# HIGH RESOLUTION $^1$H-NMR AND $^{13}$C-NMR SPECTRA OF SATURATED PYRROLIZIDINE MONOESTER ALKALOIDS

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ABSTRACT.—$^1$H-nmr spectra of saturated pyrrolizidine monoester alkaloids and the aminoalcohols trachelanthamidine (**4**), isoretronecanol (**10**), supinidine (**11**) and curassanecine (**12**) have been determined at 270 MHz in $CDCl_3$ and $C_6D_6$. Also chemical shifts and coupling constants are tabulated. Evidence is presented that viridiflorates and trachelanthates can be differentiated by means of a) chemical shifts of the magnetically non-equivalent isopropyl methyl groups in $C_6D_6$ and b) chemical shifts and patterns of the H–4' and H–9 signals. $^{13}$C-nmr spectra of these substances measured at 67.89 MHz are also reported. Chemical shift trends are presented and another method for distinguishing viridifloric and trachelanthic esters on the basis of the chemical shifts of the methyl carbons is discussed.

The chemistry of the pyrrolizidine alkaloids is of considerable importance due to their wide distribution in the plant kingdom, their hepatotoxicity and carcinogenicity and their more recent discovery in specialized organs of Lepidoptera (1, 2). In structural studies on pyrrolizidine alkaloids considerable use has already been made of nmr spectrometry (3–5). Such work has generally been carried out at 60 or 100 MHz where many signals, particularly those of the ring protons, overlap and coupling constants are determined with difficulty.

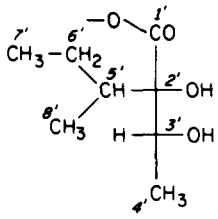
In our work on pyrrolizidine alkaloids from *Heliotropium ovalifolium* (6) we have already shown the advantage of operating at higher magnetic fields. More recently our study of saturated pyrrolizidine monoester alkaloids in *Heliotropium curassavicum* (7–9) at 270 MHz has led to generalizations which may be useful in identification and structure elucidation of closely related ester alkaloids. In the following discussion we present this information. We also discuss the $^{13}$C-nmr spectra from which useful information can be extracted also.

## RESULTS AND DISCUSSION

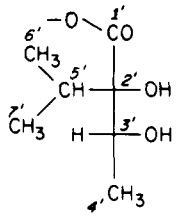
*A. $^1$H-NMR Studies.*—Chemical shifts and coupling constants, obtained at 270 MHz, for the alkaloids (7–9) curassavine (**1**), coromandaline (**2**), heliovicine (**3**), heliocurassavinine (**5**), heliocurassavine (**7**), heliocoromandaline (**8**), heliocurassavicine (**9**) and the amino alcohols (7–9) trachelanthamidine (**4**), isoretronecanol (**10**), supinidine (**11**) and curassanecine (**12**) are listed in tables 1–3. Important regions of the spectra are presented in figures 1–4. All signals were assigned by decoupling experiments.

To demonstrate the validity of the assignments in the tables, we illustrate the procedure for the case of curassavine (**1**) beginning with the necic acid moiety. Identification of the three proton triplet at $\delta$ 0.89 ($CDCl_3$ solution) with H–7' is obvious as is that of the one proton quartet at $\delta$ 4.00 with H–3'. Irradiation at the frequency of H–3' collapses the three proton doublet at $\delta$ 1.27 (H–4'). Hence the three proton doublet at $\delta$ 0.93 is that of H–8'. Irradiation at the frequency of H–7' collapses the multiplet at $\delta$ 1.22 (H–6') to a doublet; subsequent irradiation at the frequency of H–6' collapses not only the H–7' *t* to a singlet but simplifies a signal near $\delta$ 1.87 (H–5'). The multiplet of H–5' is also simplified, this time to a *t*, by irradiation at the frequency of H–8'.

As regards the necine moiety, irradiation at the center of the AB part (4.20*dd* and 4.27*dd*–H–9) of an ABX system collapsed a multiplet at $\delta$ 2.14 to a broad quartet, thus locating H–1. Irradiation at the frequency of the latter collapsed the H–9 signals to *d*'s, a broad quartet at $\delta$ 3.42 (H–8) to a broad *t* and simplified signals near $\delta$ 2.05 and 1.83 (H–2). Irradiation at the frequency of H–8 not only reduced the multiplicity of H–1, but collapsed multiplets at $\delta$ 2.03 and 1.60 (H–7)



$R_1$



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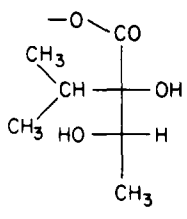

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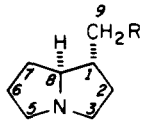

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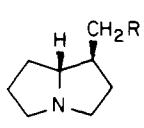
2 R=$R_2$
3 R=$R_3$
4 R=OH



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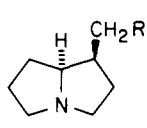

7 R=$R_1$
8 R=$R_2$
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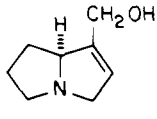
10 R=OH



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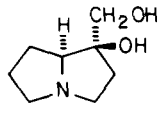

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to two *dt*'s. Irradiation at the frequency of a *dt* at δ 3.28 also simplified the H-2 multiplets and collapsed a *dt* at δ 2.60 to a broad triplet, thus identifying these two *dt*'s as originating from H-3α and H-3β. Conversely irradiation at the frequency of H-3β collapsed the signal of H-3α to a broad *t* and simplified the multiplets of H-2. Very careful irradiation of the multiplet near δ 2.05 (H-2d) or 1.83 (H-2u) also collapsed the multiplets of H-3α and H-3β, this time to narrowly split *dd*'s.

