Phytochemistry, Vol. 22, No. 3, pp. 774–776, 1983.
Printed in Great Britain.

0031-9422/83/030774-03$03.00/0

ANGELICOIDENOL, A BICYCLIC MONOTERPENE FROM THE SEEDS OF *PLEUROSPERMUM ANGELICOIDES*

UMAR MAHMOOD, SHEO B. SINGH and RAGHUNATH S. THAKUR

Central Institute of Medicinal and Aromatic Plants, Lucknow 226016, India

(*Received* 2 *August* 1982)

Key Word Index—*Pleurospermum angelicoides*; Umbelliferae; angelicoidenol; 5-exo-hydroxyborneol; 5-exo-methoxyborneol.

Abstract—From the methanol extract of the defatted seeds of *Pleurospermum angelicoides*, a new bicyclic monoterpene has been isolated which was characterized by spectral data and chemical reactions.

INTRODUCTION

Pleurospermum angelicoides is a herb found at high altitude in the Himalayan tract of the Kumaoun region [1]. The seeds of this plant have a pleasant odour. Since no chemical work on this plant has been reported, a detailed investigation on its chemical constituents was undertaken. Recently we have reported [2] a new phenylpropanoid, 1-propenyl-2,3,4-trimethoxybenzene, along with other constituents from this source. In continuation of our work, we now report the isolation and characterization of a new bicyclic dihydroxy monoterpene designated as angelicoidenol (**1a**).

RESULTS AND DISCUSSION

Si gel chromatography of the methanol extract of *P. angelicoides* seeds provided angelicoidenol, (**1a**), mp 255–257° sublimed at 181°, $[\alpha]_D$ −16.12° was analysed for $C_{10}H_{18}O_2$ (M^+ at *m/z* 170.1301). The IR spectrum of this compound showed bands at 3330 and 1020 (OH), 1380 and 1365 cm^{-1} (gem-dimethyl) and the complex pattern of bands in 1320–850 cm^{-1} region was similar to hydroxybornane [3]. Compound **1a** formed a diacetate (**1b**) (M^+ at *m/z* 254) at room temperature when treated with acetic anhydride–pyridine.

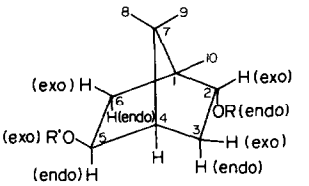
The structure of the compound was substantiated by the ^{13}C NMR spectrum of **1a** in pyridine-d_5 which exhibited nine lines for ten carbon atoms. The actual assignment was derived on the basis of a SFORD experiment and residual C–H coupling which was comparable with borneol [4] (Table 1). The high resolution mass spectrum showed ions at *m/z* 155 and 152 due to loss of a methyl group and water, respectively, from the M^+ ion. The mass fragments, which are identical with hydroxybornanes [3, 5], are depicted in Scheme 1. The ion at *m/z* 111 (base peak) confirmed it to be a 2,5-dihydroxybornane [3].

The structure and stereochemistry was deduced by an extensive ^1H NMR study of **1a** in pyridine-d_5, which showed a complex pattern due to the diagonal arrangement of the hydroxy groups allowing all the protons to have different orientation. It showed singlets at δ 0.90, 1.05 and 1.40 for C-8, C-9 and C-10 methyl groups. The signal at 1.15 (*dd*, J = 13.5 and 3.5 Hz) could be assigned to endo-H-3 and the other *dd* at 1.72 (J = 13 and 3 Hz) to exo-H-6. The doublet at 1.95 (J = 5 Hz) can safely be assigned to H-4. Apparently H-4 may couple with endo-H-5, exo-H-3 and endo-H-3 but showed only a doublet due to coupling with exo-H-3. The dihedral angle [6] of

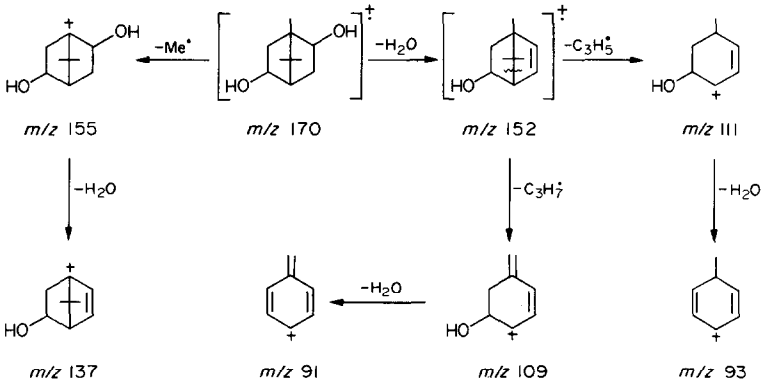
Table 1. ^{13}C NMR (25.2 MHz) spectral data of angelicoidenol (**1a**) in pyridine-d_5 with δ-values relative to TMS as int. standard

