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催吐萝芙木中生物碱的研究

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摘 要:从催吐萝芙木根的乙醇提取物中分离得到15个吲哚生物碱,利用波谱(ESI-MS,^{1}H NMR,^{13}C NMR)等技术分别鉴定为利血平(**1**),四氢鸭脚木碱(**2**),异山德维辛碱(**3**),利血平酸甲酯(**4**),萝芙木碱(**5**),山德维辛碱(**6**),异育亨宾(**7**),霹雳萝芙木碱(**8**),α-育亨宾(**9**),育亨宾(**10**),催吐萝芙木定(**11**),四叶萝芙新碱(**12**),harman(**13**),mauiensine(**14**),12-hydroxymauiensine(**15**)。其中化合物**13**~**15**是首次从该植物中分离到。

关键词:吲哚生物碱;催吐萝芙木

中图分类号:R284.1 **文献标识码**:A

Indole Alkaloids from *Rauwolfia vomitoria*

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Abstract: Fifteen indole alkaloids were isolated from the roots of *Rauwolfia vomitoria*. On the basis of spectroscopic evidence, their structures were identified as reserpine (**1**), tetrahydroalstonine (**2**), isosandwicine (**3**), methyl reserpate (**4**), ajmaline (**5**), sandwicine (**6**), isorauhimbine (**7**), perakine (**8**), α-yohimbine (**9**), yohimbine (**10**), mitoridine (**11**), tetraphyllicine (**12**), harman (**13**), mauiensine (**14**), and 12-hydroxymauiensine (**15**). Compounds **13**~**15** were isolated from this plant for the first time.

Key words: indole alkaloids; *Rauwolfia vomitoria*

Introduction

Rauwolfia vomitoria (Apocynaceae) is mainly distributed in the west of Africa. In recent years, it was transplanted in the south and southwests of China, especially in Guangxi and Yunnan provinces. It has rich indole alkalodis which are the most important source of the hypotensive. Moreover, some of alkaloids are also used to treat arrhythmia[1]. The chemical properties of the *Rauwolfia vomitoria* have been exhaustively investigated abroad[2], but there has few reports in China. In order to discover their new activities, we researched the chemical constituents of *R. vomitoria* and indentified the structures.

Experimental

Apparatus

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 Hz and DRX-500 Hz spectrometers with TMS as internal standard. The ESI-MS was carried out on a VG Autospec-3000 spectrometer. Silica gel (200~300, 300~400 mesh) from Qingdao Haiyang Chem. Ind. Co. Ltd. and Sephadex LH-20 from Amersham Biosciences AB, Sweden, were used for column chromatography.

Plant material

The roots of *R. vomitoria* were collected in Xishuangbanna, Yunnan, China and identified by Zhang Shuncheng (Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences). A voucher specimen (No. 128) is deposited in our laboratory.

Extraction and isolation

The air-dried roots (7.0 kg) of *R. vomitoria* were extracted with 90% EtOH under refluxing to give a crude extract. The ethanolic extracts were submitted to acid-base treatment to obtain the crude alkaloids (112 g), which was subjected to column chromatography over Si gel eluting with $CHCl_3$/ MeOH (100:0~0:100) to give four fractions. Fraction 1 was subjected to repeated

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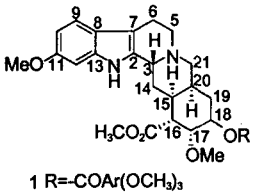
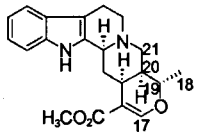
column chromatography over Si gel with $CHCl_3$/MeOH (30∶1) and petroleum ether/EtOAc (10∶1) to get compounds **1** (80 mg) and **2** (15 mg). Fraction 2 was subjected to column chromatography over Si gel with petroleum ether/EtOAc/ diethylamine (15∶1∶0.1), followed by separation over Sephadex LH-20 eluted with acetone to obtain compounds **7** (10 mg), **8** (50 mg), **9** (7 mg), and **13** (8 mg). Fraction 3 was subjected to column chromatography over Si gel with $CHCl_3$/ diethylamine (100∶2.5 ~ 100∶4) and petroleum ether/EtOAc (8∶2) to yield compounds **3** (7 mg), **4** (20 mg), **5** (6 mg), and **6** (10 mg). Fraction 4 was subjected to repeated column chromatography over Si gel with $CHCl_3$/ MeOH (8∶2), petroleum ether/EtOAc/ diethylamine (9∶1∶0.2) to obtain compounds **10** (8 mg), **11** (15 mg), **12** (9 mg), **14** (7 mg), and **15** (5 mg).



