fatty acid (500 mg) with 5-methylhexanol (1000 mg) with a drop of conc. H_2SO_4 for 3 hr at 150° gave the corresponding esters (950 mg).

Synthesis of 2-ethylhexyl esters. Esterification of the fatty acids with 2-ethylhexanol [3] as above gave the corresponding esters.

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CONSTITUENTS OF THE ESSENTIAL OIL OF *ARTEMISIA REHAN*

BERHANU ABEGAZ* and PAULOS G. YOHANNES
Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia

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Key Word Index—*Artemisia rehan*; Asteraceae; essential oil; davanone; eudalene; GC/MS analysis.

Abstract—The composition of the essential oil of *A. rehan* has been studied. A total of 22 components were identified, the major components being davanone and camphor, and the occurrence of eudalene is noted for the first time. The characteristic blue colour of the oil is due to chamazulene.

INTRODUCTION

Artemisia rehan Chiov is an odorous herb which is widespread in and native to Ethiopia. Although numerous reports appear in the literature on the chemistry of different species of *Artemisia* no studies have been reported on *A. rehan*. In this paper we report our findings on the chemical constituents of the oil obtained by steam distillation of the whole plant.

RESULTS AND DISCUSSION

The essential oil from the whole plant, obtained by steam distillation of fresh material, was separated on silica gel with hexane and ethyl acetate to separate the hydrocarbons from the oxygenated derivatives. The fractions were then subjected to GC and GC/MS. Identification was confirmed by comparison of R_t values with those of standard compounds as well as by computerized matching of acquired mass spectra with stored NBS mass spectral library in the data system of the GC/MS. A total of 22 components representing 87% of the oil were identified (see Table 1). Among the main components, davanone **1** and chamazulene **2** were isolated by CC and identified on the basis of IR, ^1H NMR and mass spectra. The spectra obtained were identical with literature values [1, 2] for these compounds. The results of the analysis of the essential oil show that camphor (24%) and davanone (44%) are the major constituents of the oil. Davanone **1** is also reported to occur in the oil of *A. pallens* [3, 4] and in one of the genotypes of *Tanacetum vulgare* [5]. Capillary GC/MS analysis of the oil showed the presence of two additional components (0.6% and trace) which gave very similar mass spectra to that of the major constituent, davanone. These are designated in the table as davanone-isomer-1 and davanone-isomer-2. It is not entirely clear whether these are diastereomeric compounds or closely related structures such as artemone **3**. It has been shown that synthetic davanone diastereomers can be separated on a capillary column

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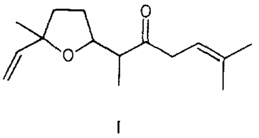
*Address all correspondence to this author at: Department of Chemistry, Boston University, Boston, MA 02215, U.S.A.

Table 1. Constituents of the essential oil of *A. rehan*

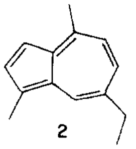
Compound	% of oil	Method of identification	Compound	% of oil	Method of identification
Bornyl acetate	1.76	GC/MS	Eudesmol	0.81	GC/MS
Camphene	0.01	GC	Linalol	3.88	GC/MS
Camphor	23.49	GC/MS	Limonene	0.25	GC
Chamazulene	0.26	MS, IR, NMR	Mentol	0.63	GC
1, 8-Cineole	0.50	GC	Menthone	0.35	GC
Davanone-isomer-1	0.60	GC/MS	Myrcene	0.33	GC/MS
Davanone-isomer-2	trace	GC/MS	α-Pinene	0.04	GC
Davanone	44.36	GC/MS, IR, NMR	β-Pinene	0.30	GC
cis-Ethyl cinnamate	1.38	GC/MS	γ-Terpinene	0.65	GC
trans-Ethyl cinnamate	2.93	GC/MS	Terpinene-4-ol	5.16	GC/MS
Eudalene	2.05	GC/MS	α-Terpineol	trace	GC/MS
Total recovered				86.74	

[6, 7]. The co-occurrence of artemone and davanone in the oil of *A. pallens* [8] and the observation that both compounds exhibit similar mass spectra are also documented. Attempts are currently under way in our laboratory to isolate and determine the structures of the minor components.