TABLE 1. Chemical shifts of protons of the pyrrolizidine nucleus.[a]

| Compound | H1[b] | H2[b] | H3[c] | H5[c] | H6[c] | H7[b] | H8[d] | H9[e] | ΔH9 |
|---|---|---|---|---|---|---|---|---|---|
| 1 ($CDCl_3$) | 2.14 | C.2.05,1.83 | 3.28,2.50 | 3.07,2.66 | 1.85 | 2.03.1.60 | 3.42 | 4.27,4.20 | 0.07 |
| 1 ($C_6D_6$) | C.1.65 | C.1.53 | 3.07,2.12 | 2.91,2.24 | 1.47 | C.1.60 | 3.33 | 4.07,4.00 | 0.07 |
| 2 ($CDCl_3$) | C.2.19 | C.2.05,1.87 | 3.36,2.62 | 3.14,2.70 | 1.89 | 2.16,1.63 | 3.52 | 4.27,4.22 | 0.05 |
| 2 ($C_6D_6$) | C.1.62 | C.1.53 | 3.09,2.08 | 2.91,2.21 | 1.44 | C.1.58 | 3.39 | 4.07,3.99 | 0.08 |
| 3 ($CDCl_3$) | 2.28 | C.2.13,1.93 | 3.39,2.62 | 3.11,2.76 | 1.86 | 2.10,1.60 | 3.44 | 4.61,4.02 | 0.59 |
| 3 ($C_6D_6$) | C.1.63 | C.1.50 | 3.14,2.08 | 2.88,2.25 | 1.41 | C.1.60 | 3.26 | 4.31,3.75 | 0.56 |
| 5 ($CDCl_3$) | 2.28 | C.2.13,1.89 | 3.41,2.62 | 3.14,2.77 | 1.91 | 2.10,1.60 | 3.51 | 4.60,4.05 | 0.55 |
| 5 ($C_6D_6$) | C.1.56 | C.1.49 | 3.12,1.98 | 2.83,2.20 | 1.36 | 1.54 | 3.30 | 4.26,3.72 | 0.54 |
| 7 ($CDCl_3$) | C.2.17 | C.2.04,1.93 | 3.39,2.63 | 3.17,2.72 | 1.90 | 2.06,1.65 | 3.57 | 4.24*d* | 0.00 |
| 7 ($C_6D_6$) | C.1.65 | C.1.56 | 3.14,2.12 | 2.94,2.23 | 1.49 | C.1.61 | 3.46 | 4.11,3.98 | 0.13 |
| 8 ($CDCl_3$) | C.2.21 | C.2.10,1.97 | 3.48,2.66 | 3.26,2.74 | 1.96 | 2.17,1.67 | 3.74 | 4.31,4.24 | 0.07 |
| 8 ($C_6D_6$) | 1.66 | C.1.36 | 3.04,1.89 | 2.84,2.04 | C.1.29 | C.1.43 | 3.47 | 4.09,3.93 | 0.16 |
| 9 ($CDCl_3$) | 2.28 | C.2.12, C.1.98 | 3.50,2.65 | 3.21,2.79 | C.1.95 | 2.09,1.64 | 3.62 | 4.59,4.06 | 0.53 |
| 9 ($C_6D_6$) | 1.63 | C.1.50 | 3.17,2.00 | 2.87,2.19 | 1.37 | C.1.54 | 3.38 | 4.25,3.77 | 0.48 |
| 4 | C.1.99 | C.1.97,1.63 | 3.14,2.52 | 2.96,2.60 | 1.79 | 1.93,1.53 | 3.21 | 3.61*d* | 0.00 |
| 10 | 2.05 | 1.99,1.70 | 3.22,2.58 | 3.04,2.64 | 1.84 | 2.01,1.58 | 3.33 | 3.63 | 0.00 |
| 11 | — | 5.50*br* | 3.88,3.32*dd* | 3.09,2.53 | 1.76*qn* | 1.97,1.52*sx* | C.4.19*br* | C.4.15,4.24 | 0.09 |
| 12[f] | — | 2.30,2.22*dt* | 335.,3.00 | 3.11,2.78 | 1.79 | 2.39,2.03 | 3.86*t* | 3.98*s* | 0.00 |

[a]Measured in $CDCl_3$ when not specified otherwise using $Me_4Si$ as internal standard; chemical shifts are accurately measured when not prefixed by c, [b]multiplet, [c]doublet of a triplet, [d]quartet broad, [e]doublet of a doublet, unless specified otherwise. [f]in $C_5D_5N$.

