Alkaloids from *Consolida oliveriana*

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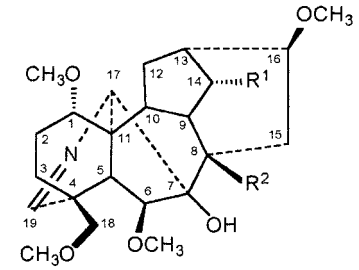
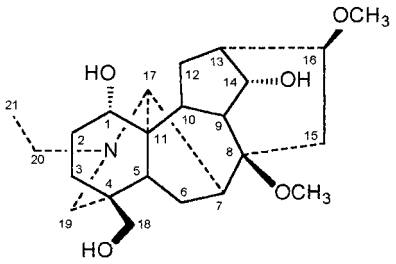
Four new diterpenoid alkaloids, olivimine (**1**), olividine (**2**), 8-*O*-methylcolumbianine (**3**), and 7α-hydroxycossonidine (**4**), were isolated from the aerial parts of *Consolida oliveriana*. Compounds **1** and **2**, **3**, and **4** belong to the lycoctonine-azomethine, aconitine, and hetisine types, respectively, and their structures were elucidated by spectral data interpretation.

In connection with studies of species in the genera *Delphinium*, *Aconitum*, and *Consolida*, which possess diverse biological activities,[1] in the present investigation we have isolated from the aerial parts of *Consolida oliveriana* (DC.) Schröd. (Ranunculaceae) the already known alkaloids ajaconine, anthranoyllycoctonine, browniine, consolidine, 14-*O*-deacetylpubescenine, delcosine, delphatine, delsoline, dihydroajaconine, gigactonine, 18-hydroxy-14-*O*-methylgadesine, lycoctonine, 19-oxodelphatine, pubescenine, and takaosamine, together with the new alkaloids olivimine (**1**), olividine (**2**), 8-*O*-methylcolumbianine (**3**), and 7α-hydroxycossonidine (**4**). The known alkaloids were identified by analysis of their ^{1}H and ^{13}C NMR spectra and comparison with published data. In a previous study on this species, the structure elucidation of the new norditerpenoid alkaloid consolidine was reported, in addition to the isolation of the known alkaloids ajaconine, delsoline, gigactonine, and pubescenine.[2]

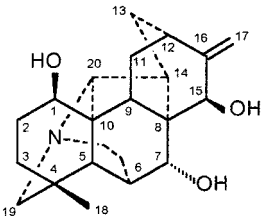


1 $R^1 = OCH_3$; $R^2 = OH$

2 $R^1 = OAc$; $R^2 = OCH_3$



3



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Results and Discussion

Analysis of the NMR spectra of olivimine (**1**) ($C_{24}H_{37}NO_7$) and olividine (**2**) (C_{26} $H_{39}NO_8$) indicated that they are norditerpenoid alkaloids belonging to the lycoctonine type with an C(19)═N azomethine group.[3] The NMR spectra of **1** (Table 1) did not show signals for angular methyl and *N*-ethyl groups, although they gave singlet resonances for four secondary methoxyl groups at *δ* 3.15, 3.35, 3.38, and 3.43 and for two quaternary oxygenated carbons at *δ* 77.3 and 86.4 that could be attributed to a tertiary α-glycolic system, which is characteristic of a lycoctonine-type alkaloid.[3] Moreover, compound **1** gave signals for an azomethine function at *δ* 7.29 (s; *δ* 164.5 d) and for a primary methoxyl group at *δ* 3.34 (s; *δ* 59.0 q; *δ* 74.2 t) which was located at C-18 following the usual substitution pattern in norditerpenoid alkaloids.[3,4] The one-proton signals at *δ* 3.63, 3.28 (each d, $J = 9.3$ Hz, *δ* 74.2 t), assigned to the nonequivalent C-18 methylene protons, gave three-bond connectivities in the HMBC experiment with methoxyl (*δ* 59.0), methylene (*δ* 24.2), and methine (*δ* 44.8) carbons that have consequently been assigned to CH_3O-18, C-3, and C-5, respectively. Further correlations were also observed in the HMBC experiment between the azomethine proton with C-18 and the methine amine-carbon at *δ* 64.4 (*δ* 3.78 s), and long-range coupling in the ^{1}H−^{1}H COSY spectrum with the one-proton signal at *δ* 3.78 (Table 1, Supporting Information), permitting the azomethine group to be located at C(19)═N and the latter pair of signals to be attributed to C-17 and H-17. The secondary methoxyl groups were located at C-1, C-6, C-14, and C-16 on the basis of their ^{1}H and ^{13}C NMR resonances and were corroborated by the analysis of the 2D NMR spectral data. Thus, the triplet signal observed at *δ* 3.65 (t, $J = 4.5$ Hz) in the ^{1}H NMR spectrum, which is characteristic of the H-14*β* proton, showed C−H long-range correlations with the carbon resonances at *δ* 57.7 q, 77.3 s, and *δ* 82.3 d, in accordance

