respectively, for tetraludin B diacetate (**2b**).

When tetraludin C was oxidized with periodic acid, the product obtained was identical with the pyruvic acid derivative (**2c**) obtained from tetraludin B. Mild hydrolysis of **2c** from **3a** with sodium bicarbonate gave **2f**. This indicated that the two melampolides **2a** and **3a** are diasteroisomeric and only differ in the chirality at C-2′ and/or C-3′ of the 2-methyl-2,3-dihydroxybutyrate side chain (**A**) at C-8.

Applying Bohlmann's procedure [1] for the isolation of root constituents of *Tetragonotheca ludoviciana*, *T. repanda*, *T. helianthoides* and *T. texana* provided the known C-17 acetylenes **4** and **6** [1] from each species. The compounds were identified by 270 MHz ^{1}H NMR, UV and MS spectral methods. Compounds **4** and **6** were correlated also by MnO_2 oxidation of **4** to give **6**. From non-polar fractions of areal parts of *T. ludoviciana*, the acetate **5** was isolated in low yield and identified by acetylation of alcohol **4**. The acetylation product of **4** gave IR, UV and NMR spectra identical with those of the natural acetate **5**.

EXPERIMENTAL

Tetragonotheca ludoviciana (T. and G.) Gray, was collected in August, 1977 at Tarrant Co., Texas (Bacon and Bragg 1652, voucher at UTA). Dried leaves (582 g) were extracted and worked up as previously described, providing 9.0 g of crude syrup which was chromatographed over 250 g of Si gel using $CHCl_3$ and mixtures of $CHCl_3$–Me_2CO (2.5, 5.0, 10.0, 20.0, 40.0 and 80.0%) as eluant; 250 ml fractions were taken and all fractions were monitored by TLC.

Tetraludin A (**1a**). Chromatography fractions 16–17 provided 0.7 g of an oily compound. IR ν_{max}^{Film} cm^{-1}: 3500 (OH); 1760 (γ-lactone), 1740 (ester), 1715 (α,β-unsaturated ester), 1665, 1625 (double bonds). CD: (c, 1.6 × 10^{-4}; MeOH), 25°, $[\theta]_{213}$

-43687, $[\theta]_{260}$ -1165. Low resolution MS *m/e* (rel. int.): 466 (M^+, 0.7%), 422 (M − Me—CH=O, 2.1); 362 (M − HOAc–Me—CH=O, 13.5); 350 (M − $C_5H_8O_3$, 4.0); 333 (M − $C_5H_9O_4$, 3.5); 332 (M − $C_5H_{10}O_4$, 3.8); 291 (M − $C_5H_9O_4$ —CH_2=C=O or M − $C_5H_8O_3$—Me—CO_2, 29.9); 274 ($C_{16}H_{18}O_4$, 17.9); 273 ($C_{16}H_{17}O_4$, 41.0); 272 ($C_{16}H_{16}O_4$, 85.9); 259 ($C_{15}H_{18}O_4$, 33.0); 258 ($C_{15}H_{14}O_4$, 17.3); 240 ($C_{16}H_{16}O_4$—MeOH, 18.7); 241 ($C_{16}H_{17}O_4$—MeOH, 16.5); 242 ($C_{16}H_{18}O_4$—MeOH, 14.3); 213 ($C_{14}H_{13}O_2$, 41.0); 45 (Me—CH=$\overset{+}{O}$H, 41.5); 43 (Me—C=O, 100.0). (Calc. for $C_{21}H_{26}O_9$: MW, 422.1569. Found: MW (MS), 422.1578). Acetylation of **1a** (100 mg) with Ac_2O–Py at room temp. for 5 hr gave **1b**; IR ν_{max} cm^{-1}: 3500, 1765, 1740, 1710, 1665, 1720.

Pyruvate (**1c**). Periodic acid (200 mg) was stirred with 10 ml Et_2O for 1 hr, and decanted over a soln of 150 mg tetraludin A (**1a**) in Et_2O, the reaction being monitored by TLC. When the reaction was completed the ethereal soln was washed with H_2O, dried and the solvent evapd. The reaction mixture was then chromatographed over Si gel. IR ν_{max} cm^{-1}: 1765, 1740, 1715.

Hydrolysis of the pyruvate **1c**. A soln of 100 mg **1c** in 4 ml EtOH was treated with 25 mg $NaHCO_3$ at room temp. After 2 hr, the reaction mixture was worked up to give **1f**. IR ν_{max} cm^{-1}: 3500, 1765, 1740, 1715, 1670, 1620.

Oxidation of **1a**. Tetraludin A (100 mg) was dissolved in 5 ml Me_2CO, cooled at 5° and Jones' reagent was added. The reaction was monitored by TLC, the reaction mixture worked up in the usual manner and chromatographed over Si gel. The less polar compound was identified as the pyruvate **1c**, and the more polar compound was identified as polydalin. IR ν_{max} cm^{-1}: 3450, 1765, 1740, 1715, 1710.

