Available online at www.sciencedirect.com
SCIENCE DIRECT®
Phytochemistry 66 (2005) 1656–1661
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Lanostane triterpenoids from the inedible mushroom *Fomitopsis spraguei*

Dang Ngoc Quang [a,b], Yuuki Arakawa [a], Toshihiro Hashimoto [a], Yoshinori Asakawa [a,*]

[a] *Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan*
[b] *Faculty of Chemistry, Hanoi University of Education, 136 Xuan Thuy Road, Cau Giay, Hanoi, Vietnam*

Received 7 February 2005; received in revised form 28 March 2005
Available online 6 July 2005

Abstract

Investigation of the methanolic extract of the inedible mushroom *Fomitopsis spraguei* (Polyporaceae) led to the isolation of five lanostane-type triterpenoids (**1**–**5**): three new compounds named fomitopsins A–C (**2**–**4**), and two known compounds, quercinic acid C (**1**) and 3α-carboxyacetyl-12β-hydroxyquercinic acid (**5**). Their structures were determined by 2D NMR, MS, IR, UV spectra, and X-ray crystallographic analyses. An X-ray crystal structure analysis of quercinic acid C (**1**) established its stereochemistry as 3*R*,12*R*-dihydroxy-24*R*-methyl-23-oxo-25*S*-lanost-8-en-26-oic acid.

Keywords: Fungi; Lanostane; Triterpenoid; *Fomitopsis spraguei*

1. Introduction

Fungal species of the Polyporaceae are known to produce 24-methyl-lanostanes with a carboxyl group at C-26, and some possess a carboxyacetoxyl group at C-3 (Adam et al., 1967; Bryce et al., 1967; Cheung et al., 1973; Yokoyama and Natori, 1974; Rösecke and König, 2000). Fomlactones A–C from *Fomes cajanderi* contain a 12,23 epoxy ring together with a 26,23-lactone (He et al., 2003). So far, these compounds have been shown to possess interesting biological activities, such as anti-inflammatory activity (Giner-Larza et al., 2000; Kamo et al., 2003), antimicrobial activity (Keller et al., 1996; Bae and Min, 2000), anti-HIV activity (Li et al., 1993), and DNA polymerase and DNA topoisomerase inhibitory activity (Mizushina et al., 2004). In the course of our investigation of biologically active substances from inedible fungi, we previously reported the isolation of several lanostane triterpenoids from *Daldinia concentrica* (Quang et al., 2002) and *Tyromyces fissilis* (Quang et al., 2003, 2004). In continuation of this work, we report here the isolation of five lanostane triterpenoids (**1**–**5**) from *Fomitopsis spraguei* and the revised structure of quercinic acid C (**1**) based on the results of an X-ray crystallographic analysis.

2. Results and discussion

Fresh fruitbodies of *F. spraguei* were cut into small slices and extracted with MeOH. The methanolic extract was concentrated and repeatedly chromatographed on silica gel, a reversed-phase column and finally preparative HPLC to obtain five compounds (**1**–**5**). In some cases, substances could not be purified by conventional separation methods, and thus methylation by trimethyldiazomethane was carried out, followed by separation to obtain **7**–**9** as methyl esters of compounds **3**–**5**. These procedures were performed after the presence of a

* Corresponding author. Tel.: +88 622 9611; fax: +88 655 3051.
E-mail address: asakawa@ph.bunri-u.ac.jp (Y. Asakawa).

