Phytochemistry, Vol. 21, No. 8, pp. 2009–2011, 1982.
Printed in Great Britain.

0031-9422/82/082009-03$03.00/0

VOLATILE COMPONENTS OF *ARTEMISIA CAPILLARIS*

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(*Revised received* 4 *January* 1982)

Key Word Index—*Artemisia capillaris*; Compositae; capillene; dehydrofalcarinone; dehydrofalcarinol; 5-phenyl-1, 3-pentadiyne; aesculetin dimethyl ether; terpenes.

Abstract—Terpenoid and acetylenic components not reported previously in *Artemisia capillaris* have been identified, including *p*-cymene, 5-phenyl-1, 3-diyne, dehydrofalcarinone and dehydrofalcarinol. The distribution of volatile components in different parts of the plant is described.

INTRODUCTION

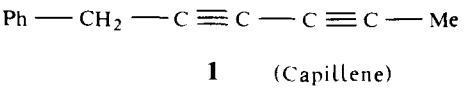
Capillene (**1**) and several other acetylenes have been isolated from the steam-distilled essential oil of the aerial parts of *Artemisia capillaris* Thunb. [1–7]. Another acetylene has been isolated from the ether extract of the roots [8], and aesculetin dimethyl ether has been isolated from the hot water extract of the seeds [9]. The present investigation has been undertaken to identify volatile components not reported previously in this plant and to elucidate their distribution within the plant.

RESULTS AND DISCUSSION

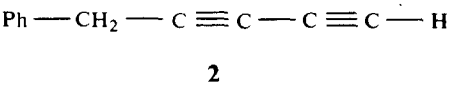
The plant was separated into seeds, fine stems and leaves, stems and roots; each part was macerated with *n*-hexane–ether (1:1), and the volatile components of each extract were examined by GC. The table shows the retention time, the results of identification and the relative percentage of thirty-one components (as peaks) on the GC trace. Components 1–4, 6, 8, 11, 12 and 13 have been identified by GC/MS as terpenoids, and 14, 15, 23 and 27 as previously reported acetylenes [1–4]. Component 29 was isolated by CC and identified by analytical and spectral data as aesculetin dimethyl ether (6, 7-dimethoxycoumarin) [9]. The GC/MS data show that 7, 30 and 31 are previously unidentified acetylenes. 7 was isolated by CC and TLC and its identity as 5-phenyl-1, 3-pentadiyne (**2**) was supported by the IR, UV, GC/MS, ^{1}H NMR and ^{13}C NMR spectral data. **2** was first isolated from *Artemisia dracunculus* L. [10], and it is expectable that **2** should coexist with capillene (**1**) in the same plant.

Components 30 and 31, especially the latter, are major components of the roots; they are so unstable that purification is very difficult. They were purified by repeated CC on Si gel. Because the MS spectra of the purified 30 and 31 gave little information about their structures, they were hydrogenated on Pt–C for the determination of their skeletons. The perhydro compounds were identified as heptadeca-3-one and heptadeca-3-ol respectively by analytical and spectral data. Eventually 30 and 31 were identified as dehydrofalcarinone (**6**) and dehydrofalcarinol (**7**), respectively, from the data on their perhydro derivatives and from NMR spectra.

6 was earlier isolated from the roots of *Artemisia campestris* L. by Bohlmann [11]. It is so unstable that it was converted to a MeOH adduct, and the structure was suggested by spectral data and established by synthesis. **7** was isolated first from *Artemisia atrata*



1 (Capillene)



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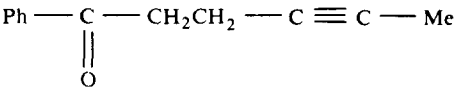
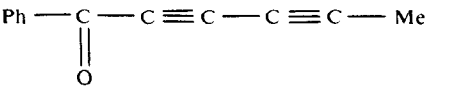
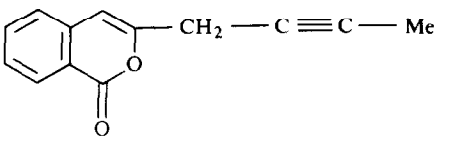


3 (Capillone)



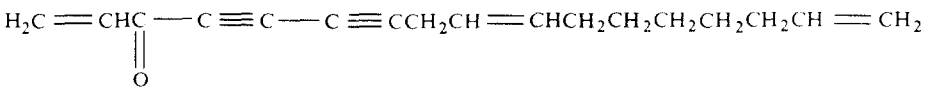
4 (Capillin)



5 (Capillarin)

Lam. by Bohlmann, and the structure was determined by ^{1}H NMR spectroscopy [12]. In our case these two acetylenes have been identified mainly by ^{13}C NMR spectra.

