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(−)-1(10),11-EREMOPHILADIEN-9β-OL FROM THE LIVERWORT *MARCHANTIA POLYMORPHA* SSP. *AQUATICA*

ANGELA RIECK, NILS BÜLOW, CHRISTIANE FRICKE, YÜCEL SARITAS and WILFRIED A. KÖNIG*

Institut für Organische Chemie, Universität Hamburg, D-20146 Hamburg, Germany

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Key Word Index—*Marchantia polymorpha* ssp. *aquatica*; Marchantiales; Hepaticae; sesquiterpenes; 1(10),11-eremophiladien-9β-ol.

Abstract—A new eremophilane-type sesquiterpenoid, (−)-1(10),11-eremophiladien-9β-ol, was isolated from the liverwort *Marchantia polymorpha* ssp. *aquatica*. Structure elucidation was performed by means of spectroscopic methods and chemical conversion to known eremophilone. The configuration was proved by NOE measurements and comparison of the products obtained by dehydration and hydrogenation of the alcohol with the hydrogenation products of both enantiomers of eremophilene and valencene by enantioselective gas chromatography with cyclodextrin derivatives.

INTRODUCTION

Marchantia polymorpha ssp. *aquatica* [Nees] Burgeff is a large thalloid and widespread liverwort growing on wet sites and adjacent to container plants in plant nurseries. In many reports [1–13] the presence of terpenoic and aromatic compounds in *Marchantia polymorpha* L. was described. In this paper we report on the isolation and characterization of a new sesquiterpene alcohol (−)-1(10),11-eremophiladien-9β-ol (**1**) from the subspecies *M. aquatica*.

RESULTS AND DISCUSSION

1(10),11-Eremophiladien-9β-ol (**1**) was isolated as an oil and showed a weak woody scent. The elemental composition $C_{15}H_{24}O$ was determined by high resolution mass spectral analysis. The ^1H NMR and ^{13}C NMR spectra of **1** indicated signals of one secondary methyl group (δ 0.88, *d*, *J* = 6.1 Hz, H-15; δ 15.6, C-15), one tertiary methyl group (δ 1.11, *s*, H-14; δ 24.1, C-14) and an isopropenyl group (δ 4.70, 4.68, each 1H, *br s*, H-12; δ 108.8, C-12; δ 1.71, *s*, H-13; δ 20.5, C-13; δ 149.7, C-11). The NMR spectra also showed signals characteristic of a secondary alcohol group (δ 4.38, *dd*, *J* = 7.8 Hz and 4 Hz, H-9; δ 75.1, C-9), a trisubstituted double bond (δ 5.67, *t*, *J* = 3.6 Hz, H-1; δ 126.9, C-1; δ 145.4, C-10), four methylene groups (δ 2.13, *m*, H-8β, δ 1.55, *m*, H-8α; δ 37.9, C-8; δ 2.08, *m*, H-2; δ 25.4, C-2; δ 1.72, *m*, H-6β, δ 1.51, *dd*, *J* = 12.7 Hz, H-6α; δ 40.0, C-6; δ 1.48, *m*, H-3; δ 26.9, C-3) and two methine protons (δ 1.84, *m*, H-7; δ 38.3, C-7; δ 1.51, *m*, H-4; δ 37.4, C-4). Additional NMR techniques as ^1H-^1H and ^1H-^{13}C correlated 2D NMR and long range measurements confirmed the structure of **1**. The relative stereochemistry of **1** was elucidated using NOE difference spectroscopy (Fig. 1). Irradiation of the tertiary methyl group enhanced the H-6α signal while irradiation of the secondary methyl group enhanced the H-6β signal. Saturation of the H-9 resonance enhanced the signals due to H-7 and H-1.

