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Triterpenoids from *Fuscoporia obliqua*

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Abstract: Two new lanosta triterpenoids, 3ß,22 α -dihydroxy-lanosta-8,24E-diene-25-peroxide, 3ß,22 α ,25-trihydroxy lanosta-8,24E-diene were isolated from the petroleum ether extracts of *Fuscoporia obliqua* and their structures had been determined by spectral data, chemical method and X-ray crystallographic analysis.

Keywords: *Fuscoporia obliqua*, Polyporaceae, fungi, triterpeneperoxide, 3ß,22 α -dihydroxy-lanosta-8,24E-ene-25-peroxide, 3ß,22 α ,25-trihydroxy-lanosta-8,24E-diene.

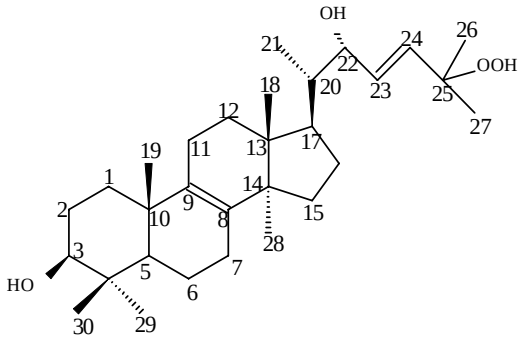
Fuscoporia obliqua is the birch tree fungus. It had been reported to contain several triterpenes of the lanostane type and pigment[1-3]. In the course of systematic study of its chemical composition, we isolated two novel triterpenoids named 3ß,22 α -dihydroxy-lanosta-8,24E-diene-25-peroxide (compound Ⅰ), 3ß,22 α ,25-trihydroxy-lanosta-8,24E-diene (compound Ⅱ). The isolation and structure elucidation of these compounds are reported in this paper.

Compound Ⅰ, m.p.196-198℃, $[\alpha]_D^{20}$+56.4 ($CHCl_3$, c 0.055), was obtained as a colorless slice crystal and showed a violet spot with 1% vanillin H_2SO_4 on TLC after heating. The molecular formula $C_{30}H_{50}O_4$, was established by HREIMS, which gave $[M^+]$ at *m/z* 474.3723 (calcd. 474.3709). The IR spectrum absorption at 3400 cm^{-1} suggested the presence of hydroxyl group. The peaks (*m/z* 343,329,311,299,281 and 109) in the EI MS spectrum and signals in ^{1}HNMR spectrum, which clearly showed eight methyl signals (δ 0.81,0.98,1.06,1.07,1.23,1.31,1.55 and 1.55 respectively) and two oxymethine signals (δ 4.60 dd, J=3.7, 6.5 Hz, H-22 ,3.43 dd, J=7, 10Hz, H-3), revealed the characteristics of lanosta skeleton. When the ^{1}HNMR spectral data of compound Ⅰ was compared with that of lanosterol[4,5], the only difference is that in the side chain of compound Ⅰ existed *trans* double bond (δ 6.35,d,J=15Hz and δ 6.15,dd,J=15, 6.5Hz). The ^{13}CNMR, DEPT and HREI MS spectra of compound Ⅰ also displayed it contained following 30 singals of carbons, two oxymethine carbons δ 78.1 (C-3), 74.1 (C-22), four olefinic carbons δ 134.4 (C-8), 134.4 (C-9), 136.7 (C-23), 129.9 (C-24), a quarternary carbon bearing oxygen δ 81.2 (C-25). Furthermore, the intense peaks at *m/z* 441 (M^+-33) and *m/z* 373 (M^+-101) in the EIMS spectrum revealed the existence of -OOH in 25- position. Thus, the structure of compound Ⅰ can be established as **Figure**

A.

The relative configuration of compound Ⅰ was determined by X-ray crystallographic analysis , compared with the known configuration of the parent skeleton (18,19 methyl were in ß configuration and 28 methyl was in α configuration), the structure of compound Ⅰ was shown in **Figure A**.

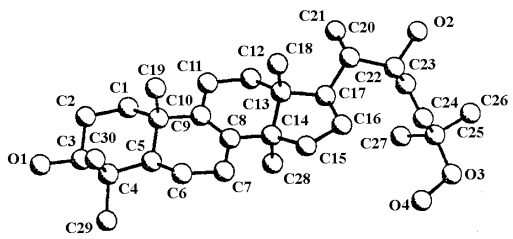
Figure A the structure of compound Ⅰ



Single crystal X-ray diffraction data were colleted by using a MAC Science DIP 2030k Image Plate with graphite monochromate, Moka radiation. The crystal belongs to monoclinic,space group $P2_1$. Accurate cell parameters are as follows: a=8,505 (1), b=10.446 (1), c=15.763 (1)Å, b=90.358 (4)° , V=1400.41 (23)$Å^3$, Z=2. There were 1546 reflections of which 1500 were observed the position of 31 nonhydrogen atoms were obtained directly from E-map. The structure was solved with NOMCSDP software package. Positions of the other nonhydrogen atoms were obtained and the kind of atoms were determined by using the least square calculation and the difference Fourier method in turn. Positions of all hydrogen atoms were obtained by geometric calculation and difference Fourier method.

