SHORT PAPER

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Abietane diterpenes from *Rabdosia serra (maxim) hara*†

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Three new abietane diterpenoids which were assigned the structures of 16-hydroxyhorminone, 16-acetoxy horminone, and 6,12,15-trihydroxy-5,8,11,13-abietetriene-7-one were isolated, together with horminone, 16-acetoxy-7-0-acetylhorminone, β-sitosterol, stigmasterol, ursolic acid and palmitic acid from the leaves of *Rabdosia serra (maxim) hara*.

Keywords: abietane diterpenes, *Rabdosia serra (maxim) hara*

Rabdosia serra(maxim) hara, is a Chinese traditional medicine which is used for the treatment of hepatitis, enteritis, acute cholecystitis and dysentery. It is a perennial herb distributed mainly in middle and southeastern parts of China.[1] In previous reports, four diterpenoids, rabdoserrin A, rabdoserrin B, excisanin A and kamebakaurin which belong to the ent-kaurene series of diterpenoids have been isolated from this source.[2,3] We now describe the isolation and structure identification of five abietane diterpenes from the dried leaves of this herb. Three are novel compounds are 16-hydroxyhorminone **3**, 16-acetoxyhorminone **4** and 6,12,15-trihydroxy-5,8,11,13-abietetriene-7-one **5**. In addition, two known abietane quinones, horminone **1**, 16-acetoxy-7-0-acetylhorminone **2** and β-sitosterol, stigmasterol, ursolic acid, palmitic acid were identified.

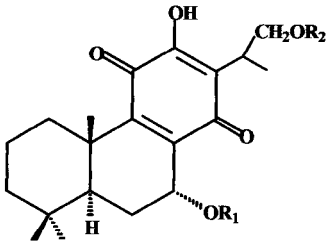
Results and discussion

Compounds **1–2** were identified by comparison of their spectroscopic data (UV, IR, ^{1}H NMR, ^{13}C NMR and MS) with the data of published compounds.[4,5]

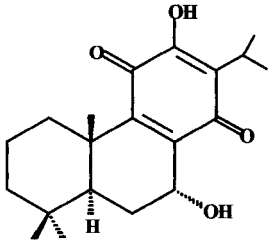
The spectroscopic data indicated that compounds **3-4** had a similar constitution and were related to compound **1**. Compound **3** was obtained as a yellow amorphous powder. Its EIMS showed a molecular ion peaks at *m/z* 348. The ^{13}C NMR showed that it possessed four CH_3, five CH_2, three CH and eight quarternary carbons. By combining the MS data and the ^{13}C NMR, the molecular formula was established as $C_{20}H_{28}O_5$. This was confirmed by HRMS (*m/z* 349.2017, M+H). Compound **3** possessed IR absorption bands for hydroxy groups (3397cm^{-1}) and there were characteristic peaks due to the quinonid structure (1681, 1654, 1627, 1602 cm^{-1}). The presence of the quinone was further confirmed by the typical UV absorption maxim at 214 and 273 nm and by ^{13}C NMR signals at 119.4, 143.4, 148.2, 151.9, 183.4, 188.7[4]. Its UV, IR, ^{1}H NMR, ^{13}C NMR were very similar to those of **1**, and this suggested that **3** and **1** had almost the some constitution.[5] The significant differences between **3** and **1** were the absence of two ester group absorption (1740, 1720 cm^{-1}) in the IR and the disappearance of two acetoxy group signal (1.97, s, 3H; 2.00, s, 3H) from the ^{1}H NMR of the former. The absence of two acetoxy group of **3** caused the upfield shift of the signal for H-7β from δ: 5.90 to 4.71 and 16-H from 4.21 to 3.29 (Table 1). Thus **3** was shown to 16-hydroxyhorminone.