1 R=-COAr(OCH$_3$)$_3$
4 R=H



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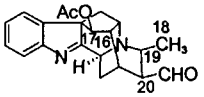
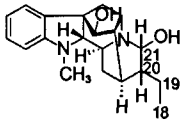
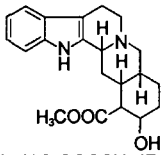


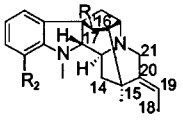
8



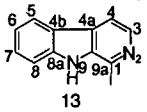
3 17α-OH,20β-H,21α-H
5 17β-OH,20α-H,21β-H
6 17α-OH,20α-H,21β-H



7 3β-H,15α -H,16β-COOCH$_3$,17α-OH,20α-H
9 3α-H,15α -H,16β-COOCH$_3$,17α-OH,20α-H
10 3α-H,15α -H,16α-COOCH$_3$,17α-OH,20β-H



11 R$_1$=O,R$_2$=OH 14 R$_1$=β-OH,R$_2$=H
12 R$_1$=α-OH,R$_2$=H 15 R$_1$=β-OH,R$_2$=H



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Results and Identification

Compound 1 White needles (CH_3COCH_3-CH_3OH), ESI-MS *m/z*:608 [M]$^+$; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.04 (1H, s, H-3), 3.17 (2H, m, H-5β and H-21β), 3.03 (1H, dd, *J* = 11.6, 3.3 Hz, H-5α), 2.69 (1H, dd, *J* = 11.1, 4.6 Hz, H-6α), 2.46 (1H, m, H-6β), 7.32 (3H, m, H-9, H-2′ and H-6′), 6.76 (1H, d, *J* = 8.5 Hz, H-10), 6.82 (1H, s, H-12), 1.84 (2H, m, H-14), 3.91 (1H, m, H-17), 4.46 (1H, s, H-18), 2.95 (1H, m, H-21α), 3.91 (9H, s, OCH_3), 3.81 (6H, s, OCH_3), 3.49 (3H, s, OCH_3), 7.68 (1H, s, NH). The ^{13}C NMR data see Table 1. Compound **1** was determined to be reserpine[3].

Compound 2 White amorphous powder, ESI-MS *m/z*:352 [M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.34 (1H, br d, *J* = 11.1 Hz, H-3), 3.10 (1H, br d, *J* = 12.2 Hz, H-5β), 2.96 (1H, m, H-5α), 2.75 (2H, m, H-6α and H-21α), 2.54 (1H, m, H-6β), 7.45 (1H, d, *J* = 7.5 Hz, H-9), 7.14 ~ 7.06 (2H, m, H-10 and H-11), 7.25 (1H, *J* = 7.7 Hz, H-12), 1.70 (2H, m, H-14), 7.58 (1H, s, H-17), 1.40 (3H, d, *J* = 6.1 Hz, H-18), 4.52 (1H, m, H-19), 1.53 (1H, m, H-20), 2.96 (1H, d, *J* = 8.7 Hz, H-21β), 3.76 (3H, s, $COOCH_3$). The ^{13}C NMR data see Table 1. Compound **2** was determined to be tetrahydroalstonine[3].

Compound 3 White amorphous powder, ESI-MS *m/z*:326 [M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.01 (1H, s, H-2), 3.51 (2H, m, H-3 and H-5), 1.98 (1H, br d, *J* = 12.5 Hz, H-6β), 1.29 (1H, br d, *J* = 12.5 Hz, H-6α), 7.04 (1H, d, *J* = 7.0 Hz, H-9), 6.77 (1H, t, *J* = 7.0 Hz, H-10), 7.12 (1H, t, *J* = 7.0 Hz, H-11), 6.69 (1H, d, *J* = 7.0 Hz, H-12), 1.68 (2H, m, H-14α and H-14α), 1.93 (1H, m, H-15), 2.35 (1H, m, H-16), 4.70 (1H, d, *J* = 9.2 Hz, H-17), 0.98 (3H, t, *J* = 7.3 Hz, H-18), 1.38 (2H, m, H-19 and H-20), 3.99 (1H, d, *J* = 6.8 Hz, H-21), 2.80 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **3** was determined to be isosandwicine[4].