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Table 1. ^{1}H and ^{13}C NMR Data for Compounds **1**−**4** in $CDCl_3$[a]

	1		**2**		**3**		**4**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1α							4.20 (br s, $W_{1/2}$ = 6.0 Hz)	65.9 d
1*β*	3.22 (t, 3.8)	81.6 d	3.20 (t, 4.6)	81.5 d	3.75 (t, 3.5)	72.1 d		
2α	1.77[b]	20.7 t	1.68[b]	21.7 t	1.59 (m)	29.8 t	1.78 (m)	27.0 t
2*β*	1.36 (dddd, 12.6, 12.6, 10.8, 3.4)	20.7 t	1.48 (dddd, 12.0, 11.6, 10.5, 3.4)	21.7 t	1.57 (m)	29.8 t	1.75 (m)	27.0 t
3α	1.55 (ddd, 11.4, 11.4, 6.5)	24.2 t	1.66[b]	25.1 t	1.92 (m)	26.2 t	1.31 (m)	27.6 t
3*β*	1.80 (ddd, 13.4, 8.7, 3.0)	24.2 t	1.66[b]	25.1 t	1.92 (m)	26.2 t	1.80 (m)	27.6 t
4		50.5 s		48.6 s		37.9 s		37.2 s
5	1.83 (s)	44.8 d	1.69 (s)	48.8 d	1.87 (d, 6.9)	41.1 d	1.93 (s)	54.3 d
6α	3.78 (s)	91.1 d	3.66 (s)	91.6 d	1.81 (m)	23.7 t	3.39 (br s, $W_{1/2}$ = 7.0 Hz)	71.1 d
6*β*					1.51 (m)	23.7 t		
7		86.4 s		89.1 s	2.44 (d, 7.6)	39.1 d	3.97 (d, 2.7)	67.1 d
8		77.3 s		79.9 s		78.9 s		50.5 s
9	2.38 (dd, 4.6, 7.3)	38.4 d	3.14 (dd, 6.8, 4.7)	40.6 d	2.11 (t, 5.7)	45.3 d	1.97 (m)	39.8 d
10	1.94 (ddd, 11.7, 11.7, 6.6)	43.3 d	2.03[b]	43.5 d	1.91 (m)	43.8 d		53.8 s
11α		47.5 s		48.2 s		49.0 s	1.95 (m)	26.5 t
11*β*							1.78 (m)	26.5 t
12α	1.47 (dd, 13.5, 4.8)	30.4 t	1.47 (br d, 7.9)	29.1 t	1.65 (m)	29.7 t	2.25 (m)	33.6 d
12*β*	2.02 (ddd, 11.8, 11.8, 7.5)	30.4 t	2.02[b]	29.1 t	2.04 (ddd, 14.1, 11.6, 7.7)	29.7 t		
13α	2.83 t (6.0)	43.0 d	2.55 (t, 6.3)	36.8 d	2.37[b]	40.1 d	1.08 (dt, 13.5, 2.8)	32.4 t
13*β*							1.76 (m)	32.4 t
14*β*	3.65 (t, 4.5)	84.2 d	4.81 (t, 3.9)	75.2 d	4.12 (t, 4.6)	75.5 d	2.18 (br d, 11.1)	38.1 d
15α	2.86 (dd, 14.8, 8.6)	32.9 t	2.79 (dd, 15.7, 8.7)	28.7 t	2.17 (m)	37.2 t	4.51 (s)	65.9 d
15*β*	1.74 (dd, 14.5, 7.7)	32.9 t	2.00 (dd, 16.0, 6.4)	28.7 t	2.17 (m)	37.2 t		
16	3.28 (t, 10.1)	82.3 d	3.39 (t, 9.0)	82.2 d	3.38 (t, 8.9)	82.9 d		155.1 s
17	3.78 (s)	64.4 d	3.87 (d, 2.4)	65.4 d	2.73 (s)	63.7 d	*Z*-5.00 (s)	109.2 t
17							*E*-4.97 (s)	109.2 t
18 A	3.63 (d, 9.3)	74.2 t	3.50 (d, 9.3)	75.5 t	3.48 (d, 10.5)	68.4 t	1.04 (s)	28.3 q
18 B	3.28 (d, 9.3)	74.2 t	3.44 (d, 9.3)	75.5 t	3.32 (d, 10.5)	68.4 t		
19 A	7.29 (s)	164.5 d	7.52 (s)	167.7 d	2.37 (d, 11.2)	56.5 t	2.49 (d, 12.6)	62.3 t
19 B					2.09 (d, 11.2)	56.5 t	2.43 (d, 12.5)	62.3 t
20 A					2.55 (m)	48.4 t	2.45 (s)	74.9 d
20 B					2.49 (m)	48.4 t		
21					1.14 (t)	13.0 q		
CH_3O-1α	3.15 (s)	56.2 q	3.15 (s)	56.0 q				
CH_3O-6*β*	3.38 (s)	57.9 q	3.40 (s)	59.4 q				
CH_3O-8			3.50 (s)	52.4 q	3.19 (s)	48.6 q		
CH_3O-14α	3.43 (s)	57.7 q						
CH_3COO-14α			2.05 (s)	21.3 q				
CH_3O-16*β*	3.35 (s)	56.2 q	3.33 (s)	56.2 q	3.39 (s)	56.5 q		
CH_3O-18	3.34 (s)	59.0 q	3.39 (s)	59.4 q				
HO-8	4.15 (s)							

