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ALKALOIDS FROM *DACTYLICAPNOS TORULOSA**

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Key Word Index—*Dactylicapnos torulosa*; Fumariaceae; dactylicapnosine; dactylicapnosinine; dactyline; 8-hydroxydihydrosanguinarine; dactylidine; NMR; X-ray analysis.

Abstract—Phytochemical investigation of *Dactylicapnos torulosa* yielded two known compounds, (−)-*cis*-*N*-methylstylopiumchloride and hydrastinine chloride; and five new alkaloids, dactyline, 8-hydroxydihydrosanguinarine and dactylidine, as well as dactylicapnosine and dactylicapnosinine with novel C–N–O–C moieties. All structures were elucidated by spectroscopical methods. The structure of dactylicapnosine was also determined by single crystal X-ray diffraction analysis.

INTRODUCTION

From the Chinese medicinal plant *Dactylicapnos torulosa* (Hook f. et Thomas) Hutchins, alkaloids belonging to the berberine, benzo[c]phenanthridine, phthalideisoquinoline, procumbine and *seco*-phthalideisoquinoline types have been previously isolated [1,2]. During the present investigation five new alkaloids, named dactylicapnosine (**1**), dactylicapnosinine (**2**), dactyline (**3**), 8-hydroxydihydrosanguinarine (**4**) and dactylidine (**5**) were isolated, together with the two known alkaloids, (−)-*cis*-*N*-methylstylopium chloride (**6**) and hydrastinine chloride (**7**). Their structures were elucidated mainly by spectroscopy. The structure of dactylicapnosine (**1**) was also established by single crystal X-ray diffraction analysis. The ^{13}C NMR data were assigned by evaluation of C,H-COSY, C,H-COLOC, DEPT and NOE-difference experiments.

RESULTS AND DISCUSSION

Dactylicapnosine (**1**), obtained as orange plates, shows a strong green fluorescence in solution; UV λ_{max}^{MeOH} nm log(ε): 381 (4.60), 300 (4.59); λ_{max}^{MeOH}/KOH nm log(ε): 293 (4.49). On the basis of an ion at *m/z* 795 $[M + 1]^+$ in the FAB mass spectrum of **1** a M_r of 794 was inferred, whereas in its HR-EI mass spectrum a fragment with *m/z* 397.1146 appears as the highest mass ion, corresponding to $C_{21}H_{19}NO_7$. From the NMR spectra (C,H-COSY, DEPT and C,H-COLOC, as well as NOE-differences described in Fig. 1) a substructure of *seco*-phthalideisoquinoline is derived (see structure **1** in Fig. 1 without ring A–E). The disappearance of the UV absorption at 381 nm upon addition of KOH provides evidence for this moiety. Furthermore, from the NMR spectra, the presence of the following moieties were deduced: one phenyl ring with two protons in *para*-positions and a methylenedioxy group (ring A), another phenyl ring with two neighbouring protons and two methoxy groups *ortho* to each other (ring **B**), and a -CH(1)-CH(2)-CH(3)-moiety. In NOE-difference experiments, a positive NOE was observed between 1-H and one of the two protons on ring A (H-7), and between H-3 and H-4. Thus, the moiety -CH(1)-CH(2)-CH(3)- forms a five-membered ring (ring C) attached to ring A. The protons of an *N*-methyl group at δ3.0 give rise to a cross-signal in C,H-COLOC with carbon C-2 at δ80.8; thus, this nitrogen atom should be located at C-2. Apart from the moieties discussed above, there is a carbonyl group at δ164.4 and a quaternary carbon at δ108.2. Because of the chemical shift of C-5′ (δ118.9), the carbonyl group should be directly attached to C-5′. Because the carbon C-α appears at δ108.2 and lacks a sp^2 partner carbon atom, this carbon should be considered as aliphatic and attached to two oxygen atoms. Furthermore, because of the chemical shift, it is not likely that C-6′ (at δ136.8) bears an oxygen atom. It is not possible for C-3 to be connected directly with the oxygen atom, otherwise ring D would be an oxazolidine; the chemical shift of C-α would be at a lower field than observed and there would also be a NOE effect between N-Me and H-1′, as expected with the help of molecular models. Consequently, the carbon C-α should be located between

*Part 2 in the series Alkaloids from *Dactylicapnos torulosa*. For Part 1 see ref. [2].