Analysis result indicated that compound Ⅰ belongs to lanosta triterpenoid and had the chemical formular of C30H50O4 (the final reliable factors were Rf=0.045, Rw=0.051, S=6.729). In this compound, ring A is in chair,ring B and C are in semi-chair and ring D is in envelope configuration. Furthermore, ring A with B and ring C with D were all trans-fused . The result also showed that 3,22-position were substituted by hydroxyl and 25-position by peroxide. Its X-ray structure was displayed in **Figure B**.

Figure B The X-ray structure of compound Ⅰ



Compound Ⅱ, m.p. 241℃, $[\alpha]_D^{20}$ +308.5 ($CHCl_3$, c 0.07), was obtained as a colorless slice crystal and showed a violet spot then turned to yellow green spot with 1% vanillin H_2SO_4 on TLC after heating. The molecular formula $C_{30}H_{50}O_3$ was established by HREIMS, which gave [M^+] at 458.3767 (cacld. 458.3759). In the EIMS spectrum, the base peak at *m/z* 343 together with the intense peak at *m/z* 440 (M^+-H_2O), 425 (M^+-H_2O-CH_3), 325,311,299,281 and 109 revealed the characteristics of lanosta skeleton. The IR, ^{1}HNMR ,^{13}CNMR, DEPT spectra were very similar to those of compound Ⅱ except for molecular weight, thus we deduced the structure of this compound can be established as **Figure C**.

However, the structure of natural product, which was identical to compound Ⅱ had been reported by Finn scientists[6], but the configuration of 22-position was not reported. In order to determine the configuration of this compound, we conducted the reduction of compound Ⅰ with $NaBH_4$ in methanol for 15 min., only one product yielded . Its Rf values of TLC, and IR spectrum with those of compound Ⅱ were identical, and the mixed melt point of reduced compound Ⅰ and compound Ⅱ was unchanged. Thus the structure of compound Ⅱ was established as **Figure C**.

Figure C the structure of compound Ⅱ

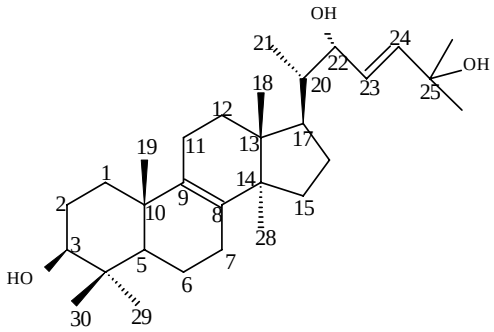


Table 1. ^{13}CNMR spectra data for compounds Ⅰ and Ⅱ in pyridine-d_6

No.	Ⅰ	Ⅱ	No.	Ⅰ	Ⅱ
1	36.1	36.1	16	31.4	31.4
2	27.8	27.8	17	43.7	43.7
3	78.1	78.1	18	16.2	16.2
4	39.5	39.5	19	19.4	19.4
5	50.9	50.9	20	47.9	47.9
6	18.7	18.7	21	13.4	13.4
7	26.9	26.9	22	74.1	74.0
8	134.4	134.4	23	136.7	141.0
9	134.4	134.4	24	129.9	126.3
10	37.4	37.4	25	81.2	69.8
11	21.3	21.3	26	25.6	30.9
12	27.6	27.6	27	25.2	30.9
13	45.1	45.1	28	28.6	28.6
14	49.7	49.7	29	16.3	16.3
15	31.4	31.4	30	24.3	24.3

Table 2. ^{1}HNMR spectra data for compounds Ⅰ and Ⅱ in pyridine-d_6

No.	Ⅰ	Ⅱ	No.	Ⅰ	Ⅱ
3	3.43,dd (J=7,10)	3.43,dd (J=7,10)	23	6.16,dd (J=6.5,15)	6.31,dd (J=6.5,15)
18	0.81,s	0.81,s	24	6.35,d (J=15)	6.25,d (J=15)
19	0.98,s	0.93,s	26	1.55,s	1.55,s
21	1.31,d (J=6.7)	1.29,d (J=6.7)	27	1.55,s	1.54,s
			28	1.07,s	1.07,s
22	4.60,dd (J=3.7,6.5)	4.61,dd (J=3.7,6.5)	29	1.06,s	1.05,s
			30	1.23,s	1.23,s

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