0031-9422/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2005.05.020

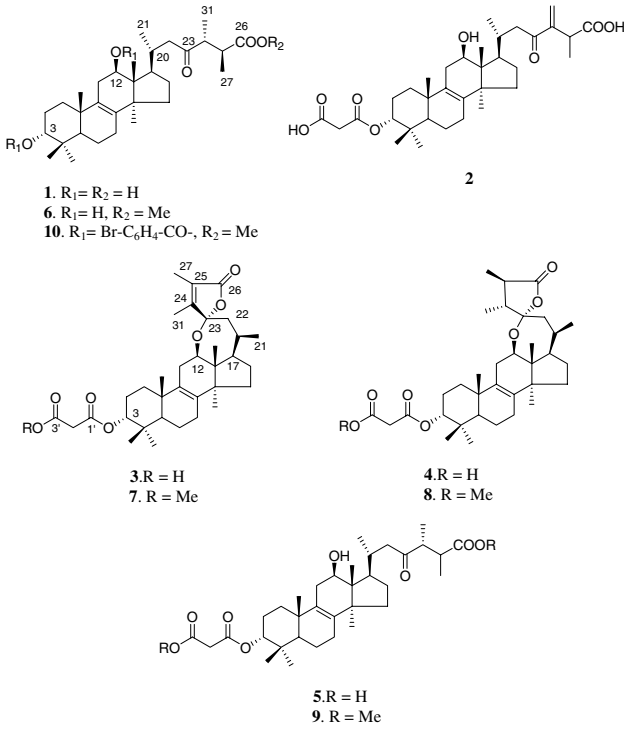

Fig. 1. Structures of **1**–**10**.

carboxylic group was confirmed by IR and the absence of a carbomethoxyl group was confirmed by NMR spectra.

The spectral data of compound **1** were identical to those of a previously reported lanostane, quercinic acid C (3β,12β-dihydroxy-24-methyl-23-oxolanost-8-en-26-oic acid) from *Daedalea quercina* (Rösecke and König, 2000). However, the stereochemistry of the hydroxyl group at C-3 should be *a*-configuration (axial) since H-3 (equatorial) appears as a broad singlet and C-3 appears at 74.6 (Rösecke and König, 2000). To confirm the stereochemistry of quercinic acid C it was converted to its methyl ester (**6**), which was treated with *p*-bromobenzoyl chloride in pyridine to yield the dibenzoate **10** as white crystals. An X-ray crystallographic analysis of **10** (Fig. 2) revealed the structure and stereochemistry of quercinic acid C (**1**) as 3*R*, 12*R*-dihydroxy-24*R*-methyl-23-oxo-25*S* lanost- 8-en-26-oic acid, as shown in Fig. 1.

Fomitopsin A (**2**) was obtained as an oil. Its molecular formula was established as $C_{34}H_{50}O_8$ by HRFABMS. The IR spectrum showed the presence of a carboxyl group (2500–3400 cm^{-1}, 1728 cm^{-1}). Its ^1H NMR spectrum (CD_3OD) showed the signals of two *exo*-methylenes, two secondary methyl groups and five tertiary methyl groups. The ^{13}C NMR spectrum showed a conjugated ketone, a carboxylic group, two olefinic carbons and two oxygenated carbons. The *exo*-methylene group was deduced to be located at C-24 based on long-range correlation between H-31 and C-23, C-24 and C-25 in the HMBC spectrum. The signals observed in the ^1H and ^{13}C NMR spectra were closely related to those of compound **1**, indicating that **2** also has a lanostane structure, except for the presence of the *exo*-methylene in place of a methyl group at C-24. Another difference is the unit at C-3. The signals of this side chain at C-3 were not observed in CD_3OD. However, the fragments in EIMS provided some evidence for the presence of a carboxyacetyloxy partial structure at C-3, since