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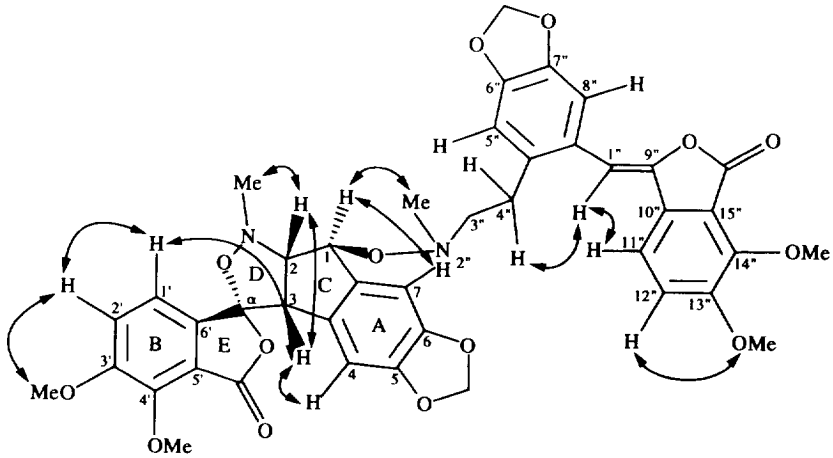

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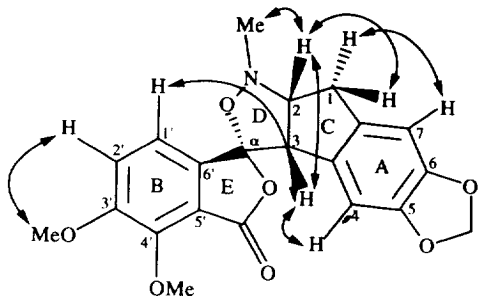

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Fig. 1. Structures of alkaloids **1** and **2** (↔ is for NOE signal).

C-3 and C-6′. Ring D with a C–N–O–C sequence and the lactone ring E were established. The protons H-2 and H-3 are *cis*-oriented, because the coupling constant between them is 7 Hz and a positive NOE effect was detected. Otherwise, the coupling constant would not be significant. As the coupling constant between H-1 and H-2 is too small to be resolved, the dihedral angle between these protons is close to 90°. From the NOE effects between H-3 and H-1′, the relative configuration of C-α was determined. The structure of **1** was finally verified by single crystal X-ray diffractometry (Fig. 2). The crystal data and the atomic coordinates are deposited at the Cambridge Crystallography Data Centre, U.K.

The molecular formula $C_{21}H_{19}NO_7$ of dactylicapnosinine (**2**) was deduced from the $[M]^+$ *m/z* 397.1165 in the HR-EI mass spectrum. The ^1H and ^{13}C NMR data resemble those of **1** as far as the rings A–D are concerned. The difference is that C-1 in **2** appears as a methylene group. From the C, H-COLOC cross-signals and from the NOE-difference results (Fig. 1), the structure of **2** was elucidated. Because $[\alpha] = 0°$, this compound may be a racemate.

The biogenesis of alkaloids **1** and **2** remains unknown. Alkaloid **2** consists of an indanoisoxazolidine derivative, which is formed possibly from the rearrangement of a substance with an indanobenzazepine skeleton. Indanobenzazepine alkaloids, such as ribasidine [3, 4], himalayine and limogine [5], as well as grandiflorine [6], have been isolated. Probably, alkaloid **2** is synthesized from an indanobenzazepine alkaloid by rearrangement; alkaloid **1** is formed from a derivative of **2** and a *seco*-phthalideisoquinoline alkaloid.

Dactyline (**3**), a white powder, shows a weak peak at *m/z* 397 in the EI mass spectrum and a peak at *m/z* 396.1720 in the HR-EI mass spectrum ($[M - H]^+$, corresponding to $C_{22}H_{24}N_2O_5$). In the ^1H NMR spectrum of **3**, two methoxy groups are detected at δ3.83 (*s*, 3′-OMe) and 3.87 (*s*, 4′-OMe), and two protons of a methylenedioxy group (attached to C-7 and C-8 as revealed by an HMBC experiment) at δ5.80 (*d*) and 5.83 (*d*). An isolated methylene group $-CH_2-$ (C-1) appears at δ3.36 (*d*) and 3.21 (*d*) with a geminal coupling constant of 14 Hz. Two *N*-methyls appear as singlets at δ3.25 (*s*) and 3.36 (*s*), and an ethylene moiety is formed by two neighbouring methylene groups, one at δ3.0 and δ3.24 (each *ddd*, 2H, H-5), the other one at δ3.37 and 3.47 (each *ddd*, 2H, H-6). In the ^{13}C NMR spectrum, an aliphatic quaternary carbon (C-2) is located at δ88.5 and a carbonyl group at δ169.3. From the NMR data and molecular formula, an amide carbonyl group was assumed. Further

Table 1. NMR data of alkaloid **1** ($CDCl_3$)

