PERGAMON

Phytochemistry 52 (1999) 523–527

PHYTOCHEMISTRY

Alkaloidal and other constituents from the root bark of *Clausena excavata*

Tian-Shung Wu[a,*], Shiow-Chyn Huang[b], Pei-Lin Wu[a], Chang-Sheng Kuoh[c]

[a]*Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, ROC*
[b]*Department of Pharmacy, Chia Nan College of Pharmacy and Science, Tainan Hsien, Taiwan, ROC*
[c]*Department of Biology, National Cheng Kung University, Tainan, Taiwan, ROC*

Received 11 August 1998; received in revised form 29 January 1999

Abstract

Ten new carbazole alkaloids, clausine-M, -N, -O, -P, -Q, -R, -S, -U, -V and clausenatine-A, together with 39 known compounds were isolated and identified from the acetone extract of the root bark of *Clausena excavata*. Their structures have been elucidated by spectroscopic analyses. This is the first report of a decarboxylated carbazole alkaloid from a natural source. The presence of a C_{23}-skeleton carbazole alkaloid in a plant of *Clausena* genus is also reported for the first time. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Clausena excavata; Rutaceae; Carbazole alkaloid

1. Introduction

Clausena excavata is a wild shrub which has been claimed to be a useful folk medicine in the treatment of snake-bites and as a detoxification agent (Sasaki, 1924). In a continuing collaborative search for naturally occurring antiplatelet agents, we have isolated bioactive constituents from the stem bark (Wu, Huang & Wu, 1996a) and leaves (Wu et al., 1993) of *C. excavata*. In this study the acetone extract of the root bark of *C. excavata* was concentrated and subjected to purification by column chromatography to afford ten new carbazole alkaloids, clausine-M (**1**), -N (**2**), -O (**3**), -P (**4**), -Q (**5**), -R (**6**), -S (**7**), -U (**8**), -V (**9**) and clausenatine-A (**10**) together with 27 known carbazole alkaloids, 2-hydroxy-3-formyl-7-methoxycarbazole (**11**) (Chaichantipyuth, Pummangura, Naowsaran & Thauyavuth, 1988), glycozolidal (**12**) (Wu et al., 1996a), heptaphylline (**13**) (Wu et al., 1996a), murrayafoline-A (**14**) (Furukawa, Wu, Ohta & Kuoh, 1985), 3-methylcarbazole (**15**) (Wu et al., 1996a), girinimbine (**16**) (Furukawa et al., 1985), mukonal (**17**) (Wu et al., 1996a), mukonidine (**18**) (Wu et al., 1996a), mukonine (**19**) (Wu et al., 1996a), methyl carbazole-3-carboxylate (**20**) (Wu et al., 1996a), murrayanine (**21**) (Wu et al., 1996a), 3-formylcarbazole (**22**) (Li, McChesney & El-Feraly, 1991), clausine-C (**23**) (Wu, Huang & Wu, 1996b), -E (**24**) (Wu et al., 1996a), -F (**25**) (Wu & Huang, 1992), -K (**26**) (Wu et al., 1996a), -T (**27**) (Wu, Huang & Wu, 1997), -W (**28**) (Wu et al., 1997), furoclausine-A (**29**) (Wu et al., 1997), -B (**30**) (Wu et al., 1997), clausevatine-D (**31**) (Wu, Huang & Wu, 1998), -E (**32**) (Wu et al., 1998), -F (**33**) (Wu et al., 1998), -G (**34**) (Wu et al., 1998), clausamine-A (**35**) (Wu et al., 1998), carbazomarine-A (**36**) (Wu, Huang & Wu, 1996c) and 2,7-dihydroxy-3-formyl-1-(3′-methyl-2′-butenyl)carbazole (**37**) (Kumar, Valliparum, Adehajo & Reisch, 1995); 10 known coumarins, claucavatin-A (**38**) (Huang, Wu & Wu, 1997), -B (**39**) (Huang et al., 1997), kinocoumarin (**40**) (Huang et al., 1997), clausenidin (**41**) (Huang et al., 1997), clausarin (**42**) (Huang et al., 1997), nordentatin (**43**) (Huang et al., 1997), xanthoxyletin (**44**) (Huang et al., 1997), xanthyletin (**45**) (Huang et al., 1997), osthol (**46**) (Huang et al., 1997) and cedrelopsin (**47**) (Huang et al., 1997); and

---

* Corresponding author.

