TATSIRINE, A DITERPENOID ALKALOID FROM *DELPHINIUM TATSIENENSE* FRANCH

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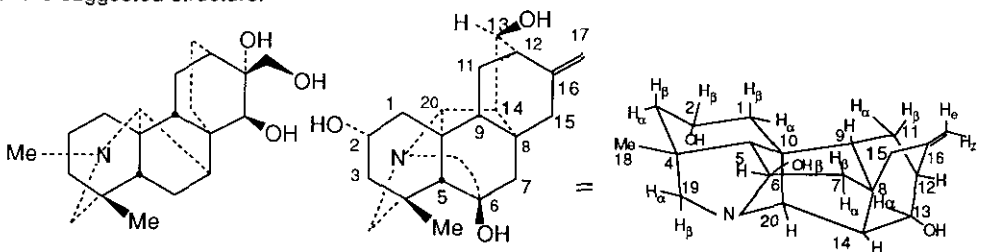
Abstract – Tatsirine, isolated from the roots of Delphinium tatsienense, has been assigned structure (2). The structure was established on the basis of homonuclear ^1H COSY, fixed-evolution HETCOR, two-dimensional nOe and selective INEPT studies on 5.

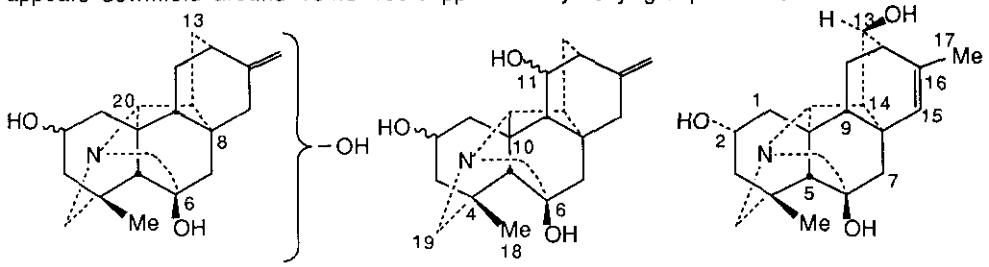
We have reported in earlier communications the structure determination of the alkaloids deltatsine,[1] delelatine,[2] tatsidine,[3,4] tatsiensine[5] and tatsinine[6] isolated from the roots of *Delphinium tatsienense* Franch (Family Ranunculaceae). The plant also contains the norditerpenoid alkaloids browniine, deacetylambiguine, delcosine, lycoctonine and the diterpenoid alkaloids ajaconine, hetisine and hetisinone. From the polar alkaloidal fraction E_1,[5] two diterpenoid alkaloids were obtained by preparative tlc on alumina. One of these has been identified as dictyzine (**1**) and the other alkaloid designated as *tatsirine* has been assigned structure (**2**). We describe here the complete ^1H and ^{13}C nmr spectral analysis of **2** which is the basis of the suggested structure.



1 **2**

The mass spectrum of tatsirine indicated the molecular formula $C_{20}H_{27}NO_3$. The ^{13}C nmr spectrum (FX-60) showed 19 signals for 20 carbon atoms of tatsirine at ppm: 149.1, 106.6, 97.9, 70.6, 67.4, 66.7, 60.9(2C), 51.8, 49.4, 48.5, 44.8, 42.9, 42.3, 41.6, 36.8, 33.9, 32.4, 31.2 and 22.4. The signals at 149.1 and 106.6 ppm suggested that the alkaloid is of the 'hetisine' type, and these could be assigned to C-16 and C-17, respectively, of the exocyclic methylene group. The two broad singlets (δ 4.73 and 4.85) in the ^1H nmr spectrum supported the presence of the exocyclic methylene group. The signal at 97.9 ppm is clearly due to the carbinolamine carbon as in geyrinine,[7] and spirasine XII[8] which indicated the placement of one of the three hydroxyl groups at C-6. The remaining two hydroxyl groups can be located at C-1, C-2, C-3, C-7, C-11, C-13 or C-15. In hetisine-type alkaloids possessing a hydroxyl group at C-15, the signal for C-16

appears downfield around 154.5–156.0 ppm.[9] A hydroxyl group at C-15 in tatsirine is therefore dis-