TABLE 2. Chemical shifts of protons in necic acid portion.[a]

| Compound | H-3'[b] | H-4'[c] | H-5'[d] | H-6'[c] | H-7'[c] | H-8'[c] | ΔH6', 7' |
|---|---|---|---|---|---|---|---|
| **1** | 4.00 | 1.27 | C.1.87 | 1.22*m* | 0.89*t* | 0.93 | — |
| **1** ($C_6D_6$) | 4.13 | 1.39 | 2.01 | 1.13*m* | 0.92*t* | 1.01 | — |
| **7** | 3.99 | 1.27 | C.1.84 | 1.25*m* | 0.90*t* | 0.93 | — |
| **7** ($C_6D_6$) | 4.15 | 1.41 | 2.04 | 1.12*m* | 0.93*t* | 1.02 | — |
| **2** | 3.97 | 1.27 | 2.12 | 0.94*m* | 0.88 | — | 0.06 |
| **2** ($C_6D_6$) | 4.11 | 1.39 | 2.28 | 1.05 | 1.00 | — | 0.05 |
| **8** | 3.99 | 1.27 | 2.16 | 0.94 | 0.88 | — | 0.06 |
| **8** ($C_6D_6$) | 4.08 | 1.37 | 2.27 | 1.05 | 0.99 | — | 0.06 |
| **3** | 4.04 | 1.19 | 2.09 | 0.95 | 0.93 | — | 0.02 |
| **3** ($C_6D_6$) | 4.25 | 1.33 | 2.28 | 1.17 | 1.01 | — | 0.16 |
| **5** | 4.04 | 1.19 | 2.09 | 0.95 | 0.93 | — | 0.02 |
| **5** ($C_6D_6$) | 4.23 | 1.31 | 2.25 | 1.16 | 1.00 | — | 0.16 |
| **9** | 4.05 | 1.19 | 2.07 | 0.94 | 0.93 | — | 0.01 |
| **9** ($C_6D_6$) | 4.27 | 1.33 | 2.24 | 1.17 | 1.01 | — | 0.16 |
| Curassavic acid[e] | 4.06 | 1.36 | 1.87 | 1.39*m* | 0.92*t* | 0.93 | — |
| ($C_5D_5N$) | 4.59 | 1.70 | 2.37 | 1.94*m* | 0.97*t* | 1.21 | — |
| (+) Viridifloric acid[e] | 4.07 | 1.33 | 2.17 | 0.96 | 0.95 | — | 0.01 |
| ($C_5D_5N$) | 4.58 | 1.69 | 2.66 | 1.34 | 1.23 | — | 0.11 |
| (−) Trachelanthic acid | 4.22 | 1.26 | 2.01 | 0.99 | 0.97 | — | 0.02 |
| ($C_5D_5N$) | 4.57 | 1.57 | 2.56 | 1.30 | 1.26 | — | 0.04 |

[a]Measured in $CDCl_3$ unless specified otherwise using $Me_4Si$ as internal standard; in ppm from standard; $J_{3',4'}=6.5$, $J_{\text{all others}}=7$Hz. [b]quartet, [c]doublet, [d]multiplet unless specified otherwise, [e]All peaks broadened in $CDCl_3$.

Finally, H–5 and H–6 were located as follows. Irradiation at the frequency of H–7d ($\delta$ 2.03) collapsed the multiplet of H–7u at 1.60 to a *dt*, collapsed the quartet of H–8 to a broadened *t* and simplified a two proton multiplet at $\delta$ 1.85 (H–6). Irradiation at the latter's frequency not only collapsed the two H–7 multiplets to *dd*'s, but also collapsed two *dt*'s at $\delta$ 3.07 and $\delta$ 2.66 to *d*'s, thus identifying these signals as those of H–5$\alpha$ and H–5$\beta$. Conversely, irradiation at the frequency of H–5$\alpha$ (or H–5$\beta$) collapsed at *dt* of H–5$\beta$ (or H–5$\alpha$) to a *t* and simplified the H–6 multiplet.

Decoupling experiments were also carried out in $C_6D_6$ solution for all compounds. In the case of **1**, H–3$\alpha$,$\beta$, H–5$\alpha$,$\beta$, H–8, and the AB system of H–9 experienced diamagnetic solvent shifts, whereas H–3', H–4' and H–5' were shifted downfield. H–7' and H–8' were well separated in $C_6D_6$, but H–1, H–2 and H–7 were poorly resolved.

TABLE 3. Coupling constants.[a]