Table 1 ^{1}H NMR data of compounds **1**, **3**, **4**, (200 MHz, $CDCl_3$, TMS)

H	**1**	**3**	**4**
1β	2.72 m ($w_{1/2}$=20, J^2=13)	2.67 m ($w_{1/2}$=20, J^2=13)	2.66 m ($w_{1/2}$=20, J^2=12)
7β	5.90 (3)	4.71 (3)	4.72 (3)
12-OH	7.26 s	7.24 s	7.24 s
15	3.34 sextet (7)	3.36 sextet (7.4)	3.33 sextet (7)
16	4.29 4.21 dd (7, 11)	3.84 3.79 dd (7.6, 11)	4.32 4.23 dd (7, 11)
17-Me	1.24 d (8)	1.23 d (7.6)	1.22 d (8)
18-Me	0.85 s	0.87 s	0.85 s
19-Me	0.85 s	0.95 s	0.95 s
20-Me	1.21 s	1.18 s	1.21 s
OAc	1.97 s 2.00 s		1.99 s



R1=R$_2$=Ac **1**
R1=R$_2$=H **3**
R1=H, R$_2$=Ac **4**



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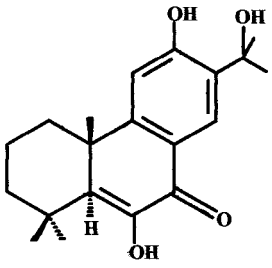

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Compound **4**, a yellow amorphous powder, was assigned the molecular formula $C_{22}H_{30}O_6$ by EIMS (*m/z* 390), ^{13}C NMR and HRMS (*m/z* 391.2127, M+H). Its IR spectrum showed peaks for a hydroxy groups (3370 cm^{-1}) and an ester group (1737 cm^{-1}). Comparison of the ^{1}H NMR spectra of **4** with that of **1** showed the lack of an acetoxy signal at δ: 2.00 in **4** and the upfield shift of the H-7β from δ: 5.90 in the latter

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

to 4.72 in the former. Therefore, the chemical constitution of **4** was established as 16-acetoxyhorminone. The ^{1}HNMR of **1**, **3**, **4** are given in Table 1.

Compound **5** was white crystals. The EIMS indicated a molecular formula $C_{20}H_{26}O_4$ (*m/z* 330), and the HRMS (*m/z* 331.1902, M+H) confirmed this information. The ^{13}CNMR(DEPT) revealed the presence of five CH_3, three CH_2, two Ch and 10 quaternery carbon atoms. The ^{1}H NMR indicated an abietane structure with signals at δ 1.68, and 1.66 (each 3H, s, H-16, H-17) and three emthyl singlets one at 1.63(H-20), and two others at δ 1.37 and δ 1.25 (H-18 and H-19). This suggested that there was a hydroxyl group at C-6 as observed in similar compounds.[6] The signal at δ 7.50(1H, s, H-14), suggested the presence of a carbonyl group at C-7. The absence of a signal at δ 3.03 and the type of singlet of two methyl groups (C-16, C-17) suggested the presences of a hydroxyl group at C-15 which was further confimed by the ^{13}C NMR (δ 76.01, C-15). The ^{1}H NMR, ^{13}C NMR signals were compatible with the proposed structure for compound **5**.

Experimental

M.p.s.: uncorr. UV: EtOH. IR: KBr; ^{1}H and ^{13}C NMR: 200 and 400 MHz respectively, $CDCl_3$ with TMS as int. standard; MS: EI, 70ev.

R. serra leaves were collected in Fujian Province of China and identified by Huang Xingsheng, a botanist at this institute where a voucher specimen has been deposited.

Dried and powdered leaves (4.8 kg) were extracted with EtOH at room temperature and the solvent was evaporated. The residue (284 g) was dissolved in MeOH and decolourized by treatment with active charcoal (200 g) when the solvent was warm. The filtrate was concentrated to about 300 ml and mixed with silica gel (250 g). The mixture was submitted to cc(silica gel) eluting with increasing proportions of Me_2CO-petrol ether. Fractions were monitored by TLC. All fractions were purified by further silia-gel column chromatography or preparative TLC (silia gel), to yield in order of increasing polarity: (**2**)(42 mg), (**1**)(38 mg), (**4**)(22 mg), (**3**)(38 mg), (**4**)(23 mg), β-sitosterol(312 mg), stigmasterol(630 mg), palmitic acid(27 mg), ursolic acid(2.1 g).