3 **4** **5**

counted. In alkaloids bearing a hydroxyl group at C-7, e.g. sadosine,[10] the signal for C-8 appears around 48.3 ppm. As the C-8 signal in tatsirine appears at 44.8 ppm, C-7 does not bear a hydroxyl group. When a hydroxyl group is present at C-1, e.g. hanamisine, hypognavine and hypognavinol, the adjacent quaternary carbon at C-10 appears in the range 52.0–55.0 ppm.[9,11] As the C-10 signal in tatsirine is seen at 49.4 ppm, C-1 does not appear to bear a hydroxyl group. When no hydroxyl group is present at C-1, C-2 or C-3 in ring A, the signal for C-2 appears around 19.8 ppm.[8,12] Since there is no resonance for a methylene carbon around this region, C-2 must bear a hydroxyl group. No hetisine-type alkaloids have been isolated so far, which are substituted by a hydroxyl group at C-3 only. In the case of alkaloids which bear hydroxyl groups at the C-2 and C-3 positions, the signal for C-4 appears around 51.0 ppm (e.g. geyrinine).[7] The quaternary carbon resonance for C-4 in tatsirine appears at 36.8 ppm. Therefore tatsirine is not a C-2, C-3 -diol. The above evidence leads to the location of the third hydroxyl group at C-11 or C-13 and the partial structure (**3**). On the basis of the existing spectral data, it was difficult to make a choice between the two alternative structures **4** and **2** (stereochemistry of the hydroxyl groups not yet defined). *We therefore decided to carry out high-field nmr studies. The sample* (~8 mg) recovered after the preliminary nmr spectral determination was dissolved in methylene chloride-acetone and passed through alumina and eluted with methylene chloride-5% methanol. This afforded a homogeneous compound (~6 mg) (**5**), which was taken for detailed nmr experiments. Spectral data of the recovered sample, showed that the exocyclic methylene group had migrated into the ring as in **5**. This was seen in the disappearance of the signals assignable to the exocyclic methylene protons, with the appearance of a single vinyl resonance in the ^1H nmr spectrum (CD_3OD; δ 5.54, s) (Table 1). Furthermore, a second methyl singlet was also apparent due to a vinylic methyl group (δ 1.83). In the ^{13}C nmr spectrum (CD_3OD; Table 2), the two vinylic carbons had shifted to δ 144.1 (s) and 124.1 (d) in CD_3OD (δ 143.2 and 123.4 in CD_2Cl_2). An APT spectrum confirmed the multiplicity of these olefinic carbons. In CD_3OD, the carbinolamine carbon C-6 appeared at 100.7 ppm. Isomerization of the double bond must have taken place owing to the exposure of tatsirine to traces of acid in $CDCl_3$ while recording of the original ^{13}C nmr spectrum, followed by contact with alumina.

The ^{13}C nmr spectrum (CD_3OD), exhibited only eighteen signals, and two additional resonances were under the solvent peak. One of these signals appearing at 49.8 ppm due to C-9 was observed in an APT experiment as a methine, and was also revealed in the fixed-evolution HETCOR spectrum (Figure 1). The last resonance attributed to C-8, could not be seen in the APT spectrum and therefore must be due to a quaternary carbon. This signal was revealed using CD_2Cl_2 as solvent (Table 2) but was not observed in CD_3OD.