Carbon No.	Borneol [4]	**1a**	Multiplicity (SFORD)	J (residual C–H(Hz)
1	49.4	50.8	*s*	—
2	77.0	75.0	*d*	52.5
3	38.9	37.1*	*dd*	16.5, 11.1, 15.4
4	45.2	53.7	*d*	26.2
5	28.2	75.0	*d*	52.5
6	26.0	39.6*	*dd*	22.4, 12.2, 21.9
7	47.9	47.9	*s*	—
8	18.8	21.8†	*q*	17
9	20.2	20.2†	*q*	11
10	13.4	13.5	*q*	13

*, †Assignments with the same sign can be reversed.



Ia R = R' = H
Ib R = R' = Ac
Ic R = H, R' = Me



Scheme 1.

the other two protons did not allow them to couple with H-4. An eight line signal at 2.20–2.50 (*ddd*, J = 13.5, 9.5 and 5 Hz) was due to exo-H-3 and a symmetrical double doublet at 2.80–3.05 (J = 13 and 8.5 Hz) was assigned to endo-H-6. The exo-H-2 was found to be resonating at 4.50 (*ddd*, J = 9.5, 3.5 and 2 Hz) and the endo-H-5 appeared at 4.29 as a double doublet due to coupling with the exo-H-6 (J = 3 Hz) and endo-H-6 (J = 8.5 Hz). A broad singlet at 5.80 (exchanged with D_2O) was assignable to two hydroxyl groups. The chemical shift and J values are very close to Anet's theoretical values [6]. The ^{1}H NMR assignments were also confirmed by decoupling experiments on individual protons.

On the basis of the above data the structure of angelicoidenol was assigned as 5-exo-hydroxyborneol or 1, 7, 7-trimethyl-2-endo-5-exo-dihydroxybicyclo(2, 2, 1) heptane (**1a**).

Compound **1a** on refluxing with 7% methanolic sulphuric acid for 6 hr. was converted into 5-exo-methoxyborneol (**1c**) which showed the signals in its

Table 2. ^{1}H NMR (90 MHz) chemical shifts (δ-values relative to TMS as int. standard) of angelicoidenol (**1a**) and its derivatives in different solvents

	1a (pyridine-d_5)	**1a** (DMSO-d_6)	**1a*** ($CDCl_3$)	**1b** ($CDCl_3$)	**1c** ($CDCl_3$)
C-8 Me	0.90 *s*	0.75 *s*	0.76 *s*	0.84 *s*	0.72 *s*
C-9 Me	1.05 *s*	0.75 *s*	0.81 *s*	0.86 *s*	0.78 *s*
C-10 Me	1.40 *s*	1.00 *s*	1.04 *s*	1.00 *s*	0.92 *s*
C-2 H (exo)	4.50 *ddd* (9.5, 3.5, 2)	3.60 *m*	3.83 *m*	4.72 *m*	3.80 *ddd* (9.5, 3.5, 1.5)
C-3 H (exo)	2.20–2.50 *ddd* (13.5, 9.5, 5)	1.90–2.30 *m*	2.1–2.50 *m*	2.10–2.50 *m*	2.01–2.40 *m*
H (endo)	1.15 *dd* (13.5, 3.5)	1.15–1.30 *m*	1.25–1.50 *m*	1.18–1.32 *m*	1.08–1.29 *m*
C-4 H	1.95 *d* (5)	1.50 *d* (5)	1.73 *d* (5)	1.85 *d* (5)	1.79 *d* (5)
C-5 H (endo)	4.19 *dd* (8.5, 3)	3.60 *m*	3.83 *m*	4.56 *dd* (9, 3)	3.25 *dd* (8.5, 3.5)
C-6 H (exo)	1.72 *dd* (13, 3)	—	—	1.48–1.70 *m*	1.48–1.70 *m*
H (endo)	2.8–3.05 *dd*, (13, 8.5)	1.90–2.30 *m*	2.10–2.50 *m*	2.10–2.50 *m*	2.01–2.40 *m*
Others	5.80 *br s* (2 × OH) D_2O exchangeable	—	—	1.95, 1.98 *s* (2 × OCOMe)	3.15 *s* (OMe)

*Literature data [3].

^{1}H NMR spectrum ($CDCl_3$) for the exo-H-2 as a triple doublet centred at δ 3.80 (J = 9.5, 3.5 and 1.5 Hz). The signal for the endo-H-5 was shifted to 3.25 (*dd*, J = 8.5, 3.5 Hz) and the additional signal for the methoxy group appeared at 3.15. It was, therefore, characterized as 5-exo-methoxyborneol.

