Constituents of *Clausena excavata*. Isolation and Structural Elucidation of New Carbazole Alkaloids

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Constituents of the roots, the stem bark, and the leaves of *Clausena excavata* BURM. f. (Rutaceae) grown in a greenhouse at Okitsu Branch, Fruit Tree Research Station, Shizuoka, were studied. New carbazole alkaloids named clauszoline-H (1), -I (2), and -J (4) from the roots, clauszoline-K (6) and -L (7) from the stem bark, and clauszoline-M (8) from the leaves were isolated, together with known carbazoles and coumarins, and their structures were elucidated by spectroscopic methods.

Key words *Clausena excavata*; carbazole alkaloid; clauszoline; coumarin; Rutaceae

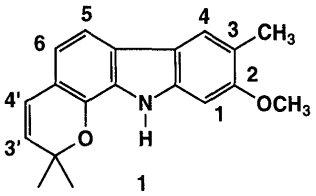
In our previous paper[1] on the chemical constituents in *Clausena excavata* BURM. f. (Rutaceae), the structures of seven new carbazole alkaloids, clauszoline-A, -B, -C, -D, -E, -F, and -G, and a new coumarin, 5-geranyloxy-7-hydroxycoumarin isolated from the stem bark of *C. excavata* collected in Singapore, were described. Further studies of components in the roots, stem bark, and leaves of *C. excavata* cultivated in a greenhouse in Shizuoka, Japan resulted in the isolation of six new carbazole alkaloids, together with several known carbazole alkaloids and coumarins. In the present paper, the isolation and characterization of the six new carbazole alkaloids, clauszoline-H (**1**), -I (**2**), -J (**4**), -K (**6**), -L (**7**), and -M (**8**), are described.

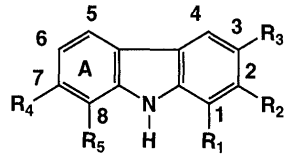
Results and Discussion

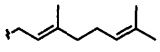
The acetone extracts of the roots, the stem bark, and the leaves of *Clausena excavata* were fractionated by combinations of silica gel column chromatographies and preparative TLC to give six new alkaloids, together with known components (Charts 1, 2, and Experimental).

Structure of Clauszolines The presence of the carbazole chromophore in all the new alkaloids was suggested by the following UV absorption bands, accompanied with some minor bands,[2] together with IR bands due to an NH group (see Experimental). (a) Sharp UV absorption bands at λ_{max} 227—258 nm and at λ_{max} 264—324 nm, and a broad band at λ_{max} 301—394 nm with strong, medium, and weak intensities, respectively, were suggestive of the 3-methylcarbazole structure. (b) In the case of 3-formylcarbazoles, sharp absorption bands at λ_{max} 232—242 nm (strong) and at λ_{max} 272—306 nm (strong), and a broad band at λ_{max} 322—376 nm (weak), were seen. (c) 3-Carboxy- or 3-carbomethoxycarbazoles revealed analogous UV absorptions having two high-intensity bands at λ_{max} 236—248 nm and λ_{max} 269—282 nm, along with some low-intensity shoulder bands at λ_{max} 306—338 nm. The structure and location of the substituent in each alkaloid will be discussed below.

Structure of Clauszoline-H (1) Clauszoline-H was obtained as a colorless powder. The high-resolution mass spectrum (HR-MS) gave the molecular formula as $C_{19}H_{19}NO_2$. The ^{1}H-NMR spectrum showed two singlets (3H × 2) at δ 2.34 and 3.90 due to an aryl methyl and methoxy protons as well as an imino group [δ 8.02 (1H, br s)]. A singlet (6H) at δ 1.50 assignable to geminal dimethyls attached to an oxygenated carbon, and AB-type





	R_1	R_2	R_3	R_4	R_5
2	OH	H	$COOCH_3$	H	H
3	OCH_3	H	COOH	H	H
4	H	OCH_3	COOH	OCH_3	H
5	H	OCH_3	$COOCH_3$	OCH_3	H
6	H	H	CHO	OCH_3	H
7	H	H	$COOCH_3$	OCH_3	H
8	H	OH	CHO	H	OH
9		OH	CHO	H	OH