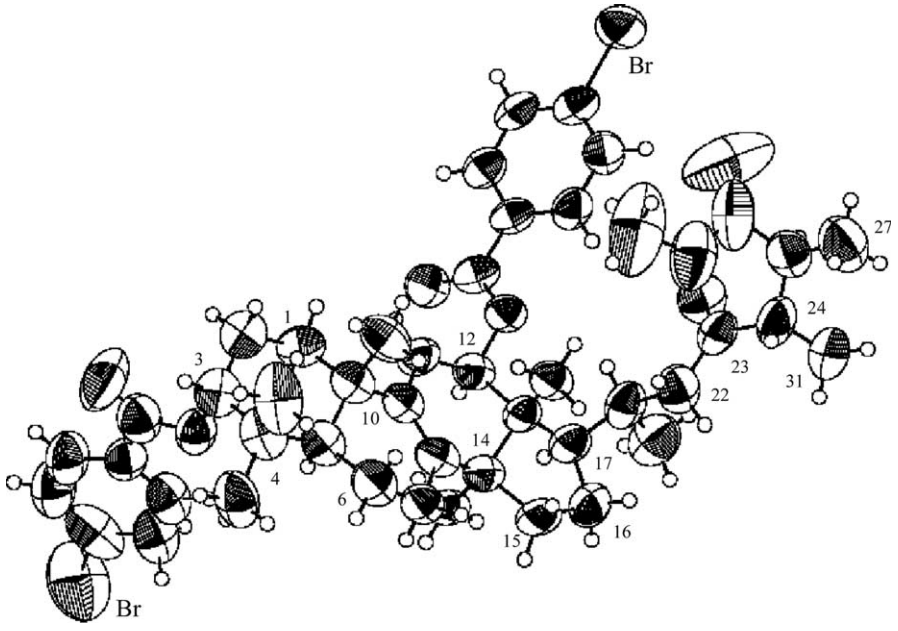

Fig. 2. ORTEP drawing of **10**.

fragments were observed at *m/z* 542 (M-CO2) and 525 (M-HAc-1). When $CDCl_3$ was used as a solvent, this compound and its methyl ester decomposed. Since we did not have enough compound **2** for further measurements, we could not observe the full NMR data of the carboxyacetyloxy group at C-3. Thus, fomitopsin A (**2**) was determined to be 3-carboxyacetyloxy-24-exomethylene-12β-hydroxy-23-oxo-lanost-8-en-26-oic acid.

Fomitopsin B–C (**3**–**4**) and **5** could not be isolated in a pure state and were methylated to yield two new compounds **7**, **8** and a known lanostane triterpenoid **9** (Yokoyama and Natori, 1974). No methoxyl groups were present in the NMR spectra of the unmethylated material. In addition, ^{13}C NMR spectral data of **9** were reported for the first time in Table 2.

The fomitopsin B methyl ester (**7**) was obtained as white crystals, and HRFABMS revealed the molecular formula of $C_{35}H_{50}O_7$. The signals observed in NMR spectra resembled those of **1** and **2**, suggesting that **7** also has a lanostane skeleton. In addition, the presence of an unsaturated lactone group was supported by signals at 179.6 and 1766 cm^{-1} in the ^{13}C NMR and IR spectra, respectively, and by the HMBC correlations between C-26 and Me-27 and Me-31, the olefinics C-24 and C-25 and two vinyl methyls H-27 and H-31. Furthermore, an HMBC correlation between H-3 and C-1′ established the presence of a carboxyacetyl group at C-3. The relative stereochemistry of **7** was deduced from the NOESY spectrum, in which H-3 was equatorial, whereas H-12 was axial based on NOE correlation from H-3 to H-29, and H-12 to H-17 and H-30. The structure and stereochemistry of fomitopsin B methyl ester (**7**) was established by an X-ray crystallographic analysis (Fig. 3) as 12β,23-epoxy-3α-carbomethoxyacetyloxy-24- methyllanost-8,24-dien-26,23-olide.

Fomitopsin C methyl ester (**8**) had spectral data similar to those of **7** except for the presence of two hydrogen atoms at C-24 (δ_H 2.12) and C-25 (δ_H 2.38). The stereochemistry of the two methyl groups at C-27 and C-31 were established to be β and α, respectively, based on the NOESY correlations between H-24 and H-22 and Me-27, H-25 and Me-31 and between Me-18 and Me-21. Thus, fomitopsin C methyl ester is 12*β*,23-epoxy-3α-carbomethoxyacetyloxy-24α-methyl-lanost-8-en-26,23-olide (**8**).

3. Experimental

3.1. General

NMR spectra were recorded on a Varian Unity 600 (600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR) using $CDCl_3$, CD_3OD, and C_5D_5N as solvents. Mass spectra including high-resolution FAB mass spectra were recorded on a JEOL JMS AX-500 spectrometer. IR spectra were measured on a Perkin Elmer Spectrum One FT-IR spectrometer. UV spectra were obtained on a Shimadzu UV-1650PC in MeOH solution. Specific optical rotations were measured on a JASCO DIP-1000 polarimeter with $CHCl_3$ as a solvent. X-ray reflection data were measured on a DIP Image diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Preparative medium-pressure liquid chromatography (MPLC) was performed with a Work-21 pump (Lab-Quatec Co., Ltd, Japan) and a Lobar column (Merck). HPLC was performed on a Shimadzu liquid chromatograph LC-10AS with RID-10A and SPD-10A detectors using a Waters 5C 18-AR-II or 5 SL-II column. TLC was performed on silica gel plates (Kieselgel 60 F254, Merck) and reversed-phase C_{18} silica gel plates (Merck).

