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# ESSENTIAL OIL FROM RHIZOMES OF *FERULA JAESCHKEANA**

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**Key Word Index**—*Ferula jaeschkeana*; Apiaceae; rhizome; essential oil; monoterpenoids; sesquiterpenes; GC-MS.

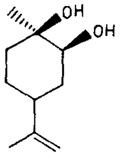
**Abstract**—Volatile components of the rhizomes of *Ferula Jaeschkeana* have been investigated to afford seven monoterpene hydrocarbons, 15 oxygenated monoterpenes, four sesquiterpene hydrocarbons and three sesquiterpene alcohols. Three new monoterpene alcohols have been isolated and their structures elucidated by spectroscopic methods and chemical transformations.

## INTRODUCTION

The genus *Ferula* comprises perennial herbs distributed from the Mediterranean region to Central Asia. Its several species are commercial sources of asafoetida, an oleo-gum resin, used as a flavouring material, a condiment and in medicine. *Ferula jaeschkeana* Vatke common to the north-west Himalayas yields a resin which is altogether different and is used mainly as an antiseptic [1]. The rhizomes of the plant, however, yield an essential oil which is used in the Indian perfumery industry [2]. The presence of several sesquiterpenoids have already been reported from the methanol extract of its rhizomes [2–4]. However, its essential oil has been investigated only cursorily [5–7]. We have recently reported the presence of *p*-menthendiols (**1**–**3**) from its oil [8]. In this paper we describe a detailed investigation of the oil after isolation and characterization of constituents by GC-MS, $^1$H NMR, $^{13}$C NMR, IR and chemical transformations.

## RESULTS AND DISCUSSION

In continuation of our efforts in searching for new sources of perfumery products [9–14], we collected rhizomes of *F. jaeschkeana* from the Kashmir valley which after hydrodistillation afforded a pale yellow oil (yield 1%). The oil after GC and GC-MS analysis afforded 44 well-resolved constituents. Seven of them were monoterpene hydrocarbons (53.03%), 15 oxygenated monoterpenes (21.5%), four sesquiterpene hydrocarbons (10.69%), three sesquiterpene alcohols (7.4%) and a few (4.8%) unidentified (Table 1). The major constituents of the oil included α-pinene (8.3%), *p*-cymene (14.3%), limonene (26.0%) and terpinen-4-ol (5.8%). The contribution of monoterpene diols (**1**–**4** and **7**, 5.5%) in imparting an exotic aroma to the oil was of particular importance. *p*-Menth-1β,4α-diol (**5**, 2.5%) did not impart any aroma, however, but its diacetate derivative produces an agreeable odour. These monoterpene diols along with sesquiterpene hydrocarbons (10.7%) and sesquiterpene alcohols (7.4%) make the oil long lasting and more attractive. Most of the constituents were identified by GC $R_t$, Kovats retention indeces and MS fragmentation but the important compounds, viz. *p*-cymene, limonene, carvacrol, cubenol, epicubenol and **1**–**3** were isolated and their $^1$H NMR and MS compared with those reported in the literature [8, 15] and with the library established by us. The structures of the new compounds (**4**, **5** and **7**) were elucidated using spectral methods and chemical transformations.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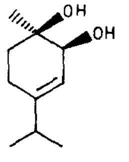
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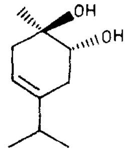
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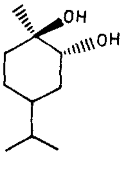
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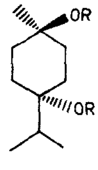
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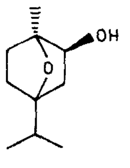
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The $^1$H NMR spectrum of **4** was, in part, similar to **3** [8]. The main difference was the absence of the broad singlet at δ5.30, which indicated that **4** is devoid of an endocyclic double bond. Compound **4** did not form an acetonide indicative of the presence of a 1,2-*trans*-diol. The H-2 appeared as a broad singlet at δ3.50 ($W_{1/2}$ = 8 Hz) as in the case of **3**. The MS and IR were in agreement with structure **4** (see Experimental). Similarly, the $^1$H NMR spectrum of **5** did not show any downfield signals except two broad singlets at δ4.6 and 4.2 which also disappeared after shaking with $D_2O$; this indicated that the molecule contained two tertiary hydroxyls. The doublet at δ0.90 collapsed to a singlet after irradiation of the double quartet at δ1.86. This showed that no hydroxyl is attached to C-7. Acetylation of **5** yielded **6** which showed two additional signals at δ2.06 and 2.07 indicating that hydroxyls are attached to C-1 and C-4. The stereochemistry at C-1 and C-4 was found to be same as that of 4-terpineol and **1**–**3** because dehydration of **5** with conc. $H_2SO_4$ yielded a mixture of 4-terpineol and α-terpinene. $^{13}$C NMR also showed two downfield signals at δ76.0 and 75.8 indicating the presence of two oxygenated carbons. These data along with MS and IR (see