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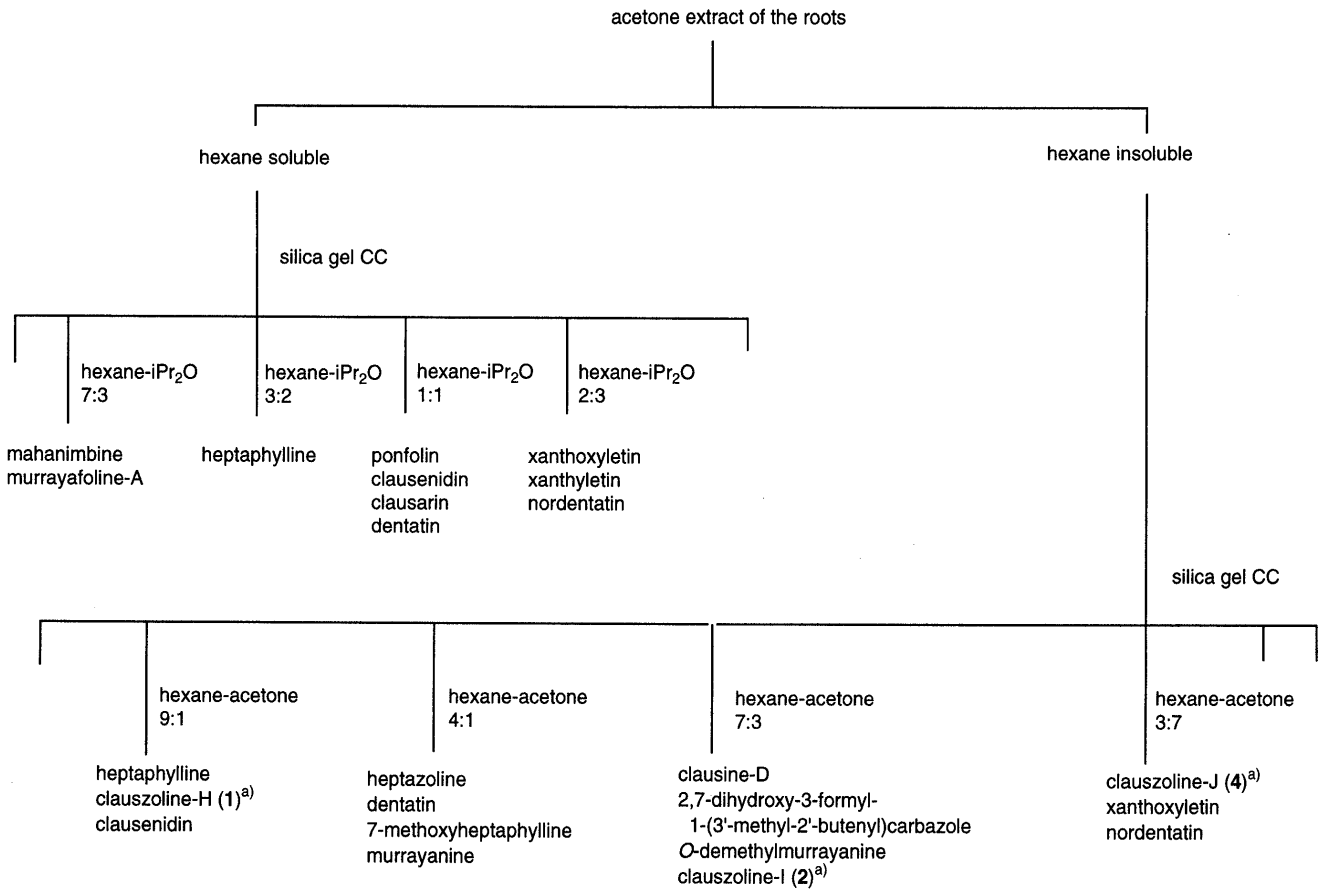

Chart 1. Isolation of Carbazole Alkaloids and Coumarins from the Roots of *Clausena excavata*
a) New carbazole alkaloid.

