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NEW MONOTERPENE DIOLS FROM ESSENTIAL OIL OF *FERULA JAESCHKEANA*

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Key word Index—*Ferula jaeschkeana*; Umbelliferae; *p*-menthene diols.

Abstract—The steam distilled oil of *F. jaeschkeana* rhizomes afforded three new *p*-menthene diols.

INTRODUCTION

Despite numerous investigations on the constituents of *F. jaeschkeana* oil [1–4] only a few monoterpenoids have been isolated and identified. In the present communication we report the characterisation of three new monoterpenoids, *p*-menth-3-ene-1,2-diol (**1a**), *p*-menth-4-ene-1,2-diol (**2**) and *p*-menth-8-ene-1,2-diol (**3**) from the essential oil of *F. jaeschkeana* rhizomes.

RESULTS AND DISCUSSION

On repeated column chromatography over silica gel, the essential oil of *F. jaeschkeana* yielded three compounds. Compound **1a** was obtained as a viscous mass and analysed for the molecular formula $C_{10}H_{18}O_2$. It did not show the molecular ion in the mass spectrum but showed a fragment ion at *m/z* 152 $[M-H_2O]^+$. Its IR spectrum exhibited a strong absorption at 3350 cm^{-1} for hydroxyls and preliminary investigations of its physical data showed the presence of a double bond indicative of one ring and one double bond in the molecule.

The presence of one tertiary, one secondary hydroxy groups and one trisubstituted double bond was established by the signals at δ 3.92 *d* (3 Hz), 5.25 *d* (3 Hz) in its ^{1}H NMR spectrum and carbon signals at δ 72.20 *s*, 74.40 *d*, 145.80 *s* and 121.00 *d* in its ^{13}C NMR spectrum. The nature of the secondary hydroxyl group was further confirmed by the formation of its monoacetate (**1b**). The C-7 Me at δ 1.20 *s* indicated the presence of a tertiary hydroxy group at C-1 and the other secondary hydroxy group was fixed at C-2 and the double bond at C-3 on the basis of couplings and ^{1}H NMR decouplings. If irradiation was done at the olefinic proton at δ 5.25 *d*, the oxymethine signal at δ 3.92 *d* changed into a singlet and vice versa. Irradiation at C-8 methine at δ 1.95 *sept* collapsed the secondary methyls into singlet at δ 0.98 and sharpened the olefinic doublet (J = 3 Hz) at δ 5.20. Further the mass spectrum fragments arose due to a retro-Diels–Alder fragmentation which was in agreement with the proposed structure (**1a**).

Stereochemistry of Me group at C-1 has been fixed axial since C_5 is upfield (δ 24.00) due to 1,5-diaxial interaction, γ-effect compared with the carbon chemical shifts of closely related compounds [5]. The hydroxyl at C-2 was deduced as β-axial due to the J value of 3 Hz between oxymethine and olefinic proton, and the appearance of acetoxy group at δ 2.13 (**1b**) in its ^{1}H NMR spectrum [6]. cis-configuration of both vicinal hydroxyls was also corroborated by formation of its acetonide. On the basis of the above findings structure **1a** was assigned for this compound.

Compound **2**, a viscous mass analysed for molecular formula $C_{10}H_{18}O_2$ (M^+, 170). Its IR spectrum showed absorption at 3380 cm^{-1} for hydroxy groups. The presence of one tertiary and one secondary hydroxy groups, one trisubstituted double bond, an isopropyl group and a quaternary methyl at oxygen bearing carbon were confirmed by comparing ^{1}H NMR and ^{13}C NMR spectra of **2** with compound **1a**. In its mass spectrum fragments arising due to retro-Diels–Alder fragmentation were also present.

Position of secondary hydroxyl group was located at C-2 as α-equatorial since its oxymethine appeared as a broad singlet at δ 3.70 ($W_{1/2}$ = 8 Hz) and the double bond at Δ^4 by homonuclear proton decoupling experiments in its ^{1}H NMR spectrum. It also did not form its acetonide. In its ^{13}C NMR spectrum, C-3 methylene carbon appeared upfield at δ 25.0 (*t*) due to 1,3-diaxial and γ-effects. Thus, it was characterized as **2**.

Compound **3**, a crystalline substance, mp 72° was analysed for molecular formula $C_{10}H_{18}O_2$, (M^+ 170). Its IR spectrum showed an absorption band at 3350 cm^{-1} for hydroxy groups. ^{13}C NMR spectrum of **3** indicated the presence of an exocyclic double bond, a secondary and a tertiary hydroxy bearing carbons besides two methyl and three methylene carbons. Its ^{1}H NMR spectrum also showed the terminal methylene protons as a broad singlet at δ 4.70. Its tertiary hydroxy group was located at C-1, since the C-7 methyl appeared at δ 1.25, and the vinylic methyl at δ 1.70, which established the position of the terminal methylene at C-8 in structure **3**. The signal for this methyl was also sharpened when the exomethylene was irradiated. The position of secondary hydroxyl group was fixed at C-2 as β axial by ^{1}H NMR decouplings and comparing its ^{1}H NMR data with those of compounds **1a**, **2** and the mp, optical rotation of a synthetically prepared compound [7]. On the basis of the data now available structure **3** was suggested for this compound.

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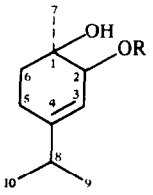
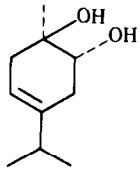
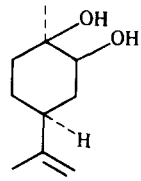


1a R = H
1b R = Ac



2



3

EXPERIMENTAL

Mps: uncorr. NMR: $CDCl_3$, TMS as int. standard. CC and TLC were performed on silica gel.