C-atom	δ_C	$\delta_H^{*,\dagger}$	In C,H-COLOC correlate with	C-atom	δ_C	δ_H^*	In C,H-COLOC correlate with
1	63.0	5.20, *s*		7″	146.8		H-5″
2	80.8	3.95, *d*	2-NCH_3	8″	110.3	7.70, *s*	
3	63.0	4.57, *d*		8″a	125.1		H-5″
3a	131.9		H-1, H-4	9″	143.0		
4	104.4	6.10, *s*		10″	134.1		H-1″
5	148.5			11″	114.4	7.10, *m*	
6	149.4		5,6-OCH_2O	12″	119.9	7.10, *m*	
7	106.2	6.80, *s*		13″	152.9		13″-OCH_3
7a	134.1		H-1	14″	148.2		14″-OCH_3
1′	117.3	7.27, *d*		15″	115.1		
2′	118.9	7.32, *d*		α	108.2		
3′	154.4		3′-OCH_3, H-1′	2-NMe	44.7	3.00, *s*	
4′	148.0		4′-OCH_3, H-2′	5,6-OCH_2O	101.6	5.95, *s*	
5′	118.9			3′-OMe	56.9	3.92, *s*	
6′	136.8		H-2′	4′-OMe	62.4	4.10, *s*	
1″	101.2	6.40, *s*		5′-COO-	164.4‡		
3″	61.9	2.90, *m*		2″-Me	44.7	2.73, *s*	
4″	31.7	2.95, *m*		6″,7″-OCH_2O	101.3	5.90, *s*	
4″a	132.5		H-8″	13″-OMe	56.9	3.92, *s*	
5″	109.9	6.70, *s*		14″-OMe	62.6	4.10, *s*	
6″	147.5		H-5, H-8	15″-COO-	164.6‡		

* Signals of corresponding H-atoms in ^1H NMR deduced from C,H-COSY.
† $J_{H2,H3} = 7$ Hz, $J_{H1',H2'} = 8$ Hz.
‡ Assignments interchangeable.

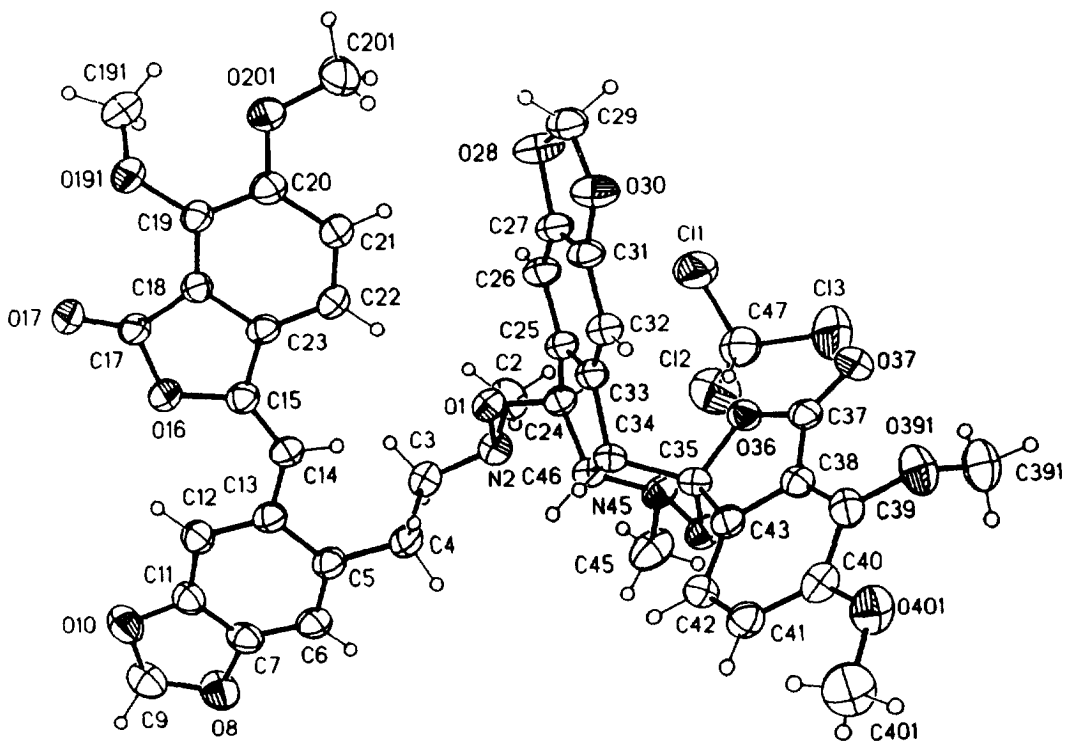


Fig. 2. Structure of alkaloid **1** deduced from X-diffractometry.

