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Monoterpene-alcohols from a mushroom *Dictyophora indusiata*

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Abstract

Five monoterpene-alcohols were isolated from a mushroom *Dictyophora indusiata*, one of which was identified as 3,7-dimethyl-1,6-octadiene-3,4-diol and its absolute configuration was determined as (3*R*,4*S*). The structures of the other four were, 4-[(3*R*,4*S*)-3-hydroxy-3,7-dimethylocta-1,6-dienyl(*Z*)-9-octadecenoate, 4-[(3*R*,4*S*)-3-hydroxy-3,7-dimethylocta-1,6-dienyl(9*Z*,12*Z*)-9,12-octadecadienoate, 3,7-dimethyl-1,6-octadiene-3,4,5-triol, bis[6-(3,4,7-trihydroxy-3,7-dimethyloctenyl) ether, as determined by means of spectral and chemical methods.

Keywords: Dictyophora indusiata; Phallaceae; Monoterpene-alcohol

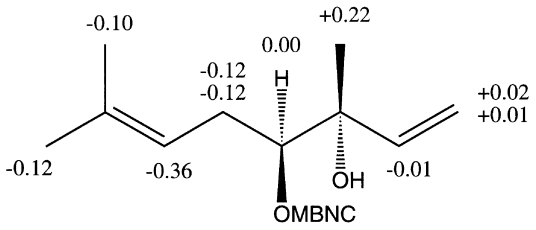
1. Introduction

Dictyophora indusiata is an edible mushroom used in Chinese food and medicine. From this mushroom, stimulators of NGF (nerve growth factor)-synthesis, dictyophorins A and B were isolated (Kawagishi et al., 1997). In the course of a screening program for other novel compounds, five monoterpene-alcohols were isolated. In this paper, the isolation and structural determination of these compounds are described.

2. Results and discussion

Air-dried fruiting bodies of *D. indusiata* were extracted with 85% EtOH. The extract after concentrating the solvent was partitioned between ethyl acetate and water. Repeated silica gel chromatography and HPLC of the EtOAc extract gave compounds **1**–**5**.

The molecular formula of **1** was determined as $C_{10}H_{18}O_2$ by HR-EIMS of the molecular ion peak at m/z 170.1311 (calcd 170.1307). The ^{1}H NMR spectral data of **1** were quite similar to those of cornusol isolated from the flower *Cornus controversa* (Table 1) (Kurihara & Kikuchi, 1978). However, the $[\alpha]^{23}_D$ of **1** was -7.4° (MeOH; *c* 7.4), while that of cornusol was 0°. Therefore we tried to determine the absolute configuration of **1**. In the NOESY spectrum of the acetonide of **1** prepared by the treatment of **1** with acetone and *p*-toluenesulfonic acid, a NOE between H-4 and H-10 was observed, indicating that the relative stereochemistry of **1** was (3*R**,4*S**). For determination of its absolute configuration of **1**, 2′-methoxy-1,1′-binaphthyl-2-carboxylic acid (MBNC) was used as described previously (Fukushi, Yajima, & Mizutani, 1994). From this method, the absolute configuration of **1** was unambiguously established as (3*R*,4*S*) (Fig. 1).



Δδ (ppm) = δ (a*R*)-MBNC ester − δ (a*S*)-MBNC ester

Fig. 1. Δδ values of MBNC esters of **1** in ^{1}H NMR ($CDCl_3$).