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Table 1. Composition of essential oil of rhizomes of *Ferula jaeschkeana* (Column: CP Sil 5)

| Peak no. | Constituents | Identified by | % |
|---|---|---|---|
| 1 | α-thujene | a, b, c | 0.72 |
| 2 | α-pinene | a, b, c | 8.32 |
| 3 | u.i. | — | 0.12 |
| 4 | u.i. | — | 0.16 |
| 5 | Δ-3-carene | a, b, c | 0.75 |
| 6 | α-phellandrene | a, b, c | 0.18 |
| 7 | p-cymene | a, b, c, d | 14.30 |
| 8 | limonene | a, b, c, d | 25.96 |
| 9 | cis-ocimene | a, b, c | 2.80 |
| 10 | u.i. | — | 0.42 |
| 11 | α-thujone | a, b, c | 0.82 |
| 12 | camphor | a, b, c | 0.36 |
| 13 | u.i. | — | 0.70 |
| 14 | u.i. | — | 0.45 |
| 15 | u.i. | — | 0.33 |
| 16 | terpinen-4-ol | a, b, c | 5.80 |
| 17 | α-terpineol | a, b, c | 1.50 |
| 18 | carvone | a, b, c | 0.42 |
| 19 | *p*-cymen-7-ol | b, c | 0.46 |
| 20 | u.i. | — | 0.32 |
| 21 | u.i. | — | 0.27 |
| 22 | terpin-4-yl acetate | a, b, c | 3.35 |
| 23 | α-terpinyl acetate | a, b, c | 0.45 |
| 24 | 2β-hydroxy-1,4-cineole | c, d, e, f | 1.35 |
| 25 | *p*-menth-1β, 4α-diol | c, d, e, f | 2.45 |
| 26 | *p*-menth-1β, 2α-diol | c, d, f | 0.75 |
| 27 | *p*-menth-3-en-1,2,-diol | c, d, e, f | 1.36 |
| 28 | *p*-menth-4-en-1,2-diol | c, d, e, f | 1.15 |
| 29 | *p*-menth-8-en-1,2-diol | c, d, e, f | 0.93 |
| 30 | carvacrol | a, b, c, d | 0.84 |
| 31 | germacrene D | c | 0.72 |
| 32 | α-gurjunene | c | 3.10 |
| 33 | *iso*-longifolene | c | 2.62 |
| 34 | δ-selinene | c | 3.45 |
| 35 | $C_{15}H_{24}$ | c | 0.42 |
| 36 | $C_{15}H_{24}$ | c | 0.38 |
| 37 | u.i. | — | 0.36 |
| 38 | $C_{15}H_{24}O$ | c | 0.42 |
| 39 | u.i. | — | 0.46 |
| 40 | u.i. | — | 0.72 |
| 41 | *epi*-cubenol | c, d, f | 3.16 |
| 42 | cubenol | c, d, f | 3.80 |
| 43 | u.i. | — | 0.32 |
| 44 | u.i. | — | 0.21 |

a = $R_t$, b = Kovats retention index, c = MS, d = $^1$H NMR, e = $^{13}$C NMR, f = IR, u.i. = unidentified.