Tetraludin B (**2a**). Chromatography fractions 18–19 (0.6 g) provided **2a**, mp 164–5°. IR ν_{max} cm^{-1}: 3450, 1765, 1740, 1715, 1665, 1620. CD: (*c*, 8.0×10^{-5}; MeOH), 25°, $[\theta]_{214}$ -101525, $[\theta]_{260}$ -2620. MS *m/e* (rel. int.): 524 (M^+, 3.0); 480 (M − Me—CH=O, 0.9); 406 (M − $C_5H_{10}O_3$, 1.9); 407 (M − $C_5H_9O_3$, 2.7); 391 (M − $C_5H_9O_4$, 1.7); 362 (M − $C_5H_{10}O_3$—Me—CH=O, 23.4); 291 ($C_{16}H_{19}O_5$, 56.9); 274 ($C_{16}H_{18}O_4$, 27.7); 273 ($C_{16}H_{17}O_4$, 90.7); 272 ($C_{16}H_{16}O_4$, 100.0); 259 ($C_{15}H_{15}O_4$, 45.2); 258 ($C_{15}H_{14}O_4$, 16.6); 240 ($C_{16}H_{16}O_4$—MeOH, 20.8); 241 ($C_{16}H_{17}O_4$—MeOH, 22.2); 242 ($C_{16}H_{18}O_4$—MeOH, 14.9); 213 ($C_{14}H_{13}O_2$, 41.5); 101 ($C_5H_9O_2$, 18.8); 83 (C_5H_7O, 48.4); 55 (C_4H_7, 32.6). (Calc. for $C_{26}H_{36}O_{11}$: C, 59.53; H, 6.92. Found: C, 59.36; H, 6.96%). Derivatives **2b** to **2f** were obtained under conditions described above for the tetraludin A derivatives. Their ^1H NMR parameters are summarized in Table 1.

Tetraludin C (**3a**). Fractions 22–24 provided, after further chromatographic purifications, **3a**, mp 172–3° (Et_2O–petrol, 9:1). IR ν_{max} cm^{-1}: 3500, 1765, 1735 and 1715. CD: (*c*, 3.5×10^{-5}; MeOH), 25°, $[\theta]_{214}$ -122765, $[\theta]_{260}$ -3593. MS *m/e* (rel. int.): 524 (M^+, 1.6); 480 (M − Me—CH=O, 1.1); 406 (M − $C_5H_{10}O_3$, 1.3); 407 (M − $C_5H_9O_3$, 1.8); 391 (M − $C_5H_9O_4$, 1.6); 362 (M − $C_5H_{10}O_3$—Me—CH=O, 20.3); 291 ($C_{16}H_{19}O_5$, 51.2); 274 ($C_{16}H_{18}O_4$, 24.9); 273 ($C_{16}H_{17}O_4$, 70.0); 272 ($C_{16}H_{16}O_4$, 100.0); 259 ($C_{15}H_{15}O_4$, 42.0); 258 ($C_{15}H_{14}O_4$, 14.1); 240 ($C_{16}H_{16}O_4$—MeOH, 18.6); 241 ($C_{16}H_{17}O_4$—MeOH), 20.7); 242 ($C_{16}H_{18}O_4$—MeOH, 12.2); 213 ($C_{14}H_{13}O_2$, 38.8); 101 ($C_5H_9O_2$, 14.1); 83 (C_5H_7O, 29.3); 55 (C_4H_7, 15.4). (Calc. for $C_{26}H_{36}O_{11}$: C, 59.3; H, 6.92. Found: C, 59.64; H, 7.18%).

Derivatives **3b** to **3d** were obtained under conditions described above for the tetraludin A derivatives. ^1H NMR parameters are summarized in Table 1.

Acetylenic constituents in Tetragonotheca *species*. Plant sources: *Tetragonotheca repanda* (Buckl.) Small (collected in Texas, Brooks Co., 30 April 1976, *Urbatch* and *Fischer* 2460; voucher at Louisiana State University Herbarium [LSU]). *T. ludoviciana* (collected in Texas, Tarrant Co., August 1977, *Bacon* and *Bragg* 1652; voucher at Herbarium of the University of Texas at Arlington). *T. helianthoides* L. (collected in Mississippi, Lamar Co., 13 July 1976, *Urbatch* 2750; voucher at LSU). *T. texana* (Gray) Englem and Gray (collected in Texas, Travis Co., W. of Austin, 30 May 1976, M.D. and M.A. *Whalen* 345; voucher at LSU).

Extractions of ground roots of the four *Tetragonotheca* species were carried out with a 2:1 mixture of Et_2O–petrol [1]. Crude fractionations were performed by CC (Si gel, activity II), beginning with petrol followed by petrol–Et_2O mixtures with increasing amounts of Et_2O (5, 10, 15, 25, 50, 100% Et_2O). Subsequent PLC (Si gel GF 254) of the crude fractions, which were monitored by TLC and UV, were carried out with Et_2O–petrol mixtures as eluants providing *ca* 20–30 mg of acetylenic constituents **4** and **6** per 100 g of roots. The UV and ^1H NMR spectral data of the acetylenic compounds were shown to be identical with data reported in the lit. for alcohol **4** and aldehyde **5** [1]. The 270 MHz ^1H NMR spectral parameters shown for alcohol **4** are given in **4a**.

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