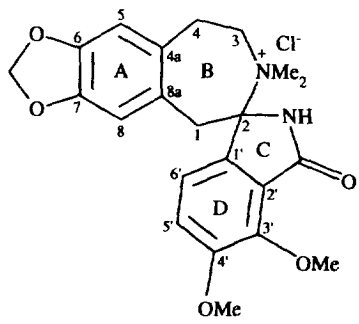
Table 2. NMR data of alkaloid **2** ($CDCl_3$)

C-atom	δ_C	δ_H	J_{HH}	In C,H-COLOC correlate with
1	31.3	2.95, *d*	15	
		3.04, *dd*	7 Hz, 15 Hz	
2	74.3	3.84, "t"	7 Hz	
3	65.1	4.48, *d*	7 Hz	
3a	129.8			H-1, H-7
4	105.3	6.20, *s*		
5	147.4			H-7
6	148.2			H-4
7	105.2	6.64, *s*		
7a	134.8			H-1, H-4
1′	117.3	7.25, *m*		
2′	119.0	7.25, *m*		
3′	154.2			3′-OCH_3
4′	148.2			4′-OCH_3
5′	118.9			H-1′
6′	138.0			
α	108.6			H-1′
2-NMe	44.3	2.90, *s*		
5,6-OCH_2O-	101.2	5.88, *d*	1 Hz	
		5.90, *d*		
3′-OMe	53.9	3.94, *s*		
4′-OMe	62.6	4.14, *s*		
5′-COO-	164.7			

moieties were recognized from ^1H, ^{13}C NMR, HMQC and HMBC experiments (Fig. 3): one phenyl ring with two neighbouring protons at δ7.19 (*d*, 1H, H-6′) and δ7.25 (*d*, 1H, H-5′) with an *ortho*-coupling constant of 8 Hz, and the two methoxy groups discussed above (ring D), and another phenyl ring with two protons in a *para*-position with chemical shifts of δ6.41 (*s*, 1H, H-8) and δ6.68 (*s*, 1H, H-5) and the methylenedioxy group (ring A). The $-CH_2-CH_2-$ and the $-CH_2-$ moieties were located on ring A due to two cross-signals [δ3.00 (H-4)—δ 110.3 (C-5) and δ3.22, (H-1)—δ 112.9 (C-8)] in the HMBC. In the same experiment, one of the protons at C-1 ($H\text{-}1_a$, δ3.22) and the aromatic protons at δ7.25 (*d*, 1H, H-5′) on ring D correlate with C-1′ (δ143.3), and proton $H\text{-}1_b$ (δ3.37) correlates with C-2 (δ88.6). Therefore, the quaternary carbon C-2 stands between C-1 and ring D. In the HR-EI mass spectrum, the prominent fragment at *m/z* 58.0680 (C_3H_8N) has a relative intensity of 43%. One of the two neighbouring methylene carbons $-CH_2-CH_2-$ appears at δ71.3. From these data, the structure of ring B is derived. With respect to its chemical shift (δ124.5), C-2′ is very likely to be attached to the carbonyl group. Accordingly, the substitution in ring C was assigned. After addition of 1% $AgNO_3$ to a solution of **3** in water, a white precipitate was observed, which was soluble in ammonia (25%). This precipitate turned to yellow on addition of 1% KBr. Thus, the anion in **3** should be chloride.

The molecular formula $C_{20}H_{15}NO_5$ of 8-hydroxydihydrosanguinarine (**4**) was deduced from the peak at *m/z* 335.0920 in its HR-EI mass spectrum. The UV absorptions of **4** resemble closely those of some known 7,8-dihydrosanguinarine alkaloids [7]. Comparing the ^1H NMR spectrum of **4** with that of 8-methoxydihydrosanguinarine [8, 9], the lack of one methoxy group is noticed in **4**, whereas an additional signal at δ4.25 (*br s*, D_2O exchangable) for an hydroxy group is confirmed by a broad absorption at 3450 cm^{-1} in its IR spectrum; thus, **4** has the structure of a pseudobase. There are many reports on pseudobases [10]. An investigation of sanguinarine in $EtOH-H_2O$ showed that **4** is one form of sanguinarine existing in solution [11]. Some of the benzo[c]phenanthridines reported with substituents at C-8 may be artefacts [7, 11]. However, the sanguinarine pseudomethanolate isolated from *Fumaria* [8], *Hunnemannia* [12] and *Hypecoum* [13], displays a significant optical rotation, so that it can be considered as a genuine natural product [7]. Alkaloid **4** with an optical rotation of $[\alpha]_D^{25} = -9°$ (MeOH, *c* 0.4) is probably an unequal mixture of enantiomers, which may have undergone racemization during extraction and isolation.