| Compound | 1 | 2 | 3 | 5 | 7 | 8 | 9 | 4 | 10 | 11 | 12[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $J_{1,2}$ | C.6.5 | 8.5 | 6.0 | | C.6.5 | 6.5 | 6.0 | | | — | — |
| $J_{2,3\alpha}$ | C.3.5 | 6.5 | 4.0 | 3.5 | C.3.5, 6.5 | C.4.5, 6.5 | C.4.0 | C.3.0, 7.0 | 4.0,6.5 | 2.0 | 2.5 |
| $J_{2,3\beta}$ | 6.0 | 5.5 | C.6.5 | 7.0 | C.4.0, 6.5 | C.3.5, 7.0 | 7.5 | 7.0 | 6.0 | 3.0 | 6.0 |
| $J_{3\alpha,3\beta}$ | 9.5 | 8.5 | 9.5 | 10.0 | 10.0 | 9.5 | 10.5 | 8.5 | 10.0 | 15.0 | 9.0 |
| $J_{5\alpha,5\beta}$ | 11.0 | 11.0 | 11.0 | 11.5 | 11.0 | 11.5 | 11.5 | 11.0 | 10.0 | 10.0 | 9.5 |
| $J_{5\alpha,6}$ | 6.5 | 6.0 | 7.0 | 6.5 | 6.5 | 6.5 | 6.5 | 6.5 | 6.5 | 5.5 | 5.0 |
| $J_{5\beta,6}$ | 6.0 | 6.5 | 6.5 | 6.0 | 6.5 | 6.5 | 6.5 | C.6.5 | 6.5 | 6.5 | 7.0 |
| $J_{6,7}$ | C.7.5 | C.7.0 | 7.0 | C.8.5 | C.6.5 | 6.5 | 7.0 | 7.0 | C.7.0 | | |
| $J_{7u,7d}$ | 11.5 | 12.0 | 12.5 | 12.0 | 11.5 | 12.5 | 12.0 | 12.0 | 12.0 | 11.5 | |
| $J_{7,8}$ | C.6.5 | 6.5 | C.6.5 | 6.5 | C.6.0 | C.5.0 | C.5.0, 7.0 | C.6.5, | C.6.0 | | 6.0,8.0 |
| $J_{1,8}$ | C.6.0 | C.6.5 | 7.0 | C.5.5 | C.6.5 | C.7.5 | 5.0 | C.6.0 | 5.5 | — | — |
| $J_{1,9u}$ | 6.5 | 6.0 | 4.5 | 4.5 | 5.5[c] | 5.5 | 5.0 | 6.5[c] | 6.0 | — | — |
| $J_{1,9d}$ | 5.5 | 5.5 | 4.5 | 4.5 | — | 5.5 | 4.0 | — | 6.0 | 2.0[d] | — |
| $J_{9u,9d}$ | 11.0 | 11.5 | 11.5 | 11.5 | — | 11.5 | 11.5 | — | 1.5 | 14.0 | — |

[a]Measured in $CDCl_3$ unless specified otherwise; *J* values in Hz. [b]in $C_5D_5N$; [c]$J_{1,9}$ (H-9's magnetically equivalent)) [d]$J_{2,9}$.

Fig. 1 shows the signals of the ring protons of our alkaloids. Invariably H–8 is farthest downfield and H–7u farthest upfield. Chemical shifts of H–3$\alpha$, H–5$\alpha$, H–5$\beta$ and H–3$\beta$ decrease in this order, a situation which contrasts with the order H–3$\alpha$, H–3$\beta$, H–5$\alpha$, H–5$\beta$ recorded previously for other pyrrolizidine alkaloids (3, 4). The H–3, H–5 and H–7 proton pairs exhibit a considerable degree of magnetic non-equivalence, the H–2 protons somewhat less so.

Fig. 2 shows the ring proton signals of the amino alcohols. The slight nonequivalence exhibited by the H–9 protons of **10** cannot be observed at lower field strengths, but H–9a and H–9b of **4** (and **6**) remain essentially equivalent even at 270 MHz. The situation is reversed for H–6, this pair being slightly non-equivalent in **4** and **6**, but equivalent in **10**. The order of decreasing chemical shift for **4**, **6** and **10** is again H–3$\alpha$, H–5$\alpha$, H–5$\beta$, H–3$\beta$ as in the derived esters. That this order seems to be associated with the removal of unsaturation is seen by comparison with the spectrum of supinidine (**11**). The non-equivalence of H–7 in the saturated and unsaturated series is not evident from previously published work.

In trachelanthates of the retronecine and heliotridine series, the isopropyl methyls are magnetically equivalent at 60 MHz, or nearly so ($\Delta\delta$ 0.02), whereas in the viridiflorates the methyl signals may differ by $\delta$ 0.04 and the chemical shift of H–4' is greater in the viridiflorates ($\delta$ 1.26–1.30) than in the trachelanthates ($\delta$ 1.16–1.20) (10). However, in the case of the viridiflorates of supinidine and (+) isoretronecanol H–4' is found at an intermediate $\delta$ 1.22–1.23 and the isopropyl methyls differ in shift by 0.03 (11). Hence $CDCl_3$ spectra at low magnetic fields are relatively unsatisfactory for distinguishing between viridiflorates and trachelanthates.

Figure 3 shows the methyl signals of our alkaloids in $CDCl_3$ and $C_6D_6$. H–7' and H–8' of the curassavates are somewhat resolved in $CDCl_3$ at 270 MHz (fig. 3a) and cleanly separated in $C_6D_6$ (fig. 3d). In $CDCl_3$ the chemical shift difference for H–6' and H–7' is 0.06 for the viridiflorates (fig. 3b) and 0.01 for the trachelanthates (fig. 3c), but in $C_6D_6$ the chemical shift differences are 0.05–0.06 for the viridiflorates (fig. 3f). H–4' is found at $\delta$ 1.37–1.39 in the viridiflorates, at $\delta$ 1.31–1.33 in the trachelanthates, and at $\delta$ 1.39–1.41 in the curassavates. Thus, in our series, and quite possibly in esters of other necine bases, viridiflorates and trachelanthates may be differentiated easily by their nmr spectra in $C_6D_6$.