[a] Chemical shifts in ppm relative to solvent ($CDCl_3$) signal. Assignments based on HMQC. Coupling constants (*J*) in Hz. ^{13}C NMR multiplicities were established by DEPT data. [b] Signals overlapped.

with the presence of CH_3O-14α, HO-8, and CH_3O-16*β* groups in the molecule. In the ^{1}H−^{1}H COSY spectrum, the signal for H-5 showed *W* coupling with the H-17 proton and a weak coupling with the one-proton resonance at *δ* 3.78 (s; *δ* 91.1 d), which clearly indicated the presence of a CH_3O-6*β* group. The remaining secondary methoxyl group was placed at CH_3O-1α on the basis of the ^{13}C NMR chemical shifts of the doublet at *δ* 81.6 (*δ* 3.22 t, *J* = 3.8 Hz).[5,6]

The NMR spectra of olividine (**2**) were very similar to those of **1** and gave signals for an azomethine group at *δ* 7.52 (*δ* 167.7 s), three secondary methoxyl groups (*δ* 3.15, 3.40 and 3.33, each s), and one primary methoxyl group (*δ* 3.39 s), which were placed in the same positions as for **1** (Table 1). In addition, a signal was evident for a tertiary methoxyl group (*δ* 3.50 s), suggesting the presence of a monomethylated α-glycolic system, and a secondary acetate group (*δ* 2.05 s; *δ* 171.2 s), which was tentatively located at CH_3COO-14α in view of the multiplicity of its geminal proton. These deductions, together with the stereochemistry of the functional groups, were fully confirmed by close inspection of the 2D NMR data (Table 2, and Tables 1 and 2, Supporting Information). The structures of both compounds **1** and **2** were further substantiated by comparison of their ^{13}C NMR values with those of related compounds such as anhweidelphinine,[6] lamarckinine,[7] ajadinine,[8] and acoseptridine.[9]

The NMR spectra of 8-*O*-methylcolumbianine (**3**) ($C_{23}H_{37}NO_5$) (Table 1) did not show resonances for an angular methyl group, but displayed signals for an *N*-ethyl group at *δ* 2.49 and 2.55 (each m, *δ* 48.4 t) and *δ* 1.14 (t, *δ* 13.0 q) and for secondary and tertiary methoxyl groups at *δ* 3.39 and 3.19 (each s; *δ* 56.5, 48.6 each q; *δ* 82.9 d, 78.9 s), which are characteristic of a norditerpenoid alkaloid.[3] The ^{13}C NMR spectrum showed the presence of only one quaternary oxygenated carbon at *δ* 78.9, pointing to an aconitine-type norditerpenoid alkaloid possessing a tertiary methoxyl at C-8.[3,4] The other oxygen functions were primary and secondary hydroxyls located at OH-18 (*δ* 3.32 and 3.48, each d, *J* = 11.2 Hz; *δ* 68.4 t); HO-1α (*δ* 3.75 t, *J* = 3.5 Hz; *δ* 72.1 d); and HO-14α (*δ* 4.12 t, *J* = 4.6 Hz; *δ* 75.5 d) as established due to their ^{1}H and ^{13}C NMR signals and 2D NMR data (Tables 1 and 2, and Tables 1 and 2, Supporting Information). The proposed structure for the alkaloid **3** was

