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Two New Abietane Quinones from *Isodon lophanthoides* var. *Micranthus*

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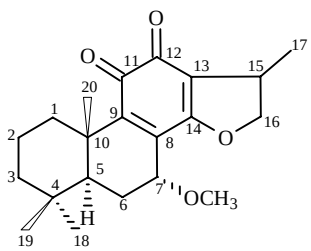
Abstract: The structures of two new abietane quinones, named micranthins A and B, were determined to be 7α-methoxy-14, 16-epoxy-8, 13-abietadiene-11, 12-dione (1) and 16-acetoxy-6, 7-dehydroroyleanone (2) respectively, which were isolated from *Isodon lophanthoides* var. *micranthus.*

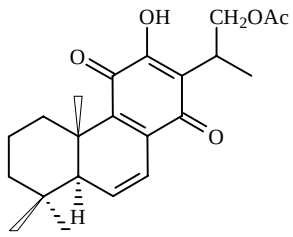
Keyword: *Isodon lophanthoides* var. *micranthus*, Labiatae, abietane quinones, micranthin A, miranthin B.

In the course of our research on bioactive compounds in genus *Isodo*n, two new abietane quinones were obtained from the 70 % acetone extract of the whole plant of *Isodon lophanthoides* var. *micranthus* (C.Y.Wu) H .W. Li, a perennial herb collected in Tengchong county, southwest of Yunnan province. This paper presents the structural elucidation of the new compounds.

Figure 1 The structures of **1** and **2**



1



2

Compound **1** had a molecular formula $C_{21}H_{28}O_4$ with eight unsaturated degrees, as deduced from its HREI mass spectrum (found 344.1987, cacld. 344.1988) and the ^1H and ^{13}C NMR data. In its DEPT spectrum, it was showed the signals of five methyls

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including one methoxyl [δ_C 57.4 (q), δ_H 3.40 (3H, s)], five methylenes, three methines including one oxymethine at [δ_C 71.9 (d), δ_H 4.01 (br. s, 1H)] and eight quaternary carbons containing four olefinic carbons [δ_C 118.5 (s), 135.9 (s), 150.2 (s), 171.8 (s)] and two carbonyl groups [δ_C 175.2 (s), 184.0 (s)]. Considering the compound isolated from the *Isodon* genus, it had an abietane diterpene skeleton and possessing an ortho-benzoquinone moiety, which was confirmed by the fact that there were ion at *m/z* 346 $[M + 2]^+$ in its mass spectrum and the typical chemical shifts of two carbonyl groups at δ_C 175.2 (s), 184.0 (s)[1]. The demands of the number of unsaturated degrees and a relative downfield methylene at δ_C 81.8 (t) displayed in ^{13}C NMR spectrum implied that except for the normal ring A, B, C, there should be an extra ring in the molecular skeleton, linking C-14 and C-16 through an oxygen bridge. The inferences were reasonablly verified by HMBC spectrum, which displayed clearly correlations between C-13 (δ_C 118.3) with H-16a/b, and C-14 (δ_C 171.8) with H-16a/b as well. The methoxy group was appointed at position C-7 by HMQC and HMBC spectral experiment. The α-orientation of 7-OCH_3 was indicated by the absence cross peak of 7β-H with 5α-H in the NOSEY spectrum. Consequently, the structure of micranthin A was elucidated as 7α-methoxy-14, 16-epoxy-8, 13-abietadiene-11, 12-dione.

Table 1 The ^{13}C NMR Data of **1** and **2** in $CDCl_3$ (100.5 MHz, δ in ppm)

carbon	**1**	**2**	carbon	**1**	**2**
1	35.6 (t)	35.3 (t)	13	118.3 (s)	118.2 (s)
2	19.0 (t)	18.9 (t)	14	171.8 (s)	185.9 (s)
3	41.3 (t)	40.7 (t)	15	34.6 (d)	29.5 (d)
4	33.3 (s)	33.5 (s)	16	81.8 (t)	66.5 (t)
5	45.7 (d)	52.3 (d)	17	18.9 (q)	15.1 (q)
6	22.1 (t)	140.3 (d)	18	33.3 (q)	32.8 (q)
7	71.9 (d)	121.5 (d)	19	22.1 (q)	23.0 (q)
8	135.9 (s)	140.9 (s)	20	18.5 (q)	15.2 (q)
9	150.2 (s)	138.8 (s)	OAc		171.2 (s)
10	40.0 (s)	39.5 (s)			21.2 (q)
11	184.0 (s)	183.1 (s)	OCH_3	57.4 (q)	
12	175.2 (s)	152.3 (s)			