The UV absorption maxima of dactylidine (**5**) at 360 (sh), 320, 251 and 204 nm, along with the general appearance of the UV spectrum, is similar to that of dihydroroemerine [14]. In the ^1H NMR, two methylenedioxy groups are detected at δ6.16 (*s*, 2H) and δ6.08 (*s*, 2H). Four protons are present in the ^1H NMR spectrum as two AB systems: two of them at δ8.12 (*d*, H-4) and 8.21 (*d*, H-5) with a common coupling constant of 6 Hz, and another AB system at δ7.30 (*d*) and δ6.88 (*d*) (J = 8 Hz), which could be assigned to H-8 and H-9 because of their shielding induced by the methylenedioxy group. Further-



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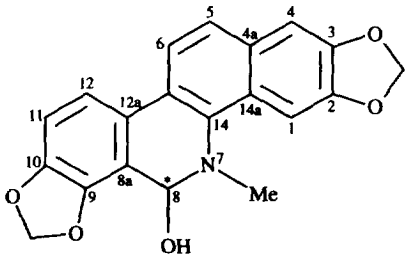

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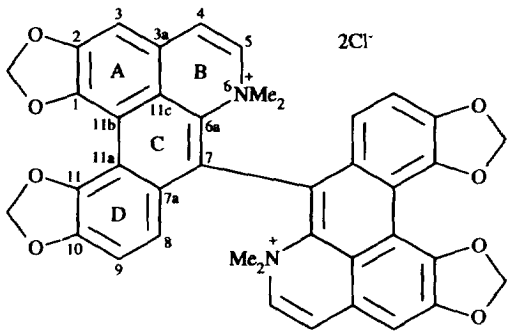

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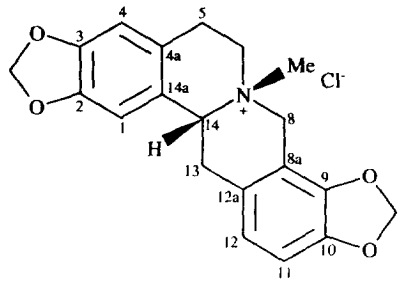

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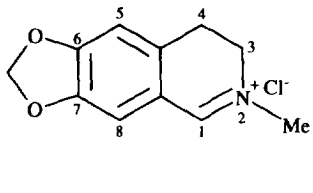

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Fig. 3. Structures of alkaloids **3**–**7**.

more, two *N*-methyl groups were observed at δ3.15 (*s*, 3H) and δ4.13 (*s*, 3H) in the ^{1}H NMR spectrum, with corresponding ^{13}C signals at δ30.8 and 46.6. Thus, compound **5** is a quarternary salt. No signal for H-7 is observed in the ^{1}H NMR; the peak at *m/z* 333.1001 (92%) in the HR-EI mass spectrum corresponds to the formula $C_{20}H_{15}NO_4$. Thus, alkaloid **5** was recognized to be an aporphine dimer with a 7,7′-linkage between the two cationic moieties (Fig. 3). The anion Cl^- in **5** was identified as described for **3**.

EXPERIMENTAL

General. Mp: uncorr. IR: KBr discs. NMR: 400 MHz (^{1}H) and 100 MHz (^{13}C), TMS as int. standard. EI-MS: 70 eV. CC: silica gel (Merck, Kieselgel 60, 70–230 mesh). Identification of anion Cl^- in **3**, **5** and **6**: 1% $AgNO_3$ and **3**: 1% KBr (aq.), NH_4OH (25%).

Plant material and extraction. See ref. [2].

Isolation. A portion (18 g) of the total alkaloidal fr. was chromatographed (CC, 300 g) with $CHCl_3$–MeOH mixts of increasing polarity (20:1, 1 l, 10:1, 1 l, 5:1, 1 l and MeOH, 2 l). Frs were collected every 500 ml to yield frs 1–6. Fr. 1 (0.04 g) was chromatographed on a column (5 g) with CH_2Cl_2– EtOAc (20:1) to give **4** (0.01 g). After recrystallization of α-hydrastine in $CHCl_3$ from fr. 2 (7 g), the mother liquid was chromatographed repeatedly on columns using CH_2Cl_2–EtOAc (10:1) to yield **1** (0.04 g) and **2** (0.02 g). Compound **3** (0.015 g) was isolated from fr. 5 (0.04 g) by CC (7 g) eluted with $CHCl_3$–MeOH (4:1). Fr. 6 (0.07 g) was submitted to CC (50 g) using $CHCl_3$–MeOH–H_2O (10:10:1) to give **5** (0.02 g) and **6** (0.01 g).

X-ray crystallography of dactylicapnosine (**1**). All X-ray data were collected on an Enraf-Nonius CAD4 diffractometer at room temp. with CuKα radiation

(λ = 1.54178 Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically as F^2 (SHELXL–93). H-atoms were located by difference electron density determination and refined by using a siding model. An empirical adsorption correction on the basis of ψ-Scans was applied.