Table 2. HMBC Data of **1**−**4** in $CDCl_3$

proton	**1**	**2**	**3**	**4**
1α				C-3, C-5
1β	C-3, C-10, CH_3O-1	C-3, C-10, C-5,[a] C-17,[a] CH_3O-1	C-3, C-10	
2α		C-3, C-4	C-3	C-10
2β	C-3	C-3, C-4	C-3	C-10
3α	C-1, C-4, C-18, C-19	C-1, C-2, C-18, C-19	C-1, C-18	C-1, C-4, C-5, C-18
3β	C-1, C-4, C-5, C-19	C-1, C-2, C-18, C-19	C-1, C-18	C-1, C-5
4				
5	C-1, C-3, C-4, C-6, C-7, C-10, C-11, C-17, C-19	C-1, C-4, C-6, C-10, C-11, C-17, C-18, C-19	C-7, C-10, C-17	C-3, C-18, C-19, C-20
6α	C-4, C-7, C-8, C-11, CH_3O-6	C-4, C-7, C-8, C-11, CH_3O-6	C-4, C-8	C-4, C-7, C-8, C-10, C-20
6β			C-4, C-5, C-8, C-11	
7			C-5, C-8, C-9, C-11, C-17	C-8, C-14
9	C-12, C-13, C-15, C-16	C-10, C-12, C-13, C-14, C-15	C-12, C-13, C-14	C-5, C-7, C-12, C-14, C-20
10	C-5, C-8, C-11, C-12, C-17	C-5, C-8, C-12, C-17	C-8, C-11, C-17	
11α				C-8, C-10, C-16
11β				C-8, C-10, C-13, C-16
12α	C-9, C-11, C-13, C-14	C-10, C-11, C-13, C-14, C-16	C-9, C-10, C-11, C-14, C-16	
12β	C-9, C-10, C-13, C-16		C-9, C-16	
13α	C-8, C-9, C-12, C-15	C-9, C-10, C-14, C-15, C-16	C-9, C-14, C-15, C-16	C-14, C-16, C-20
13β				C-11
14	C-8, C-16, CH_3O−14	C-7,[a] 8, 9,[a]13,[a] 16, 171.2 s[a]	C-8, C-16	C-9, C-10
15α	C-7, C-8, C-9, C-13, C-16	C-7, C-8, C-9, C-13, C-16	C-8, C-9, C-16	C-7, C-8, C-9, C-12, C-16, C-17
15β	C-7, C-8, C-16	C-7, C-8, C-16	C-8, C-9, C-16	
16	C-12, C-14, CH_3O-16	C-12, C-14, CH_3O-16	C-12, C-14, CH_3O-16	
17-*Z*[b]	C-5, C-6, C-7, C-8, C-19	C-5, C-6, C-7, C-8, C-19	C-5, C-6, C-8, C-19, C-20	C-12, C-15, C-16
17-*E*[b]				C-12, C-15, C-16
18 A	C-3, C-4, C-5, C-19, CH_3O-18	C-3, C-5, C-19, CH_3O-18	C-3, C-19	C-3, C-4, C-5, C-19
18 B	C-3, C-4, C-5, C-19, CH_3O-18	C-3, C-5, C-19, CH_3O-18	C-3, C-4, C-5	
19 A	C-4, C-5, C-17, C-18	C-5, C-17	C-3, C-4, C-5, C-17	C-3, C-4, C-20
19 B			C-3, C-4, C-18, C-20	C-3, C-4, C-20
20 A			C-17, C-19, C-20	C-1, C-6, C-8, C-9, C-13, C-19
20 B			C-17, C-19, C-20	
21			C-20	
CH_3O-1α	C-1	C-1		
CH_3O-6β	C-6	C-6		
CH_3O-8		C-8	C-8	
CH_3O-14α	C-14			
CH_3COO-14α		C-14, 171.2 s		
CH_3O-16β	C-16	C-16	C-16	
CH_3O-18	C-18	C-18		
HO-8	C-15			

[a] Acquired for $J = 4$ Hz. [b] Nomenclature *E*/*Z* for vinylinic protons only should be considered for compound **4**.

confirmed by comparison of the ^{13}C NMR values with those of columbianine, where the normal α and β effects on C-7, C-8, C-9, and C-15, respectively, were evident.[10]