Table 1. ^{1}H Nmr Chemical Shift Assignments of **5**

Proton No.	CD_3OD (ppm)	Multiplicity (J,Hz)	CD_2Cl_2 + 10% C_5D_5N**	Multiplicity (J, Hz)
H15	5.54	br s	5.50	s
H2β	4.14	br s, $W_{1/2}$ = 13.0	4.27	br s, $W_{1/2}$ = 12.1
H20	3.83	s	4.30	s
H13α	3.53	br s, $W_{1/2}$= 8.2	3.64	br s
H19α	3.48	d,11.4	3.88	d, 11.2
H19β	3.20	d, 11.4	3.47	d, 11.2
H12	2.42	br s	2.49	br s
H7β	2.35	d, 13.7	2.55	AB
H7α	2.22	d, 13.7	2.55	AB
H1α	1.96	br d, 14.2	2.05	br d, 12.5
H17	1.83	s	1.84	s
H3α	*1.86	m	1.96	br d, 14.7
H11α	*1.70	m	1.63	dd, 14.2, 3.4
H5	1.66	s	1.75	s
H3β	*1.56	m	#1.55	m
H1β	*1.52	m	#1.47	m
H14	*1.50	***	1.87	br s,$W_{1/2}$=7.1
H9	*1.46	***	1.51	m
H18	1.40	s	1.51	s
H11β	1.10	br t, 11.6	1.11	br t, 12.0

* The chemical shifts are read from cross sections of fixed evolution time HETCOR due to their heavy overlap in ^{1}H nmr spectrum.

\# The chemical shift is obtained from cross section COSY spectrum.

** The appearance of the H-7α,7β spin system is very sensitive to the amount of pyridine in the solvent. Thus in the initial preparation of the sample in CD_2Cl_2/10% pyridine-d_5, the H-7 methylene protons appeared as a broadened singlet (δ 2.55, 2H) with virtual coupling, but after a few days in the nmr tube, this became an AA'-system due to evaporation of some CD_2Cl_2.

*** The multiplicities of these signals were not discernible because of overlap.

Table 2. ^{13}C Nmr Chemical Shifts of **5** in CD_3OD and CD_2Cl_2

Carbon No.	δ (CD_3OD)[a] ppm		δ (CD_2Cl_2) ppm	δ (CD_2Cl_2 + 10% C_5D_5N) ppm
16	144.1	s	143.2	143.8
15	124.1	d	123.4	122.4
6	100.7	s	98.0	101.4
13	75.4	d	74.6	74.0
20	70.8	d	69.7	69.2
2	66.9	d	66.3	65.2
5	61.0	d	59.6	59.2
19	60.3	t	59.0	58.1
14 [b]	59.1	d	58.3	57.8
9 [b]	49.8[b]	d	48.8	48.8
8	a	s	48.3	48.2
10	45.9	s	45.0	44.8
12	44.0	d	42.7	42.9
3	42.4	t	41.6	41.7
7	41.8	t	41.5	40.7
4	37.6	s	36.7	36.7
1	35.0	t	34.7	34.4
18	31.1	q	30.7	30.5
11	26.3	t	25.5	25.4
17	21.8	q	21.8	21.7

[a] C-8 is under solvent peak

[b] C-14 and C-9 could not be distinguished in HETCOR and COSY in CD_3OD. The signal at 49.8 ppm was observed in an APT experiment in CD_3OD as solvent; C-14 and C-9 can be distinguished clearly in the fixed evolution HETCOR with CD_2Cl_2 + 10% pyridine-d_5 as solvent.

From the fixed-evolution HETCOR spectrum[13] (Figure 1), the carbinol carbons were readily located at δ 66.9 (C-2) and 75.4 (C-11 or C-13), one bond coupled to the methines at δ 4.14 (br s) and 3.53 (br s), re-