To assess these results compound **1** was treated with $SOCl_2$ yielding eremophila-1(10),8,11-triene (**2**) (Scheme 1). Hydrogenation of **2** caused a shift of the C-11 double bond and furnished as main products **4** and **5** which showed identical mass spectra and retention indices with the products obtained by hydrogenation of (-)-valencene (**6**) and (-)-eremophilene (**7**),

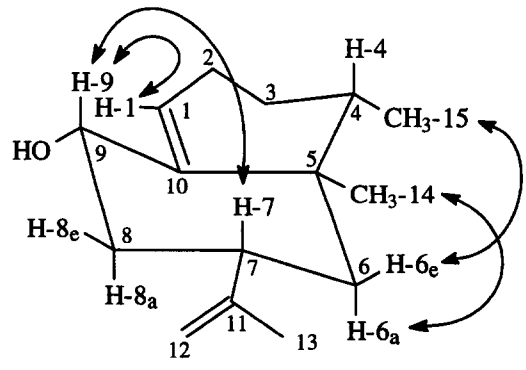
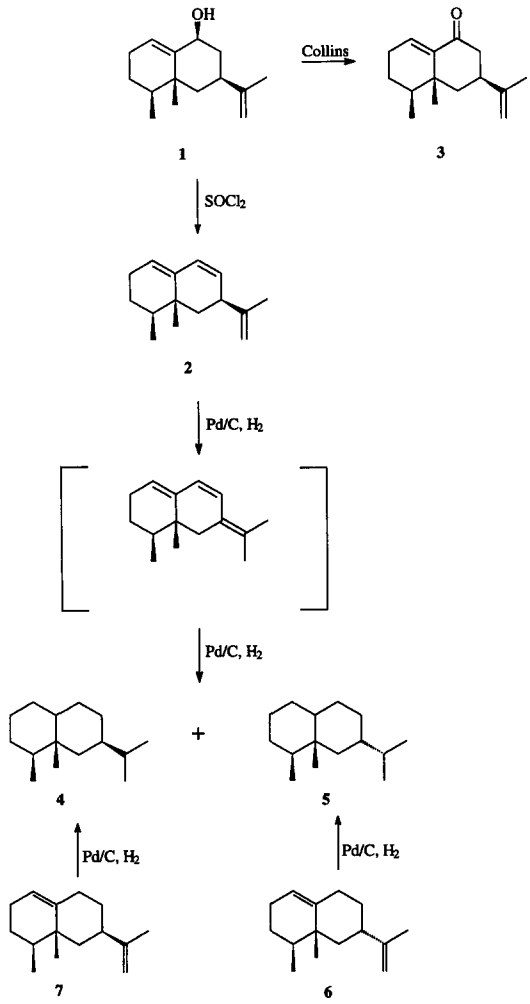


Fig. 1.

*Author to whom correspondence should be addressed.



Scheme 1.

respectively, on capillary columns coated with heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin [14], octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin and heptakis(6-*O*-methyl-2,3-di-*O*-pentyl)-β-cyclodextrin [15]. Eremophilene (**7**) has been found in *M. polymorpha* [16]. Oxidation of **1** with Collins reagent yielded the ketone **3** [17]. The ^{1}H NMR data of **3** were identical to published data for eremophilone [18, 19].

EXPERIMENTAL

Plant material. Marchantia polymorpha ssp. *aquatica* [Nees] Burgeff was collected in southern Germany (Westalb) in October 1993 and in southern Norway in August 1995. The liverworts were identified by Dr H. Muhle, University of Ulm, Germany. The collected liverworts are deposited in the Institut für Allgemeine Botanik, University of Hamburg.

Hydrodistillation. The essential oil was prepared by steam distillation (2 hr) of aq. homogenates of fresh and green plants using *n*-hexane as collection solvent. Because of the greatly differing weight the fresh material was not weighed.

Preparative GC. Isolation of **1**, **2** and **3** was performed by prep. GC on a Varian 1400 instrument, equipped with a stainless steel column (Silcosteel, Amchro) (2.05 m × 5.1 mm) with 6% octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin–polysiloxane PS-086 (1 : 1; w/w) on Chromosorb W-HP. He was used as carrier gas at a flow rate of 240 ml min^{-1}.