An additional and valuable criterion for distinguishing between trachelanthates and viridiflorates is the great difference in the degree of non-equivalence exhibited by the pair of H–9 protons (fig. 4). $\Delta\delta_{H\text{-}9's}$ are 0.05–0.07 ($CDCl_3$) and 0.08–0.16 ($C_6D_6$) for the viridiflorates, 0.53–0.59 ($CDCl_3$) and 0.48–0.56 ($C_6D_6$) for the trachelanthates, and 0–0.07 ($CDCl_3$) and 0.07–0.13 ($C_6D_6$) for the curassavates. In macrocyclic esters, the non-equivalence of H–9 is due to the rigidity of the system which prevents rotation about the C–9,0 bond. In the case of our compounds, the phenomenon is due to bulky $\alpha$-substituents in the esterifying acids which restrict rotation about the C–9, oxygen bond.

*B.* $^{13}$*C–NMR Studies.*—Although more than two hundred pyrrolizidine alkaloids have been isolated and characterized so far, use of $^{13}$C-nmr spectra has received only sporadic attention (12–15). Table 4, which lists $^{13}$C-nmr spectra of compounds **1–12**, indicates that chemical shift data can be used to discriminate between a) esters of trachelanthimidine and isoretronecanol and b) viridiflorates and trachelanthates.

The assignments in table 4 were made on the basis of proton noise-decoupled spectra (PND), single frequency off-resonance decoupled spectra (SFORD) and comparisons of chemical shifts from compound to compound.

We illustrate the method for the PND spectrum of curassavine (**1**) which exhibits 15 signals, one of which is of double intensity, for 16 carbons. The SFORD spectrum shows 2 singlets, 4 doublets, 7 triplets and 2 quartets (one with double

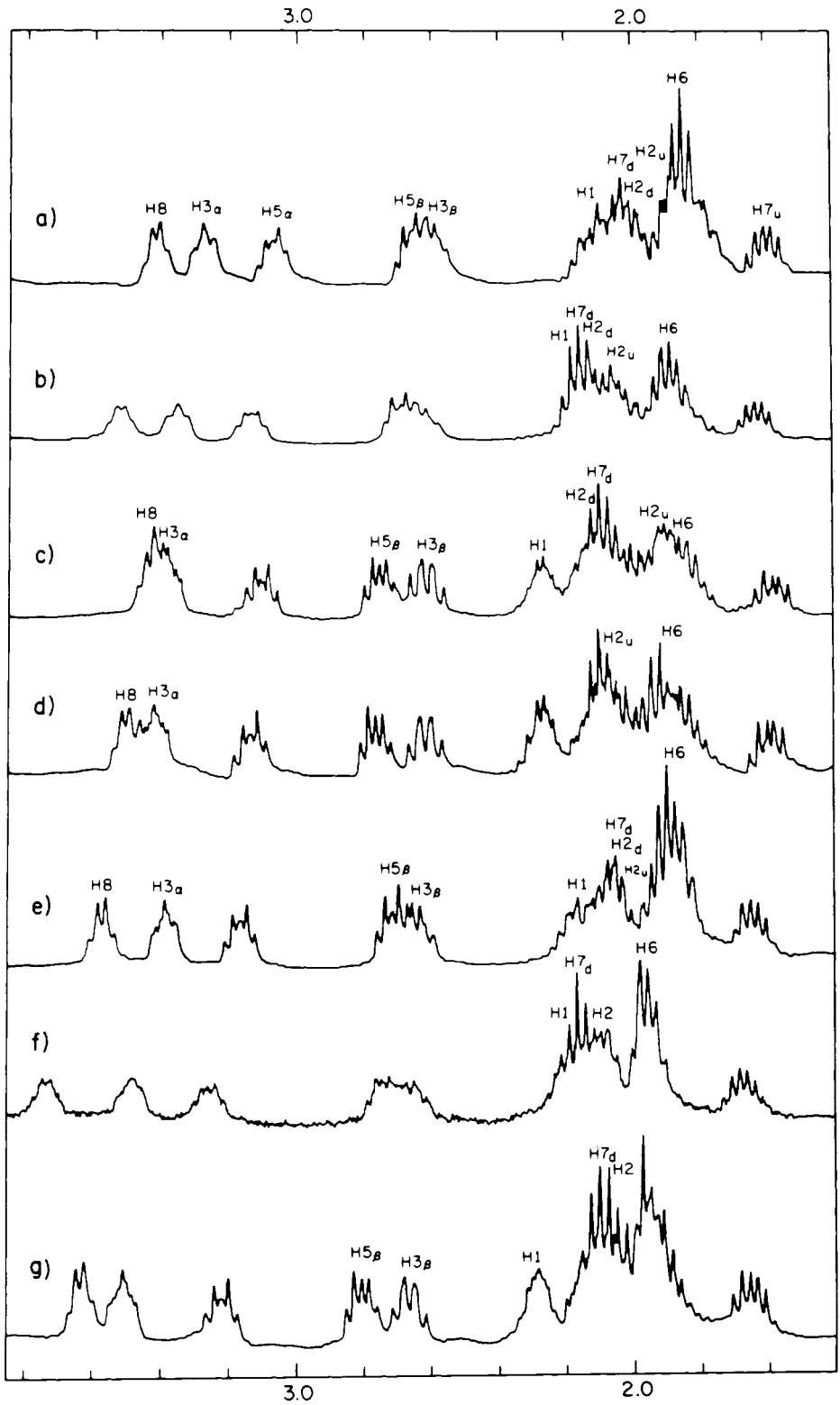


FIG. 1. $^1$H-nmr spectra ($CDCl_3$) of ester alkaloids in region δ 1.4–3.8 (ring protons). a) curassavine (**1**); b) coromandaline (**2**); c) heliovicine (**3**); d) heliocurassavinine (**5**); e) heliocurassavine (**7**); f) heliocoromandaline (**8**); g) heliocurassavicine (**9**).