0031-9422/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0031-9422(99)00220-4

Table 1
^{1}H NMR spectral data for compounds **1**-**6** and **9** (acetone-d_6, δ, multiplicity, J, Hz)

	1	**2**	**3**	**4**	**5**	**6**	**9**
H-1 or R_1	7.46 d, 8.4	7.50 d, 8.5	6.82 s	7.06 s	4.06 s (OMe)	8.89 br s (OH)	6.98 d, 2.3
H-2 or R_2	7.96 dd, 8.4,1.4	8.03 dd, 8.5,1.7	11.42 s (OH)	3.89 s (OMe)	7.38 d, 1.2	7.48 d, 1.4	3.84 s (OMe)
H-3 or R_3	3.89 s (CO_2Me)	–	9.95 s (CHO)	2.29 s (Me)	10.01 s (CHO)	3.86 s (CO_2Me)	6.76 dd, 8.4,2.3
H-4	8.64 d, 1.4	8.73 br s	8.26 s	7.76 s	8.19 d, 1.2	8.22 d, 1.4	7.84 d, 8.4
H-5	8.01 d, 8.5	8.09 d, 8.6	7.86 d, 8.0	7.54 d, 7.8	7.99 d, 8.5	7.95 d, 8.5	7.84 d, 8.4
H-6	6.81 dd, 8.5,2.2	6.88 dd, 8.6,2.0	6.77 dd, 8.0,2.4	7.03 t, 7.8	6.84 dd, 8.5,2.2	6.79 dd, 8.5,2.2	6.76 dd, 8.4,2.3
H-7 or R_4	8.51 s (OH)	3.88 s (OMe)	8.46 s (OH)	6.85 d, 7.8	8.58 s (OH)	8.41 s (OH)	3.84 s (OMe)
H-8 or R_5	6.97 d, 2.2	7.09 d, 2.0	6.93 d, 2.4	3.96 s (OMe)	7.07 d, 2.2	7.03 d, 2.2	6.98 d, 2.3
NH	10.48 br s	10.60 br s	10.46 br s	10.05 br s	10.67 br s	10.35 br s	10.13

two known flavonoids, isoliquiritigenin (**48**) (Huang et al., 1997) and 4′,7-dihydroxyflavanone (**49**) (Huang et al., 1997). Here we report the structural elucidation of ten new carbazole alkaloids by spectroscopic analyses.

2. Results and discussion

UV absorptions and a broad ^{1}H NMR signal around δ 10.5 indicated the 10 new compounds should be carbazole alkaloids (Chakraborty, 1977). For all except **4** and **9**, a carbonyl substituent was observed on C-3 due to the presence of a conjugated C=O bond in its IR spectra. It has been reported that the 3-carbonyl carbazole alkaloids were obtained from 3-methylcarbazole via oxidation (Chakraborty, 1977).

Clausine-M (**1**) was determined to have the molecular formula $C_{14}H_{11}NO_3$ by high resolution mass spectrometry. The ^{1}H NMR spectrum showed two sets of ABX aromatic protons, one at δ 6.81 (dd, J = 8.5, 2.2 Hz), 6.97 (d, J = 2.2 Hz), 8.01 (d, J = 8.5 Hz) and the other at δ 7.46 (d, J = 8.4 Hz), 7.96 (dd, J = 8.4, 1.4 Hz), 8.64 (d, J = 1.4 Hz) (Table 1). They were assigned for H-6, H-8, H-5 and H-1, H-2, H-4, respectively, owing to the downfield signals at δ 8.01 and 8.64 which were characteristic peaks for H-5 and H-4 in a 3-carbonylcarbazole system (Wu et al., 1996a). A D_2O-exchangeable hydroxyl peak at δ 8.51 exhibited a NOE with proton H-6. This supported that a phenolic hydroxyl substituent was located at C-7. A remaining methoxyl at δ 3.89 apparently was due to a carboxymethyl group on C-3. In the mass spectrum, the fragment ion at m/z 210 for [M^+-OMe] and 182 for [M^+-CO_2Me] also supported the presence of the carboxymethyl substituent. Therefore, the structure of clausine-M was deduced as **1**.