Table 3. ^1H-^1H Correlations and nOe's of **5** in CD_3OD

Observed H	nOe's (NOESY) (in CD_3OD)	Correlations (COSY) (in CD_3OD)	nOe's (NOESY) (in CD_2Cl_2 + 10% C_5D_5N)	Correlations (COSY) (in CD_2Cl_2 + 10% C_5D_5N)
H15	H7α, H7β, H17	H12, H17	H7α, H7β, H17	H17, H12
H2β	H1α, H1β, H3α, H3β	H1α, H1β, H3α,H3β	H1α, H1β, H3α, H3β	H1α, H3α, H1β, H3β
H20	H19α, H1α, H14	none	H19α, H13α, H14	none
H13α	H12, H11α, H14	H12, H14	H20, H12, H14, H11α	H12, H14
H19α	H20, H3α, H19β	H-19β	H20, H19	H19β
H19β	H19α, H18	H-19α	H19α, H18	H19α
H12	H13α, H17, H11α,H11β	H11β (w), H11α (s), H13α	H13α, H17, H11α	H13α, H11α, H11β, H9, H15
H7β	H7α, H5, H9	H7α, H9 (w)	H14, H9	none
H7α	H7β, H14	H7β		
H1α	H2β, H11α, H1β	H1β, H2β	H2β, H11α, H1β	H1β
H17	H12, H15	H15	H12, H15	H15 (long range)
H3α	H3β, H2β, H18, H19α	H3β, H2β	H2β, H3β	H3β
H5	H9, H18, H7β	none	H9	none
H11α	H12, H11β, H1α	H11β, H12	H11β, H1α, H12, H13α	H11β, H12
H 3β	H3α, H2β	H3α, H2β	H3α	H3α
H1β	H1α, H2β	H-1α, H-2β	H1α	H1α
H9	H7β, H11α, H5	H11β, H7	H5, H7	H11β
H14	H20, H7α, H13α	H13α	H20, H13α, H7α, H7β	H13α
H18	H5, H19β	none	H19β	none
H11β	H11α, H9, H12	H11α, H9, H12	H11α	H11α, H9

spectively. The lower field of these was coupled to at least three other protons as shown by the COSY spectrum (Figure 2). Moreover, the cross peak to δ ~1.6 was sufficiently broad to indicate coupling to two protons with a near identical chemical shift. The fixed-evolution HETCOR spectrum confirmed this by revealing that each of the two distinct couplings to the broad singlet at δ 4.14 (cross peaks at δ 1.96 and 1.83) was the gem partner of methylene pairs with the second proton from each located at ~1.6 ppm (Figure 1). Thus, one of the two secondary alcohols must be flanked by methylenes, and this is only possible at C-2, thereby confirming the chemical shift rationale presented earlier. The carbon signals for C-1, C-2 and C-3 were therefore confirmed as δ 35.0, 66.9 and 42.4, respectively. Furthermore, the broad singlet assigned to H-2 must be equatorial ($W_{1/2}$ = 13.0 Hz) and therefore the hydroxyl group at C-2 must be α and axial.

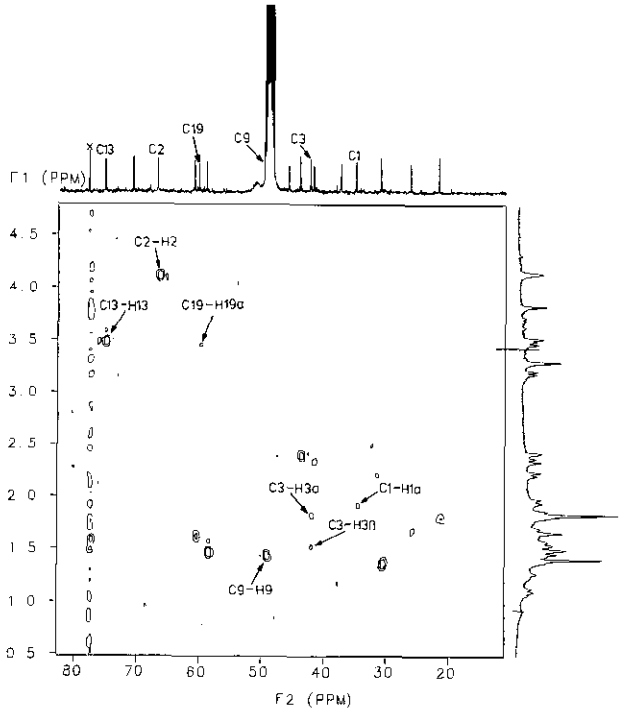


Figure 1. Fixed-evolution HETCOR Spectrum of **5** (CD_3OD). One-bond coupling between C1–H1β (δ 1.52) was revealed in the cross section.

