Buffer solution, pH	Weight of the fractions, g	Isolated, g
7.0	37.38	7.8 peganine
6.8	52.80	3.9 deoxypeganine perchlorate
6.6	31.51	14.33 deoxypeganine hydrochloride
6.4	7.73	8.80 deoxypeganine perchlorate 0.86 peganine 1.2 deoxypeganine tetrate
6.2	4.28	0.1 peganine
5.8	3.98	
5.6	2.97	
5.4	3.11	
5.2	2.53	5 harmine
5.0	3.10	
4.0	8.10	
3.0	5.50	0.46 vasicinone
2.0	3.00	4.14 vasicinone 1.3 deoxyvasicone hydrochloride
10% H_2SO_4	20.7	
Washing chloroform	210	Mixture of vasicinone and deoxyvasicinone (on TLC)

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CHARACTERISTIC INFLUENCE OF TRIFLUOROACETIC ACID ON THE CHEMICAL SHIFT ON THE SIGNAL OF A PROTON GEMINAL TO AN OH GROUP

K. L. Seitanidi and M. R. Yagudaev

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To detect and to determine the multiplicity of the masked signal of $\underline{H}-C-OH$ in the NMR spectra of complex organic compounds, recourse is usually had to esterification (acetylation and benzoylation) of the secondary OH group, in consequence of which the signal of the proton under consideration shifts downfield by 0.85-1.2 ppm [1-3]. However, the masked signal of the $\underline{H}-C-OH$ proton can be revealed without having recourse to such reactions. In particular, for this purpose it is possible to use paramagnetic shift reagents or various nonpolar solvents.

In spite of the large number of publications in which the instruments of solvents in NMR spectroscopy for resolving structural and chemical problems have been considered [4-6], trifluoroacetic acid (TFA) has not been the object of a systematic study, particularly in the case of natural compounds.

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TABLE 1. Chemical of $\underline{H}-C-OH$ Protons in $CDCl_3$ and Trifluoroacetic Acid and Their Relative Difference (Δ)

Substance	Solvent (δ, ppm)		
	$CDCl_3$	trifluoro-acetic acid	Δ
Cyclohexane	3,60	3,97	0,37
Isopropanol	4,03	4,39	0,36
Bucharidine	4,00	4,40	0,40
Perforine	4,25	4,80	0,55
Vincarine	4,21	4,91	0,70
Codonopsine	3,90	4,60	0,70
Solasodine	3,50	3,90	0,40
Imperialine	3,50	4,00	0,50
6-Hydroxyhyoscyamine	3,63	4,08	0,45
Ajmaline $H-C_{17}-OH$	4,25	5,02	0,77
$\underline{H}-O_{21}-OH$	4,45	5,26	0,81

JNM-4H-100 instrument, c = 5%, 0–TMS.

We give information on the influence of TFA on the change in the chemical shift (CS) of the $\underline{H}-C-OH$ proton in some model compounds and natural alkaloids [8] containing a secondary OH group. In solution in TFA as compared with $CDCl_3$, the $\underline{H}-C-OH$ signal is shifted downfield by 0.40–1.00 ppm (Table 1). The scatter in the values of Δ shown is evidently due to differences in the structure and stereochemistry of the compounds studied.

The paramagnetic shift of the proton under discussion can be explained from the idea of the action of it of the "reaction field of the medium" (TFA), by the formation of intermolecular hydrogen bonds between the molecules of TFA and the substance, and also by the inductive influence of the protonation of the nitrogen atoms (in nitrogen-containing compounds).

Thus, we have established that TFA is an extremely convenient solvent which enables the CS and multiplicity of the signal of the $\underline{H}-C-OH$ proton and, consequently, its orientation, to be determined.

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