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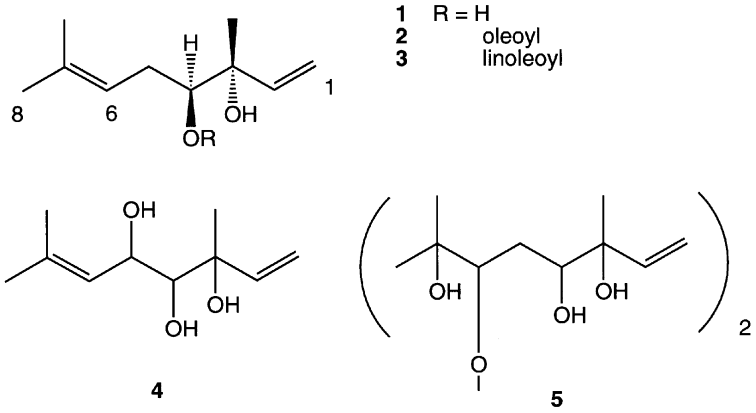

Structure 1.

The molecular formula of compound **2** was determined to be $C_{28}H_{50}O_3$ by HR-FABMS of $[M+H]^+$ peak at *m/z* 435.3840 (calcd 435.3838). Its ^{1}H NMR spectrum was similar to that of **1**. However, the spectrum of this compound showed many additional signals due to a fatty acid; a triplet methyl group at δ 0.86, two methylene groups at δ 1.90–2.10, one methylene at δ 2.29, two olefinic protons at δ 5.30–5.50 and many other methylene groups at δ 1.20–1.40. In addition, the signal of H-4 shifted from δ 3.31 to δ 4.87 as compared with **1**. These data suggested that **2** was an ester between oleic acid and the 4-OH of **1**. This structure was confirmed by preparation of **2** from **1** and oleic acid. Since all the data including the specific optical rotation (+8.0°, MeOH; *c* 1.0) of synthetic **2** were identical with those ($[\alpha]_D^{23}$ +8.1° (MeOH; *c* 0.50)) of natural **2**, the structure of **2** was determined as shown.

The ^{1}H NMR data and $[\alpha]_D^{23}$ (+8.0°, MeOH; *c* 1.0) of **3** ($C_{28}H_{48}O_3$ by HR-FABMS of $[M+H]^+$ peak at *m/z* 433.3664, calcd 433.3682) were very similar to those of **2**, suggesting that **3** might possess a linoleic acid moiety instead of the oleic acid unit of **2**. Its structure was confirmed by preparation of the compound from **1** and linoleic acid.

The molecular formula $C_{10}H_{18}O_3$ of **4** was suggested by HR-EIMS which gave a molecular ion peak at *m/z* 186.1270 (calcd 186.1256). The ^{1}H NMR and ^{13}C NMR spectra of **4** were also similar to those of **1**, but differed by 3 exchangeable protons, and 3 oxycarbons (δ 68.8, 77.2, 77.5), respectively. In the COSY spectrum of **4**,

Table 1
^{1}H NMR data for compounds **1**–**5** (in $CDCl_3$)

Position	δ ppm (multiplicity, *J* in Hz)				
	1	**2**	**3**	**4**	**5**
1	5.23 (dd, 17.16, 1.32), 5.05 (dd, 10.89, 1.32)	5.31 (dd, 17.48, 1.32), 5.14 (dd, 10.88, 1.32)	5.32 (dd, 17.15, 1.32), 5.16 (dd, 10.88, 1.32)	5.42 (d, 17.49), 5.21 (d, 10.89)	5.25 (dd, 17.49, 0.99), 5.10 (dd, l0.89, 0.99)
2	5.84 (dd, 17.16, 10.89)	5.88 (dd, 17.48, 10.88)	5.90 (dd, 17.15, 10.88)	5.96 (dd, 17.49, 10.56)	5.94 (dd, 17.49, 10.89)
4	3.31 (dd, 9.9, 3.3)	4.87 (dd, 8.57, 4.62)	4.88 (dd, 8.90, 4.62)	3.23 (d, 8.91)	4.10 (dd, 6.26, 3.96)
5	2.10 (m), 1.97 (m)	2.29 (m)	2.31 (m)	4.65 (br d, 8.58)	2.17 (ddd, 12.87, 6.60, 3.96), 1.83 (ddd, 12.87, 8.58, 6.26)
6	5.11 (dd, 7.92, 7.92)	5.05 (dd, 6.67, 6.67)	5.06 (dd, 6.67, 6.67)	5.43 (br.s)	4.03 (dd, 8.58, 6.60)
8	1.61 (s)	1.64 (s)	1.67 (s)	1.74 (s)	1.21 (s)
3-Me	1.19 (s)	1.24 (s)	1.25 (s)	1.34 (s)	1.32 (s)
8-Me	1.51 (s)	1.57 (s)	1.58 (s)	1.67 (s)	1.26 (s)
H-2′		2.29 (m)	2.31 (m)		
H-8′		1.90–2.10 (m)	1.90–2.10 (m)		
H-9′, 10′		5.30–5.50 (m)	5.30–5.50 (m)		
H-11′		1.90–2.10 (m)	2.77 (t, 5.61)		
H-12′, 13′		1.20–1.40 (m)	5.30–5.50 (m)		
H-14′		1.20–1.40 (m)	1.90–2.10 (m)		
H-18′		0.86 (t, 6.60)	0.88 (t, 6.90)		
Others		1.20–1.40 (m)	1.20–1.40 (m)		