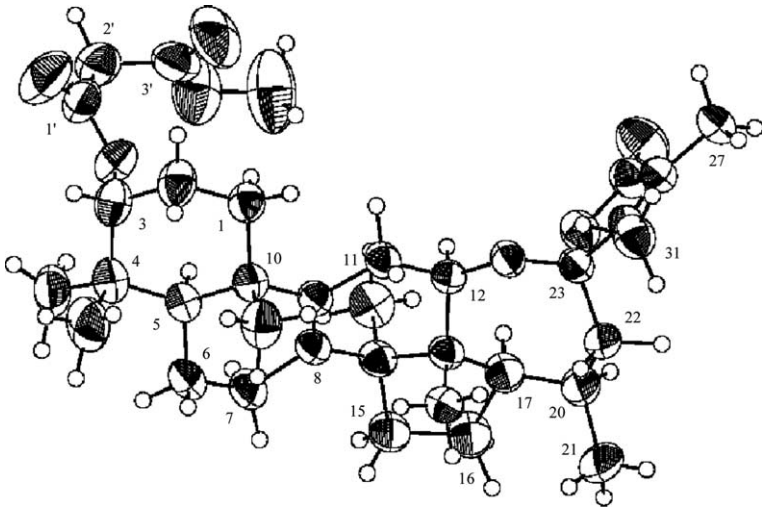

Fig. 3. ORTEP drawing of **7**.

3.2. Material

Fruitbodies of *F. spraguei* were collected at Okayama Forest Park, Okayama Prefecture, Japan in August 2001 and identified by Kazuyuki Takase (The Kansai Fungus Association). A voucher specimen (No. H01081) has been deposited at the Faculty of Pharmaceutical Sciences, Tokushima Bunri University.

3.3. Extraction and isolation

Fresh fruitbodies of *F. spraguei* (115.9 g) were extracted with MeOH. The methanolic extract was concentrated to obtain a residue (17.3 g), that was chromatographed on a SiO_2 column using MeOH–CHCl3 (1–4% MeOH) as a solvent system to give 31 fractions. Fraction 11 (470 mg) was repeatedly applied to a reversed-phase column with CH_3CN–H_2O (4:1) to give **2** (9.7 mg) and two more sub-fractions 11-5 (20 mg) and 11-6 (229 mg). Sub-fraction 11-5 was purified by MPLC with a SiO_2 column and $CHCl_3$–MeOH (15:1) to give **1** (5.5 mg). One hundred mg of sub-fraction 11-6 was methylated by $(CH_3)_3SiCHN_2$ (3 ml) and MeOH (3 ml), and then separated by SiO_2 column chromatography with EtOAc–hexane (1:1) to give **6** (59 mg) as a methyl ester of **1**. Fraction 15 (1402 mg) was purified by a reversed-phase column with CH_3CN–H_2O (6:4) to obtain 18 sub-fractions. Methylation of 50 mg of sub-fraction 15-4 (298 mg) by $(CH_3)_3SiCHN_2$ (1.5 ml) and MeOH (1.5 ml) and purification by SiO_2 column chromatography with hexane–EtOAc (6:4) gave **7** (16.6 mg) as white crystals in EtOAc. Fifty mg of sub-fraction 15-6 (204 mg) was treated the same as sub-fraction 15-4 to give **8** (2.9 mg) and **9** (18.1 mg).

3.3.1. Fomitopsin A (**2**)

$[\alpha]_D^{20} + 5.5°$ (*c* 0.4, $CHCl_3$). HRFABMS: *m/z* 609.3434 $[M + Na]^+$, $C_{34}H_{50}O_8Na$, requires 609.3403. IR (KBr) cm^{-1}: 2500–3400, 1728, 1462, 1376, 1262, 1157, 1024. ^1H and ^{13}C NMR ($CDCl_3$) (Tables 1 and 2).

