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THE NMR INVESTIGATION OF ALKALOIDS.

VII. ^{13}C NMR SPECTRA AND STRUCTURE OF "KOPSANONE" AND KOPSINILAM

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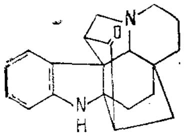
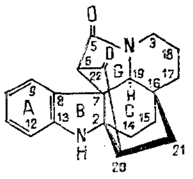
On the basis of a study of the ^{13}C NMR spectra of a base from *Vinca erecta* previously regarded as "kopsanone," and the known alkaloid kopsinilam, it has been shown that the former is 5,22-dioxokopsane.

A base with mp 284-285°C, $[\alpha]_D^{20}$ + 98.6° (c 0.18; chloroform), R_f 0.4 [5], has previously been isolated from the plant *Vinca erecta* Regel et Schmalh., for which, on the basis of its composition and an analysis of its UV, IR, and mass spectra, the structure of "kopsanone" (I) was proposed [1]. However, the later purification of this base led to a rise in the melting point to 304-305°C. In addition, the mass spectrum, the composition, and the presence in its IR spectrum of two bands corresponding to the stretching vibrations of a ketonic C=O group in a five-membered ring at 1750 cm^{-1} and of a lactam at 1670 cm^{-1} showed that this base was not "kopsanone" but 5,22-dioxokopsane (II) (kopsanone lactam) isolated previously from the plants *Pleiocarpa mutica* Benth. [2] and *Alstonia venenata* R. Br. [3], and synthesized from kopsanone [4].

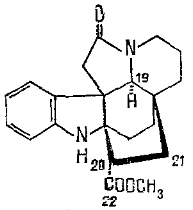
In order to investigate the structure further, we have studied the ^{13}C NMR spectrum both of the base 5,22-dioxokopsane under investigation and of the known alkaloid kopsinilam (III) [5, 6].



I



II



III

The assignment of the signals of the carbon atoms was made on the basis of an experiment with complete and incomplete decoupling of C—H interactions taking α-, β-, and γ- contributions into account [12], and also by a comparison with literature figures for the ^{13}C CSs of substances having similar structures [7-9]. The results are given in Table 1 and in Fig. 1.

In the spectrum of (II) eight signals of sp^2 carbon atoms appear in the 110-205 ppm region — six signals from an aromatic ring and two signals of carbonyl carbons (ketonic and lactamic). The signals of the sp^3 carbons resonate in the 70-19.5 ppm region, two of them

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TABLE 1. Details of the ^{13}C NMR Spectra of 5,22-Dioxokopsane and of Kopsinilam

Carbon atom	CS (ppm) and multiplicity		Carbon atom	CS (ppm) and multiplicity	
	5,22-Dioxokopsane, $CDCl_3$	Kopsinilam, Py-d_5		5,22-Dioxokopsane, $CDCl_3$	Kopsinilam, Py-d_5
C-2	69,1 s	66 5 s	C-14	33,2 t	31,6 t
C-3	40,5 t	41,9 t	C-15	23,2 t	28,5 t
C-5	165 6 s	172,3 s	C-16	32,7 s	33.3 s
C-6	62 7 d	40,1 t	C-17	19,5 t	21,0 t
C-7	55.9 s	50,0 s	C-18	33,2 t	35,4 t
C-8	130,7 s	138,6 s	C-19	65,8 d	65,7 d
C-9	119,7 d	119.5 d	C-20	52,3 d	44.[illegible] d
C-10	128,5 d	127,9 d	C-21	28,9 t	31,8 t
C-11	122.2 d	121,1 d	C-22	205,0 s	174,2 s
C-12	111,3 d	111 0 d	OCH_3	—	51.8 d
C-13	150,7 s	150,7 s			

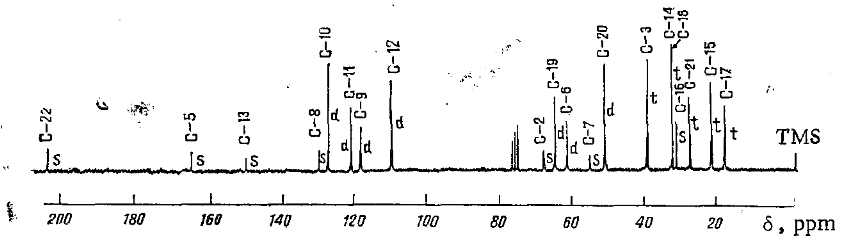

Fig. 1. ^{13}C NMR spectrum of 5,22-dioxokopsane in $CDCl_3$.

coinciding in the CS values. The presence of two signals of carbonyl carbons and an analysis of the CSs and multiplicities of the other signals together with other physiochemical and spectral characteristics show that base (II) is 5,22-dioxokopsane.