Dactylicapnosine (**1**). Yellow plates (from $CHCl_3$ in an atmosphere satd with MeOH), mp 135–136°. $[\alpha]_D^{20} = 0°$ (MeOH; *c* 0.3). UV λ_{max}^{MeOH} nm log(ε): 300 (4.59), 381 (4.60); UV λ_{max}^{MeOH} nm log(ε): 273 (4.28), 343 (4.32); UV $\lambda_{max}^{MeOH/KOH}$ nm log(ε): 293 (4.59). IR ν_{max} cm^{-1}: 2960, 2900, 2840, 2780, 1780 (C=O), 1660, 1610, 1500, 1480, 1430, 1360, 1350, 1275, 1240, 1190, 1170, 1150, 1080, 1040, 1015, 1000, 965, 940 (–CH_2O–), 870, 760, 730, 720, 690. FAB-MS (positive, *m*-nitrobenzylacohol as matrix): *m/z* 795 $[M + 1]^+$, 396, 351; HR-EIMS (rel. int): *m/z* (rel. int.): *m/z* (rel. int.) 398.1219 ($C_{21}H_{21}NO_7$, 13), 397.1146 ($C_{21}H_{19}NO_6$, 16), 383.1384 ($C_{21}H_{21}NO_6$, 9), 381.1205 ($C_{21}H_{19}NO_6$, 4), 352.0955 ($C_{20}H_{16}NO_6$, 29), 351.0881 ($C_{20}H_{15}NO_6$, 44), 340.0963 ($C_{19}H_{16}NO_6$, 31), 208 (25), 193 (40), 190 (30), 189 (50), 188 (100), 160 (40). NMR data in Table 1.

Dactylicapnosinine (**2**). Needles ($CHCl_3$–EtOAc, 2:1), mp 184.5–186°. $[\alpha]_D^{20} = 0°$ (MeOH; *c* 0.1). UV λ_{max}^{MeOH} log(ε): 299 (4.22), 240sh (4.38); UV λ_{min}^{MeOH} log(ε): 263 (3.40). IR ν_{max} cm^{-1}: 3000, 2900, 2820, 1765 (C=O), 1600, 1495, 1475, 1420, 1350, 1310, 1300, 1270, 1260, 1240, 1215, 1200, 1180, 1140, 1100, 1060, 1040, 1000, 950, 930, 910, 890, 860, 840, 810, 800, 780, 740, 720, 710, 670, 650. HR-EIMS *m/z* (rel. int.): 397.1166 $[M]^+$ (46) (cal. for $C_{21}H_{19}NO_7$: 397.1171), 352.0915 ($[M]^+$–CH_3NO, $C_{20}H_{16}NO_6$, 26), 351.0868 ($C_{20}H_{15}NO_6$, 66), 189 (40), 188 (100), 160 (60). NMR data in Table 2.

Dactyline (**3**). Needles (MeOH); mp 110° (dec.). $[\alpha]_D^{20}$:0° (MeOH; *c* 1.0). UV λ_{max}^{MeOH} log(ε): 293 (4.19). IR ν_{max} cm^{-1}: 3400 (–NH–), 1690 (C=O), 1490, 1460, 1430, 1375, 1345, 1265, 1060, 1040, 1005, 935 (–OCH_2O–). EI-MS 40 eV *m/z* (rel. int.): 396.1535 ($[M + H]^+$) (2) (cal. for $C_{22}H_{24}N_2O_5$: 396.1552), 394.1537 ($C_{22}H_{22}N_2O_5$, 4), 352.1098 ($C_{19}H_{16}N_2O_5$, 19), 351.1089 ($C_{20}H_{17}NO_5$, 94), 336.0858 ($C_{19}H_{13}NO_5$, 23), 193.0664 ($C_{14}H_9O$, 10), 192.0667 ($C_{10}H_{10}NO_3$, 100), 162.0664 ($C_{10}H_{10}NO_3$, 6), 58.0680 (C_3H_8N, 43). ^1H NMR (CD_3OD, 500 MHz): δ3.37 (*d*, 1H, H-1, J_{gem} = 12 Hz), 3.22 (*d*, 1H, H-1, J_{gem} = 12 Hz), 3.27 (*s*, 3H, *N*-CH_3), 3.20 (*s*, 3H, *N*-CH_3), 3.37 (*ddd*, 1H, H-4, *J* = 13, 4, 4 Hz), 3.47 (*ddd*, 1H, H-4, *J* = 13, 6, 6 Hz), 3.24 (*ddd*, 1H, H-5, *J* = 12, 6, 6 Hz), 3.0 (*ddd*, 1H, H-5, *J* = 12, 4, 4 Hz), 6.68 (*s*, 1H, H-6), 5.72 and 5.76 (AB, each 1H, –OCH_2O–, *J* = 1 Hz), 6.43 (*s*, 1H, H-9), 3.82 (*s*, 3H, 3′-OMe), 3.85 (*s*, 3H, 4′-OMe), 7.25 (*d*, 1H, H-5′, *J* = 8Hz), 7.20 (*d*, 1H, H-6, *J* = 8 Hz). ^{13}C NMR (CD_3OD, 125 MHz): δ42.7 (C-1), 88.6 (C-2), 57.8 (*N*-$\underline{C}H_3$), 57.9 (*N*-$\underline{C}H_3$), 71.3 (C-4), 27.2 (C-5), 131.1 (C-5a), 110.3 (C-6), 148.3 (C-7), 147.8 (C-8), 102.3 (–$O\underline{C}H_2O$–), 112.9 (C-9), 128.4 (C-9a), 143.3 (C-1′), 124.5 (C-2′), 169.2 (C=O), 148.0 (C-3′), 62.3 (3′-$O\underline{C}H_3$), 154.8 (C-4′), 57.0 (4′-$O\underline{C}H_3$), 119.5 (C-5′), 118.0 (C-6′).