Experimental) were in complete agreement with the structure **5**.

The $^1$H NMR spectrum of **7** showed a double doublet ($J = 7$ and 2 Hz) at δ3.78 indicating the presence of a secondary equitorial hydroxyl. The irradiation of this signal led to the collapse of an overlapping multiplet at δ2.12 into an obscured multiplet. Similarly, the multiplet at δ2.12 after irradiation collapsed the two doublets at δ0.96 and 0.98 into singlets as well as the double doublet at δ3.78 into a doublet. This showed that H-3 and H-7 were appearing as overlapping multiplets at δ2.12. The appearance of a highly deshielded H-10 at δ1.42 and the collapse of the double quartet at δ2.12 into a singlet when the two doublets at δ0.98 and 0.96 were irradiated indicated that **7** is a 1,4-cineole derivative. The $^{13}$C NMR also showed three downfield signals at δ94.5, 88.0 and 77.2 and a quartet at δ30.0 which supported the structure as **7**. The stereochemistry at C-1 and C-4 was assumed to be same as that of 1,4-cineole but could not be confirmed. The MS and IR data (see Experimental) were also in agreement with structure **7**.

## EXPERIMENTAL

Plant material was collected in October, 1980 from Gulmarg, in the Kashmir region of North West Himalaya. Fresh rhizomes (10 kg) after hydrodistillation yielded 100 ml oil, $d^{33}$ 0.9238, $n_D^{33}$ 1.4750, $[\alpha]_D^{20} + 15.068°$. $^1$H NMR spectra were recorded at 400 MHz, $^{13}$C NMR at 20 MHz with TMS as int std; chemical shifts are given in δ units. GC, GC-MS, IR and optical rotation methods were the same as those described previously [11]. Oil (100 ml) was chromatographed over a column of activated neutral $Al_2O_3$ using petrol (40–60°). The polarity of the eluant was increased using EtOAc in the following proportions: 99:1, 97:3, 19:1 and 9:1. The first fraction after further sepns yielded limonene (20 g) and *p*-cymene (12 g). Fractions 25–27 after further CC ($CHCl_3$–MeOH) and prep. TLC (petrol–$Me_2CO$, 9:1) gave cubinol (3 g). Similarly, fractions 29–30 after further sepns yielded epicubenol (2.8 g). Fractions 31–40 after further CC yielded two mixts. The first after TLC ($CH_2Cl_2$–MeOH, 19:1) gave **1** (600 mg), **2** (1.2 g) and **3** (950 mg) and the second after further TLC ($CHCl_3$–MeOH, 19:1) gave **4** (370 mg, $R_f$ 0.22), **7** (1.15 g, $R_f$ 0.25) and carvacrol (735 mg). The polar fractions 47–50 were concd and after crystallization from $Et_2O$ gave a solid mass which after further TLC ($CHCl_3$–MeOH, 9:1) gave **5** (2.3 g, $R_f$ 0.55).

p-*Menth*-1β,2α-*diol* (**4**). Viscous oil, IR $\nu_{max}^{neat}$ cm$^{-1}$: 3385 (OH), 3000–2860, 1465, 1380, 1050; MS *m/z* (rel. int.): 172 [$M^+$, $C_{10}H_{20}O_2$] (10); 154 $[M-H_2O]^+$ (60); 136 $[154-H_2O]^+$ (58); 107 (90), 91 (42), 71 (63), 55 (44), 43 (100); $^1$H NMR ($CDCl_3$): 3.50 (*br d* $W_{1/2}$ = 8 Hz, H-2), 1.90 (*m*, H-7), 1.80–1.50 (overlapping *m*, H-3 to H-6), 1.32 (*s*, H-10), 0.90 (*d*, $J = 7$ Hz, H-8 and 9). **4** (20 mg) was dissolved in dry $Me_2CO$ (5 ml) and conc. $H_2SO_4$ (0.5 ml) added and shaken for 2 hr. After usual work-up the reaction mixt. yielded unreacted **4** (15 mg) $[\alpha]_D^{30°} + 7°$ (*c* 1.5; MeOH).