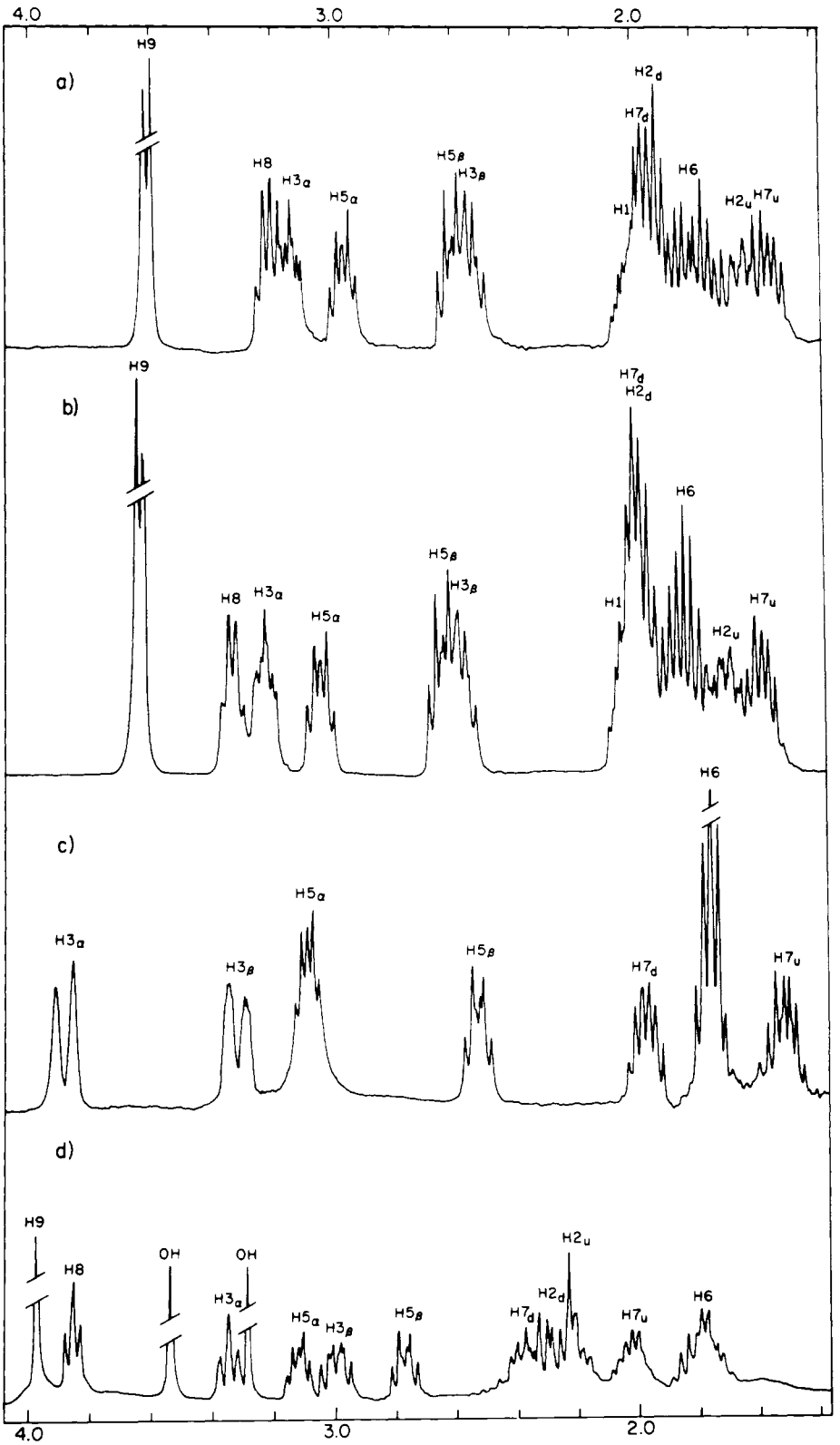


FIG. 2. $^1$H-nmr spectra of aminoalcohols in region δ 1.4–4.0. a) trachelanthamidine (**4**); b) isoretronecanol (**10**); c) supinidine (**11**); d) curassanecine (**12**).