Clausine-N (**2**) was obtained as an isomer of **1** and possessed a very similar ^{1}H NMR spectrum (Table 1). However, instead of two substituents carboxymethyl and hydroxyl as in **1**, a carboxyl on C-3 and a methoxyl on C-7 was proposed for **2**. The existence of a methoxyl substituent was proven by the fragment ion of [M^+-Me] at m/z 226 and [M^+-Me–CO] at m/z 198 in mass spectrum. Based on the above analysis, the structure of **2** was established for clausine-N.

Clausine-O (**3**) was determined to have the molecular formula $C_{13}H_9NO_3$. Two singlets at δ 9.95 (CHO) and 8.26 (H-4) in the ^{1}H NMR spectrum indicated that **3** is a 3-formylcarbazole derivative (Table 1). In the aromatic region, one set of ABX signals at δ 6.77 (dd, J = 8.0, 2.4 Hz), 6.93 (d, J = 2.4 Hz) and 7.86 (d, J = 8.0 Hz) were assigned for H-6, H-8 and H-5, respectively, leaving the remaining singlet at δ 6.82 for H-1. Due to the intramolecular hydrogen bonding with 3-CHO, an unusual downfield hydroxyl at δ 11.42 inferred that a phenolic hydroxyl was located at C-2. Thus, a signal at δ 8.46 for a hydroxyl should be present on C-7. A 2,7-dihydroxy-3-formylcarbazole alkaloid (**3**) was assigned for clausine-O, which was similar to 2-hydroxy-3-formyl-7-methoxycarbazole (**11**).

Clausine-P (**4**) was determined to have the molecular formula $C_{15}H_{15}NO_2$. From the ^{1}H NMR spectrum, a methyl singlet at δ 2.29 attached at C-3 was observed (Table 1). Three mutually coupled protons at δ 6.85 (d, J = 7.8 Hz), 7.03 (t, J = 7.8 Hz) and 7.54 (d, J = 7.8 Hz) for H-7, H-6 and H-5, respectively, and two singlets at δ 7.06 and 7.76 for H-1 and H-4 were also observed. The absence of carbonyl substituent on C-3 caused the chemical shifts of H-4 and H-5 at normal position (δ 7.06 to 7.90) (Chakraborty and Roy, 1991). The remaining two methoxyl signals at δ 3.89 and 3.96 would attach on C-2 and C-8. The full assignments of ^{1}H NMR signals were further supported by NOESY spectra which showed NOEs between 3-Me (δ 2.29) and H-4 (δ 7.76); 2-OMe (δ 3.89) and H-1 (δ 7.06); 8-OMe (δ 3.96) and H-7 (δ 6.85). Therefore, clausine-P was assigned the structure as **4**.

Clausine-Q (**5**) was another isomer of **1** and **2**. By inspection of the ^{1}H NMR spectrum (Table 1), an aldehyde peak at δ 10.01 for 3-CHO, one ABX set at δ 6.84 (dd, J = 8.5, 2.2 Hz), 7.07 (d, J = 2.2 Hz) and 7.99 (d, J = 8.5 Hz) for H-6, H-8 and H-5, respectively and two meta-coupled protons at δ 7.38 and 8.19

Table 2
^{1}H NMR spectral data for compounds **7**, **8** and **10** (acetone-d_6, δ, multiplicity, *J*, Hz)

	7	8	10
H-1 or R_1	1.86 s (3-Me) 3.05 dd, 14.0,8.6 and 3.28 dd, 14.0,4.0 (H-1′) 4.30 br. s (2′-OH) 4.49 m (H-2′) 4.74 & 4.92 s (H-4′)	1.29,1.30 s (3′-Me) 2.85 dd, 14.0,10.0 and 3.34 dd, 14.0,2.0 (H-1′) 3.69 s (OH) 3.75 m (H-2′) 4.12 d, 5.0 (OH)	1.50,1.53,1.83 s (Me) 3.65 d, 6.9 (2H, H-1′) 3.75 m (4H, H-4′ and H-5′) 5.03 m (1H, H-6′) 5.38 m (1H, H-2′)
2-OH	11.81 s	11.77 s	11.77 s
3-CHO	9.98 s	9.94 s	9.98 s
H-4	8.35 s	8.15 s	8.35 s
H-5	8.07 d, 8.0	7.85 d, 8.3	8.08 d, 8.0
H-6	7.37 t, 8.0	6.76 dd, 8.3,2.0	7.22 t, 8.0
H-7 or 7-OH	7.21 t, 8.0	8.51 s (OH)	7.37 t, 8.0
H-8	7.53 d, 8.0	6.96 d, 2.0	7.49 d, 8.0
NH	10.64 br. s	10.45 br. s	10.57 br. s