The fourth new compound, 7α-hydroxycossonidine (**4**) ($C_{20}H_{27}NO_3$), proved to be a hetisine-type diterpenoid alkaloid possessing three secondary hydroxyl groups at C-1, C-7, and C-15. The NMR spectra gave typical signals of a diterpenoid alkaloid with an angular methyl group at δ 1.04 (s; δ 28.3 q) and an exocyclic methylene at δ 5.00, 4.97 (each s; δ 109.2 t) (Table 1). In the HMBC spectrum, the angular methyl signal gave C−H long-range connectivities with ^{13}C NMR resonances at δ 27.6 t, 37.2 s, δ 54.3 d, and δ 62.3 t, enabling these signals to be ascribed to C-3, C-4, C-5, and C-19, respectively. The one-proton resonance at δ 3.39 (br s, $W_{1/2} = 7.0$ Hz; δ 71.1 d) was assigned to H-6 by taking into account the correlations observed in the ^1H−^1H COSY spectrum with H-5, δ 1.93 (s; δ 54.3 d) and with the one-proton resonance at δ 2.45 (s; δ 74.9 d) for H-20 (*W* coupling) (Table 1, Supporting Information). Additionally, a further correlation was obtained from the same experiment between H-6 and the carbinyl proton signal at δ 3.97 (d; $J = 2.7$ Hz; δ 67.1 d), permitting one of the hydroxyl groups to be located at C-7. A HO-7α stereochemistry was deduced from the correlations shown in the ROESY spectrum between the H-7β signal with H-5 and the one-proton resonance at δ 1.97 (m; δ 38.9 d) assigned to H-9 (Table 4, Supporting Information). A secondary hydroxyl group was placed at HO-1β, on the basis of the three-bond connectivities encountered in the HMBC spectrum between the carbinyl proton signal at δ 4.20 (br s; $W_{1/2} = 6.0$ Hz; δ 65.9 d) with C-3 and C-5 and because of the spatial correlation in the ROESY spectrum with the H-20 signal. The other carbinyl proton signal at δ 4.51 (s; δ 65.9 d) gave, among others, three-bond connectivities with the C-7 and C-17 carbon resonances in the HMBC experiment and a correlation in the ROESY spectrum with the one-proton resonance at δ 2.18 (br d, $J = 11.1$ Hz; δ 38.1 d) that was assigned to H-14, because of the three-bond correlation shown in the HMBC experiment between H-9 and H-7β with the ^{13}C NMR signal at δ 38.1, for C-14. These observations were consistent with the presence of a HO-15β function in the molecule. The remaining NMR signals were in agreement with the proposed structure of **4**, and the assignments were made on the basis of the 2D NMR data (Table 2, and Tables 1 and 2, Supporting Information) and by comparison with the spectra of cossonidine.[11] Thus, stronger high-field chemical shifts observed in carbons C-14 ($\Delta\delta = -5.5$) and C-15 ($\Delta\delta = -5.7$) than in carbons C-5 ($\Delta\delta = -2.3$) and C-9 ($\Delta\delta = -1.6$) were noteworthy when compared with those of cossonidine due to the γ-gauche effect exerted by the alcohol group at C-7 over C-14 and C-15 in the α configuration.[12,13]

