^{13}C NMR OF ISOPIMARANE DITERPENES: 8,9-EPOXYKETONES

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The ^{13}C NMR data for some 8,9-epoxy-7-keto-isopimaranes are presented. The main effects observed on the carbon chemical shifts upon epoxidation are discussed.

INTRODUCTION

As part of our continuing studies on the ^{13}C NMR of isopimarane diterpenoids[1] , we have studied the main effects observed upon substitution on several positions of the isopimaranes framework[2] , in order to establish parameters for structural elucidation in this class of terpenoids. We hereby discuss some of the effects caused by epoxidation of the 8,9-double bond of a series of 7-keto-12-oxy and 7,11-diketo-isopimaranes.

EXPERIMENTAL

The precursors for the epoxidation reaction were available either directly from natural sources[3], or through reactions of previously isolated substances[4]. The epoxidations were performed by reaction with alkaline hydrogen peroxide under standard conditions.

The ^{13}C NMR spectra of the diterpenes were recorded at 25.2 MHz using a Varian XL - 100 spectrometer in the FT mode. The acquisition parameters were as follows: pulse width, 17 s ; acquisition time, 0.6 s ; spectral width, 6150 Hz, pulse repetition time, 2.0s; number of transients, 6000; and number of data points, 8192. The spectra were obtained from deuteriochloroform solution (5-15% w/v) with 1% TMS as internal reference.

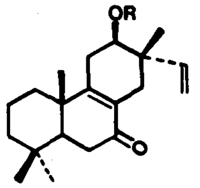
The ^{13}C NMR spectra were recorded in the proton-noise decoupled mode, affording the chemical shift values (δ), which are referred in ppm relative to TMS (data in table I). The substitution pattern of each carbon from the diterpenic framework was obtained through the SFORD mode.

RESULTS AND DISCUSSION

Considering the enone moiety present at the herein investigated isopimaranes, the effects observed upon the epoxidation reaction on the chemical shifts of C-8 and C-9 are clearly distinct. While the former undergoes the expected shift according to the substitution pattern (ca. - 55 ppm), the later is strongly shielded (ca.-98 ppm). Compounds 7 and 8 are excluded from this analysis as the mutual interference of the two carbonyl groups at C-7 and C-11 leads to shifts out of the range of those observed for the other compounds.

Analysis of the effects on the allylic carbons (as the related to the enone system double bond) reveals that C-10 and C-14 are clearly shielded upon epoxidation (ca.-2 and -3 ppm, respectively). The keto carbon at C-7 is deshielded (ca. 8 ppm) in compounds 1 - 6, due to the supression of the resonance effect of the double bond.

The most important effect of the epoxyde function arises from its tendency to shield the carbons which have, at least, one hydrogen situated three carbons away and bearing a SYNAXIAL relationship to it (GAMMA EFFECT)[5]. In compounds 1-8, the effect is nitid at C-5 (ca. -8 ppm), proving the ALPHA stereochemistry of the epoxide group, and noticeably lacking for C-12 in compounds 1-6. While this may seem unexpected at first glance, it is certainly due to the conformation adopted by the C-ring in these compounds, precluding the required SYNAXIAL relationship between the epoxyde oxigen and the hydrogen at C-12. On the other side, the shielding effect observed at C-17 methyl carbon, due to a GAMMA interaction with the oxygen at C-12, can be explained by a correct spatial relationship between the two centers induced upon the epoxidation reaction.



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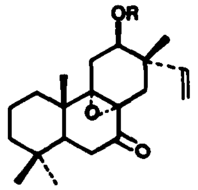
3 R=Ac



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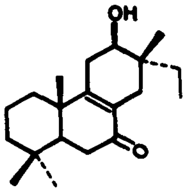

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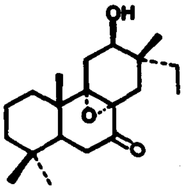

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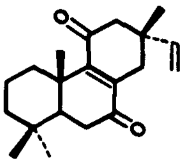

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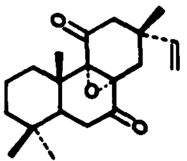

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Table 1. ^{13}C chemical shifts (δ) of diterpenes 1-8*

	1	2	3	4	5	6	7	8
C-1	35.6	35.7	35.3	35.6	35.9	35.7	35.9	35.7
C-2	18.3	18.4	18.4	18.8	18.5	18.5	18.5	18.4
C-3	41.1	41.0	41.0	41.0	41.1	41.1	40.8	41.1
C-4	32.9	33.1	33.0	33.0	33.1	33.1	32.8	33.4
C-5	49.9	41.7	50.0	41.6	50.0	41.8	49.7	41.9
C-6	35.1	34.4	35.1	34.0	35.3	34.4	35.0	35.2
C-7	199.8	207.7	198.8	207.0	199.6	207.8	200.4	204.0
C-8	128.0	73.9	128.1	72.3	128.4	73.9	141.5	69.8
C-9	163.3	63.8	161.4	63.9	162.9	64.5	154.9	72.0
C-10	39.3	37.8	39.4	37.6	39.4	37.6	39.0	36.7
C-11	30.9	32.8	30.5	32.1	31.2	31.2	201.6	204.5
C-12	70.1	69.5	73.2	73.5	71.5	70.5	50.5	47.6
C-13	39.3	39.4	37.9	37.1	35.3	35.0	37.8	40.4
C-14	30.7	27.0	28.5	25.4	30.8	28.1	34.8	32.8
C-15	144.0	144.7	142.3	143.8	30.9	30.6	144.5	145.7
C-16	112.9	115.1	113.4	113.4	7.7	7.6	112.3	111.1
C-17	19.8	15.0	22.3	18.3	21.3	16.9	26.4	25.0
C-18	32.2	32.4	32.3	32.5	32.3	32.5	32.8	32.4
C-19	21.1	20.6	21.2	21.0	19.0	20.6	21.2	20.6
C-20	17.6	16.9	17.4	16.7	17.9	16.9	17.3	16.1

*Values in ppm from TMS.

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