

Note

Sesquiterpenoids of Acorane Type from the Liverwort *Bazzania tridens*

Chia-Li Wu* (吳嘉麗) and Jyh-Rong Chen (陳志容)
 Department of Chemistry, Tamkang University, Tamsui, Taiwan 251, R.O.C.

Three sesquiterpenoids of acorane type-(+)-acorenone B (5), (+)-acorenone-7 α -ol (6), and 4-acorenone-3-one (7)-were identified from the Shanlin Chi liverwort species *Bazzania tridens*. Among them, the alcohol 6 is novel, and the dextro-enantiomer 5 is isolated from nature for the first time.

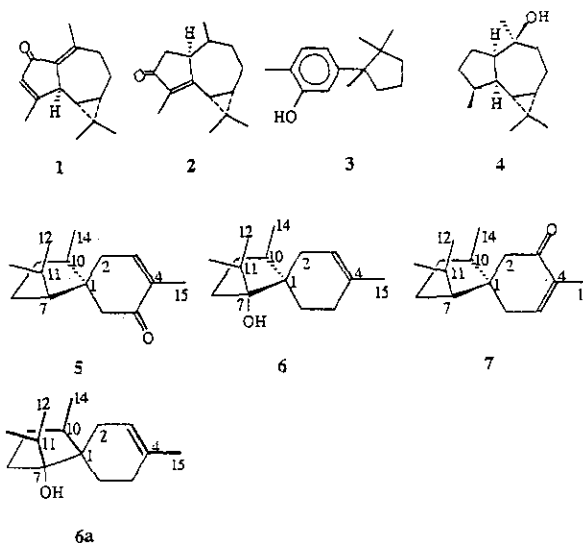
INTRODUCTION

The leafy liverwort, *Bazzania tridens*, is distributed widely in most parts of southeast Asia. We reported the chemical constituents of several specimens of this species collected from locations in Taiwan and Japan.^{1,2} There appeared a great variation of constituents among the specimens examined, such that specimens collected from varied localities contain varied sesquiterpenoids, many of them even new structures.^{1,3,4} A common point was found after a comparison of six Taiwanese and three Japanese specimens either tridensenone (1) or cyclocolorenone (2), two sesquiterpenes of closely related structures, is invariably present as one major component in nearly all *B. tridens* specimens examined. Five of six Taiwanese and one Japanese specimen biosynthesized cyclocolorenone (2) and the other two Japanese specimens produced tridensenone (1) as the major component.^{1,2}

In further work on *B. tridens* collected at Shanlin Chi (altitude 1700 m), we found that other than cyclocolorenone (2) two major components were δ -cupareneol (3) and ledol (4). Three sesquiterpenoids of acorane type, 5-7, were characterized as minor components. Among them, the dextro-enantiomer of 5 was isolated from nature for the first time and compound 6 is a novel alcohol of acorane skeleton. Here we present spectral evidence for these three acoranes.

RESULTS AND DISCUSSION

Compounds 5 and 6 were isolated from the EtOAc/hexane (1 : 4) elution of the crude oil on a silica-gel column and further purified on a Sep-Pak cartridge in preparative GC.⁵ The spiro-skeleton was recognized by the presence of a quaternary carbon without a tertiary methyl group on it. A sesquiterpene acorane skeleton was indicated in a HMBC (¹H-detected multiple-bond heteronuclear multiple-quantum coherence) experiment. A subsequent comparison of



spectral data of spiro-enone 5 with those (¹H and ¹³C NMR and mass spectra) of synthetic (+)-acorenone B^{6,7} confirmed the identity of these two compounds. (-)-Acorenone B is an uncommon essential oil component and reported only from the higher plant *Bothriochloa intermedia*.⁸ Optical data of the isolated liverwort component are consistent with that of synthetic (+)-acorenone B,⁹ hence the absolute configuration of 5 is shown as depicted. The positive enantiomer of acorenone B is unreported as a natural product. As chemical shifts of certain protons were not previously assigned, a more complete assignment of each proton appears in Table 1.