Experimental Section

General Experimental Procedures. The optical rotations were obtained on a Perkin-Elmer 241 polarimeter, 1 dm cell. IR spectra were recorded with a Perkin-Elmer 1600 spectrophotometer. 1D and 2D NMR spectra were recorded using Bruker AMX-500 and WP-200 SY spectrometers; δ values in parts per million relative to solvent ($CDCl_3$) signal. DEPT, $^1H-^1H$ COSY, HMQC, HMBC ($J = 8$ Hz), and ROESY (spin lock 500 ms) experiments were carried out with the pulse sequences given by Bruker. Mass spectra were measured with a Micromass Autospec instrument. Alumina Merck Art. 1077 and 1101 were used for column chromatography and preparative TLC, respectively. Zones on TLC plates were visualized with Dragendorff's reagent.

Plant Material. *Consolida oliveriana* was collected and identified near Pazarkik in eastern Turkey at an altitude of 980 m, by Prof. Julián Molero Briones, Botany Departament, Faculty of Pharmacy, University of Barcelona, where a voucher specimen (BCF-37810) has been deposited.

Extraction and Isolation. Dried powdered aerial parts of the plant (3.9 kg) were defatted with hexane (7 L) over one month and extracted repeatedly with 80% ethanol (7 L) at room temperature over one week. After removing the solvent under a vacuum, the EtOH extract (280 g) was treated with 0.1 M H_2SO_4 and filtered. The acidic solution was subjected to a pH gradient extraction using 10% NaOH, and the aqueous phases were extracted with CH_2Cl_2 to obtain a neutral residue at pH 7 (10.6 g) and a basic residue at pH 12 (2.2 g). The neutral residue was subjected to column chromatography over alumina (6.5 × 15 cm), eluting with EtOAc (100%) and EtOAc−MeOH (90:10), to afford 57 fractions of 300 mL each. Fractions 1−28, eluted with EtOAc (100%), were combined to obtain three alkaloidal residues that were individually subjected to further alumina column chromatography to yield olividine (**2**, 1.6 mg) from fractions 1−5; olivimine (**1**, 12 mg) from fractions 6−10, and consolidine (60 mg), delphatine (7 mg), delsoline (10 mg), and pubescenine (5 mg) from fractions 11−28. Fractions 29−57, eluted with EtOAc−MeOH (90:10), were combined and chromatographed over another alumina column using EtOAc−MeOH (90:10) as mobile phase to yield anthranoyllycoctonine (1.5 mg), browniine (3 mg), 14-*O*-deacetylpubescenine (6.5 mg), delcosine (8 mg), gigactonine (8.5 mg), 18-hydroxy-14-*O*-methylgadesine (3 mg), lycoctonine (2 mg), 19-oxodelphatine (12 mg), pubescenine (5 mg), takaosamine (2.5 mg), and 8-*O*-methylcolumbianine (**3**, 4 mg). The basic residue was chromatographed over a Sephadex LH-20 column using hexane−CH_2Cl_2−MeOH (40:30:30) as mobile phase to obtain an alkaloidal residue (1.5 g). This material was then subjected to alumina column chromatography (4.5 × 7 cm), eluting with EtOAc−MeOH (90:10), to yield ajaconine (300 mg), delphatine (6 mg), dihydroajaconine (10 mg), lycoctonine (4 mg), and 7α-hydroxycossonidine (**4**, 3 mg). The new alkaloids were further purified by preparative TLC over alumina plates.