p-*Menth*-1β,4α-*diol* (**5**). Colourless crystals, mp 153°, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3300 (OH), 2960–2850, 1455, 1435, 1350, 1200, 1030; MS *m/z* (rel. int.): 172 [$M^+$, $C_{10}H_{20}O_2$] (5), 154 $[M-H_2O]^+$ (18), 136 $[154-H_2O]^+$ (5), 127 (60), 109 (50), 99 (25), 81 (35), 71 (55), 57 (58), 43 (100); $^1$H NMR ($CD_3OD$): 4.60 (*br s*, OH), 4.20 (*br s*, OH), 1.86 (*qq*, $J = 7$ Hz, H-7), 0.90 (*d*, $J = 7$ Hz, H-8 and 9), 1.17 (*s*, H-10), 1.85, 1.74, 1.52, 1.35 (overlapping *m*, H-2, 3, 5 and 6). $^{13}$C NMR ($CD_3OD$): 17.5 (C-8 and C-9), 30.8 (C-10), 35.3 (C-7), 76.0 and 75.8 (C-1 and C-4), 39.5, 30.8, 27.2 (C-2, 3, 5 and 6); $[\alpha]_D^{22°} + 1.2°$ (MeOH; *c* 1.0). Acetylation of **5** (20 mg) after usual work-up yielded **6** (18 mg). **6**: $^1$H NMR ($CDCl_3$): 0.90 (*d*, $J = 7$ Hz, H-8 and 9), 1.20 (*s*; H-10), 2.08 (*s*, 2 × OAc), 2.5–1.40 (H-2, 3, 5, 6 and 7).

*Dehydration of* **5**. **5** (20 mg) was dissolved in MeOH (2 ml) and conc $H_2SO_4$ (0.05 ml) added. Refluxing of the mixt. was carried out for 3 hr. After usual work-up and TLC sepns 4-terpineol (10 mg) and α-terpinene (6 mg) were obtained.

2β-*Hydroxy*-1,4-*cineole* (**7**). Colourless crystals, mp 75°, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3250 (OH), 2980–2850, 1450, 1435, 1370, 1205, 1100, 1050: MS *m/z* (rel. int.) 170 [$M^+$, $C_{10}H_{18}O_2$] (8), 152 $[M-H_2O]^+$ (2), 145 (8), 127 (10), 109 (13), 97 (13), 83 (18), 71 (23), 55 (20), 43 (100); $^1$H NMR ($CDCl_3$): 3.78 (*dd*, $J = 7$ and 2 Hz, H-2), 2.12 (overlapping *m*, H-3 and 7), 1.60–1.35 (overlapping *m*, H-5 and 6), 1.42 (s, H-10), 0.96 and 0.98 (2 d, $J = 7$ Hz, H-8 and 9). $^{13}$C NMR ($CDCl_3$): 94.5 and 88.0 (C-1 and 4), 77.2 (C-2), 45.6 (C-3), 32.6 (C-7), 16.2 and 18.0 (C-8 and 9), 30.0 (C-10), 32.6 and 33.1 C-5 and 6).