Compound 4 Yellow amorphous powder, ESI-MS *m/z*:414 [M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.44 (1H, s, H-3), 3.17 (2H, m, H-5β and H-21β), 3.00 (1H, m, H-5α), 2.69 (1H, m, H-6β), 2.51 (1H, m, H-6β), 7.31 (1H, d, *J* = 8.6 Hz, H-9), 6.75 (1H, d, *J* = 8.6 Hz, H-10), 6.83 (1H, s, H-12), 3.53 (2H, m, H-17 and H-18), 2.95 (1H, m, H-21α), 3.83 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 3.57 (3H, s, OCH_3), 8.00 (1H, s, NH). The ^{13}C NMR data see Table 1. Compound 4 was determined to be methyl reserpate[3].

Compound 5 Colorless needles ($CHCl_3$-CH_3OH),

ESI-MS *m/z*:326[M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ:2.63 (1H, s, H-2), 3.57 (1H, br d, J = 9.6 Hz, H-3), 3.00 (1H, m, H-5), 2.03 (1H, br d, J = 12.0 Hz, H-6α), 1.92 (1H, dd, J = 12.0, 4.8 Hz, H-6β), 7.44 (1H, d, J = 7.3 Hz, H-9), 6.75 (1H, t, J = 7.3 Hz, H-10), 7.12 (1H, t, J = 7.3 Hz, H-11), 6.63 (1H, d, J = 7.3 Hz, H-12), 1.82 (1H, m, H-14β), 1.47 (3H, m, H-14β, H-19′ and H-20), 2.25 (1H, br s, H-15), 1.85 (1H, s, H-16), 4.41 (1H, s, H-17), 0.94 (3H, t, J = 6.8 Hz, H-18), 1.40 (1H, m, H-19), 4.23 (1H, br s, H-21), 2.77 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **5** was determined to be ajmaline[4].

Compound 6 White amorphous powder, ESI-MS *m/z*:326[M]$^+$; ^{1}H NMR ($CDCl_3$: CD_3OD = 1 : 1, 400 MHz) δ:3.13 (1H, s, H-2), 3.19 (2H, m, H-3 and H-5), 2.02 (1H, m, H-6α), 1.31 ~ 1.42 (5H, m, H-6β, H-14β, H-19, H-19′ and H-20), 7.08 (1H, d, J = 7.1 Hz, H-9), 6.81 (1H, t, J = 7.1 Hz, H-10), 7.16 (1H, t, J = 7.1 Hz, H-11), 6.65 (1H, d, J = 7.1 Hz, H-12), 1.69 (1H, br s, H-14α), 2.23 (1H, m, H-15), 2.26 (1H, m, H-16), 4.87 (1H, d, J = 9.2 Hz, H-17), 0.97 (3H, t, J = 6.8 Hz, H-18), 4.61 (1H, s, H-21), 2.80 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **6** was determined to be sandwicine[5].

Compound 7 Yellow amorphous powder, ESI-MS *m/z*:354[M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.57 (1H, s, H-3), 3.23 (2H, m, H-5α and H-21β), 3.07 (1H, d, J = 11.6 Hz, H-5β), 2.98 (2H, m, H-6β H-21α), 7.45 (1H, d, J = 7.6 Hz, H-9), 7.11 (1H, t, J = 7.6 Hz, H-10), 7.17 (1H, t, J = 7.6 Hz, H-11), 7.36 (1H, d, J = 7.6 Hz, H-12), 2.40 (1H, m, H-16), 4.11 (1H, m, H-17), 3.87 (3H, s, $COOCH_3$), 8.40 (1H, s, NH). The ^{13}C NMR data see Table 1. Compound **7** was determined to be isorauhimbine[3,6].