8-*Hydroxydihydrosanguinarine* (**4**). Yellow powder, mp 170° (dec.). $[\alpha]_D^{20}$ – 9° (MeOH; *c* 0.4). UV λ_{max}^{MeOH} log(ε): 350sh (3.45), 325 (3.94), 284 (4.31), 235 (4.28). IR ν_{max} cm^{-1}: 3450 (-OH), 3000-2700, 1650, 1600, 1500, 1460, 1440, 1350, 1340, 1290, 1200, 1040, 940 (–OCH_2O–). HR-EIMS *m/z* (rel. int.): 335.0920 $[M]^+$ (3) (cal. for $C_{20}H_{15}NO_5$: 335.0920), 318 ($[M]^+$ – HO) (100). ^1H NMR (300 MHz, $CDCl_3$): δ7.13 (*s*, 1H, H-1), 7.71 (*s*,1H, H-4), 7.49 (*d*, 1H, H-5, *J* = 9 Hz), 7.77 (*d*, 1H, H-6, *J* = 9 Hz), 2.80 (*s*, 3H, *N*-$C\underline{H}_3$), 5.40 (*s*, 1H, H-8), 6.94 (*d*, 1H, H-11, *J* = 8 Hz), 7.42 (*d*, 1H, H-12, *J* = 8 Hz), 7.97 (*s*, 1H, –OH), 6.06 and 6.07 (AB, each 1H, –$OC\underline{H}_2O$–), 6.13 (*d*, 2H, –$OC\underline{H}_2O$–, *J* = 1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ89.7 (C-8), 44.8 (*N*-$\underline{C}H_3$), 105.0 (-$O\underline{C}H_2O$-), 105.7 (-$O\underline{C}H_2O$-), 104.4 (C-1), 108.5 (C-4), 124.0 (C-5), 127.6 (C-6), 120.2 (C-2), 112.8 (C-11), 151.9, 151.3, 151.0, 149.1 (C-2, C-3, C-9, C-10), 141.9 (C-14), 134.9, 130.6, 129.5, 126.5 (C-4a, C-13, C-14a, C-12a), 116.8 (C-8a).

Dactylidine (**5**). Orange powder, mp > 300° (carbonization). UV λ_{max}^{MeOH} log(ε): 360sh (4.12), 320 (4.21), 251 (4.69), 204 (4.79); UV λ_{max}^{MeOH} log(ε): 283 (4.00), 227 (4.49). IR ν_{max} cm^{-1}: 1660, 1605, 1585, 1500, 1470, 1445, 1360, 1280, 1230, 1180, 1045, 1000, 975, 930, 915. HR-EIMS *m/z* (rel. int.): 333.1001 $[M]^+$ (92) (cal. for $C_{20}H_{15}NO_4$: 333.1001), 332.0921 ($C_{20}H_{14}NO_4$, 100), 318 (5), 317 (7). ^1H NMR (CD_3OD): δ7.56 (*s*, 1H, H-3), 8.12 (*d*, 1H, H-4, *J* = 6 Hz), 8.21 (*d*, 1H, H-5, *J* = 6 Hz), 6.80 (*s*, 1H, H-8, *J* = 8 Hz), 7.30 (*d*, 1H, H-9, *J* = 8 Hz), 6.16 (*s*, 2H, –$OC\underline{H}_2O$–) 6.08 (*s*, 2H, –$OC\underline{H}_2O$–), 3.15 (*s*, 3H, *N*-$C\underline{H}_3$), 4.13 (*s*, 3H, *N*-$C\underline{H}_3$). ^{13}C NMR (CD_3OD): δ103.8 and 104.4 (C-3, C-8), 108.6 (C-4), 137.1 (C-5), 146.7 (C-6a), 125.6 (C-9), 152.0, 154.0, 158.4, 156.3 (C-1, C-2, C-10, C-11), 140.8, 125.6, 130.4, 132.2, 122.5 (C-3a, C-7a, C-11a, C-11b, C-11c), 46.6 (2 × *N*–Me), 104.5 and 105.9 (–OCH_2O–).