3.3.2. Quercinic acid C methyl ester (**6**)

HREIMS: *m/z* 516.3819 $[M]^+$, $C_{32}H_{52}O_5$, requires 516.3815. IR (KBr) cm^{-1}: 3513, 1713, 1456, 1373, 1204, 755. ^1H NMR ($CDCl_3$): δ 4.11 (1H, *t*, *J* = 7.7

Table 1
^1H NMR spectral data of 2 (CD_3OD), **7** and **8** ($CDC1_3$, 600 MHz)

Position	**2**	**7**	**8**
1	1.51 *m*	1.38 *m*	1.48 *m*
		1.48 *m*	
2	1.54 *m*	1.69 *m*	1.68 *m*
	1.90 *m*	1.87 *m*	1.95 *m*
3	4.67 *brs*	4.70 *t* (2.8)	4.67 *t* (2.2)
5	1.54 *brd* (3.6)	1.42 *m*	1.50 *m*
6	1.54 *m*	1.49 *m*	1.52 *m*
	1. 65 *m*	1.63 *m*	1.65 *m*
7	2.05 *brs*	2.02 *m*	2.08 *m*
11	1.82 *m*	1.76 *m*	1.84 *m*
	2.54 *m*	2.37 *m*	2.38 *m*
12	4.06 *t* (7.7)	4.37 *t* (8.2)	4.35 *t* (8.2)
15	1.23 *dd* (7.4, 16.2)	1.27 *m*	1.30 *m*
	1.76 *m*	1.76 *m*	1.78 *m*
16	1.71 *m*	1.68 *m*	1.74 *m*
	1.94 *m*	1.82 *m*	1.86 *m*
17	1.96 *m*	2.77 *dd* (9.3, 18.4)	2.66 *dd* (9.1, 18.4)
18	0.77 *s*	0.81 *s*	0.82 *s*
19	1.06 *s*	1.01 *s*	1.06 *s*
20	2.41 *m*	2.38 *m*	2.20 *m*
21	0.97 *d* (6.9)	0.97 *d* (7.4)	1.02 *d* (7.4)
22	2.91 *dd* (3.0, 15.4)	1.85 *m*	1.77 *m*
	2.54 *m*	2.02 *m*	2.08 *m*
24			2.12 *m*
25	3.58 *dd* (7.1, 14.6)		2.38 *m*
27	1.29 *d* (7.1)	1.77 *d* (l.l)	1.22 *d* (7.1)
28	0.91 *s*	0.87 *s*	0.89 *s*
29	0.96 *s*	0.92 *s*	0.96 *s*
30	0.96 *s*	0.99 *s*	0.99 *s*
31	6.29 *s*	1.97 *d* (l.l)	1.12 *d* (6.9)
	5.94 *s*		
2′		3.39 *s*	3.43 *s*
3′-O*Me*		3.71 *s*	3.70 *s*

Table 2
^{13}C NMR spectral data of **2**, **9** (CD_3OD) and **7**, **8** ($CDCl_3$, 150 MHz)

Position	2	7	8	9
1	32.1	30.9	32.1	32.0
2	26.4	23.1	24.1	24.1
3	80.4	79.5	80.9	80.9
4	37.9	36.8	38.0	37.9
5	46.6	45.3	46.7	46.7
6	19.1	17.8	18.9	19.0
7	26.8	25.6	26.8	26.8
8	135.1	133.8	135.2	135.2
9	137.2	135.0	136.6	137.3
10	37.9	36.8	37.9	37.9
11	34.6	29.4	30.6	34.6
12	73.4	77.1	77.1	73.5
13	53.5	52.8	53.8	53.4
14	50.4	49.6	50.6	50.3
15	32.2	31.8	32.8	32.2
16	24.1	23.6	24.6	26.3
17	51.9	43.0	44.6	51.3
18	10.8	11.8	12.0	10.8
19	19.4	18.9	19.4	19.4
20	32.7	28.7	29.5	30.8
21	22.4	19.7	19.9	22.7
22	44.9	42.7	41.6	48.6
23	203.8	107.4	111.7	216.2
24	150.3	161.5	52.1	49.6
25	41.8	120.9	43.1	42.5
26	178.0	173.3	179.6	178.1
27	16.6	8.3	13.9	15.0
28	28.2	27.6	28.2	28.2
29	22.3	21.7	22.1	22.1
30	24.6	24.7	24.9	24.5
31	126.0	10.9	12.9	14.2
1′		166.0	167.7	167.7
2′		41.8	42.3	
3′		167.2	169.0	169.0
3′-O*Me*		52.3	52.9	52.8
26-O*Me*				52.2