(*J* = 1.2 Hz) for H-2 and H-4 suggested a 1,7-disubstituted-3-formylcarbazole alkaloid for **5**. The two substituents, OH (δ 8.58) on C-7 and OMe (δ 4.06) on C-1 were confirmed by the presence of NOE of OMe with H-2. Consequently, clausine-Q was assigned the structure **5**.

Clausine-R (**6**) was determined to have the molecular formula $C_{14}H_{11}NO_4$. The carbazole skeleton of **6** is the same as that of **5** from the ^{1}H NMR spectra (Table 1). The absence of NOE, between a methoxyl (δ 3.86) and any other protons indicated a carboxymethyl substituent located on C-3. The presence of NOE between a hydroxyl (δ 8.89) and H-2 (δ 7.48), and a second hydroxyl (δ 8.41) with H-6 (δ 6.79) and H-8 (δ 7.03) showed two hydroxyl groups at C-1 and C-7. Hence, the 1,7-dihydroxy-3-carbomethoxycarbazole alkaloid (**6**) was inferred for clausine-R.

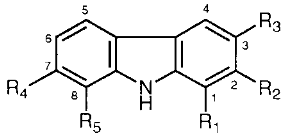
Clausine-S (**7**) was determined to have molecular formula $C_{18}H_{17}NO_3$. A formyl group (δ 9.98) on C-3, a downfield hydroxyl (δ 11.81) on C-2 and a singlet at δ 8.35 for H-4 appeared in the ^{1}H NMR spectrum as for **3** (Table 2). An unsubstituted ring A was proposed due to the four mutually coupled protons at δ 7.21 (t, *J* = 8.0 Hz), 7.37 (t, *J* = 8.0 Hz), 7.53 (d, *J* = 8.0 Hz) and 8.07 (d, *J* = 8.0 Hz). The presence of one set of -CH_2CH- ABX signals at δ 3.05 (dd, *J* = 14.0, 8.6 Hz), 3.28 (dd, *J* = 14.0, 4.0 Hz) and 4.49 (m), a terminal = CH_2 singlet at δ 4.74 (s) and 4.92 (s), an olefinic methyl at δ 1.86 (s), and a D_2O exchangeable aliphatic hydroxyl at δ 4.30 (d, *J* = 4.0 Hz) suggested a side chain, -$CH_2CH(OH)C(CH_3)=CH_2$, on C-1. This substituent was further supported by the base peak at *m*/*z* 224 [M^+-$CH(OH)C(CH_3)=CH_2$], a cleavage at the benzylic position, in the mass spectrum. On the basis of the above results, the structure of clausine-S was deduced as **7**.

Clausine-U (**8**) was determined to have the molecular formula $C_{18}H_{19}NO_5$. On comparison of the ^{1}H NMR spectrum of **8** (Table 2) with those of **3** and **7**, a 1-alkyl-2,7-dihydroxy-3-formylcarbazole alkaloid was inferred for compound **8**. The side chain on C-1 was found to be -$CH_2CH(OH)C(CH_3)_2OH$ based on the existence of two methyl singlets at δ 1.29 and 1.30 and a hydroxyl singlet at δ 3.69. The structure of clausine-U was established as **8** and the full assignment of the ^{1}H-NMR and ^{13}C-NMR signals was confirmed by HMQC, HMBC and NOESY spectra.

Clausine-V (**9**) was determined to have molecular formula $C_{14}H_{13}NO_2$. It is a symmetical carbazole alkaloid with an ABX system at δ 6.76 (dd, *J* = 8.4, 2.3 Hz), 6.98 (d, *J* = 2.3 Hz) and 7.84 (d, *J* = 8.4 Hz) together with a methoxyl signal at δ 3.84 (Table 1). Therefore, 2,7-dimethoxycarbazole alkaloid (**9**) was assigned for clausine-V.