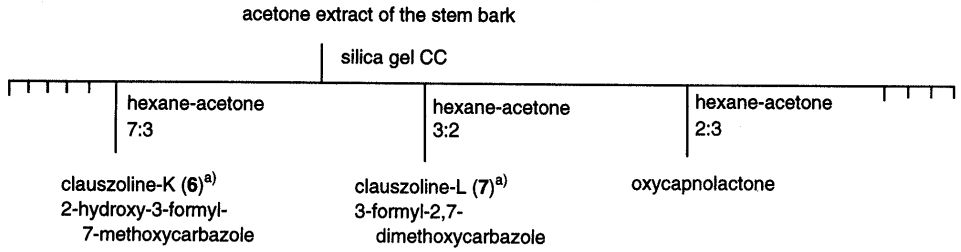

Chart 2. Isolation of Carbazole Alkaloids and Coumarins from the Stem Bark of *Clausena excavata*
a) New carbazole alkaloid.

doublets at δ 6.48 and 5.56 (each 1H, $J=9.8$ Hz) indicated the presence of a dimethylpyran ring system in the molecule. In the aromatic proton region of the ^{1}H-NMR spectrum, four aromatic protons were observed as an *ortho*-located AB-type doublet [δ 7.42, 6.84 (each 1H, $J=8.1$ Hz)], together with two 1H singlets (δ 7.71, 6.85). Among them, the lower field two signals at δ 7.42 (d) and 7.71 (s) are characteristic of H-5 and H-4 of a carbazole nucleus, respectively.[2-4] In the nuclear Overhauser effect (NOE) experiments, irradiation of the H-4 signal (δ 7.71) gave 5% and 8% enhancements of the H-5 signal (δ 7.42) and the aryl methyl signal (δ 2.34), respectively. This observation indicated the location of the aryl methyl group at C-3. Further, the observation of NOE enhancements between the methoxy (δ 3.90) and H-1 (δ 6.85) signals, and between the signals of H-4′ (δ 6.48) on a dimethylpyran ring and H-6 (δ 6.84) indicated the presence of the methoxy group at C-2 and the dimethylpyran ring fused with the 8-oxygenated carbazole nucleus at C-7 and C-8, respectively. These spectral data led us to propose the structure **1** for clauszoline-H. Clauszoline-H (**1**) is the first example of a naturally occurring 3-methyl-2,8-dioxygenated carbazole alkaloid having a dimethylpyran ring fused with the carbazole nucleus at C-7 and C-8.

Structure of Clauszoline-I (2) This compound was isolated as a pale yellow oil, $C_{14}H_{11}NO_3$. The UV spectrum (see Experimental) was similar to that of mukoeic acid (**3**)[5] isolated previously from *Murraya euchrestifolia* HAYATA.[6] The ^{1}H-NMR (acetone-d_6) spectrum revealed a D_2O-exchangeable signal at δ 10.70, a set of four-spin protons at δ 8.17 (1H, d, $J=7.7$ Hz, H-5), 7.22 (1H, t, $J=7.7$ Hz, H-6), 7.43 (1H, t, $J=7.7$ Hz, H-7), and 7.61 (1H, d, $J=7.7$ Hz, H-8), and two doublets at δ 8.38 (1H, $J=1.1$ Hz, H-4) and 7.59 (1H, $J=1.1$ Hz, H-2). These

Table 1. ^{1}H-NMR Data in $CDCl_3$ for New Carbazole Alkaloids

	1	2[a]	4[b]	6	7	8[a]
H-1	6.85	—	7.01	7.47 (d, 8.4)	7.39 (d, 8.6)	6.94
H-2	—	7.59 (d, 1.1)	—	7.91 (dd, 1.5, 8.4)	8.06 (dd, 1.8, 8.6)	—
2	3.90 (3H, OCH_3)	—	3.88 (3H, OCH_3)	—	—	11.44 (OH)
3	2.34 (3H, CH_3)	3.88 (3H, $COOCH_3$)	—	10.08 (CHO)	3.97 (3H, $COOCH_3$)	9.99 (CHO)
H-4	7.71	8.38 (d, 1.1)	8.38	8.51 (d, 1.5)	8.70 (d, 1.8)	8.40
H-5	7.42 (d, 8.1)	8.17 (d, 7.7)	7.93 (d, 8.4)	8.00 (d, 8.4)	7.99 (d, 8.4)	7.58 (d, 7.7)
H-6	6.84 (d, 8.1)	7.22 (t, 7.7)	6.76 (dd, 8.4, 2.2)	6.94 (dd, 8.4, 2.2)	6.91 (dd, 8.4, 2.2)	7.05 (t, 7.7)
H-7	—	7.43 (t, 7.7)	—	—	—	6.90 (d, 7.7)
7	—	—	3.82 (3H, OCH_3)	3.92 (3H, OCH_3)	3.91 (3H, OCH_3)	—
H-8	—	7.61 (d, 7.7)	6.96 (d, 2.2)	6.96 (d, 2.2)	6.96 (d, 2.2)	—
NH	8.02 (br)	10.70 (br)	11.26 (br)	8.29 (br)	8.18 (br)	10.63 (br)
Others	6.48 (d, 9.8, H-4′) 5.56 (d, 9.8, H-3′) 1.50 (6H, 2′-CH_3)		12.05 (br, OH)			8.86 (br, OH)

Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. All signals correspond to 1H, observed as a singlet, unless otherwise stated. *a*) Spectra were taken in acetone-d_6. *b*) A spectrum was taken in DMSO-d_6.

spectral data, coupled with biogenetic considerations,[2-4] suggested the presence of a 1-oxygenated-3-substituted carbazole skeleton having no substituent in the A-ring.[2-4] Further, the presence of a carbomethoxy group at C-3 was indicated by an IR band at ν_{max} 1703 cm^{-1}, two significant mass fragments at m/z 210 [$M^+ - \cdot OCH_3$] and 182 [$M^+ - \cdot COOCH_3$] in the EI-MS, and the ^{1}H-NMR signal at δ 3.88 (3H, s). On the basis of these spectral data, we assigned the structure **2** to clauszoline-I.

Structure of Clauszoline-J (4) This compound was obtained as pale yellow prisms, mp 252—256 °C, $C_{15}H_{13}NO_4$. In the ^{1}H-NMR spectrum, ABC-type signals at δ 7.93 (1H, d, J=8.4 Hz), 6.76 (1H, dd, J=8.4, 2.2 Hz), and 6.96 (1H, d, J=2.2 Hz), two 1H-singlet signals at δ 8.38 and 7.01 were observed in the aromatic proton region, along with two methoxy signals [δ 3.88 and 3.82]. The presence of a carboxy group was indicated by the IR bands at ν_{max} 3315 (br), 1666 cm^{-1} and two characteristic mass fragments at m/z 254 [$M^+ - \cdot OH$] and 226 [$M^+ - \cdot COOH$] in the EI-MS. In the NOE experiments, irradiation of the NH signal at δ 11.26 showed enhancements at the H-1 (δ 7.01) and the H-8 (δ 6.96) signals, respectively. Irradiation of the H-4 signal at δ 8.38 showed an enhancement of the H-5 signal (δ 7.93). Irradiation of the methoxy signal at δ 3.82 caused 5% and 13% enhancements of the H-6 (δ 6.76) and H-8 (δ 6.96) signals, respectively. Further, a 16% enhancement of the H-1 signal at δ 7.01 appeared on irradiation of the methoxy signal at δ 3.88. Based on these results, we assigned structure **4** to clauszoline-J, corresponding to a demethylated derivative of clauszoline-C (**5**).[1]

Structure of Clauszoline-K (6) This compound was obtained as a colorless powder, $C_{14}H_{11}NO_2$. A lower-field 1H singlet at δ 10.08 in the ^{1}H-NMR spectrum and an IR band at ν_{max} 1680 cm^{-1} suggested the presence of a formyl group in the molecule. The remaining ^{1}H-NMR signals were observed as two sets of ABC-type signals, as well as a methoxy group (δ 3.92). One set, which appeared at δ 7.47 (1H, d, J=8.4 Hz), 7.91 (1H, dd, J=8.4, 1.5 Hz), and 8.51 (1H, d, J=1.5 Hz), was assignable to H-1, H-2, and H-4, respectively, because the most deshielded doublet at δ 8.51 was due to H-4, located *ortho* to the formyl group.[7] The signals of the other three-spin system at δ 6.94 (1H, dd, J=8.4, 2.2 Hz), 6.96 (1H, d, J=2.2 Hz), and 8.00 (1H, d, J=8.4 Hz) were assigned to H-6, H-8, and deshielded H-5, respectively. The presence of the methoxy group at C-7 on the carbazole nucleus was indicated by the appearance of NOE enhancements between the methoxy (δ 3.92) and H-6 (δ 6.94) signals, and between the methoxy (δ 3.92) and H-8 (δ 6.96) signals. These spectral data indicated this alkaloid to have structure **6**.