Hz, H-12), 3.64 (3H, *s*, 26-CO*Me*), 3.44 (1H, *t*, *J* = 2.5 Hz, H-3), 1.15 (3H, *d*, *J* = 6.9 Hz, H-27), 1.07 (3H, *d*, *J* = 6.9 Hz, H-31), 1.00 (3H, *s*, H-19), 0.98 (3H, *d*, *J* = 6.3 Hz, H-21), 0.97 (3H, *s*, H-28), 0.91 (3H, *s*, H-30), 0.87 (3H, *s*, H-29), 0.72 (3H, *s*, H-18). ^{13}C NMR ($CDCl_3$): δ 213.7 (C-23), 176.5 (C-26), 135.8 (C-9), 133.5 (C-8), 75.9 (C-3), 72.8 (C-12), 52.5 (C-13), 51.8 (26-CO*Me*), 49.9 (C-17), 49.1 (C-14), 48.3 (C-24), 47.8 (C-22), 44.1 (C-5), 40.8 (C-25), 37.5 (C-4), 36.7 (C-10), 33.6 (C-11), 31.1 (C-15), 30.2 (C-1, C-20), 28.0 (C-28), 26.1 (C-2), 25.7 (C-7), 25.6 (C-16), 24.0 (C-30), 22.3 (C-21), 22.1 (C-29), 18.9 (C-19), 18.0 (C-6), 14.4 (C-27), 13.6 (C-31), 9.7 (C-18).

3.3.3. Fomitopsin B methyl ester (7)

White crystals (Et_2O). M.p. 220–225 °C. $[\alpha]_D^{20} + 4.3°$ (*c* 0.2, $CHCl_3$). HRFABMS: *m/z* 583.3656 $[M + H]^+$, $C_{35}H_{51}O_7$, requires 583.3635. IR (KBr) cm^{-1}: 1766, 1438, 1376, 1320, 1259, 1155, 1061, 965. ^1H and ^{13}C NMR ($CDCl_3$) (Tables 1 and 2).

3.3.4. Fomitopsin C methyl ester (8)

$[\alpha]_D^{20} - 15.3°$ (*c* 0.4, $CHCl_3$). HRFABMS: *m/z* 584.3717 $[M]^+$, $C_{35}H_{52}O_7$, requires 584.3713. IR (KBr) cm^{-1}: 1733, 1456, 1379, 1215, 1156, 1023, 944. ^1H and ^{13}C NMR ($CDCl_3$) (Tables 1 and 2).

3.3.5. Benzoylation of 6 (10)

To a solution of compound **6** (20 mg) in pyridine (2 ml) was added *p*-bromobenzoyl chloride (43.9 mg), and the reaction mixture was stirred at room temperature for 24 h. Work-up as usual gave a residue, which was purified by silica gel column chromatography (hexane–EtOAc, 4:1) to give **10** (29.2 mg) as white crystals in EtOAc. M.p. 172–180 °C. HRFABMS: *m/z* 903.2423 $[M + Na]^+$, $C_{46}H_{58}O_7Br_2Na$, requires 903.2447. IR (KBr) cm^{-1}: 1785, 1715, 1590, 1456, 1397, 1273, 1103, 846. ^1H NMR ($CDCl_3$): δ 7.93, 7.88, 7.61, 7.56 (4H, *d*, *J* = 8.8 Hz, dibenzoates), 5.48 (1H, *t*, *J* = 7.7 Hz, H-12), 4.91 (1H, *t*, *J* = 2.5 Hz, H-3), 3.64 (3H, *s*, 26-O*Me*), 2.79 (1H, *dd*, *J* = 7.1, 9.3 Hz, H-25), 2.73 (1H,