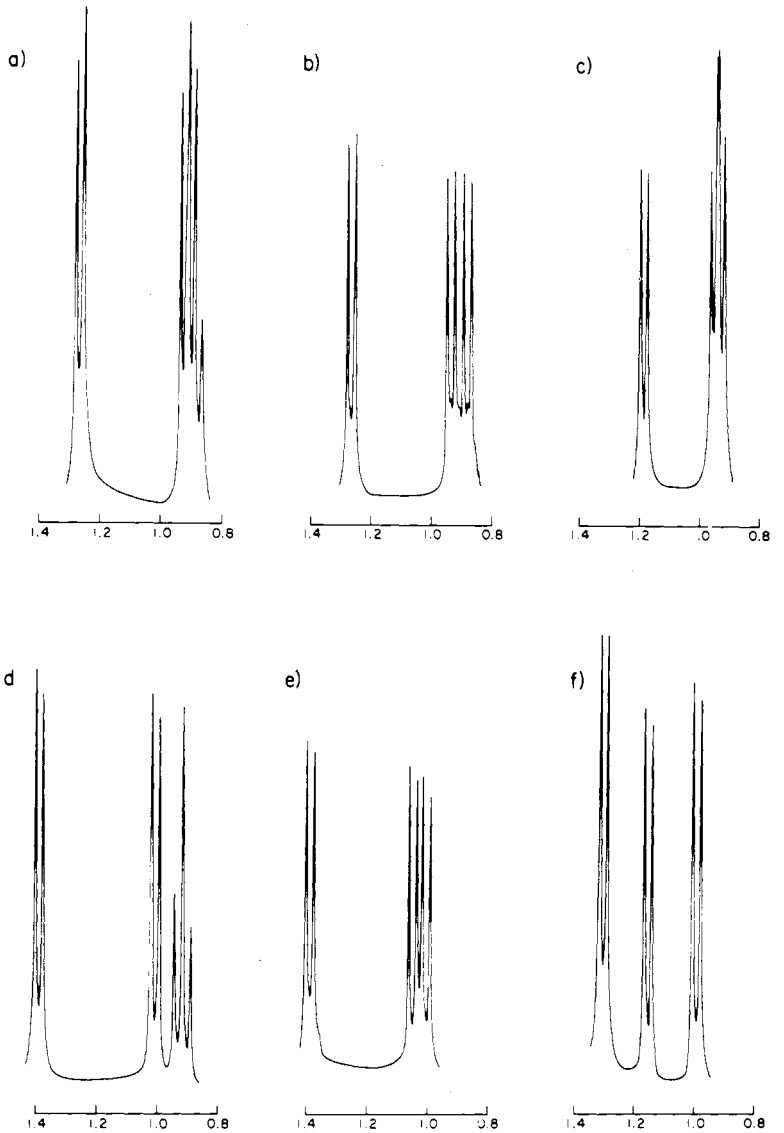


FIG. 3. $^1$H-nmr spectra (methyl region) of ester alkaloids. a) curassavates-curassavine (**1**), heliocurassavine (**7**) in $CDCl_3$; b) viridiflorates-coromandaline (**2**), heliocoromandaline (**8**) in $CDCl_3$; c) trachelanthates-heliovicine (**3**), heliocurassavinine (**5**), heliocurassavicine (**9**) in $CDCl_3$; d) curassavates **1**, **7** in $C_6D_6$; e) viridiflorates **2**, **8** in $C_6D_6$; f) trachelanthates **3**, **5**, **9** in $C_6D_6$.

intensity). The singlets at $\delta$ 174.82 and 84.24 were assigned to C–1′ and C–2′, respectively. The doublet at $\delta$ 70.97 was assigned to C–3′ as it is absent in the free base trachelanthamidine (**4**) and slightly shifted to 71.05 in coromandaline (**2**) and 69.08 in heliovicine (**3**) due to the change in esterifying moieties. These and some other assignments were confirmed by decoupling experiments. By comparison of the chemical shifts in **2–10** the doublets at $\delta$ 68.02 and 44.76 were assigned to C–8 and C–1, respectively. The doublet at $\delta$ 39.06 was assigned to C–5′ as it is shifted upfield by ca. 6.0 ppm in **2** and **3**. Comparison of the spectrum of **1** with those of **2–10** permitted assignment of the following triplets: 67.48 to C–9; 54.54 to C–3, 54.24 to C–5, 31.63 to C–7, 30.27 to C–2 and 25.63 to C–6. The triplet at $\delta$ 24.77 could be assigned to C–6′ as it is only found in one

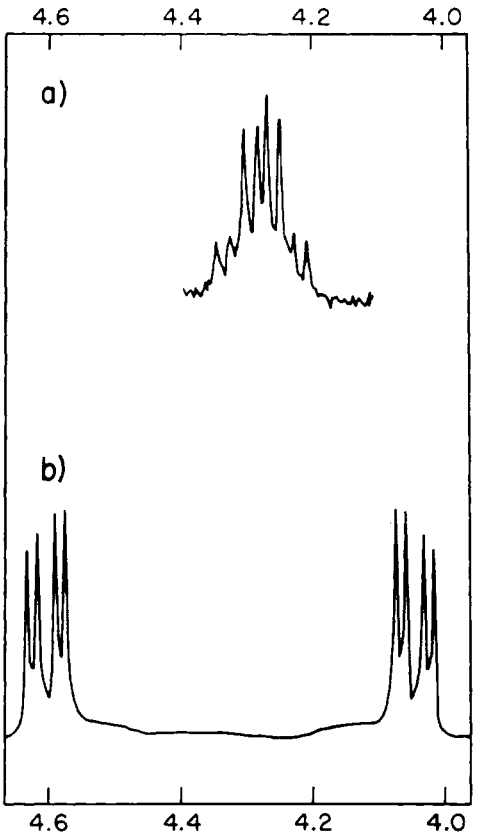


FIG. 4. H-9 signals ($CDCl_3$) of a) viridiflorates; b) trachelanthates.

other compound, namely **7**. The quartet at 17.35 was assigned to C-4' and the quartet at 12.09 (double intensity) to C-7' and C-8'.