Compound **2** gave a molecular formula $C_{22}H_{28}O_5$ in its HREI mass spectrum (found 372.1955, calcd. 372.1937) and the ^1H and ^{13}C NMR data. Its NMR signals were very similar to those of a known compound 16-acetoxy-7α-methoxyroyleanone[2,3]. The only difference was that one methylene at δ_C 22.2 (t), one methoxy at δ_C 57.3 (q) and one oxygen-bearing methine at δ_C 70.8 (d) in the known compound were disappeared, while two olefinic carbons at δ_C 140.3 (d) and 121.5 (d) in the downfield were observed in ^{13}C NMR spectrum of **2**. It can be deduced that compound **2** was a 6, 7- dehydro derivative of the 16-acetoxy-7α-methoxyroyleanone. The result was verified by spectral data of HMBC experiment, in which correlations between C-5 with H-6, H-7, and C-8 with H-6, H-7 were clearly shown. Thus the structure of miranthin B was

determined to be 16-acetoxy-6, 7- dehydroroyleanone.

Compound **1**, $C_{21}H_{28}O_4$, red oil, $[\alpha]_D^{25}$ –14.30 (*c* 0.07, $CHCl_3$); UV λ_{max}: 240, 285, 423 nm; IR ν_{max}: 3443, 2958, 2929, 1626, 1462, 1412, 1388, 1295, 1154, 1087, 937 cm^{-1}; ^1H NMR (400 MHz, in $CDCl_3$) δ: 4.83 (t, 1H, *J* = 9.0 Hz, H-16a), 4.21 (t, 1H, *J* = 9.0 Hz, H-16b), 4.01 (br s, 1H, H-7β), 3.44 (m, 1H, H-15), 3.40 (br s, 3H, OCH_3), 2.59 (br d, 1H, *J* = 13.4 Hz, H-1α), 2.02 (br d, 1H, *J* = 13.4 Hz, H-6β), 1.65 (m, 1H, H-2α), 1.46 (br s, 1H, H-6α), 1.42 (br d, 1H, *J* = 13.4 Hz , H-5α), 1.26 (d, 3H, *J* = 6.8 Hz, Me-17), 1.19 (s, 3H, Me-20), 0.98 (m, 1H, H-1β), 0.91 (s, 3H, Me-18), 0.88 (s, 3H, Me-19); EIMS *m/z* : 346 $[M+2]^+$ (24) , 344 $[M]^+$ (16), 314 (100), 301 (28), 285 (23), 269 (32), 245 (29), 229 (21), 219 (31), 203 (17), 187 (15), 149 (11), 109 (24), 69 (43); ^{13}C NMR data see **Table 1**.

Compound **2**, $C_{22}H_{28}O_5$, red oil, $[\alpha]_D^{25}$ -316.72 (*c* 0. 62, $CHCl_3$); UV λ_{max}: 228, 261, 351 nm; IR ν_{max}: 3431, 2956, 2931, 2870, 1740, 1639, 1460, 1374, 1330, 1255, 1162, 1036, 981, 962, 962, 937, 715 cm^{-1}; ^1H NMR (400 MHz, in $CDCl_3$) δ: 6.77 (dd, 1H, *J* = 10.0, 3.1 Hz, H-7), 6.45 (dd, 1H, *J* = 10.0, 3.1 Hz, H-6), 4.27 (dd, 1H, *J* = 10.6, 7.3 Hz, H-17a), 4.20 (dd, 1H, *J* = 10.6,7.3 Hz, H-17b), 3.34 (sextet, 1H, *J* = 7.3 Hz H-15), 2.87 (m, 1H, H-1β), 2.12 (t, 1H, *J* = 3.1 Hz, H-5α), 1.98 (s, 3H, Ac),1.62 (m, 2H, H-2), 1.42 (m, 2H, H-3), 1.21 (m, 1H, H-1α), 1.20 (d, 3H, *J* = 7.3 Hz, Me-16), 1.01 (s, 3H, Me-20), 0.99 (s, 3H, Me-18), 0.95 (s, 3H, Me-19); EIMS *m/z*: 372 $[M]^+$ (64), 330 (31), 312 (91), 297 (61), 284 (20), 269 (36), 256 (40), 243 (100), 229 (91), 217 (41), 201 (41), 187 (40), 173 (21), 159 (22), 141 (29), 128 (41), 115 (39), 105 (25), 91 (35), 83 (54), 69 (53), 55 (52); ^{13}C NMR data see **Table 1**.

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