The low-field AB-system (δ 3.48, 3.20, J_{AB} = 11.4 Hz) characteristic of the C-19 methylene enabled confirmation of the C-19 resonance at δ 60.3 in a cross section from the fixed-evolution HETCOR spectrum. The lower-field proton of this gem pair showed nOe's in the NOESY spectrum to the broad singlet at δ 3.83 (shown to be a methine proton from the fixed-evolution HETCOR and APT spectra with the carbon resonance at δ 70.8) and the previously assigned H-3 proton at δ 1.83, which is overlapped by the vinyl methyl group (Table 3). The other H-19 proton (δ 3.20) showed an nOe only to its gem partner and the C-18 methyl group. The two H-19 protons were therefore distinguished, and the methine protons at δ 3.83 must therefore be H-20. In Table 1 and diagram 2, H-19α and H-19β indicate the pseudo-axial and pseudo-equatorial protons, respectively, in the boat conformation of the ring formed by C-4, C-5, C-10, C-20, N and C-19. The boat should be viewed in the conventional way.

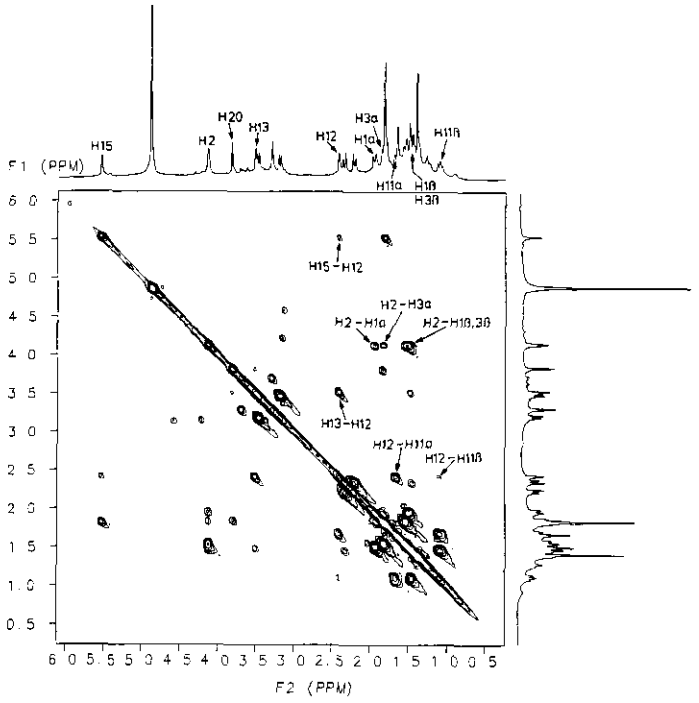


Figure 2. COSY Spectrum of **5** (CD_3OD).

As C-6 is part of the carbinolamine functionality, C-7 most likely is an isolated methylene (C-8 also is quaternary), accounting for the second, higher-field AB system (^1H: δ 2.22, 2.35 J_{AB} = 13.7 Hz; ^{13}C: 41.8). This was supported in a somewhat round-about way. The vinylic methyl group showed an nOe with the olefinic proton as well as a methine (^1H: δ 2.42, br s; ^{13}C: 44.0) which must therefore be H-12. This latter proton also showed allylic coupling to H-15. The H-12 resonance was also coupled to the methine of a secondary alcohol (^1H: δ 3.53, br s; ^{13}C: δ 75.4) and a methylene pair, as confirmed by the cross section in the fixed-evolution HETCOR spectrum (^1H: δ ~1.7 and 1.1; ^{13}C: 26.3) (Figure 1). One member of this methylene pair was overlapped with H-5 (δ ~1.6). *Therefore, H-12 must be adjacent to the vinyl system* (C-16 and C-15) and a methylene group, and the secondary carbinol group (also adjacent to H-12 by the COSY spectrum) must therefore be located at C-11 or C-13, though these are not yet distinguished. The second isolated AB-system can only be located at C-7 since all other methylenes are accounted for. The lower-field H-7 resonance showed an nOe to the methine proton δ 1.66 which correlated with the methine carbon at δ 61.0. This methine also showed an nOe to the C-18 methyl group and must therefore be H-5, and the lower-field H-7 proton must be H-7β. Furthermore, both H-5 and H-7β showed nOe's to another *proton in a severely overlapped region of the spectrum* (δ ~ 1.5) which correlated with a methine carbon (δ 49.8) and therefore must be H-9. Thus H-5, H-7β and H-9 showed the expected 1,3-diaxial nOe's.