In a similar way assignments were made for **2**–**12**. Going from **1** to **2** the change in necic acid produces an upfield shift of C-9 by $\delta$ 0.4 and the expected changes in acid signals. On comparing **3** with **2** it is observed that C-1, C-6 and

TABLE 4. $^{13}$C-nmr spectra.[a]

| | 1 | 2 | 3 | 5 | 7 | 8 | 9 | 4 | 10[b] | 11 | 12[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C-1*d*.... | 44.76 | 44.76 | 44.11 | 44.16 | 44.71 | 44.67 | 44.19 | 48.14 | 48.22 | 137.84*s*[c] | 80.32*s*[c] |
| C-2*t*.... | 31.63 | 31.47 | 31.13 | 31.06 | 31.44 | 31.25 | 30.92 | 31.95 | 31.81 | 121.02*d* | 39.15 |
| C-3*t*.... | 54.54 | 54.49 | 54.35 | 54.34 | 54.51 | 54.40 | 54.32 | 54.79 | 54.78 | 59.97 | 55.66 |
| C-5*t*.... | 54.24 | 54.19 | 54.24 | 54.18 | 54.23 | 54.16 | 54.19 | 54.53 | 54.52 | 56.64 | 53.29 |
| C-6*t*.... | 25.63 | 25.61 | 25.03 | 25.03 | 25.58 | 25.56 | 25.06 | 25.75 | 25.69 | 25.90 | 25.42 |
| C-7*t*.... | 30.27 | 30.21 | 29.29 | 29.26 | 30.11 | 29.99 | 29.93 | 30.08 | 29.92 | 30.43 | 27.84 |
| C-8*d*.... | 68.02 | 68.00 | 68.22 | 68.15 | 68.13 | 67.97 | 68.14 | 69.92 | 68.16 | 71.27 | 70.80 |
| C-9*t*.... | 67.48 | 67.07 | 66.85 | 66.64 | 66.85 | 66.33 | 65.96 | 65.25 | 64.97 | 61.90 | 68.38 |
| C-1'*s*... | 174.82 | 174.65 | 175.53 | 175.48 | 174.71 | 174.56[c] | 175.45 | | | | |
| C-2'*s*... | 84.24 | 83.69 | 83.37 | 83.36 | 84.38 | 83.45 | 83.45 | | | | |
| C-3'*d*... | 70.9 | 71.05 | 69.08 | 69.14 | 71.15 | 71.24 | 69.19 | | | | |
| C-4'*q*... | 17.35 | 17.36 | 17.36 | 17.37 | 17.36 | 17.27 | 17.29 | | | | |
| C-5'*d*... | 39.06 | 32.23 | 32.64 | 32.66 | 39.09 | 32.23 | 32.77 | | | | |
| C-6'*q*... | 24.77*t* | 15.99 | 16.94 | 16.91 | 24.85*t* | 15.96 | 17.00 | | | | |
| C-7'*q*... | 12.09 | 17.84 | 17.25 | 17.25 | 12.09 | 17.85 | 17.29 | | | | |
| C-8'*q*... | 12.09 | — | — | — | 12.09 | — | — | | | | |

[a]Measured in $CDCl_3$ unless specified otherwise relative to $Me_4Si$ as internal standard; [b]All signals weak due to very low concentration. [c]Very weak. [d]in $C_5D_5N$

*s*-singlet, *d*-doublet, *t*-triplet, *q*-quartet in the rows unless specified othersie.

C–7 are shifted upfield, whereas the other ring carbons are affected only slightly, and that the change in configuration from 2'*R*, 3'*R* to 2'*R*, 3'*S* also results in a significant upfield shift of C–3'. $\Delta\delta_{C\text{-}6',C\text{-}7'}$ is 1.85 for **2** and only 0.3 for **3**. In the isoretronecanol derivatives **7**, **8** and **9** C–9 is shifted upfield by $\delta$ 0.63, 0.74 and 0.89 relative to its position in the trachelanthamidine analogs **1**, **2** and **3**, whereas C–9 of the laburnine derivative **5** is upfield of C–9 of **3** by only 0.2. Shifts in going from **8** to **9** parallel those observed in going from **2** to **3**. The spectra of **4** and **6** are almost identical.

In addition to the significant difference in C–9 chemical shift for isoretronecanol esters on the one hand and trachelanthamidine esters on the other, table 4 reveals that viridiflorates and trachelanthates can be distinguished as follows: a) In viridiflorates, the isopropyl methyl carbons tend to be significantly more non-equivalent ($\Delta\delta$ 1.85) than in trachelanthates ($\Delta\delta \leq 0.35$); b) in viridiflorates the chemical shift of C–3' is greater than in trachelanthates ($\sim\delta$ 71 as compared with $\sim\delta$ 69). It is also interesting that C–7' and C–8' of the curassavates are magnetically equivalent.

## EXPERIMENTAL

$^1$H-nmr spectra were run at 270 MHz in the Fourier mode on a Bruker HX–270 spectrometer in conjunction with a Nicolet 1189 computer. $^{13}$C-nmr spectra were run at 67.89 MHz on the same instrument. Spectra were run at 25° in $CDCl_3$, $C_6D_6$ or $C_5D_5N$ on samples in 5 mm o.d. tubes with $(CH_3)_4Si$ as internal standard.

*Received 14 September 1981*

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