Enantioselective capillary GC. Capillary columns with cyclodextrin derivatives were prepared as described earlier [20].

NMR-spectroscopy. NMR spectra were measured in $CDCl_3$ using TMS as internal standard.

GC-MS. Electron impact (70 eV) GC-MS measurements were carried out on a Hewlett-Packard HP 5890 gas chromatograph coupled to a VG Analytical VG 70-250S mass spectrometer.

(−)-1(10),11-*Eremophiladien-9β-ol* (**1**). $[\alpha]_D^{22} - 81$ (*c* 0.2); ^{1}H NMR (400 MHz): δ 5.67 (1H, *t*, *J* = 3.6 Hz, H-1), 4.70, 4.68 (each 1H, *br s*, H-12), 4.38 (1H, *dd*, *J* = 7.8 Hz, *J* = 4 Hz, H-9), 2.13 (1H, *m*, H-8β), 2.08 (2H, *m*, H-2), 1.84 (1H, *m*, H-7), 1.72 (1H, *m*, H-6β), 1.71 (3H, *s*, H-13), 1.55 (1H, *m*, H-8α), 1.51 (1H, *dd*, *J* = 12.7 Hz, H-6α), 1.51 (1H, *m*, H-4), 1.48 (2H, *m*, H-3), 1.11 (3H, *s*, H-14), 0.88 (3H, *d*, *J* = 6.1 Hz, H-15); ^{13}C NMR (100 MHz): δ 149.7 (C-11), 145.4 (C-10), 126.9 (C-1), 108.8 (C-12), 75.1 (C-9), 40.0 (C-6), 38.3 (C-7), 37.9 (C-8), 37.4 (C-4), 36.8 (C-5), 26.9 (C-3), 25.4 (C-2), 24.1 (C-14), 20.5 (C-13), 15.6 (C-15); MS (EI, 70 eV), *m/z* (rel. int.): 220 (5) [M]$^+$, 205 (42), 202 (35), 161 (33), 145 (34), 121 (35), 119 (45), 109 (36), 107 (62), 105 (55), 95 (47), 93 (54), 91 (50), 81 (52), 79 (40), 77 (33), 69 (35), 67 (47), 55 (63), 43 (32), 41 (100).

Eremophila-1(10),8,11-*triene* (**2**). To a soln of **1** (2 mg) in pyridine (1 ml) $SOCl_2$ (0.1 ml) was added and the mixture left for 10 min at 0°. To the reaction mixture 10% $NaHCO_3$-soln was added and extracted with *n*-hexane. The main reaction product **2** (approx. 0.5 mg) was isolated by prep. GC. Optical rotation measurements failed because of insufficient sample amount. ^{1}H NMR (400 MHz): δ 6.0 (1H, *bd*, *J* = 10 Hz), 5.54 (1H, *bd*, *J* = 5.1 Hz), 5.52 (1H, *ddd*, *J* = 10 Hz, *J* = 5.2 Hz, *J* = 2 Hz), 4.74, 4.72 (each 1H, *br s*), 1.76 (3H, *s*), 0.91 (3H, *s*), 0.89 (3H, *d*, *J* = 6.6 Hz); MS (EI, 70 eV), *m/z* (rel. int.): 202 (20) [M]$^+$, 145 (21), 134 (31), 119 (100), 105 (38), 93 (26), 91 (45), 77 (23), 41 (35).

Eremophilone (**3**). The alcohol **1** was oxidized with Collins reagent according to the method of Ratcliffe [17]. The ketone **3** was isolated by prep. GC and identified by ^{1}H NMR spectroscopy. The data are in accordance with published data of eremophilone [18, 19]. Optical rotation measurements of **3** failed because of insufficient sample amount.

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