Eudalene **4**, a non-terpenoid aromatic compound, whose occurrence in plants and essential oils has not been reported previously was identified as a component of the oil of *A. rehan*. Eudalene may very well be an artefact arising by the loss of one carbon from a labile and highly functionalized sesquiterpenoid precursor.



1



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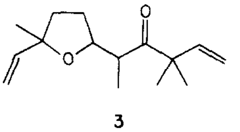

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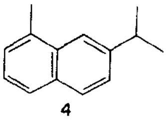

4

Chamazulene **2**, which is responsible for the blue colour of the oil has also been identified in other essential oils [9] and is believed to be an artefact formed during steam distillation.

EXPERIMENTAL

Isolation of essential oil and chromatographic analysis. Plants were collected around Addis Ababa and identified at the University Herbarium. Steam distillation of fresh whole plant material gave a dark blue oil (0.20%, density 0.912). The oil was separated on Si gel which was successively eluted with hexane and EtOAc. The oil as well as the various fractions were analysed by GC with dual FID detector using two columns packed with 10% Carbowax 20 M (1.5 m × 3 mm stainless steel) and 10% UCON (1.5 m × 3 mm copper). Analyses were performed either isothermally at 180° or by programming from 70 to 200° at 2°/min. Injector temp. was 200° and detector, 250°. N_2 at 30 ml/min was used as carrier gas. GC/MS analysis was carried out using 50-m WCOT sp1000 glass capillary column.

Isolation and characterization of davanone. The combined EtOAc fractions 2 and 3 (550 mg), containing the major component of the oil chromatographed on a column of Si gel and eluted with mixtures of EtOAc–hexane in the ratio 1:20–1:1. Davanone **1** was isolated and had $[\alpha]_D^{21}+69°$; IR ν_{max}^{neat} cm^{-1}: 1710, 1640, 915, 990. ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.88 (3 H, *d*, $J = 7$ Hz), 1.17 (3 H, *s*), 1.57 (3 H, *s*), 1.70 (3 H, *s*), 2.60 (1 H, *m*), 3.08 (2 H, *br d*, $J = 7$ Hz), 3.88 (1 H, *m*), 4.96 (1 H, *dd*, $J = 10$, 2 Hz), 5.04 (2 H, *dd*, $J = 16$, 2 Hz), 5.78 (1 H, *dd*, $J = 10$, 16 Hz). MS, 70 eV, m/z (rel. int.): 236 (M^+), 111 (100), 93 (50), 55 (27), 69 (24), 94 (18).

Isolation and characterization of chamazulene. The hexane fractions from CC contained the blue component and gave a single spot on TLC (*n*-hexane–EtOAc, 26:1, R_f 0.59) and on GC UCON column. This was identified as chamazulene on the basis of its spectra: IR ν_{max}^{neat} cm^{-1}: 3100, 2975; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.33 (3 H, *t*, $J = 7$ Hz), 2.55 (3 H, *s*), 2.75 (3 H, *s*), 2.71 (2 H, *q*, $J = 7$ Hz), 6.55 (1 H, *d*, $J = 10$ Hz), 7.05 (1 H, *d*, $J = 4$ Hz), 7.15 (1 H, *dd*, $J = 10$, 2 Hz), 7.45 (1 H, *d*, $J = 4$ Hz), 7.93 (1 H, *d*, $J = 2$ Hz). MS, 70 eV, m/z (rel. int.): 184 (M^+), 169 (100), 184 (66), 153 (44), 155 (38), 128 (34), 152 (34), 77 (32), 155 (31).

Mass spectral data. MS, 70 eV, m/z (rel. int.): *Davanone-isomer-1*: 236 (M^+, 4), 180 (11), 125 (25), 111 (93), 93 (100), 81 (49), 69 (68), 55 (54), 43 (55). *Davanone-isomer-2*: 236 (M^+, 4), 180 (3) 125 (5), 111 (100), 93 (52), 81 (11), 69 (51), 55 (39). *Eudalene*: 184 (M^+, 98), 183 (22), 169 (100), 155 (26), 153 (29), 152 (22), 128 (17), 115 (12).