Compound 8 White amorphous powder, ESI-MS *m/z*:350[M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ:4.16 (1H, d, J = 8.8 Hz, H-3), 3.61 (1H, dd, J = 6.4, 11.2 Hz, H-5), 1.67 (1H, d, J = 4.9 Hz, H-6α), 2.79 (1H, dd, J = 4.9, 11.2 Hz, H-6β), 7.59 (1H, d, J = 7.6 Hz, H-9), 7.37 (1H, t, J = 7.6 Hz, H-10), 7.21 (1H, t, J = 7.6 Hz, H-11), 7.46 (1H, d, J = 7.6 Hz, H-12), 1.74 (1H, m, H-14β), 1.61 (1H, m, H-14α), 2.86 (1H, t, J = 4.7 Hz, H-15), 2.47 (1H, t, J = 5.9 Hz, H-16), 4.92 (1H, s, H-17), 1.27 (3H, d, J = 6.6 Hz, H-18), 3.31 (1H, m, H-19), 2.15 (1H, m, H-20), 2.15 (3H, s, OCOMe), 9.82 (1H, s, CHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 182.6 (s, C-2), 56.8 (d, C-3), 56.2 (d, C-5), 37.3 (t, C-6), 64.8 (s, C-7), 136.1 (s, C-8), 128.7 (d, C-9), 123.8 (d, C-10), 125.5 (d, C-11), 121.0 (d, C-12), 156.4 (s, C-13), 22.5 (t, C-14), 26.1 (d, C-15), 49.8 (d, C-16), 77.9 (d, C-17), 18.8 (q, C-18), 51.5 (d, C-19), 48.6 (d, C-20), 170.0 (s, OCOMe), 21.0 (q, OCOMe), 201.6 (d, CHO). Compound **8** was identified as perakine by comparison of the NMR data[7].

Compound 9 Yellow amorphous powder, ESI-MS *m/z*:354[M]$^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.10 (1H, d, J = 11.2 Hz, H-3), 2.94 (3H, m, H-5α, H-6β and H-21α), 2.54 (2H, m, H-5β, H-16), 2.81 (1H, d, J = 11.2 Hz, H-6α), 7.42 (1H, d, J = 7.6 Hz, H-9), 7.03 (1H, t, J = 7.6 Hz, H-10), 7.09 (1H, t, J = 7.6 Hz, H-11), 7.26 (1H, d, J = 7.6 Hz, H-12), 2.30 (1H, m, H-15), 3.94 (1H, m, H-17), 2.03 (2H, m, H-18α and H-19β), 1.34 (1H, m, H-18β), 1.65 (1H, m, H-19α), 2.01 (1H, m, H-20), 2.62 (1H, m, H-21β), 3.79 (3H, s, $COOCH_3$). The ^{13}C NMR data see Table 1. Compound **9** was determined to be α-yohimbine[3,6].

Compound 10 Yellow amorphous powder, ESI-MS *m/z*:354[M]$^+$; ^{1}H NMR ($CDCl_3$, 500 MHz) δ:3.28 (1H, d, J = 11.1 Hz, H-3), 3.07 (1H, m, H-5α), 2.58 (1H, m, H-5β), 2.71 (1H, m, H-6α), 2.92 ~ 2.89 (2H, m, H-6β and H-21α), 7.41 (1H, d, J = 8.0 Hz, H-9), 7.03 (1H, t, J = 8.0 Hz, H-10), 7.09 (1H, t, J = 8.0 Hz, H-11), 7.29 (1H, d, J = 8.0 Hz, H-12), 4.17 (1H, s, H-17), 2.23 (1H, d, J = 12.1 Hz, H-18α), 1.90 (1H, m, H-18β), 2.02 (1H, m, H-20), 2.96 (1H, m, H-21α), 2.08 (1H, d, J = 12.1 Hz, H-21β), 3.75 (3H, s, $COOCH_3$). The ^{13}C NMR data see Table 1. Compound **10** was determined to be yohimbine[3,6].

Compound 11 White amorphous powder, ESI-MS *m/z*:322[M]$^+$; ^{1}H NMR ($CDCl_3$, 500 MHz) δ:3.22 (1H, s, H-2), 3.57 (1H, d, J = 9.8 Hz, H-3), 3.14 (1H, t, J = 5.5 Hz, H-5), 1.84 (1H, br t, J = 12.5 Hz, H-6α), 2.25 (1H, br d, J = 12.5 Hz, H-6β), 6.58 (2H, d, J = 7.3 Hz, H-9 and H-10), 6.53 (1H, d, J = 7.3 Hz, H-11), 2.49 (2H, m, H-14α and H-16), 1.33 (1H, dd, J = 14.0, 4.0 Hz, H-14β), 3.08 (1H, t, J = 4.9 Hz, H-15), 1.55 (3H, d, J = 6.6 Hz, H-18), 5.22 (1H, d, J = 6.6 Hz, H-19), 3.38 (2H, br s, H-21), 2.94 (3H, s, N-CH_3). The ^{13}C

NMR data see Table 2. Compound **11** was determined to be mitoridine[8].