Structure of Clauszoline-L (7) Clauszoline-L was obtained as a colorless oil having the molecular formula $C_{15}H_{13}NO_3$, a difference of CH_2O compared with **6**. The signal pattern (two sets of ABC-type signals and a methoxy group) of the ^{1}H-NMR spectrum (Table 1) resembled that of **6**, except for the appearance of an additional methoxy signal instead of the signals assignable to the formyl group at C-3, suggesting the 7-methoxy-3-substituted carbazole nucleus for this compound, as in **6**. The additional methoxy singlet at δ 3.97 in the ^{1}H-NMR spectrum, an IR band at ν_{max} 1709 cm^{-1}, and two significant mass fragments at m/z 224 [$M^+ - \cdot OCH_3$] and 196 [$M^+ - \cdot COOCH_3$] in the EI-MS indicated the presence of a carbomethoxy group at C-3. Based on these spectral data, together with the NOE experiments (see Experimental), the structure of clauszoline-L was concluded to be **7**.

Structure of Clauszoline-M (8) Clauszoline-M was isolated as a pale yellow powder, $C_{13}H_9NO_3$. The UV spectrum (see Experimental) was similar to that of clauszoline-F (**9**),[1] which had been isolated by us from the same plant collected in Singapore, and the IR spectrum showed bands at ν_{max} 3342 (br) cm^{-1} due to hydroxy groups. The ^{1}H-NMR spectrum showed a three-spin system at δ 6.90 (1H, d, J=7.7 Hz), 7.05 (1H, t, J=7.7 Hz), and 7.58 (1H, d, J=7.7 Hz) assignable to H-7, H-6, and deshielded H-5, and two singlet signals at δ 6.94 (1H, s) and 8.40 (1H, s) assignable to H-1 and deshielded H-4, respectively. Further, an IR band at ν_{max} 1651 cm^{-1} and ^{1}H-NMR signals at δ 9.99 (1H, s, CHO) and 11.44 (1H, s, OH, D_2O-exchangeable) indicated the presence of strongly hydrogen-bonded formyl and hydroxy groups located *ortho* with respect to each other. These results led us to conclude that clauszoline-M has the structure **8**.

Other carbazole alkaloids and coumarins isolated from the same plant material were fully characterized as mahanimbine,[8] murrayafoline-A,[6] heptaphylline,[9] ponfolin,[10] clausenidin,[11] clausarin,[12] dentatin,[13] xanthoxyletin,[14] xanthyletin,[15] nordentatin,[13] heptazoline,[16] 7-methoxyheptaphylline,[17] murrayanine,[18] clausine-D,[19] 2,7-dihydroxy-3-formyl-1-(3′-methyl-2′-butenyl)carbazole,[20] *O*-demethylmurrayanine,[21] 2-hydroxy-3-formyl-7-methoxycarbazole,[17] 3-formyl-2,7-dimethoxycarbazole,[22] and oxycapnolactone[23] by comparisons of ^{1}H-NMR and IR spectra with those of authentic samples or with spectroscopic data reported in the literature.[8-23]

Carbazole alkaloids lacking the oxygenated substituent at C-2, as in the cases of clauszoline-K (**6**) and -L (**7**), could not be detected in the stem bark of *C. excavata* collected in Singapore.[1] The native variation of the constituents of this plant is very interesting from a biogenetic viewpoint.

Experimental

Melting points were measured on a micromelting point hot-stage apparatus (Yanagimoto). ^{1}H-NMR spectra were recorded on an A-400 (JEOL) spectrometer in $CDCl_3$, unless otherwise stated. Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. All MS were taken under electron impact (EI) conditions using an M-80 (Hitachi) having a direct inlet system. UV spectra were recorded on a UVIDEC-610C double-beam spectrophotometer (JASCO) in MeOH, IR spectra on an IR-230 (JASCO) in $CHCl_3$, and optical rotations on a DIP-370 (JASCO) in $CHCl_3$ at 25 °C. Preparative TLC was done on Kieselgel 60 F_{254} (Merck).

