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SOME NMDR STUDIES ON TAXININE AND DERIVATIVES

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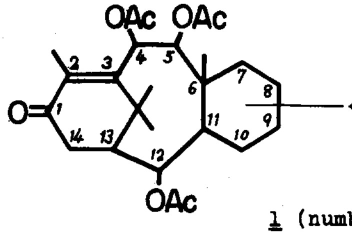
The NMDR (nuclear magnetic double resonance) data* on taxinine and derivatives given in the following permits one to extend structure 1[1] to the full structure 2. Only the results on three key compounds will be discussed here.



{$=CH_2$ and $O{\cdot}CO{\cdot}CH{=}CH{\cdot}C_6H_5$ attached to adjacent positions on ring C.

1 (numbering system is tentative)

The following notations are used in Figs. 1-3.
Abbreviations: dif., diffuse; s., singlet; d., doublet; t., triplet; q., quartet; m., multiplet.
Numbers on protons: ppm value, TMS internal reference.
Numbers between protons; J constant, cps.
Arrow: direction of arrow indicates which proton was spin-

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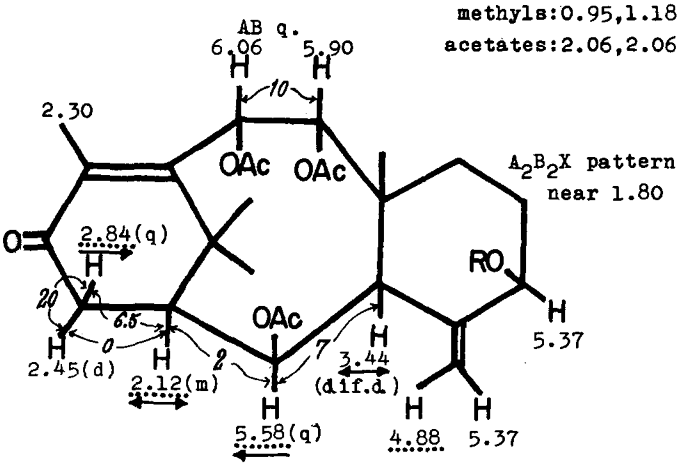
* NMR and NMDR spectra were obtained on a Varian HR-100 model; decoupling experiments were carried out as described in Varian Technical Information Bulletin, Vol.III, No.3 ins. 1471. All spectra were obtained at 100 Mc.

decoupled; e.g., in Fig.1, the left-pointed arrow by the 5.58 ppm proton shows that C_{13}-H had been decoupled (thus reducing the 5.58 ppm quartet to a doublet). An arrow pointing both ways means that protons on both sides had been decoupled.

....: shows the proton that was irradiated with the strong H_2 frequency; thus dotted lines and direction of arrows are complementary.

* : indicates chemical shifts clarified by NMDR. For example, in oxotaxinine(Fig.3) the 1.87 ppm C_6-Me singlet is superposed on methylene signals. Since the broad singlet at 5.27 ppm (C_9-H) became sharp in NMDR traces measured at 340 cps, the C_8-methylene is at ca. 1.85 ppm (527 - 340 = 187).

FIG.1. Taxinine (in $CDCl_3$)

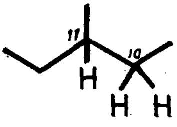


methyls:0.95,1.18,1.79
acetates:2.06,2.06,2.08

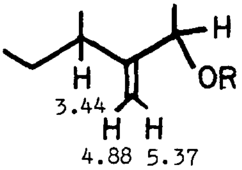
2 R:$COCH=CHC_6H_5$

1) AB quartet (J=10 - 13 cps) due to C_4 and C_5 protons is a common feature seen in all taxinine derivatives.

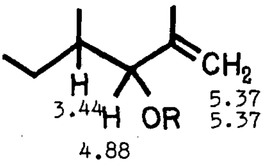
2) C_{11}-H signal: Preliminary NMDR measurements had shown that C_{11}-H became a singlet when C_{12}-H was decoupled, but this alone is not sufficient to eliminate moieties such as 3 since C_{11}-H could be equatorial and bisectional in relation to the adjacent C_{10}methylene. Alterations in bond angles in a strained system might well result in very weak coupling in the system $CH-CH_2$. However, 3 can be discarded in view of the observation that C_{11}-H is weakly coupled to a signal at the low field of 4.88 ppm. Accordingly, two possibilities 4 and 5 come into consideration.