sequences of –CHOH–CHOH–CH═C$(CH_3)_2$ and CH_2═CH– were observed. Therefore, the structure of **4** was determined as shown. HMBC correlation of the compound confirmed the structure (data not shown), although its stereochemistry remains undetermined.

The molecular formula of **5** was suggested to be $C_{20}H_{38}O_7$ based upon the HR-FABMS of its $[M+H]^+$ peak at *m/z* 391.2688 (calcd 391.2696). Although the ^{1}H NMR spectrum of **5** was again similar to **1**, **5** had an additional oxymethine signal at δ 4.03, instead of the H-6 olefinic methine of **1**. Furthermore, 10 carbons including 4 oxycarbons were observed in the ^{13}C NMR spectrum of **5**. Acetylation of **5** with acetic anhydride, pyridine and 4-dimethyl aminopyridine (DMAP) gave a hexa-acetate, indicating **5** was a symmetric dimer of a monoterpene-triol. In the ^{1}H NMR spectrum of the hexa-acetate, the H-4 signal was shifted to δ 5.14 from δ 4.10 in **5** and the chemical shift of H-6 did not change after acetylation. These data allowed us to conclude that the structure of **5** was as shown, although as for compound **4**, its stereochemistry has not yet been determined.

3. Experimental

^{1}H NMR: 270 (JEOL EX-270 spectrometer) or 500 MHz (JEOL Lambda-500 spectrometer) as int. standard. ^{13}C NMR: 125 MHz. A JASCO grating infrared spectrophotometer was used to record the IR spectra. The specific rotations were recorded by using a JASCO DIP-1000 polarimeter.

Mature fruiting bodies of *Dictyophora indusiata* (Vent.: Pers.) Fisch were collected from bamboo groves in Japan and China and identified by one of the authors (J.L.). A voucher specimen of the organism is located in the Jilin Institute of Biology, Changchun, China.

3.1. Extraction and isolation

Air dried fruiting bodies of *D. indusiata* (1.2 kg) were extracted with 85% EtOH (15 l, 5 times) and the solvent was concd under red. pres. and partitioned between EtOAc and H_2O. The residue (20.2 g) obtained after removing EtOAc was fractionated by repeated silica gel CC and HPLC to give **1** (620.3 mg), **2** (80.2 mg), **3** (15.0 mg), **4** (1.8 mg) as colorless oil and **5** (2.4 mg) as colorless oils.