Extraction and Isolation The plant material used in this study, *Clausena excavata* BURM. f. (Rutaceae), was grown in a greenhouse at the Okitsu Branch, Fruit Tree Research Station, Ministry of Agriculture, Forestry and Fisheries, Shimizu, Shizuoka (No. 84598).

a) From the Root: The acetone extract of the dried roots (200 g) was evaporated under reduced pressure to give an oily residue, which was extracted with hexane. The hexane-soluble portion was subjected to silica gel chromatography; elution with hexane–iso-Pr_2O (4:1, 7:3, 3:2, 1:1, and 2:3) and acetone successively gave 6 fractions. Each fraction was further subjected to silica gel column chromatography and preparative TLC with appropriate combinations of hexane, CH_2Cl_2, acetone, EtOAc, $CHCl_3$, and MeOH as developing solvents. From the hexane–iso-Pr_2O (7:3) eluate: mahanimbine (2 mg), murrayafoline-A (2 mg). From the hexane–iso-Pr_2O (3:2) eluate: heptaphylline (2 mg). From the hexane–iso-Pr_2O (1:1) eluate: ponfolin (4 mg), clausenidin (16.8 mg), clausarin (5.3 mg), dentatin (53.9 mg). From the hexane–iso-Pr_2O (2:3) eluate: xanthoxyletin (28.3 mg), xanthyletin (30.8 mg), nordentatin (34.3 mg). The hexane-insoluble portion was also chromatographed over silica gel with hexane, hexane–acetone (9:1, 4:1, 7:3, and 3:7), acetone, and MeOH successively to give 7 fractions. Each fraction was further treated in the same manner as described above. From the hexane–acetone (9:1) eluate: heptaphylline (5.5 mg), clauszoline-H (**1**) (3.4 mg), clausenidin (1.2 mg). From the hexane–acetone (4:1) eluate: heptazoline (4.6 mg), dentatin (8 mg), 7-methoxyheptaphylline (2.5 mg), murrayanine (6.4 mg). From the hexane–acetone (7:3) eluate: clausine-D (1.9 mg), 2,7-dihydroxy-3-formyl-1-(3′-methyl-2′-butenyl)carbazole (4.9 mg), *O*-demethylmurrayanine (2.4 mg), clauszoline-I (**2**) (1.9 mg). From the hexane–acetone (3:7) eluate: clauszoline-J (**4**) (1.9 mg), xanthoxyletin (1.2 mg), nordentatin (2.2 mg).

b) From the Stem Bark: The acetone extract of dried stem bark (70 g) was subjected to silica gel chromatography. Elution with hexane–acetone (9:1, 4:1, 7:3, 3:2, 2:3, and 1:4), acetone, $CHCl_3$–MeOH (3:1), and MeOH successively gave 12 fractions. Each fraction was further subjected to silica gel column chromatography and preparative TLC (developed with an appropriate mixture of hexane, CH_2Cl_2, acetone, EtOAc, $CHCl_3$, benzene, iso-Pr_2O, and MeOH). From the hexane–acetone (7:3) eluate: clauszoline-K (**6**) (1.3 mg), 2-hydroxy-3-formyl-7-methoxycarbazole (1.0 mg). From the hexane–acetone (3:2) eluate: clauszoline-L (**7**) (1.0 mg), 3-formyl-2,7-dimethoxycarbazole (1.1 mg). From the hexane–acetone (2:3) eluate: oxycapnolactone (1.0 mg).

c) From the Leaves[24]: The acetone extract of the leaves (70 g) was subjected to silica gel column chromatography. Successive elutions with hexane–acetone (9:1, 4:1, 3:1, 7:3, 3:2, 2:3, and 1:4), acetone, and MeOH gave 9 fractions. The hexane–acetone (7:3) eluate was further separated by repeated preparative TLC (silica gel) using iso-Pr_2O, $CHCl_3$–acetone (19:1) to afford clauszoline-M (**8**) (1.0 mg).

Known components were fully characterized by UV, IR, ^{1}H-NMR, and MS analyses.