3



4

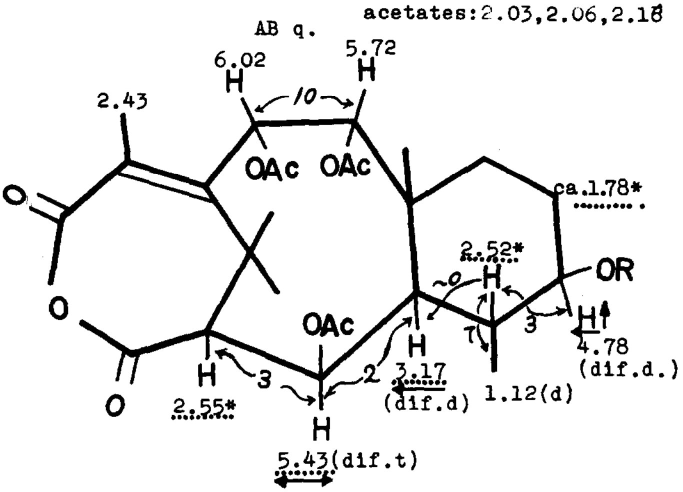


5

The A_2B_2X type pattern near 1.80 ppm was in favor of 4 but results were not conclusive since it was overlapped by a methyl singlet.

FIG.2. Acid Anhydride from Tetrahydrotaxinine[1](in $CDCl_3$)

methyls:0.93,1.49,1.75
acetates:2.03,2.06,2.18

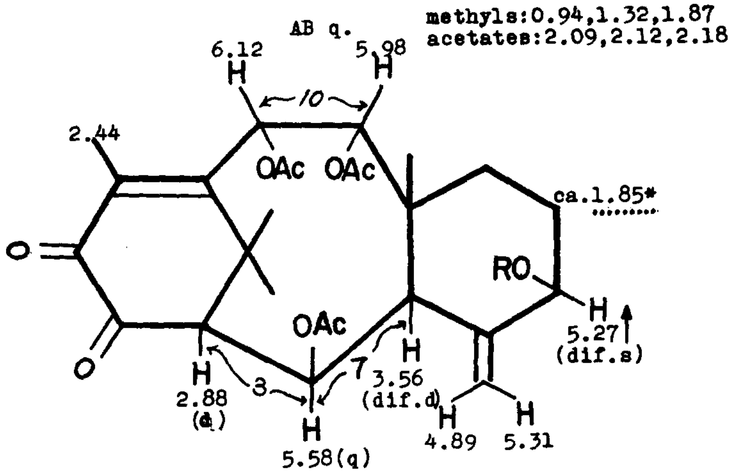


R : $CO\cdot CH_2CH_2C_6H_5$
ca.2.45 2.94

6

Part structure 4 should be adopted since in the acid anhydride 6, the diffuse doublet at 4.78 ppm, which is the proton alpha to the dihydrocinnamate group, is spin-coupled both to signals at ca. 2.52 (methine H) and 1.78 ppm (methylene H). Decoupling of C_{10}-H (230 cps) changes the C_9-H signal to a diffuse singlet, whereas decoupling of C_8-methylene (300 cps) changes the signal to a sharper doublet. Apparently, coupling between the C_8-methylene and C_9-H occurs to a slight extent only. C_{12}-H is a diffuse triplet resulting from overlap of two pairs of doublets.

FIG.3. Oxotaxinine[1] (in $CDCl_3$)



methyls: 0.94, 1.32, 1.87
acetates: 2.09, 2.12, 2.18

7 R:CO-CH=CHC_6H_5

The diffuse singlet at 5.27 ppm becomes sharper upon irradiation of the signal near 1.85 ppm (A_2B_2X type pattern) The weak coupling between the C_8 and C_9 protons is a common observance in all taxinine derivatives having the skeletal structure intact. Only in seco-taxinol derivatives[1] does it appear as a quartet.

REFERENCES

1. M. Kurono, Y. Nakadaira, S. Onuma, K. Sasaki and K. Nakanishi, 2153 (1963).