3.2. (3R,4S)-3,7-Dimethyl-1,6-octadien-3,4-diol *1*

^{13}C NMR ($CDCl_3$); δ 17.8 (8-Me), 24.2 (3-Me), 25.7 (8), 30.5 (5), 75.3 (3), 77.8 (4), 113.8 (1), 121.1 (6), 133.7 (7), 140.9 (2), IR ν_{max}^{film} cm^{-1}: 3421, 2973, 2927, 1112, 1068, 921, 837. FABMS (positive; matrix, 3-nitrobenzyl alcohol) *m/z* 153. For the ^{1}H NMR spectrum, see Table 1.

3.3. 4-[(3R,4S)-3-Hydroxy-3,7-dimethylocta-1,6-dienyl (Z)-9-octadecenoate *2*

IR ν_{max}^{film} cm^{-1}: 3448, 2929, 2857, 1735, 1413, 1174. FABMS (positive; matrix, 3-nitrobenzyl alcohol) *m/z* 435. For the ^{1}H NMR spectrum, see Table 1.

3.4. 4-[(3R,4S)-3-Hydroxy-3,7-dimethylocta-1,6-dienyl (9Z,12Z)-9,12-octadecadienoate *3*

IR ν_{max}^{film} cm^{-1}: 3489, 2925, 2854, 1729, 1456, 1413, 1176. FABMS (positive; matrix, 3-nitrobenzyl alcohol) *m/z* 433. For the ^{1}H NMR spectrum, see Table 1.

3.5. 3,7-Dimethyl-1,6-octadien-3,4,5-triol *4*

^{13}C NMR ($CDCl_3$); δ 18.3 (8-Me), 25.5 (3-Me), 25.7 (8), 68.8 (3 or 4 or 5), 77.2 (4 or 5 or 3), 77.5 (5 or 3 or 4), 113.4 (1), 124.5 (6), 136.7 (7), 141.9 (2). IR ν_{max}^{film} cm^{-1}: 3367, 2925, 1093, 1072, 871. FABMS (positive; matrix, 3-nitrobenzyl alcohol) *m/z* 209. For the ^{1}H NMR spectrum, see Table 1.

3.6. Bis[6-(3,4,7-trihydroxy-3,7-dimethyloctenyl) ether *5*

^{13}C NMR ($CDCl_3$); δ 19.4 (3-Me), 24.4 (8), 27.3 (8-Me), 34.6 (5), 71.0 (7), 77.5 (4), 83.3 (6), 84.9 (3), 113.4 (1), 143.2 (2). IR ν_{max}^{film} cm^{-1}: 3405, 2976, 2931, 1708, 1375, 1091, 1055. FABMS (positive; matrix, 3-nitrobenzyl alcohol) *m/z* 391, 373. For the ^{1}H NMR spectrum, see Table 1.

3.7. Acetonide formation of *1*

Compound **1** (5.0 mg) was dissolved in acetone (1.0 ml) and to the solution was added *p*-toluenesulphonic acid (2.0 mg). The mixture was refluxed with stirring for 8 h and partitioned between EtOAc and water. The EtOAc extract was purified by silica gel chromatography to afford the acetonide of **1** (4.5 mg).

3.8. MBNC-ester formation of *1*

Compound **1** (5.0 mg) was dissolved in CH_2Cl_2 (0.2 ml) and to the solution was added (a*S*)-MBNC (10 mg), DCC (7.0 mg) and DMAP (1.0 mg). The reaction mixture was stirred at room temperature for 8 h and then purified by silica gel CC and HPLC to afford the (a*S*)-MBNC-ester of **1** (3.0 mg). A similar reaction using (a*R*)-MBNC gave the (a*R*)-MBNC-ester of **1** (3.0 mg).

3.9. Fatty acid-ester formation of *1*

Compound **1** (5.0 mg) was dissolved in CH_2Cl_2 (0.2 ml) and to the solution was added oleic acid (10.0 mg), DCC (7.0 mg) and DMAP (1.0 mg). The reaction mixture was stirred at room temperature for 8 h and then purified by silica gel CC and HPLC to afford **2** (5.0 mg). A similar reaction using linoleic acid gave **3**.

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