Clauszoline-H (1) Colorless powder. UV λ_{max} nm: 230, 258, 288, 310, 323, 348, 363. IR ν_{max} cm^{-1}: 3471. EI-MS *m/z* (%): 293 (M^+, 54), 278 (100), 263 (14), 248 (6), 234 (10), 204 (4). NOE: irradiation of 3-CH_3 (δ 2.34) gave 11% NOE at H-4 (δ 7.71); irradiation of 2-OCH_3 (δ 3.90) gave 19% NOE at H-1 (δ 6.85); irradiation of H-4′ (δ 6.48) gave 8% NOE at H-6 (δ 6.84) and 8% NOE at H-3′ (δ 5.56); irradiation of H-4 (δ 7.71) gave 5% NOE at H-5 (δ 7.42) and 8% NOE at 3-CH_3 (δ 2.34). HR-MS Calcd for $C_{19}H_{19}NO_2$: 293.1414. Found: 293.1410.

Clauszoline-I (2) Pale yellow oil. UV λ_{max} nm: 223 (sh), 238, 247 (sh), 269, 275, 312, 322, 336. IR ν_{max} cm^{-1}: 3465, 3340 (br), 1703. EI-MS *m/z* (%): 241 (M^+, 100), 227 (4), 210 (57), 182 (18), 154 (11). HR-MS Calcd for $C_{14}H_{11}NO_3$: 241.0738. Found: 241.0739.

Clauszoline-J (4) Pale yellow prisms. mp 252—256 °C (from acetone). UV λ_{max} nm: 240, 276, 308, 318. IR (KBr) ν_{max} cm^{-1}: 3315, 1666, 1618, 1577. EI-MS *m/z* (%): 271 (M^+, 100), 256 (45), 254 (3), 241 (15), 227 (12), 226 (4), 212 (28), 210 (11), 196 (8), 184 (17), 169 (23). NOE: Irradiation of NH (δ 11.26) gave 4% NOE at H-1 (δ 7.01) and 5% NOE at H-8 (δ 6.96); irradiation of H-4 (δ 8.38) gave 5% NOE at H-5 (δ 7.93); irradiation of 7-OCH_3 (δ 3.82) gave 5% NOE at H-6 (δ 6.76) and 13% NOE at H-8 (δ 6.96); irradiation of 2-OCH_3 (δ 3.88) gave 16% NOE at H-1 (δ 7.01); irradiation of H-1 (δ 7.01) gave 1% NOE at NH (δ 11.26). HR-MS Calcd for $C_{15}H_{13}NO_4$: 271.0843. Found: 271.0848.

Clauszoline-K (6) Colorless powder. UV λ_{max} nm: 226 (sh), 232, 252 (sh), 293, 324. IR ν_{max} cm^{-1}: 3465, 1680, 1607. EI-MS *m/z* (%): 225 (M^+, 100), 210 (32), 196 (12), 182 (43), 162 (36). NOE: irradiation of 7-OCH_3 (δ 3.92) gave 3% NOE at H-6 (δ 6.94) and 3% NOE at H-8 (δ 6.96). HR-MS Calcd for $C_{14}H_{11}NO_2$: 225.0790. Found: 225.0818.

Clauszoline-L (7) Colorless oil. UV λ_{max} nm: 218, 238 (sh), 248, 281, 320 (sh). IR ν_{max} cm^{-1}: 3469, 1709, 1610. EI-MS *m/z* (%): 255 (M^+, 28), 240 (16), 224 (16), 212 (12), 196 (28), 181 (14), 163 (13). NOE: irradiation of 7-OCH_3 (δ 3.91) gave 6% NOE at H-6 (δ 6.91) and 11% NOE at H-8 (δ 6.96). HR-MS Calcd for $C_{15}H_{13}NO_3$: 255.0894. Found: 255.0873.

Clauszoline-M (8) Pale yellow powder. UV λ_{max} nm: 217, 240, 275, 290, 356. IR (KBr) ν_{max} nm: 217, 240, 275, 290, 356. IR (KBr) ν_{max} cm^{-1}: 3342 (br), 1651, 1620, 1581. EI-MS *m/z* (%): 227 (M^+, 100), 226 (60), 210 (20), 198 (23), 170 (26). HR-MS Calcd for $C_{13}H_9NO_3$: 227.0582. Found: 227.0587.

Added in Proof (October 4, 1996) After this paper submitted, clauszoline-I (**2**) and -J (**4**) were also isolated recently by Wu T.-S., *et al.* [Wu T.-S., Huang S.-C., Wu P.-L., Teng C.-M., *Phytochemistry*, **43**, 133—140 (1996)].

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