For compound 6, both ¹H and ¹³C NMR spectra (Table 1) indicate that the oxygenated function was not in conjugation with the double bond, but appeared as an isolated tertiary hydroxyl group. Its position was revealed in the HMBC data shown in structure 6a. Confirmation of the stereochemistry and assignment of chemical shifts of protons at C₂, C₅ and C₈ were derived from both NOE difference and NOESY observations (Fig. 1). The absolute configuration of this acorenone 6 (also with dextro-rotation) is assumed identical to that of (+)-acorenone B. Compound 6 unre-

Table 1. ^1H and ^{13}C NMR Data of (+)-Acorenone B (5) and (+)-Acoren-7 α -ol (6)

C	5			6		
	δ_{C}	δ_{H}	J/Hz	δ_{C}	δ_{H}	J/Hz
1	48.2			49.2		
2	25.7	2.08(α)	br d, J_{20}	45.3	1.58(α)	br d, $J_{15.5}$
		2.28(β)	br d, J_{20}		1.7 (β)	br d, $J_{15.5}$
3	144.1	6.63	br s	121.5	5.3	br s
4	135.2			139.7		
5	200.4			35.9	1.56	*
					2.14	dt, $J_{12,4}$
6	49.2	2.21	d, J_{17}	38.7	1.58	*
		2.67	d, J_{17}		1.58	*
7	56.7	1.3	*	85.4		
8	25.0	1.35(α)	*	23.2	1.88(α)	br d, J_{20}
		1.73(β)	*		1.97(β)	br d, J_{20}
9	29.6	1.23(α)	*	27.4	1.36	*
		1.75(β)	*		1.37	*
10	45.9	1.63	br q, $J_{6.5}$	37.7	1.61	*
11	29.0	1.62	septet, $J_{6.5}$	37.9	1.63	*
12	21.1	0.84	d, $J_{6.5}$	17.6	0.91	d, J
13	23.9	0.92	d, $J_{6.5}$	17.6	0.93	d, J
14	16.9	0.75	d, $J_{6.5}$	16.0	0.87	d, $J_{6.5}$
15	15.4	1.71	br s	20.5	1.78	br s

* Overlapped or obscured peaks

ported previously is thus named (1R, 7S, 10R)-(+)-acoren-7 α -ol. Its ^1H and ^{13}C NMR data were assigned on the basis of ^{13}C -DEPT, ^1H - ^1H COSY, HMQC, HMBC and NOESY spectra observed.

The third acorane-type component was recognized from the GC-MS data. The signal that eluted about half a minute earlier (DBWAX capillary column) than that of acorenone B (5) showed mass fragments similar to those of acorenone B, but with distinctive intensities. As the four isomeric acorenones were synthesized and their mass spectra were published,⁶ upon comparison the third component that eluted slightly earlier than acorenone B (5) was identified as 4-acoren-3-one (7), isolated from several plant species.¹⁰

Hydrocarbons of acorane type are rarely reported as liverwort components, and no oxygenated acoranones were

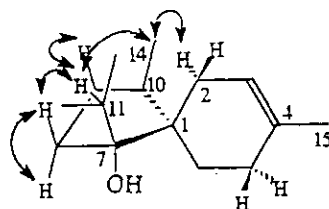


Fig. 1. NOE observed for compound 6.

found in liverworts.

EXPERIMENTAL SECTION

General

NMR spectra (500 MHz for ^1H) were measured in CDCl_3 . A fused silica capillary column (DBWAX, 30 m \times 0.25 mm) was used for both GC and GC-MS (70 eV). The column temperature was programmed from 50 $^\circ\text{C}$ to 220 $^\circ\text{C}$ at 5 $^\circ\text{C min}^{-1}$. IR spectra were measured of KBr pellets and UV spectra recorded in MeOH. Optical data were measured of CDCl_3 solutions.

Plant Materials

Bazzania tridens (Reinw. *et al.* Trev.) was collected in 1991 September at Shanlin Chi, Nantow Hsien, Taiwan and identified by Dr. K. Yamada (Ise-shi, Japan). Voucher specimens are deposited at the Department of Chemistry, Tamkang University.

Extraction and Isolation

For GC and GC-MS examinations, cleaned and dried specimens (5 g) were ground mechanically and extracted with EtOAc. After filtration through a small silica column, the concentrated filtrate was subjected to analysis. From GC analysis, the total area for sesquiterpene hydrocarbons was about 25% and the rest was oxygenated sesquiterpenes. The sesquiterpenes identified according to the GC eluting order were: β -barbatene (1.6%, area ratio), β -bazzanene (5.1%), γ -cuprenene (10%), cuparene (6.9%), ledol (4) (14.3%), acoren-7 α -ol (6), (3.5%), 4-acoren-3-one (7) (2.7%), acorenone-B (5) (5.7%), cyclocolorenone (2) (10.7%), albicanol (3.3%), a drimane lactone? (M^+ 234, base 219) (10.2%) and δ -cuparenol (3) (18.3%).