Compound **3,** $C_{20}H_{28}O_5$, yellow amorphous powder; UV λ/nm (log ε, EtOH): 217 (3.89), 274 (3.96); IR ν/cm^{-1}: 3383, 2916, 1681, 1654, 1627, 1602, 1270, 1242; HRMS *m/z* $[M+H]^+$ $^{349.2017,\ C_{20}H_{29}O_5}$ (calcd 349.2015); EIMS 70eV, *m/z*: 348$[M]^+$ (9), 330$[M-H_2O]^+$ (21), 315$[M-H_2O\text{-}Me]^+$ (12), 312$[M-2H_2O]^+$ (6), 300$[M-H_2O\text{-}2Me]^+$ (100), 297$[M-2H_2O\text{-}Me]^+$ (7), 285$[M-H_2O\text{-}3Me]^+$ (11); ^{13}C NMR (200MHz, $CDCl_3$): δ 35.7 (t, C-1), 18.8 (t, C-2), 41.0 (t, C-3), 39.1 (s, C-4), 45.6 (d, C-5), 25.8 (t, C-6), 63.0 (d, C-7), 143.0 (s, C-8), 148.2 (s, C-9), 39.2 (s, C-10), 183.4 (s, C-11), 152.2 (s, C-12), 120.9 (s, C-13), 189.3 (s, C-14), 32.3 (d, C-15), 65.2 (t, C-16), 18.4 (q, C-17), 33.1 (q, C-18), 21.7 (q, C-19), 14.5 (q, C-20).

Compound **4,** $C_{22}H_{30}O_6$, yellow amorphous powder; UV λ/nm (log ε, EtOH): 214 , 273; IR ν/cm^{-1}: 3370, 2915, 1737, 1671, 1653, 1627, 1600, 1725–1221; HRMS *m/z* $[M+1]^+$ 391.2127. $C_{22}H_{30}O_6$ (clacd 3921.2121); EIMS (probe) 70eV, *m/z*: 390$[M]^+$ (9), 372$[M-H_2O]^+$ (2), 331$[M-41\text{-}H_2O]^+$ (22), 330$[M-42\text{-}H_2O]^+$ (100), 315$[M-42\text{-}H_2O\text{-}Me]^+$ (20), 312$[M-42\text{-}2H_2O]^+$ (22), 297$[M-42\text{-}2H_2O\text{-}Me]^+$ (11); ^{13}C NMR (200MHz, $CDCl_3$): δ 35.8 (t, C-1), 18.8 (t, C-2), 41.1 (t, C-3), 39.2 (s, C-4), 45.7 (d, C-5), 25.7 (t, C-6), 63.1 (d, C-7), 143.4 (s, C-8), 148.2 (s, C-9), 39.2 (s, C-10), 183.4 (s, C-11), 151.9 (s, C-12), 119.6 (s, C-13), 188.7 (s, C-14), 29.2 (d, C-15), 66.2 (t, C-16), 18.4 (q, C-17), 33.1 (q, C-18), 21.7 (q, C-19), 14.9 (q, C-20), 170.0(s, -COMe), 20.9(q, -COMe)

Compound **5,** $C_{24}H_{34}O_5$, white crystal; m.p. 152–154°C HRMS *m/z* $[M+1]^1$ 331.1902, $C_{20}H_{27}O_4$ (calcd 331.1909); EIMS (70 eV), *m/z*: 330$[M]^+$ (8), 312$[M-H_2O]^+$ (98), 297$[M-H_2O\text{-}CH_3]^+$ (79), 242$[M-H_2O\text{-}C_5H_{10}]^+$ (100); ^{1}H NMR (500MHz, $CDCl_3$): δ 3.46 (1β-H, $w_{1/2}$=19, J^2=12), 1.39 (1 a-H, m), 2.06 (2β-H, m), 1.61 (2a-H, m), 6.30 (C_{11}-H, s), 7.50 (C_{14}-H, s), 1.68 (C_{16}-H, 3H, s), 1.66 (C_{17}-H, 3H, s), 1.37 (C_{18}-H, 3H, s), 1.25 (C_{19}-H, 3H, s), 1.63 (C_{20}-H, 3H, s). ^{13}C NMR (500MHz, $CDCl_3$): δ 41.3 (t, C-1), 19.3 (t, C-2), 35.0 (t, C-3), 38.6 (s, C-4), 174.5 (s, C-5), 143.1 (s, C-6), 184.9 (s, C-7), 123.5 (s, C-8), 138.3 (s, C-9), 42.8 (s, C-10), 115.0 (d, C-11), 148.4 (s, C-12), 131.3 (c, C-13), 124.0 (d, C-14), 76.0 (s, C-15), 31.3 (q, C-16), 31.2 (q, C-17), 33.6 (q, C-18), 25.1 (q, C-19), 30.3 (q, C-20).

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