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GERMACRANE AND EUDESMANE DERIVATIVES FROM *CALEA RETICULATA**

FERDINAND BOHLMANN, NALEEN BORTHAKUR, ROBERT M. KING† and HAROLD ROBINSON†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, W. Germany; †Smithsonian Institution, Department of Botany, Stop No. 166, Washington, DC 20560, U.S.A.

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Key Word Index—*Calea recticulata*; Compositae; sesquiterpenes; germacra-4(15),5,10(14)-trien-1-one; eudesmane derivative; 6-epi-β-verbesinol coumarate.

Abstract—*Calea reticulata* afforded in addition to known compounds two new sesquiterpenes. These were germacrane and eudesmane derivatives, identified as germacra-4(15), 5, 10(14)-trien-1-one and 6-epi-β-verbesinol coumarate, respectively.

The aerial parts of *Calea reticulata* Gardn. afforded germacrene D, the triyneneepoxides **1** and **2** [1] and ichthyotherol (**3**) [2]. Furthermore, a sesquiterpene ketone was present, molecular formula $C_{15}H_{22}O$. The ^1H NMR spectrum (Table 1) showed that it was probably a derivative of germacrene D as the typical signals of H-5, H-6, H-12, H-13 and H-15 were nearly identical with those of germacrene D. A pair of downfield shifted narrowly split signals at δ 5.51 and 5.71 indicated a methylene ketone which was supported by the IR band at 1680 cm^{-1}. Spin decoupling allowed the assignment of all signals, which led to the structure **4**. The roots gave germacrene D and γ-humulene as well as a sesquiterpene coumarate, its ^1H NMR spectral data led to the structure **5**. (Table 2). The nature of the ester residue followed from the typical pairs of doublets, while the presence of an eudesmane derivative was indicated by comparing the ^1H NMR spectral data with those of β-verbesinol coumarate [3, 4]. However, the large couplings $J_{5,6}$ and $J_{6,7}$ clearly showed that the ester group was α-orien-

Table 1. ^1H NMR spectral data of compound **4** (400 MHz, $CDCl_3$, TMS as int. standard)

H-2	3.03 *m*	H-9	2.32 *m*
H-2′	2.50 *ddd*	H-9′	2.38 *dd br*
H-3	2.77 *ddd*	H-11	1.48 *dq*
H-3′	2.32 *mm*	H-12	0.88 *d*
H-5	5.75 *d*	H-13	0.81 *d*
H-6	5.25 *dd*	H-14	4.82 *s br*
H-7	1.78 *dddd*	H-14′	4.73 *s br*
H-8	1.96 *dddd*	H-15	5.71 *s br*
H-8′	1.55 *m*	H-15′	5.51 *d*

J (Hz): 2, 2′ = 12.5; 2, 3 = 10; 2′, 3 = 4; 2′, 3′ = 7; 3, 3′ = 13; 5, 6 = 15.5; 6, 7 = 10; 7, 8 = 10; 7. 8′ = 3.5; 7, 11 = 11, 12 = 11, 13 = 7; 8, 8′ = 15; 8, 9 = 4; 8, 9′ = 12; 8′, 9 = 5; 8′, 9′ ~ 1.5; 9, 9′ = 12.5; 9, 14 = 1.5.

Table 2. ^1H NMR spectral data of compound **5** (400 MHz, $CDCl_3$, TMS as int. standard)

HA5	2.11 *d*	H-2′,6′	6.84 *d br*
H-6	5.18 *dd*	H-3′,5′	7.39 *d br*
H-7	2.29 *m*	H-7′	7.59 *d br*
H-12 H-13	0.92 *d*	H-8′	6.29 *d*
H-14	0.80 *s*		
H-15	4.76 *s br*		
H-15′	4.36 *s br*		

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*Part 431 in the series "Naturally Occurring Terpene Derivatives". For Part 430 see Bohlmann, F., Ahmed, M. and Jakupovic, J. (1982) *Phytochemistry* **21**, 1793.