The key remaining question is the location of the third hydroxyl group with the carbinol signal at δ 3.53 (br s) correlating with the methine at δ 75.4 in the fixed evolution HETCOR spectrum. The COSY spectrum revealed that this proton is coupled to the two other methine protons, one of which was assigned to H-12 (known to be methines from the HETCOR and APT spectra) and therefore the third hydroxyl group must be located at either C-11 or C-13. The major difficulty was the near overlap in the resonances for H-9 and H-14 in CD_3OD, CD_2Cl_2 and $CDCl_3$. Thus it was impossible to decide if the second coupled partner at the

carbinol proton was H-9 or H-14. Nevertheless, given the narrow half-width of this carbinol singlet,[8] it could be deduced that the carbinol proton occupied a pseudo-axial position (α) in the boat conformation of the ring defined by C-8, C-9, C-11, C-12, C-13, C-14, with the hydroxyl group pseudo-equatorial (β) pointing to the exterior face of the molecule. This result suggests that the hydroxyl occupies the C-13β position.

An important clue to the location of the hydroxyl group was the observation of an nOe between the H-7β proton and H-9, and an nOe between the H-7α proton and H-14 in the 2D-nOe spectrum. From the location of these cross peaks, it was clear that H-9 was slightly upfield from H-14, though overlapped. Equally important was the observation of an nOe from H-20 to the H-14 proton, though no coupling could be observed between these two vicinal protons even with a long range COSY, $\Delta = 0.300$ μs, due to the 90° dihedral angle, confirming H-14 as the downfield of the two (Figure 3). It is clear from the 2D-nOe spectrum that the carbinol methine proton of this last hydroxyl group showed an nOe with H-14. Thus this group must be located at C-13. If a hydroxyl group was located at C-11 with the carbinol H-11 showing only small coupling to its vicinal partner (and therefore on the interior of the molecule), an nOe to H-14 would be impossible and would have been observed to H-9, which was not the case.