Clausenatine-A (**10**) was determined to have the molecular formula $C_{23}H_{25}NO_2$. By comparison of the ^{1}H NMR spectrum with that of **7**, the difference between them was shown to be the substituent on C-1 (Table 2). Instead of five-carbon unit, a 10-carbon side chain, consisting of head-to-tail linkage of two prenyl groups, three methyls at δ 1.50, 1.53 and 1.83, three methylenes at δ 3.65 (2H, d, *J* = 6.9 Hz) and 3.75 (4 H, m), and two vinyl protons at δ 5.03 (m) and 5.38 (m), was attached on C-1. Thus, the structure of clausenatine-A was deduced as **10**.

This represents the first isolation of a decarboxylated carbazole alkaloid (**9**) from a natural source. The presence of a C_{23} skeleton carbazole alkaloid (**10**) in a plant of the *Clausena* genus is also reported here for the first time. Chakraborty reported that the genus *Glycosmis* has been found to elaborate simple carbazoles with a C_{13}-skeleton, *Clausena* C_{13}- and C_{18}-skeletons, and *Murraya* C_{13}-, C_{18}- and C_{23}-skeletons (Chakraborty, 1977). Our results show that the use of C_{13}, C_{18} and C_{23} unit carbazole alkaloids for the chemotaxonomy of genera of *Glycosmis*, *Murraya* and *Clausena* must be reconsidered.



	R_1	R_2	R_3	R_4	R_5
1:	H	H	CO_2Me	OH	H
2:	H	H	CO_2H	OMe	H
3:	H	OH	CHO	OH	H
4:	H	OMe	Me	H	OMe
5:	OMe	H	CHO	OH	H
6:	OH	H	CO_2Me	OH	H
7:	$CH_2CH(OH)C(CH_3){=}CH_2$	OH	CHO	H	H
8:	$CH_2CH(OH)C(CH_3)_2OH$	OH	CHO	OH	H
9:	H	OMe	H	OMe	H
10:	$CH_2CH{=}C(CH_3)(CH_2)_2CH{=}C(CH_3)_2$	OH	CHO	H	H

3. Experimental

Mps: uncorr. UV: in MeOH. IR: in KBr. ^1H (400 MHz) and ^{13}C NMR (100 MHz): in acetone-d_6 and TMS as internal reference. MS: a direct inlet system.

3.1. Plant material

C. excavata was collected from San Dei Men, Pingtung Hsien, Taiwan, in June 1989 and verified by Professor C.S. Kuoh. A specimen of this plant is deposited in the herbarium of National Cheng Kung University, Tainan, Taiwan.

3.2. Extraction and isolation

The acetone extract of the root bark of *C. excavata* (0.8 kg) was subjected to chromatography on a silica gel column eluted with $CHCl_3$–MeOH (25:1) to give nine fractions. Fr. 2 was chromatographed on silica gel using C_6H_6-Me_2CO (19:1) as eluent to afford **41** (7.4 g), **44** (8.1 g), **11** (4.4 g), **43** (4.5 g), **12** (46.3 mg), **37** (4.0 mg), **42** (5.2 g), **9** (6.5 mg), **13** (0.22 g), **14** (26.2 mg), **15** (2.8 mg), **10** (0.5 mg), **16** (18.4 mg), **38** (19.0 mg), **4** (2.3 mg), **17** (30.0 mg), **45** (23.7 mg), **18** (0.3 mg), **46** (15.7 mg), **19** (1.6 mg), **20** (1.0 mg), **21** (2.1 mg), **39** (14.8 mg), **40** (14.8 mg), **22** (15.2 mg), **7** (0.5 mg), **23** (3.4 mg), **47** (1.1 mg) and **36** (4.0 mg), successively. Fr. 3 yielded **24** (1.6 g) and **25** (0.14 g) after chromatography eluting with $CHCl_3$–Me_2CO (30:1) and fr. 4 gave **48** (4.2 mg), **49** (25.8 mg), **1** (2.1 mg), **3** (0.5 mg), **5** (0.7 mg) and **31** (1.0 mg) after chromatography eluting with C_6H_6–Me_2CO (4:1). Fr. 5 afforded crystalline **26** (3.1 g) and **35** (1.5 mg), **32** (10.4 mg). Fr. 6 yielded **6** (1.5 mg), **8** (0.8 mg), **29** (5.8 mg), **33** (1.0 mg), **34** (0.5 mg), **27** (0.5 mg) and **30** (0.3 mg) after chromatography eluting with *i*-Pr_2O–MeOH (9:1). Finally, **2** (1.0 mg) and **28** (10.8 mg) was obtained from fr. 7 by chromatography using $CHCl_3$–MeOH (19:1) as eluent.