As can be seen from Table 1, the seeds contain the greatest amount of oil. The seeds and fine stems and leaves contain much aromatic C-11–C-13 acetylenes (7, 14, 15, 23 and 27) and aesculetin dimethyl ether (29); capillene (14) is the most abundant substance, and the content of aliphatic acetylenes is very low.



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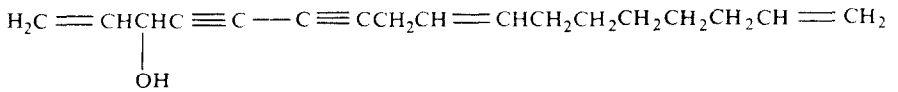

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Table 1. Distribution and identification of volatile components of *Artemisia capillaris*

Peak no.	R_t (sec)*	Confirmed identity†	Relative %‡			
			Seed	Fine stem and leaf	Stem	Root
1	2.5	α-Pinene	0.50	0.46	0.34	0.03
2	3.1	β-Pinene	8.93	6.03	1.45	0.17
3	3.8	*p*-Cymene	4.71	2.22	1.02	0.07
4	4.4	Δ^3-Carene	9.15	4.16	0.80	trace
5	5.7	Unknown	0.15	trace	0.07	
6	8.1	α-Terpineol	0.33	0.30	0.15	0.64
7	12.2	5-Phenyl-1, 3-pentadiyne (**2**)	6.03	1.94	0.29	0.09
8	13.3	Acetylborneol	0.41	0.72	0.53	0.27
9	16.1	Unknown	0.31	trace	0.62	0.05
10	17.2	Unknown	0.22	0.36	0.45	0.73
11	18.1	Methyleugenol	0.46		0.13	
12	19.1	β-Elemene	0.49	1.38	1.69	4.09
13	20.5	β-Caryophyllene	6.01	7.17	4.45	3.43
14	22.4	Capillene (**1**)	33.53	25.66	8.42	13.75
15	24.0	Capillone (**3**)	1.82	2.21	2.35	1.26
16	25.0		0.18	0.46	0.50	0.18
17	25.8					0.23
18	26.4		0.20	0.41	0.62	trace
19	27.3	Unknown	0.25	0.36	1.20	0.41
20	28.5		0.35	0.64	0.43	0.34
21	29.4		0.24	1.10	2.97	0.13
22	31.0		0.43	1.64	2.57	0.77
23	32.8	Capillin (**4**)	3.14	6.43	4.81	0.80
24	33.4		0.16	0.40	0.16	0.30
25	34.5	Unknown	0.20	0.52	0.27	0.68
26	36.1		0.18	0.43	0.32	
27	38.1	Capillarin (**5**)	9.64	14.20	2.81	1.54
28	39.7	Unknown	0.45	0.26	1.07	0.26
29	41.5	Aesculetin dimethyl ether	5.76	3.41	2.26	0.45
30	46.1	Dehydrofalcarinone (**6**)	2.17	6.31	14.31	1.98
31	47.2	Dehydrofalcarinol (**7**)	3.61	9.32	43.04	67.36

*GC; 5% silicone OV-101, temp. programmed 130–200° at 3°/min.

†Identified by GC/MS (1% silicone OV-101, temp. programmed 70–200° at 3°/min.

‡Calculated from GC peak area.

Although the amount of oil in the roots and the stems is less, the main components are aliphatic C-17 acetylenes (30 and 31).

EXPERIMENTAL

Plant material and oil removal. A. capillaris (2 kg) harvested in the suburbs of Tokyo at the termination of flowering was separated into: seeds (660 g), fine stems and leaves (238 g), stems (478 g) and roots (410 g). Each part was chopped and macerated (×4) with *n*-hexane–Et_2O (1:1), and 35.7 g, 6.5 g, 3.3 g and 7.4 g of oil was obtained respectively.

Component separation and identification. Each extract was submitted to GC/MS (1% silicone OV-101, 2 m × 3 mm, temp. programmed 130–200° at 3°/min, He) and MS were compared with those of authentic specimens. After identification of components by MS, the GC relative retention times of authentic specimens were also checked. The results are shown in Table 1.