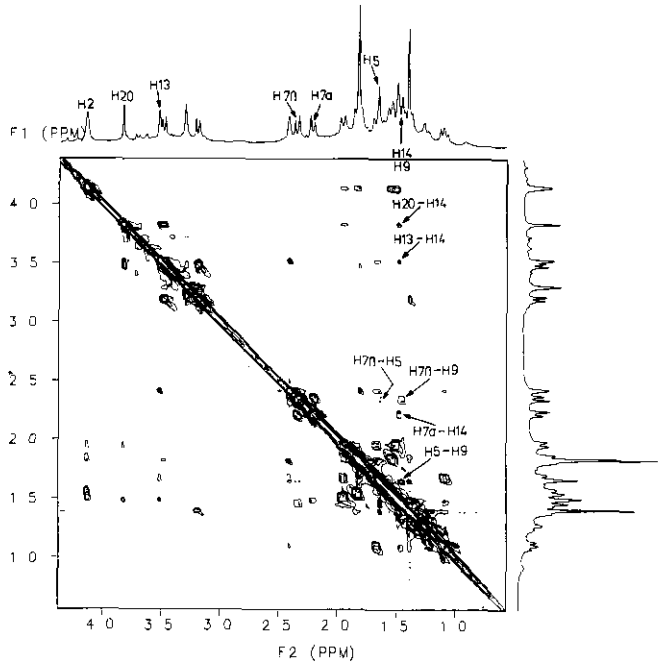


Figure 3. 2D nOe Spectrum of ***5*** *(CD_3OD).*

We sought to confirm this assignment by selective INEPT experiments which proved to be far less definitive, but clearly supported the assignment of the third hydroxyl group at C-13 and not C-11. Saturation of the carbinol signal at δ 3.53, now assigned to H-13 showed a strong polarization transfer to C-20 (as expected), but also showed a polarization transfer to C-10, four bonds removed (unexpected). This result of course, does not distinguish a C-11 from a C-13 hydroxyl group, since we cannot tell which polarization transfer traversed three and which traversed four bonds. However, on saturation of H-20, polarization transfers were observed to C-1, C-10 and the carbinol carbon at δ 75.4, therefore favoring the secondary alcohol at C-13.

Confirmation regarding location of the hydroxyl group at C-13 was obtained by repeating the proton nmr experiments in CD_2Cl_2, with 10% pyridine-d_5 which eliminated the near magnetic equivalence at H-9 and H-14 (Table 1). In this solvent system, one of the methines appeared in an overlapped region of the spectrum at δ 1.40–1.60 along with H-3β and H-1β, while the other methine was a broadened singlet at δ 1.87 ($W_{1/2}$ = 7.1 Hz). Clearly this latter signal must represent the methine vicinal to the hydroxyl group in question since the carbinol proton (H-11 or H-13) is a singlet with only weak coupling to this methine, and H-20 is also a singlet. (If this broadened singlet was adjacent to a methylene group rather than the carbinol methine, it would have appeared as a broadened doublet or doublet of doublets). Indeed, the dramatic downfield shift to δ 1.87 of this proton upon addition of pyridine (compared to δ 1.5 in CD_3OD) in contrast to the chemical shift of the other methine (remains ~δ 1.5) also supports the conclusion that this broad singlet is the resonance of the methine vicinal to the hydroxyl groups in question.

This broad singlet (H-14) showed coupling to the carbinol proton (H-13) in the long range COSY (Δ = 200 μs) spectrum (Table 4), confirming its vicinal relationship (with small coupling with H-13) to the hydroxyl group. In the long range COSY spectrum, coupling was also observed between H-20 and the carbinol proton, also indicating that the hydroxyl group must be at C-13. It should be noted that no coupling was ever observed between H-20 and H-14 in the long range COSY spectra using delays of Δ = 200, 300 and 400 μs.

Table 4. Long Range COSY (D3 = 0.200) of **5** (in CD_2Cl_2 + 10% C_5D_5N)

Observed H	Long Range Correlations
H15	H17
H20	H13α, H5, H19α
H19α	H7*, H5, H20
H13α	H20
H19β	H18
H3β	H1β
H14	H9, H13α
H9	H14, H5
H5	H9, H19β. H20

* Zig-zag coupling.

The other methine (H-9) would then be adjacent to a methylene group and molecular models indicate that coupling to one of the protons of this methylene should be significant since it would have a dihedral angle close to 0°. Location of the upfield methine adjacent to a methylene would further confirm the structure assignment of **5**, by locating the remaining hydroxyl group at either C-11 or C-13. A HETCOR spectrum revealed that the broadened singlet at δ 1.87 was one-bond coupled to the methine carbon at δ 57.8 while the overlapped methine at δ 1.40–1.60 was one-bond coupled to the methine at δ 48.8. These assignments strongly indicated that the hydroxyl group was located at C-13 since the ^{13}C chemical shift of δ 48.8 for the overlapped methine multiplet in the ^1H nmr spectrum best fits the assignment of C-9. This assignment was confirmed by a 2D-nOe experiment (Table 3) which showed an nOe between H-20 and the broadened singlet at δ 1.87, which must therefore be H-14.