Compound 12 White amorphous powder, ESI-MS *m/z*:308 $[M]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.07 (1H, s, H-2), 3.64 (1H, d, J = 9.6 Hz, H-3), 2.90 (1H, t, J = 5.0 Hz, H-5), 2.05 (1H, d, J = 12.0 Hz, H-6α), 1.23 (1H, d, J = 12.0 Hz, H-6β), 7.07 (1H, d, J = 7.2 Hz, H-9), 6.77 (1H, t, J = 7.2Hz, H-10), 7.13 (1H, t, J = 7.2 Hz, H-11), 6.63 (1H, d, J = 7.2 Hz, H-12), 1.78 (1H, t, J = 14.0 Hz, H-14α), 2.08 (1H, d, J = 14.0 Hz, H-14β), 2.98 (1H, t, J = 4.5 Hz, H-15), 2.44 (1H, m, H-16), 4.70 (1H, d, J = 9.2 Hz, H-17), 1.68 (3H, d, J = 6.7 Hz, H-18), 5.19 (1H, d, J = 6.7 Hz, H-19), 3.34 (1H, dd, J = 15.0, 4.5 Hz, H-21α), 3.44 (1H, d, J = 15.0 Hz, H-21β), 2.79 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **12** was determined to be tetraphyllicine[4,9].

Compound 13 White amorphous powder, ESI-MS *m/z*:182 $[M]^+$; ^{1}H NMR (Me_2CO-d_6, 500 MHz) δ: 8.26 (1H, d, J = 5.3 Hz, H-3), 7.89 (1H, d, J = 5.3 Hz, H-4), 8.18 (1H, d, J = 7.8 Hz, H-5), 7.24 (1H, t, J = 7.6 Hz, H-6), 7.51 (1H, t, J = 7.5 Hz, H-7), 7.59 (1H, d, J = 8.2 Hz, H-8), 10.77 (1H, br s, H-9), 2.79 (3H, s, H-1′); ^{13}C NMR (Me_2CO-d_6, 100 MHz) δ: 143.1 (s, C-1), 138.6 (d, C-3), 113.2 (d, C-4), 122.5 (s, C-4a), 128.3 (s, C-4b), 122.3 (d, C-5), 128.5 (d, C-6), 120.1 (d, C-7), 112.7 (d, C-8), 141.6 (s, C-8a), 135.7 (s, C-9a), 20.7 (q, C-1′). Compound **13** was identified as harman by comparison of the NMR data[10].

Compound 14 White amorphous powder, ESI-MS *m/z*:308 $[M]^+$; ^{1}H NMR ($CDCl_3$: CD_3OD = 1:1, 400 MHz) δ: 2.51 (1H, s, H-2), 3.32 (1H, d, J = 9.8 Hz, H-3), 2.89 (1H, t, J = 5.6 Hz, H-5), 2.07 (1H, t, J = 5.6 Hz, H-6α), 1.69 (1H, m, H-6β), 7.36 (1H, d, J = 7.2 Hz, H-9), 6.63 (1H, t, J = 7.2 Hz, H-10), 7.00 (1H, t, J = 7.2 Hz, H-11), 6.50 (1H, d, J = 7.2 Hz, H-12), 1.81 (1H, d, J = 5.0 Hz, H-14α), 1.51 (1H, m, H-14β), 2.99 (1H, t, J = 5.0 Hz, H-15), 1.88 (1H, s, H-16), 4.24 (1H, s, H-17), 1.52 (3H, d, J = 6.1 Hz, H-18), 5.13 (1H, d, J = 6.1 Hz, H-19), 3.01 ~ 3.33 (2H, m, H-21), 2.62 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **14** was determined to be mauiensine[4,9].