The whole plant of *B. tridens* was powdered with liquid N_2 and extracted with hexane. The crude extract (1.5 g) was chromatographed on a silica-gel column with a hexane-EtOAc gradient. The 20% eluate (600 mg) was repeatedly chromatographed on another silica column and eluted with benzene. From one fraction (38 mg) two spiro-sesquiterpenoids 6 (6 mg) and 7 (7 mg) were obtained upon further PGC collection.⁵ Pure δ -cuparenol (3) (4 mg) was yielded from another fraction (125 mg) after further PTLT purification. A later fraction (64 mg) was identified to contain the known sesquiterpene alcohol, ledol (4) as the major component. Cyclocolorenone (2) (50 mg) was furnished from the EtOAc/hexane (3:7) eluate and further purified on a column (Sephadex LH-20) with $\text{CHCl}_3/\text{MeOH}$. The identities of δ -

cuparenol (3) and cyclocolorone (2) were confirmed upon comparison with authentic samples. ^1H NMR spectrum of ledol (4) agreed satisfactorily with those reported.¹¹ Compound 4 has the same NMR data as those isolated from another liverwort *Cephaloziella* sp. in our laboratory; these spectra will be discussed in a paper on *Cephaloziella* sp.

(+)-Acorenone B (5): $[\alpha]_{\text{D}} + 12.3^\circ$ (*c* 0.25, CHCl_3) (lit., 17.3°)⁹; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 1674; $\lambda_{\text{max}}/\text{nm}$ (MeOH) 240 ($\log \epsilon$ 3.52); *m/z* (rel. int.) 220 (M^+ , 20%), 135 (80), 109 (100), 82 (70), 69 (65), 55 (50), 43 (58) and 41 (70).⁶

(+)-Acoren-7 α -ol (6) $[\alpha]_{\text{D}} + 18.7^\circ$ (*c* 0.15, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3470; *m/z* (rel. int.) 222 (M^+ , < 1), 204 (10), 179 (25), 161 (65), 121 (45), 69 (55), 43 (100) and 41 (55).

4-Acoren-3-one (7): *m/z* (rel. int.) 220 (M^+ , 12%), 135 (65), 109 (88), 82 (100), 69 (74), 55 (65), 43 (90) and 41 (87).⁶

ACKNOWLEDGMENTS

We thank Dr. Khosaku Yamada (Ise-shi, Japan) for identification of the specimen and Miss S.-C. Lin (Institute of Chemistry, Academia Sinica) for the NMR measurements and the National Science Council of the Republic of China for support.

Received December 29, 1994.

Key Words

Bazzania tridens; Lepidoziaceae; Liverwort: (+)-acorenone B; (+)-acoren-7 α -ol.

REFERENCES

1. Wu, C.-L.; Chen, C.-L. *Phytochemistry* **1992**, *31*, 4213.
2. Wu, C.-L. *J. Chin. Chem. Soc.* **1992**, *39*, 655.
3. Wu, C.-L.; Chang, S.-J.; Tori, M.; Furuta, H.; Sumida, A.; Asakawa, Y. *J. Chin. Chem. Soc.* **1990**, *37*, 387.
4. Toyota, M.; Asakawa, Y.; Takamoto, T. *Phytochemistry* **1981**, *20*, 2359.
5. Wei, H.-C.; Wu, C.-L. *J. Chromatog.* **1990**, *555*, 302.
6. Kutschan, R.; Schiebel, H.-M.; Schroder, N.; Wolf, H. *Chem. Ber.* **1977**, *110*, 1615.
7. Woif, H.; Kolleck, M.; Rascher, W. *Chem. Ber.* **1976**, *109*, 2805.
8. McClure, R. J.; Schorno, K. S.; Bertrand, J. A.; Zalkow, L. H. *J. Chem. Soc. Chem. Commun.* **1968**, 1135.
9. Fusao, K.; Yoshiya, A.; Michiharu, K. *J. Chem. Soc. Perkin Trans. 1* **1992**, 229.
10. Connolly, J. D.; Hill, R. A. *Dictionary of Terpenoids*; Chapman & Hall: London, **1991**, Vol. 1, p 598.
11. Miyazawa, M.; Uemura, T.; Kameoka, H. *Phytochemistry* **1994**, *37*, 1027.