In the ^{13}C NMR spectra of kopsinilam (III) eight signals of sp^2 carbon atoms are observed in the 110-175 ppm region and six signals of an aromatic ring and two C=O signals (one of a lactam and one of an ester grouping). The 13 sp^3 carbon atoms of base (III) give signals in the 67-20 ppm region the number and multiplicity of which agree completely with its structure. A comparison of the CSs of the carbon atoms present in the α-, β-, and γ-positions to the lactam, the cyclic ketone, and the ester C=O groups shows that the influences of the C=O groups on the α-, β-, and γ-carbon atoms in the (II) and (III) are different. Thus, the lactam carbonyl in kopsinilam makes an α-contribution to the CS of the C-6 carbon atom of approximately +4-5 ppm, since, in similar alkaloids containing no lactam C=O in ring G the CS of the C-6 carbon atom amounts to 34-37 ppm [8]. At the same time, the β-contribution of this C=O to the CS of the spirocarbon C-7 of kopsinilam proves to be negative and equal approximately to –6 ppm [7-9]. The β-contribution to the CS of the C-6 carbon atom of the carbon atom of the methylene group in the five-membered ring of the indolizidone fragment of kopsinilam is similar to that in the six-membered ring of quinolizidone in which the lactam C=O makes a strong-field contribution of –4.9 ppm [10]. Although the β-contribution of the C=O of the 5-membered ring in cyclopentanone as compared with cyclopentane is also negative [11], either this contribution to the CS of the C-7 carbon of 5,22-dioxokopsane is positive or the C-7 carbon atom in (II) is affected by the strain caused by the cyclopentanone ring, as a result of which the signal of the C-7 carbon atom in 5,22-dioxokopsane resonates at 55.9 ppm. At the same time, a comparison of the figures in Table 1 show that the CS of C-6 carbon atom in 5,22-dioxokopsane is 62.7 ppm and such a pronounced downfield shift of it in comparison with those of kopsinilam and other compounds close in structure [7-9] is due both to the total (about +15 ppm) α-contribution of the lactam and cyclopentanone C=O groups [11], and also, obviously, to the strain created by the cyclopentanone ring. As can be seen from a comparison of the figures in Table 1, the γ-contributions of the cylic C=O in 5,22-dioxokopsane and the ester C=O in kopsinilam to the CSs of the C-2 carbon atom differ and the corresponding contribution to the CSs of the C-18 carbon atoms in bases (II) and (III) are extremely close. Furthermore, the γ-contribution of the C=O group of the cyclopentanone ring in (II) has a substantial effect on the C-8 sp^2 carbon atom of the aromatic ring, leading to an upfield shift of its signal by 8 ppm.

The carbon atoms of ring C together with C-20 and C-21 of kopsinilam form a bicyclo-[2.2.2.]octane system. In such a system an endo-$COOCH_3$ substituent shows the following contributions: α = +15.76 ppm, β = +3.37 and +1.92 ppm, depending on the degree of substitution of the β-carbon atoms, and γ = −4.22 ppm when the substituent is in the syn position to the γ-carbon atom and −0.85 ppm when the substituent and the carbon atom are in the anti position [12]. We made an assignment of the signals of C-14, C-15, and C-21 methylene carbon atoms of kopsinilam by taking these contributions into account.

EXPERIMENTAL

The ^{13}C NMR spectra of 5,22-dioxokopsane were obtained on a Bruker WM-250 spectrometer in $CDCl_3$ (0 — TMS, $\delta_{TMS} = \delta_{CDCl_3} + 76.91$ ppm), and those of kopsinilam, it has been shown instrument in Py-d_5, 0 — TMS in the pulsed regime followed by Fourier transformation under conditions of complete and incomplete decoupling of off-resonance C—H interactions.

CONCLUSION

On the basis of the results of a study of the ^{13}C NMR spectra of a base from *Vinca erecta* previously considered to be "kopsanone" and the known kopsinilam on a Varian CFT-20 that the former is 5,22-dioxokopsane.

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