Isolation and identification of component 29. The seed oil (12 g) was extracted twice with C_6H_6, the C_6H_6-insoluble residue (2.7 g) was extracted with $CHCl_3$, and the $CHCl_3$ solution was chromatographed on Si gel with $CHCl_3$ elution. The eluted solid (0.45 g) was recrystallized from EtOH, mp 144–145°, analytical results: found: C, 63.79; H, 4.78%, Calc. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (lactone), 1625, 1585, 1487 (C_6H_6); UV λ_{max}^{EtOH} nm (log ϵ): 230 (3.950), 252 (3.458), 296 (3.429), 343 (3.760); ^1H NMR (100 MHz, $CDCl_3$): δ 3.92 (3H, *s*, OCH_3), 3.94 (3H, *s*, OCH_3), 6.26 (H, *d*, J = 3.8 Hz, =CH– at 3), 7.65 (H, *d*, J = 3.8 Hz, –CH= at 4), 6.79, 6.89 (H, *s*, C-5 or C-8); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 56.3 (OCH_3), 99.8 (C-8), 108.1 (C-5), 111.4 (C-10), 113.3 (C-3), 143.3 (C-4), 161.1 (>C=O). These data indicate 29 is aesculetin dimethyl ether [9].

Isolation and identification of component 7. The seed oil (22.5 g) was distilled under vacuum, a fraction boiling at 72–81°/0.5 mm Hg (2.23 g) was chromatographed on Si gel with $CHCl_3$ and gradient MeOH elution. Subsequently, the combined $CHCl_3$ eluted fraction was rechromatographed on a Si gel layer (1.5 mm) developed with *n*-pentane. A major band (R_f 0.42) on TLC gave **2** (45 mg), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3310, 2100 (–C≡CH), 2250 (–C≡C–), 3040 (–C_6H_5); UV λ_{max}^{EtOH} nm: 226, 238, 247, 252, 257, 264, 267; GC/MS: 70 eV, *m/z* (rel. int.): 140 $(M)^+$ (75.5), 139 $(M-1)^+$ (100), 95 (49.6), 77 $(C_6H_5)^+$ (9.8), 63 $(-CH_2C{\equiv}CC{\equiv}CH)^+$ (27.8), 43 (42.0); ^1H NMR (100 MHz, $CDCl_3$): δ 3.61 (2H, *d*, J = 1.2 Hz, $-CH_2-$ at 5), 1.97 (H, *t*, J = 1.2 Hz, ≡CH at 1), 7.26 (–C_6H_5); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 25.3 (C-1), 65.7, 66.7, 68.3, 75.5 (C-2, C-3, C-4, C-5), 134.8 (C_6H_6 C-1′), 127.8 (C_6H_6 C-2′, C-6′), 128.6, 128.4 (C_6H_6 C-3′, C-5′), 126.9 (C_6H_6 C-4′).

Isolation of components 30 *and* 31. The extracts from the roots (9 g) were chromatographed on Si gel (145 g) with gradient elution (*n*-hexane, *n*-hexane–C_6H_6, C_6H_6, C_6H_6–Et_2O, Et_2O), and 50 fractions were collected, which were assayed by GC. Component 30 was mainly present in fraction 16 eluted with *n*-hexane–C_6H_6 (7:3) and component 31 mainly in fraction 39 eluted with C_6H_6–Et_2O (9:1). Rechromatography on Si gel of fraction 16 and fraction 39 gave both pure substances as pale yellow oils.