3.3. Clausine-M (*1*)

Yellowish needles, mp 200—203° (acetone). HR-MS: calcd for $C_{14}H_{11}NO_3$, *m/z* 241.0739 $[M]^+$, found 241.0738. UV λ_{max} nm: 219, 239 (sh), 249, 283, 309 (sh), 318 (sh). IR ν_{max} cm^{-1}: 3375, 3330, 1690, 1610. EIMS *m/z* (rel. int.): 241 (M^+, 100), 210 (65), 182 (37), 153 (11). ^{13}C NMR (acetone-d_6) δ 51.9 (3-CO_2Me), 97.8 (C-8), 110.3 (C-6), 110.9 (C-1), 116.9 (C-5a), 121.7 (C-4a), 121.9 (C-4), 122.0 (C-5), 124.3 (C-3), 126.4 (C-2), 143.3 (C-1a), 143.8 (C-8a), 158.2 (C-7), 168.1 (C=O).

3.4. Clausine-N (*2*)

Yellowish powder, mp 215—218° (acetone). UV λ_{max} nm: 216, 237 (sh), 249, 277, 307, 317. IR ν_{max} cm^{-1}: 3400, 1670, 1610. EIMS *m/z* (rel. int): 241 (M^+, 100), 226 (30), 198 (40), 153 (13).

3.5. Clausine-O (*3*)

Yellowish needles, mp > 280° (acetone). UV λ_{max} nm: 200, 223, 240, 252 (sh), 291 (sh), 301, 321 (sh), 340. IR ν_{max} cm^{-1}: 3375, 3330, 1620. EIMS *m/z* (rel. int.): 227 (M^+, 100), 226 (50), 198 (10), 170 (26).

3.6. Clausine-P (*4*)

Yellow oil. HR-MS: calcd for $C_{15}H_{15}NO_2$, *m/z* 241.1103 $[M]^+$, found 241.1104. UV λ_{max} nm: 212, 236 (sh), 239, 251 (sh), 261 (sh), 290 (sh), 298, 317, 330. IR ν_{max} cm^{-1}: 3400, 1635. EIMS *m/z* (rel. int.): 241 (M^+, 100), 226 (44), 211 (15), 198 (30), 183 (18).

3.7. Clausine-Q (*5*)

Brown powder, mp 85–87° (acetone). UV λ_{max} nm: 201, 242, 252 (sh), 286, 297 (sh), 325 (sh), 338. IR ν_{max} cm^{-1}: 3375, 3330, 1660, 1610. EIMS *m/z* (rel. int.): 241 (M^+, 100), 227 (20), 226 (31), 170 (11).

3.8. Clausine-R (*6*)

Yellowish needles, mp 178–181° (acetone). HR-MS: calcd for $C_{14}H_{11}NO_4$, *m/z* 257.0688 $[M]^+$, found 257.0689. UV λ_{max} nm: 214, 241, 252, 282, 320 (sh), 333. IR ν_{max} cm^{-1}: 3350, 1695, 1620. EIMS *m/z* (rel. int.): 257 (M^+, 100), 226 (50), 198 (24), 170 (19).

3.9. Clausine-S (7)

Yellowish oil. $[\alpha]_D = +159.09°$ (*c* 0.0022, MeOH). HR-MS: calcd for $C_{18}H_{17}NO_3$, *m*/*z* 295.1208 $[M]^+$, found 295.1207. UV λ_{max} nm: 203, 236, 249, 279, 291 (sh), 299, 329 (sh), 343. IR ν_{max} cm^{-1}: 3350, 1630, 1615. EIMS *m*/*z* (rel. int.): 295 (M^+, 19), 277 (5), 262 (8), 225 (50), 224 (100), 167 (19), 149 (26).