A comparative ^{1}H NMR study of **1a** in different solvents, e.g. $CDCl_3$, DMSO-d_6 and pyridine-d_5, indicated that the latter was a better solvent since the clear splitting of signals was seen. A clear separation of the exo-H-3 at δ 2.20–2.50 and the endo-H-6 at 2.8–3.05 were observed while these signals appeared as multiplets at *ca* 2.10–2.50 in $CDCl_3$ and DMSO-d_6. The –CHOH signals were also separated in this solvent.

Although **1a** has been synthesized previously [3, 7] this report constitutes the first example of any naturally occurring dihydroxybornane.

EXPERIMENTAL

Mp (sealed capillary) is uncorr. TLC was carried out on Si gel G and the spots were visualized by I_2 vapour or Vanillin–H_2SO_4 spray. The homogeneity of the compounds was routinely checked on TLC and GC.

Extraction and isolation. The seeds of *P. angelicoides* (1.5 kg) collected from Dondital in Kumaon region (voucher specimen has been deposited in the Botany Department) were steam distilled and the residue was air dried and powdered. The powder was extracted successively with *n*-hexane (4 × 5 l.) and MeOH (3 × 5 l.) at room temp. The MeOH extract was then concd *in vacuo* to afford a residue (40 g). Si gel (1 kg) CC of the MeOH extract afforded angelicoidenol (**1a**) from the $CHCl_3$–MeOH (95:5) eluates, 180 mg, mp 255–257° ($CHCl_3$) $[\alpha]_D^{25}$ – 16.12° (MeOH; *c* 0.46). IR ν_{max}^{KBr} cm^{-1}: 3330, 2940, 1380, 1365, 1285, 1178, 1092, 1068, 1030, 995, 950, 855. High resolution MS *m/z* (rel. int.): 170. 1031 $[M]^+$, $C_{10}H_{18}O_2$, (1.4), 155.1062 $[C_9H_{15}O_2]^+$ (6.9), 152.1195 $[C_{10}H_{16}O]^+$ (4), 137.0967 $[C_9H_{13}O]^+$ (12), 126.1038 $[C_8H_{14}O]^+$ (17), 125.0966 $[C_8H_{13}O]^+$ (29), 111.0806 $[C_7H_{11}O]^+$ (100), 109.1011 $[C_8H_{13}]^+$ (49), 109.0649 $[C_7H_9O]^+$ (11), 93.0702 $[C_7H_9]^+$ (8), 83.0491 $[C_5H_7O]^+$ (7), 83.0856 $[C_6H_{11}]^+$ (11), 55.0544 $[C_4H_7]^+$ (21), 43.0463 $[C_3H_7]^+$ (13), 41.0331 $[C_3H_5]^+$ (44). ^{13}C NMR (see Table 1), ^{1}H NMR (see Table 2).

Acetylation of **1a**. Compound **1a** (30 mg) on treatment with Ac_2O–pyridine (1 ml each at room temp. formed a diacetate which, on usual working-up, gave **1b** (32 mg) as a colourless viscous oil, $[\alpha]_D^{25}$ – 13.2° ($CHCl_3$; *c* 0.46). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2990, 1725, 1465, 1380, 1250, 1218, 1030. MS *m/z* (rel. int.): 254 $[M]^+$ (25), 195 (31), 168 (27), 152 (28), 137 (27), 135 (27), 132 (69), 126 (31), 119 (57), 109 (73), 108 (62), 93 (38), 43 (100).

Methylation of **1a**. Compound **1a** (98 mg) was refluxed with methanolic H_2SO_4 (7%, 20 ml, 6 hr). The reaction was monitored by TLC and found to contain five compounds. This reaction mixture was extracted with cold hexane (3 × 25 ml) when four compounds having higher R_f were extracted, while the compound of lower R_f remained in the reaction mixture. It was then diluted with H_2O (20 ml) and the MeOH was removed *in vacuo* and extracted with $CHCl_3$ (3 × 20 ml). This extract was dried (Na_2SO_4) and the solvent was removed to afford a viscous mass which was purified by prep. TLC to provide a residue, **1c**, 17 mg. IR ν_{max}^{neat} cm^{-1}: 3400, 2940, 2865, 1448, 1387, 1370, 1205, 1099, 1060, 1020, 992, 912, 852.

Acknowledgements—We are grateful to Dr. A. Hussain, Director, for providing the necessary facilities and to C.S.I.R., New Delhi, for financial assistance to one of us (U.M).

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