There are very few examples of hetisine-type diterpenoid alkaloids in which a hydroxyl group at C-13 is located in a β-position (equatorial hydroxyl in the boat conformation of ring formed by carbons 8, 9, 11, 12, 13, 14).[14] Two recent examples are the alkaloids spirasine XIII and spirasine XV, isolated from *Spiraea japonica* L. var. *fortunei* (Pl.) Rehd. (Rosaceae).[8] The facile isomerization of the exocyclic double bond of tatsirine (**2**) to afford **5** can be explained by the formation of a carbonium ion (with traces of HCl from $CDCl_3$), which is stabilized with the suitably placed β-hydroxyl group to form an oxitane. On alumina, the

more stable isomer (**5**) is readily formed by loss of a proton from C-15. Similar isomerizations of the exocyclic methylene group take place under more drastic conditions, e.g. kaurene to isokaurene (with HCl and treatment with boiling KOH)[18] or hetisine to give a mixture of isomeric products (boiling with aq. H_2SO_4).[19]

EXPERIMENTAL

General: – ^1H and ^{13}C nmr spectra were recorded on a Varian XL-400 spectrometer (93.94 KG, 400 MHz for ^1H, 100 MHz for ^{13}C) and also on Perkin-Elmer EM-390 and JEOL FT model FX-60 in the solvents indicated in Tables 1–4.

Nmr multipulse sequence: – Spectra of **5** were run on 4 mg of sample in a 125 μL cylindrical cavity nmr tube (Wilmad). All 1D and 2D pulse sequences were run using standard Varian software, version 6.1c, except a fixed evolution HETCOR[13] experiment which was added to the sequence library according to Reynolds' program. A fixed evolution HETCOR experiment was utilized to enhance the sensitivity for detecting correlations between methylene carbons and their one-bond coupled, magnetically nonequivalent protons. ^{13}C-Multiplicities were assigned with an APT experiment and ^{13}C assignments were completed using a fixed evolution HETCOR experiment for one-bond heteronuclear couplings (^1H, ^{13}C), and a selective INEPT sequence for two- and three-bond heteronuclear couplings (^1H, ^{13}C). The evolution time in the HETCOR experiment was fixed at 19 ms with a refocusing interval of 2.47 ms. Selective INEPT experiments were recorded with the excitation and refocusing delays optimized for different coupling constants according to the formulae $\Delta 1 = 1/2J$ and $\Delta 2 = 1/3J$, respectively.[20]

Isolation of dictyzine (**1**) and tatsirine (**2**): – The crude alkaloidal fraction E_1 (15 g) (see Experimental section in Ref. 5) was chromatographed on alumina (Act. III; 700 g) and eluted with toluene containing increasing amounts of methanol. Fractions (500 ml each) were collected and the chromatographic separation was monitored by tlc (alumina). The last fractions (87–99) obtained by elution with toluene:methylene chloride:methanol (4:4:2) afforded a mixture of polar alkaloids (2.5 g). The crude alkaloid (1.7 g) was chromatographed on six preparative alumina plates. This was repeated on three alumina plates to afford dictyzine (**1**, 80 mg) mp 181–182°; $[\alpha]^{26}_D$ -100° (c, 0.49, EtOH); Found: C, 72.71; H, 9.72: Calcd. for $C_{21}H_{33}NO_3$ C, 72.58; H, 9.57. Ms: m/z 347(M^+, 40%), 330(20), 316(18), 312(15), 304(25), 256(35), 214(15), 172(100). Mixture mp., ir (nujol) and carbon-13 nmr[21] spectral comparison with an authentic sample showed them to be identical.

Chromatographic separation of a fraction obtained by preparative tlc on a column of alumina and elution with toluene containing 2% methanol afforded tatsirine (**2**, 8 mg; mp 260–263°). Eims: m/z 329(M^+, 75%), 312(29), 301(34), 294(19), 242(37), 193(9), 178(34), 160(49), 119(17), 84(100); Cims: 330(M^+ +1). ^{13}C Nmr ($CDCl_3$ + drop MeOH) ppm: 149.1, 106.6, 97.9, 70.6, 67.4, 66.7, 60.9(2c), 51.8, 49.4, 48.5, 44.8, 42.9, 42.3, 41.6, 36.8, 33.9, 32.4, 31.2, 22.4. ^1H Nmr (C_5D_5N): δ 1.55 (3H, s, CH_3), 4.72, 4.85 (each 1H, brs, H-17).

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