dd, J = 7.1, 9.3 Hz, H-24), 2.67 (1H, *brd*, J = 16.8 Hz, H-22), 2.35 (1H, *dd*, J = 10.2, 16.8 Hz, H-22), 1.15 (3H, *d*, J = 7.1 Hz, H-27), 1.10 (3H, *s*, H-30), 1.06 (3H, *s*, H-19), 1.01 (3H, *d*, J = 7.1 Hz, H-31), 0.99 (3H, *s*, H-29), 0.97 (3H, *s*, H-18), 0.94 (3H, *s*, H-28), 0.73 (3H, *d*, J = 6.3 Hz, H-21). ^{13}C NMR ($CDCl_3$): δ 212.9 (C-23), 176.5 (C-26), 165.8 and 165.3 (dibenzoates), 135.1 (C-9), 133.8 (C-8), 131.8, 131.7, 131.4, 131.0, 129.8, 129.6, 128.0, 127.8 (dibenzoates), 78.9 (C-3), 77.7 (C-12), 52.3 (C-13), 51.8 (26-O*Me*), 49.8 (C-17), 48.4 (C-24), 48.0 (C-14), 47.6 (C-22), 45.8 (C-5), 41.0 (C-25), 37.2 (C-4), 36.8 (C-10), 31.1 (C-1), 31.0 (C-15), 30.3 (C-11), 29.0 (C-20), 27.8 (C-28), 25.6 (C-7), 25.2 (C-16), 24.3 (C-30), 23.3 (C-2), 22.4 (C-21), 21.8 (C-29), 19.0 (C-19), 17.9 (C-6), 14.5 (C-27), 13.5 (C-31), 11.5 (C-18).

3.3.6. Crystal data for 7

Data collection: DIP Image plate. Cell refinement: Scalepack (HKL). Data reduction: maXus (Mackay et al., 1999). Program(s) used to refine structure: *SHELXL*-97 (Sheldrick, 1997). Refinement: on F^2 full matrix least-squares. Diffractometer: DIP Image plate. $C_{35}H_{50}O_7$, MW 582.778, orthorhombic, $P2_12_12_1$, a = 7.7140 (2) Å, b = 15.1050 (5) Å, c = 27.7570 (10) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 3234.2 (2) Å^3, Z = 4, Mo Kα radiation, γ = 0.71073 Å, μ = 0.082 mm^{-1}, 6095 reflections, 380 parameters; only coordinates of H atoms refined, R = 0.0536, R_w = 0.1320, S = 1.047.

3.3.7. Crystal data for 10

Data collection: DIP Image plate. Cell refinement: Scalepack (HKL). Data reduction: maXus (Mackay et al., 1999). Program(s) used to refine structure: *SHELXL*-97 (Sheldrick, 1997). Refinement: on F^2 full matrix least-squares. Diffractometer: DIP Image plate. $C_{50}H_{66}Br_2O_9$, MW 970.887, hexagonal, $P6_1$, a = 21.6190 (12)Å, b = 21.62 Å, c = 17.6060 (7) Å, α = 90.00°, β = 90.00°, γ = 120.00°, V = 7126.3 (5) Å^3, Z = 6, Mo Kα radiation, γ = 0.71073 Å, μ = 1.760 mm^{-1}, 4613 reflections, 516 parameters; only coordinates of H atoms refined, R = 0.0763, R_w = 0.2028, S = 1.087.

Crystallographic data for **7** (Deposition No. CCDC 255163) and **10** (Deposition No. CCDC 256065) have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, by applying to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial support from JSPS (Japan Society for the Promotion of Science) in the form of a postdoctoral fellowship to D.N. Quang (No. P04162) from 2004 to 2006 is gratefully acknowledged. We thank Dr. M. Tanaka, Mr. S. Takaoka and Miss Y. Okamoto (TBU, Japan) for recording NMR, X-ray and mass spectra, respectively. We also thank Mr. Kazuyuki Takase (The Kansai Fungus Association) for collecting and identifying the sample materials.