3.10. Clausine-U (**8**)

Yellowish powder, mp 255–257° (acetone). $[\alpha]_D = -72.85°$ (*c* 0.0151, MeOH). HR-MS: calcd for $C_{18}H_{19}NO_5$, *m*/*z* 329.1263 $[M]^+$, found 329.1264. UV λ_{max} nm: 201, 221, 240 (sh), 245, 254, 288 (sh), 303, 324 (sh), 339. IR ν_{max} cm^{-1}: 3400, 1620. EIMS *m*/*z* (rel. int.): 329 (M^+, 52), 270 (24), 240 (100), 196 (15), 183 (23), 154 (18). ^{13}C NMR (acetone-d_6) δ 25.3 and 26.1 (2 × 3′-Me), 27.5 (C-1′), 73.2 (C-3′), 79.3 (C-2′), 98.4 (C-8), 109.4 (C-1), 110.2 (C-6), 115.8 (C-3), 117.3 (C-5a), 118.7 (C-4a), 121.2 (C-5), 124.7 (C-4), 145.4 (C-8a), 147.6 (C-1a), 157.6 (C-7), 158.4 (C-2), 196.7 (3-CHO).

3.11. Clausine-V (**9**)

Colorless powder, mp 228–230° (acetone). HR-MS: calcd for $C_{14}H_{13}NO_2$, *m*/*z* 227.0937 $[M]^+$, found 227.0949. UV λ_{max} nm: 208, 236, 261, 311, 319. IR ν_{max} cm^{-1}: 3380, 1615. EIMS *m*/*z* (rel. int.): 227 (M^+, 100), 212 (85), 184 (22), 169 (33).

3.12. Clausenatine-A (**10**)

Yellowish powder, mp >280° (acetone). HR-MS: calcd for $C_{23}H_{25}NO_2$, *m*/*z* 347.1885 $[M]^+$, found 347.1884. UV λ_{max} nm: 202, 228, 237 (sh), 249, 278, 293 (sh), 297, 342. IR ν_{max} cm^{-1}: 3400, 1630, 1620. EIMS *m*/*z* (rel. int.): 347 (M^+, 55), 278 (35), 262 (18), 224 (100), 211 (18), 167 (28).

Acknowledgements

We thank the National Science Council, ROC (NSC 81-0420-B-006-10) for support of this research.

References

Chaichantipyuth, C., Pummangura, S., Naowsaran, K., & Thauyavuth, D. (1988). *Journal of Natural Products*, *51*, 1285.

Chakraborty, D. P. (1977). *Fortschritte der Chemie Organischer Naturstoffe*, *34*, 299.

Chakraborty, D. P., & Roy, S. (1991). *Fortschritte der Chemie Organischer Naturstoffe*, *57*, 71.

Furukawa, H., Wu, T. S., Ohta, T., & Kuoh, C. S. (1985). *Chemical Pharmaceutical Bulletin*, *33*, 4132.

Huang, S. C., Wu, P. L., & Wu, T. S. (1997). *Phytochemistry*, *44*, 179.

Kumar, V., Vallipuram, K., Adehajo, A. C., & Reisch, J. (1995). *Phytochemistry*, *40*, 1563.

Li, W. S., McChesney, J. D., & El-Feraly, F. S. (1991). *Phytochemistry*, *30*, 343.

Sasaki, S. (1924). In *Khoyo Taiwan Minkan Yakyo Shokubutsu Shi* (p. 36). Taipei: Khobunkan.

Wu, T. S., & Huang, S. C. (1992). *Chemical Pharmaceutical Bulletin*, *40*, 1069.

Wu, T. S., Huang, S. C., Lai, J. S., Teng, C. M., Ko, F. N., & Kuoh, C. S. (1993). *Phytochemistry*, *32*, 449.

Wu, T. S., Huang, S. C., & Wu, P. L. (1996a). *Phytochemistry*, *43*, 133.

Wu, T. S., Huang, S. C., & Wu, P. L. (1996b). *Phytochemistry*, *43*, 1427.

Wu, T. S., Huang, S. C., & Wu, P. L. (1996c). *Tetrahedron Letters*, *37*, 7819.

Wu, T. S., Huang, S. C., & Wu, P. L. (1997). *Heterocycles*, *45*, 969.

Wu, T. S., Huang, S. C., Wu, P. L. (1998). *Chemical Pharmaceutical Bulletin*, *46*, 1459.