Hydrogenation and identification of component 30. Purified 30 (80 mg) was hydrogenated on 5% Pt–C (30 mg) in EtOH (5 ml) and purified by TLC on Si gel, giving colourless crystals of heptadeca-3-one. Found: C, 79.73; H, 13.50%, Calc. for $C_{17}H_{34}O$: C, 80.24; H, 13.47%. GC/MS: 70 eV, *m/z* (rel. int.): 254 $(M)^+$ (3.8), 225 $(M-C_2H_5)^+$ (35.9), 72 (100), 73 (52.8), 85 (30.2), 57 $(C_2H_5C{=}O)^+$ (77.6), 29 $(C_2H_5)^+$ (30.2); ^1H NMR (100 MHz, $CDCl_3$): δ 0.88 (3H, *t*, J = 3.5 Hz, $-CH_3$ at 17), 1.05 (3H, *t*, J = 4 Hz, $-CH_3$ at 1), 1.26 (22H, *t*, $-CH_2-$ at 6–16), 1.55 (2H, *br*, $-CH_2-$ at 5), 2.38 (2H, *t*, J = 3.5 Hz, $-CH_2-$ at 4), 2.42 (2H, *q*, J = 3.5 Hz, $-CH_2-$ at 2); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 7.9 (C-1), 35.9 (C-2), 211 (C-3), 42.4 (C-4), 24.0 (C-5), 29.45 (C-6), 29.7 (C-7–C-13), 29.37 (C-14), 31.9 (C-15), 22.7 (C-16), 14.1 (C-17). The original material, dehydrofalcarinone (**6**) was obtained as an unstable pale yellow oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 (>C=O), 2250 (C≡C); UV λ_{max}^{EtOH} nm: 223, 262, 277, 293; GC/MS: 70 eV, *m/z* (rel. int.): 240 $(M)^+$ (6.9), 55 $(CH_2{=}CHC{=}O)^+$ (100), 41 $(CH_2{=}CHCH_2)^+$ (72.7); ^1H NMR (100 MHz, $CDCl_3$): δ 1.36 (6H, *t*, $-CH_2-$ at 12, 13, 14), 2.06 (4H, *t*, $=CCH_2-$ at 11, 15), 3.14 (2H, *t*, $=CCH_2C=$ at 8), 4.8–6.52 (6H, –CH=CH– at 1, 2; 9, 10; 16, 17); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 133.7 (C-1), 137.8 (C-2), 177.5 (C-3), 63.6, 70.7, 77.1 (C-4, C-5, C-6), 88.0 (C-7), 18.0 (C-8), 133.9, 120.8 (C-9, C-10), 27.2 (C-11), 28.68, 28.73, 28.99 (C-12, C-13, C-14), 33.7 (C-15), 138.8 (C-16), 114.3 (C-17).

Hydrogenation and identification of component 31. Purified 31 (55 mg) was hydrogenated on 5% Pt–C (20 mg) in EtOH (5 ml), and purified by TLC on Si gel, giving heptadeca-3-ol as a colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (–OH); GC/MS: 70 eV, *m/z* (rel. int.): 256 $(M)^+$ (1.6), 238 $(M-H_2O)^+$ (3.3), 227 $(M-C_2H_5)^+$ (8.2), 59 $(C_2H_5C{=}OH)^+$ (100); ^1H NMR (100 MHz, $CDCl_3$): δ 0.93 (3H, *t*, J = 6.5 Hz, $-CH_3$ at 1), 0.92 (3H, *t*, J = 6.5 Hz, $-CH_3$ at 17), 1.26 (24H, $-CH_2-$ at 5 ~ 16), 1.39, 1.41 (4H, $-CH_2-$ at 2, 4), 2.23 (H, *s*, OH), 3.5 (H, *br*, >CH–O at 3); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 9.9 (C-1), 30.2 (C-2), 73.4 (C-3), 37.0 (C-4), 25.7 (C-5), 29.7 (C-6–C-13), 29.4 (C-14), 32.0 (C-15), 22.7 (C-16), 14.1 (C-17). The original acetylene **7** was an unstable pale yellow oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (–OH), 2270 (–C≡C–); UV λ_{max}^{EtOH} nm: 208, 220, 232, 257; GC/MS: 70 eV, *m/z* (rel. int.): 242 $(M)^+$ (1.0), 67 (43.1), 55 (78.4), 41 $(CH_2{=}CHCH_2)^+$ (100), 27 $(CH_2{=}CH)^+$ (60.8); ^1H NMR (100 MHz, $CDCl_3$): δ 1.36 (6H, *t*, $-CH_2-$ at 12, 13, 14), 2.04 (4H, *d*, J = 3.5 Hz, $=CCH_2-$ at 11, 15), 2.52 (H, *s*, –OH), 3.03 (2H, *d*, J = 3.5 Hz, $=CCH_2C=$ at 8), 4.8–6.2 (6H, –CH=CH– at 1, 2; 9, 10; 16, 17); ^{13}C NMR (25.05 MHz, $CDCl_3$): δ 136.1 (C-1), 116.9 (C-2), 63.4 (C-3), 74.3 (C-4), 71.2, 64.1 (C-5, C-6), 80.1 (C-7), 17.7 (C-8), 132.9, 122.0 (C-9, C-10), 27.1 (C-11), 29.1, 28.8, 28.7 (C-12, C-13, C-14), 33.7 (C-15), 138.9 (C-16), 114.2 (C-17).

Acknowledgements—The authors are grateful to Dr. K. Sakai and Mr. A. Abe, Toray Research Center, for ^1H and ^{13}C NMR spectra.

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