(–)-cis-N-*Methylstylopium chloride* (**6**). Yellow powder; mp 210° (dec.); lit. mp 270° (dec.) [15]. $[\alpha]_D^{25}$ –125° (MeOH; *c* 0.2); lit. $[\alpha]_D^{25}$ –120° [16]. UV λ_{max}^{MeOH} log(ε): 290 (4.00), 241 (4.4), identical to that of (–)-*cis*-*N*-methylstylopium iodide [17]. IR ν_{max} cm^{-1}: 1630, 1485, 1470, 1380, 1275, 1230, 1060, 1040, 990, 940, 890, 850, 810: HR-EIMS *m/z* (rel. int.): 339.1464 ($[M + 1]^+$, $C_{20}H_{21}NO_4$) (3), 337.1295 ($[M - 1]^+$, $C_{20}H_{19}NO_4$), (3), 324.1175 ($[M - CH_3 + 1]^+$, $C_{19}H_{18}NO_4$) (19), 323.1164 ($[M - CH_3]^+$) (68), 322.1068 ($[M - CH_4]^+$, $C_{19}H_{16}NO_4$) (54), 148 (100). ^1H NMR ($CDCl_3$): δ6.73 (*s*, 1H, H-1), 6.65 (*s*, 3H, H-4), 3.34 (*dd*, 1H, H-5, *J* = 18, 10 Hz), 3.13 (*dd*, 1H, H-5, *J* = 18, 10 Hz), 3.74 (*m*, 1H, H-6), 4.24 (*dd*, 1H, H-6, *J* = 10, 10 Hz), 5.24 (*d*, 1H, H-8, *J* = 16 Hz), 5.01 (*d*, 1H, H-8, *J* = 16 Hz), 6.73 (*d*, 1H, H-11, *J* = 8 Hz), 6.58 (*d*, 1H, H-12, *J* = 8 Hz), 3.43 (*dd*, 1H, H-13, H = 18, 6 Hz), 3.02 (*dd*, 1H, H-13, *J* = 18, 10 Hz). 5.84 (*dd*, 1H, H-14, *J* = 10, 6 Hz), 5.97, 5.96, 5.94, 5.93 (each 1H, 2 × –OCH_2O–), 3.68 (*s*, 3H, N–$C\underline{H}_3$). ^{13}C NMR (CD_3OD): δ109.0 (C-1), 147.3 (C-2), 148.6 (C-3), 107.1 (C-4), 121.7 (C-4a), 144.5 (C-9), 146.7 (C-10), 108.9 (C-11), 121.0 (C-12), 121.5 (C-12a), 33.6 (C-13), 65.3 (C-14), 124.8 (C-14a), 102.1 and 101.7 (2 × –$O\underline{C}H_2O$–), 50.0 (*N*–Me).

Hydrastinine chloride (**7**). Orange powder, mp 172° (dec.). UV λ_{max}^{MeOH} log(ε): 366 (3.92), 307 (3.84), 251 (4.32), almost the same as that in EtOH [18]. IR ν_{max} cm^{-1}: 2890, 2880, 2860, 1670, 1500, 1390, 1350, 1290, 1260,

1250, 1220, 1170, 1160, 1100, 1030, 920. ^{1}H NMR (CD_3OD, 300 MHz): δ8.90 (*s*, 1H, H-1), 3.75 (*s*, 3H, *N*-CH_3), 4.00 (*t*, 2H, H-3), 3.23 (*t*, 2H, H-4), 7.0 (*s*, 1H, H-5), 6.20 (*s*, 2H, –O$\underline{CH_2}$O–), 7.25 (*s*, 1H, H-8). ^{13}C NMR (CD_3OD, 75 MHz): δ166.1 (C-1), 47.5 (*N*-$\underline{CH_3}$), 50.5 (C-3), 26.4 (C-4), 136.2 (C-4a), 109.8 (C-5), 157.4 (C-6), 149.1 (C-7), 112.6 (C-8), 119.6 (C-8a), 104.6, (–O–$\underline{CH_2}$O–).

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