Extraction and identification. F. jaeschkeana rhizomes (10 kg, fresh) collected from Gulmarg, Kashmir, was cut into small pieces and steam-distilled. It yielded a pale yellow oil (1%, 100 ml) which was chromatographed over a column of activated neutral Al_2O_3 (2 kg, Grade 1) and eluted with petrol, and petrol–EtOAc (99:1), (97:3), (95:5) and (9:1). 10 fractions of each were collected and fractions 31–40 having same TLC pattern were mixed and concd. It (20 g) was rechromatographed over Si gel column (400 g) and eluted with $CHCl_3$ and $CHCl_3$–MeOH (1–5%) mixtures, respectively, followed by prep. TLC. It resulted in the isolation of three compounds, *p*-menth-3-ene-1,2-diol (**1a**), R_f 0.18; *p*-menth-4-ene-1,2-diol (**2**) R_f 0.29, *p*-menth-8-ene 1,2 diol (**3**), R_f 0.25 solvent system CH_2Cl_2–MeOH (95:5). These gave violet, violet and red colour spots when TLC plates were sprayed with a 1% soln of vanillin–H_2SO_4 and heated for 10 min at 110°.

Compound **1a**, a viscous mass, molecular formula $C_{10}H_{18}O_2$, $[\alpha]_D^{25}$ −2.5° ($CHCl_3$; *c*2.0); IR ν_{max}^{neat} cm^{-1}: 3350, 2920, 2850, 1640, 1370, 1100, 970, 920, 870 and 840. ^1H NMR: δ 0.98 (6H, *d*, J = 7 Hz), 1.20 (3H, *s*), 1.95 (1H, *sept* J = 7 Hz), 3.92 (1H, *d*, J = 3 Hz), 5.25 (1H, *d*, J = 3 Hz): ^{13}C NMR: δ 145.80 *s*, 121.00 *d*, 74.40 *d*, 72.20 *s*, 34.10 *d*, 33.80 *t*, 24.00 *t*, 21.00 *q*, 20.80 *q*, 20.00 *q*; MS *m/z* (rel. int.): 152 $[M-H_2O]^+$ (5), 137 (42), 119 (3), 109 (11), 108 (13), 93 (4), 82 (18), 71 (65), 67 (38), 55 (22), 43 (100). (Found: C, 70.59; H, 10.72, $C_{10}H_{18}O_2$, requires C, 70.59; H, 10.58%).

Monoacetate **1b**. Acetylation of **1a** (15 mg) in C_5H_5N and Ac_2O (0.5 ml each) at room temp. and after usual work-up yielded a viscous mass, R_f 0.32 (CH_2Cl_2–MeOH 19:1); ^1H NMR: δ 0.98 (6H, *d*, J = 7 Hz), 1.22 (3H, *s*), 2.13 (3H, *s*), 4.85 (1H, *d*, J = 3 Hz), 5.30 (1H, *d*, J = 3 Hz).

Acetonide. A mixture of compound **1a** (10 mg) in dry $(Me)_2CO$ (10 ml) and conc. H_2SO_4 (0.05 ml) was shaken at room temp. for 2 hr and after usual work-up yielded a viscous mass, R_f 0.60 $CHCl_3$–MeOH (95:5). IR ν_{max}^{neat} cm^{-1}: 2995, 1640, 1380, 1218 and 1035. ^1H NMR: δ 0.97 (6H, *d*, J = 7 Hz), 1.15 (3H, *s*), 1.32 (6H, *s*).

Compound **2**: A viscous mass, $C_{10}H_{18}O_2$ (M^+, 170): $[\alpha]_D^{25}$ +4.8° (MeOH, C 4.0); IR ν_{max}^{neat} cm^{-1}: 3380, 2950, 2880, 1650, 1440, 1370, 1100, 980 and 860; ^1H NMR δ 0.95 (6H, *d*, J = 7 Hz), 1.10 (3H, *s*), 1.95 (1H, *sept*, J = 7 Hz), 3.70 (1H, *br s*, $W_{1/2}$ = 8 Hz): ^{13}C NMR: δ 148.40 *s*, 120.50 *d*, 72.20 *d*, 70.90 *s*, 35.20 *d*, 33.00 *t*, 25.00 *t*, 25.00 *q*, 21.80 *q*, 21.80 *q*, MS *m/z* (rel. int.%): 170 (M^+, 2), 152 (3.5), 135 (4), 119 (8), 112 (48), 97 (60), 83 (45), 69 (27), 67 (15), 55 (32), 43 (100).

Compound **3**. Colourless needles (MeOH), mp 74°, $C_{10}H_{18}O_2$ (M^+, 170) $[\alpha]_D^{25}$ +29° (MeOH, *c*2.0): IR ν_{max}^{neat} cm^{-1}: 3300, 2950, 2900, 1645, 1440, 1380, 1190, 1170, 1130, 1040, 970 and 900. ^1H NMR: δ 1.25 (3H, *s*), 1.70 (3H, *s*), 3.60 (1H, *t*, J = 3.0 Hz), 4.70 (2H, *br s*): ^{13}C NMR: δ 148.40 (*s*), 109.50 (*t*), 74.00 (*d*), 66.50 (*s*), 38.00 (*d*), 34.00 (*t*), 34.50 (*t*), 27.00 (*t*), 26.20 (*q*), 21.20 (*q*); MS *m/z* (rel. int.%): 170 (5), 152 (27), 137 (12.6), 126 (10.8), 111 (15.8), 109 (22.3), 108 (33), 100 (6.7), 93 (20), 71 (100), 67 (40), 43 (70).

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