Olivimine (1): amorphous solid; $[\alpha]^{25}_D$ +77° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3462, 2940, 2824, 1651, 1462, 1385, 1321, 1200, 1091, 1037, 973, 931, 751, 664 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m/z* 451 $[M]^+$ (7), 436 $[M - CH_3]^+$ (15), 420 $[M - OCH_3]^+$ (22), 405 (23), 390 (16), 373 (12), 360 (25), 358 (16), 296 (5), 217 (5), 149 (5), 84 (73), 75 (54), 49 (100); HREIMS *m/z* 451.2578 (calcd for $C_{24}H_{37}O_7N$, 451.2570).

Olividine (2): amorphous solid; $[\alpha]^{25}_D$ +96° (*c* 0.8, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2888, 2821, 1737, 1645, 1460, 1365, 1248, 1199, 1153, 1093, 1054, 981, 909, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m/z* 493 $[M]^+$ (16), 478 (72), 464 (28), 463 (100), 462 $[M - OCH_3]^+$ (22), 450 $[M - COCH_3]^+$ (22), 448 (28), 434 $[M - OCOCH_3]^+$ (38), 433 (95), 418 (32), 402 (45), 388 (60), 84 (47), 71 (57); HREIMS *m/z* 493.2664 (calcd for C_{26} $H_{39}O_8N$, 493.2675).

8-*O*-Methylcolumbianine (3): amorphous solid; $[\alpha]^{25}_D$ −2.9° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3406, 2930, 1590, 1461, 1073, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m/z* 407 $[M]^+$ (33), 406 (5), 392 $[M - CH_3]^+$ (24), 391 (26), 390 $[M - OH]^+$ (100), 389 $[M - H_2O]^+$ (5), 376 $[M - OCH_3]^+$ (32), 374 (19), 344 (6), 223 (4), 91 (5), 58(10); HREIMS *m/z* 407.2667 (calcd for $C_{23}H_{37}O_5N$, 407.2671).

7α-Hydroxycossonidine (4): amorphous solid; $[\alpha]^{25}_D$ +25° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3365, 2929, 1685, 1567, 1455, 1410, 1132, 1078, 1035, 1009, 984, 921, 843, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m/z* 329 $[M]^+$ (46), 314 $[M - CH_3]^+$ (5), 313 (24), 312 $[M - OH]^+$ (100), 311 $[M - H_2O]^+$ (4), 301 (4), 294 (7), 175 (5), 91 (5); HREIMS *m/z* 329.1980 (calcd for $C_{20}H_{27}NO_3$, 329.1990).

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Supporting Information Available: ^{13}C NMR and DEPT spectra for compounds **1**−**4**. Table 1 ($^1H-^1H$ COSY data for compounds **1**−**4**) and Table 2 (ROESY data for compounds **1**−**4**). This material is available free of charge via the Internet at http//pubs.acs.org.

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