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## REFERENCES

1. Anon. (1948). *The Wealth of India*, p. 23. CSIR, New Delhi.
2. Gulati, B. C., Shawl, A. S. and Channa, O. N. (1976). Perfumery and Flavour Association of India, IIIrd Seminar, Calcutta, p. 1.
3. Garg, S. N., Misra, L. N., Agarwal, S. K., Mahajan, V. P. and Rastogi, S. N. (1987) *Phytochemistry* **26**, 449.
4. Garg, S. N. and Agarwal, S. K. (1987) *Planta Med.* **53**, 311.
5. Garg, S. N., Agarwal, S. K., Mahajan, V. P. and Rastogi, S. N. (1987) *J. Nat. Prod.* **50**, 253.
6. Chaudhury, S. S. and Handa, K. L. (1959). *Indian J. Pharm.* **21**, 39.
7. Vashist, V. N., Nath, Y., Nazir, B. N. and Handa, K. L. (1962) *Indian Oil Soap J.* **27**, 229.
8. Kapahi, B. K., Thappa, R. K., Agarwal, S. G. and Sarin, Y. K. (1985) *Pafai.* **7**, 23.
9. Garg, S. N. and Agarwal, S. K. (1988) *Phytochemistry* **27**, 936.
10. Misra, L. N. (1986) *Phytochemistry* **25**, 2892.
11. Misra, L. N. and Singh, S. P. (1986) *J. Nat. Prod.* **49**, 941.
12. Misra, L. N. and Husain, A. (1987) *Planta Med.* **53**, 379.
13. Chandra, A., Misra, L. N. and Thakur, R. S. (1987) *Tetrahedron Letters* **28**, 6377.
14. Ahmad, A., Siddiqui, M. S. and Misra, L. N. (1988) *Phytochemistry* **27**, 1065.
15. Misra, L. N., Shawl, A. S. and Raina, V. K. (1988) *Planta Med.* **54**, 165.
16. Swigar, A. A. and Silverstein, R. M. (1981) *Monoterpenes*. Aldrich, Milwaukee, Wisconsin.

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# VOLATILE CONSTITUENTS FROM MARINE BROWN ALGAE OF JAPANESE *DICTYOPTERIS*

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**Key Word Index**—*Dictyopteris*; brown algae; dictyopterenes; sesquiterpenes; chemotaxonomy

**Abstract**—*cis*-3-Butyl-4-vinylcyclopentene, *trans*-1-[(1*Z*)-hexenyl]-2-vinylcyclopropane, 4-[(1*E*)-hexenyl]-cyclopentene, and 6-[(1*E*)-butenyl]-cyclohepta-1,4-diene were newly identified in the essential oils from fresh *Dictyopteris prolifera* and *D. undulata*. On the other hand, the oil of *D. divaricata* was found to consist mostly of a single sesquiterpene, cubenol (over 95%) instead of the $C_{11}$-compounds. The growth-locality variation in the chemical compositions of the essential oils in the genus *Dictyopteris* was discussed.

## INTRODUCTION

We have previously reported the occurrence of 'ocean smell' which consist of dictyopterene A (**1**), dictyopterene B (**2**), dictyopterene C′ (**3**), dictyopterene D′ (**4**), and dictyoprolene (**5**) including some unidentified compounds in Japanese *Dictyopteris* [1–3]. We here describe growth-locality variation of the volatile compounds in the essential oils from this genus, *D. prolifera*, and *D. divaricata* on the basis of GC and GC/MS analyses using a capillary column, and discuss taxonomic relationships within the genus of *Dictyopteris*.

## RESULTS AND DISCUSSION

Essential oils obtained from the steam distillate of fresh fronds of *D. prolifera* (*ca* 0.09–0.1%), and *D. divaricata* (0.3–0.4%).The two oils displayed very different chromatographic profiles. In the essential oils of *D. prolifera*, *cis*-3-butyl-4-vinylcyclopentene (**6**), *trans*-1-[(1*Z*)-hexenyl]-2-vinylcyclopropane (**7**), 4-[(1*E*)-hexenyl]-cyclopentene (**8**) and 6-[(1*E*)-butenyl]-cyclohepta-1,4-diene (**9**) together with the known $C_{11}$-compounds (**1**–**5**), were newly identified by comparison of retention indices and GC/MS with those of authentic specimens syn-