Compound 15 White amorphous powder, ESI-MS *m/z*:324 $[M]^+$; ^{1}H NMR (CD3OD, 400 MHz) δ: 2.57 (1H, s, H-2), 3.68 (1H, d, J = 9.6 Hz, H-3),

Table 1 The ^{13}C NMR data of 2, 4, 7 and 9 (100 MHz), 1, 10 (125 MHz) in $CDCl_3$

Compound carbon	1	2	4	7	9	10
2	130.3	134.5	130.3	130.8	134.4	133.6
3	53.7	59.8	53.8	53.9	60.3	60.0
5	51.2	53.5	51.1	50.9	53.2	52.6
6	16.7	21.7	16.6	16.5	21.5	21.0
7	108.0	108.0	107.7	107.5	107.6	107.3
8	122.2	127.1	122.0	127.4	127.0	127.0
9	118.5	118.0	118.4	118.1	117.8	118.0
10	109.0	119.3	108.9	119.7	119.0	119.2
11	156.2	121.3	156.1	121.8	121.0	121.3
12	95.2	110.8	95.2	111.2	110.7	110.9
13	136.4	136.0	136.4	136.1	136.0	136.1
14	24.3	34.2	24.2	23.6	27.2	33.4
15	32.2	31.3	32.6	32.1	37.8	36.2
16	51.7	109.5	51.3	54.2	54.6	51.9
17	78.0	155.8	81.3	65.8	65.9	66.8
18	77.8	18.5	75.1	33.4	33.2	31.3
19	29.7	72.5	32.3	24.0	24.4	23.0
20	34.0	38.4	34.4	35.5	36.3	39.7
21	49.0	56.2	49.2	49.5	60.4	60.7
C=O	172.8	168.0	173.4	174.6	174.9	175.3
OCH_3	51.7	51.1	55.8	52.2	51.8	51.8

Compound 1 R = -COAr(OCH_3)$_3$: 165.4 (s, C=O), 125.3 (s, C-1′), 106.8 (d, C-2′, C-6′), 152.9 (s, C-3′, C-5′), 142.3 (s, C-4′), 60.9 (OMe), 60.7 (OMe).

Table 2 The ^{13}C NMR data of 3, 5, 6, 12, 14 and 15 (100 MHz), 11 (125 MHz) *

Compound carbon	3	5	6	11	12	14	15
2	76.2	79.2	75.8	79.0	76.6	79.0	78.6
3	48.1	43.1	44.9	49.8	756.0	51.8	51.5
5	48.6	52.8	53.3	53.4	50.1	55.8	53.5
6	35.0	34.6	34.5	35.1	35.9	34.7	36.4
7	54.6	56.1	54.2	58.8	53.7	55.0	56.7
8	131.6	133.1	131.2	130.9	131.8	133.0	135.7
9	119.6	122.6	120.2	121.6	119.7	122.8V	116.4
10	118.9	119.1	119.6	117.0	118.9	119.0	121.7
11	127.5	127.2	127.9	114.4	127.5	127.0	113.1
12	109.7	109.5	109.9	144.6	109.6	109.1	145.6
13	154.0	153.7	153.6	140.6	154.2	153.6	141.6
14	25.8	31.3	31.0	31.4	30.2	29.2	30.2
15	28.3	28.1	27.2	28.5	27.5	27.8	28.6
16	43.3	45.2	35.0	50.3	42.3	49.2	50.4
17	72.6	77.8	71.3	213.9	72.7	76.2	77.6
18	12.3	12.2	11.9	12.9	12.8	12.3	12.9
19	22.2	25.6	23.7	117.0	113.8	114.7	115.5
20	45.5	48.0	48.4	136.0	140.0	138.3	139.9
21	88.2	88.0	87.8	55.3	55.4	54.5	55.8
N-CH_3	34.6	34.1	34.7	36.8	34.8	33.9	37.7

* 3, 5, 11, 12 were measured in $CDCl_3$, 6, 14 were measured in $CDCl_3$: CD_3OD = 1:1, 15 was measured in CD_3OD

2.90 (1H, m, H-5), 2.17 (1H, m, H-6α), 1.88 ~ 1.92 (2H, m, H-6β and H-14α), 6.64 (1H, d, J = 6.4 Hz, H-9), 6.56 (1H, dd, J = 8.0, 6.4 Hz, H-10), 6.60 (1H, d, J = 8.0 Hz, H-11), 1.26 (1H, d, J = 12.0 Hz, H-14β), 3.15 (1H, m, H-15), 1.88 (1H, s, H-16), 4.36 (1H, s, H-17), 1.66 (3H, d, J = 6.4 Hz, H-18), 5.28 (1H, br d, J = 6.4 Hz, H-19), 3.41 ~ 3.58 (2H, m, H-21α and H-21β), 3.01 (3H, s, N-CH_3). The ^{13}C NMR data see Table 2. Compound **15** was determined to be 12-hydroxymauiensine [4,9].

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