References

Adam, H.K., Bryce, T.A., Campell, I.M., McCorkindale, N.J., 1967. Metabolites of the Polyporaceae II. Carboxyacetylquercinic acid – a novel triterpene conjugate from *Daedalea quercina*. Tetrahedron Lett., 1461–1465.

Bae, K.G., Min, T.J., 2000. The structure and antibiotic activities of hydroxy acid of lanostenol compound in *Daedalea dickinsii*. Bull. Korean Chem. Soc. 21, 1199–1201.

Bryce, T.A., Campell, I.M., McCorkindale, N.J., 1967. Metabolites of the Polyporaceae I. Novel conjugates of polyporenic acid A from *Piptoporus betulinus*. Tetrahedron 23, 3427–3434.

Cheung, H.T., Seeto, J.C.F., Watson, T.R., 1973. Triterpene metabolite of *Trametes stowardii*. Aust. J. Chem. 26, 609–618.

Giner-Larza, E.M., Manez, S., Giner-Pons, R.M., Carmen Recio, M., Rios, J.-L., 2000. On the anti-inflammatory and anti-phospholipase A2 activity of extracts from lanostane-rich species. J. Ethnopharmacol. 73, 61–69.

He, J., Feng, X.H., Lu, Y., Zhao, B., 2003. Fomlactones A–C, novel triterpene lactones from *Fomes cajanderi*. J. Nat. Prod. 66, 1249–1251.

Kamo, T., Asanoma, M., Shibata, H., Hirota, M., 2003. Anti-inflammatory lanostane-type triterpene acids from *Piptoporus belutinus*. J. Nat. Prod. 66, 1104–1106.

Keller, A.C., Maillard, M.P., Hostettman, K., 1996. Antimicrobial steroids from the fungus *Fomitopsis pinicola*. Phytochemistry 41, 1041–1046.

Li, H.Y., Sun, N.J., Kashiwada, Y., Sun, L., Snider, J.V., Cosentino, L.M., Lee, K.H., 1993. Anti-AIDS agents, 9. Suberosol, a new C31 lanostane-type triterpene and anti-HIV principle from *Polyalthia suberosa*. J. Nat. Prod. 56, 1130–1133.

Mackay, S., Gilmore, C.J., Edwards, C., Stewart, N., Shankland, K., 1999. maXus Computer Program for the Solution and Refinement of Crystal Structures. Bruker Nonius, TheNetherlands, MacScience, Japan & The University of Glasgow.

Mizushina, Y., Akihisa, T., Ukiya, M., Murakami, C., Kuriyama, I., Xu, X., Yoshida, H., Sakaguchi, K., 2004. A novel DNA topoisomerase inhibitor: dehydroebriconic acid, one of the lanostane-type triterpene acids from *Poria cocos*. Cancer Sci. 95, 354–360.

Quang, D.N., Hashimoto, T., Tanaka, M., Baumgartner, M., Stadler, M., Asakawa, Y., 2002. Chemical constituents of the ascomycete *Daldinia concentrica*. J. Nat. Prod. 65, 1869–1874.

Quang, D.N., Hashimoto, T., Tanaka, M., Asakawa, Y., 2003. Tyromycic acids F and G: two new triterpenoids from the mushroom *Tyromyces fissilis*. Chem. Pharm. Bull. 51, 1441–1443.

Quang, D.N., Hashimoto, T., Tanaka, M., Takaoka, S., Asakawa, Y., 2004. Tyromycic acids B–E, new lanostane triterpenoids from the mushroom *Tyromyces fissilis*. J. Nat. Prod. 67, 148–151.

Rösecke, J., König, W.A., 2000. Constituents of the fungi *Daedalea quercina* and *Daedaleopsis confragosa* var. tricolor. Phytochemistry 54, 757–762.

Sheldrick, G.M., 1997. *SHELXL* 97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

Yokoyama, A., Natori, S., 1974. Triterpenoids of lanostane group from fruit bodies of nine Basidiomycetes species. Chem. Pharm. Bull. 22, 877–883.