

103 mg of (–)-isocomene (3) identical with a natural sample. Compound 5 (40 mg) in Et₂O (2 ml) and H₂ atmosphere (room temp. and pres.) with 10% Pd/C afforded 37 mg of 3.

Acknowledgements—The authors are indebted to Dr. José M^a Hernández Hernández, of our Laboratory, for MS measurements.

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Phytochemistry, 1981, Vol. 20, pp. 167–169. © Pergamon Press Ltd. Printed in England.

0031-9422/81/0101-0167 \$02.00/0

CARBON-13 NMR SPECTRA OF SOME ENT-ROSANE DITERPENOIDS

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(Received 17 March 1980)

Key Word Index—Diterpenoids; *ent*-rosa-5,15-diene; *ent*-8,5-*friedo*-pimara-5,15-diene derivatives; ¹³C NMR analysis.

Abstract—The ¹³C NMR signals of the parent hydrocarbon *ent*-rosa-5,15-diene (*ent*-8,5-*friedo*-pimara-5,15-diene) and some of their oxygenated derivatives have been assigned.

INTRODUCTION

¹³C NMR spectroscopy is an excellent tool for the structural elucidation of natural substances. In the diterpene field there is already a considerable amount of information which confirms this view. Podocarpanes [1], labdanes [2,3], primaranes [4,5], abietanes [6], *ent*-kauranes [7], *ent*-beyeranes [8,9], *ent*-atisanes [10–12], *ent*-trachylobanes [13,14] and *ent*-clerodanes [15–17] have been studied among others.

The availability of a series of *ent*-rosane derivatives and our continued interest [8–11] in the applications of ¹³C NMR spectroscopy has prompted us to carry out this study. Until now, only ¹³C NMR data of rosenonolactone and some of its derivatives [18], jesromotretol [19], and partial results on rimuene [20] (the epimer at C-13 of compound 1) have been reported. This paper presents the

¹³C NMR data for the parent hydrocarbon *ent*-rosa-5,15-diene (1) and the C-11 and/or C-15 and C-16 oxygenated derivatives (2–8), many of which are natural diterpenoids [21,22].

RESULTS AND DISCUSSION

The assignments for the ¹³C NMR chemical shifts of the diterpenoids (Table 1) were made with the aid of off-resonance decoupled spectra and selective decoupling experiments, and further based on comparison of pairs of compounds, consideration of β, γ and δ substituent effects, general chemical shift arguments and literature data on related structures [4, 5, 18–20].

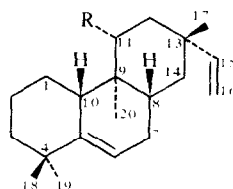
In general we have detected no unusual effects in this type of hydrocarbon skeleton. The presence of an 11-keto group (8), the different stereochemistry of the C-11

hydroxyl group (6 and 7) and the absence of any substitution in this carbon atom (1 and 3) are clearly reflected in the chemical shifts of C-1, C-8, C-10 and C-20 carbon atoms. On the other hand, a γ -gauche effect caused by the C-15 hydroxyl group is evidenced by the C-14 carbon atom chemical shifts (Table 1).

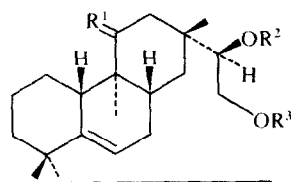
EXPERIMENTAL

All ^{13}C NMR spectra were obtained on a Varian XL-100 (15) spectrometer equipped with a Nicolet TT-100PFT accessory. The spectra were recorded at the base frequency of 25.2 MHz over a spectral width of 6 kHz with the solvent (commercial NMR grade CDCl_3) providing an internal deuterium lock. A total of 8 K data points were collected in the FID. A pulse width of $10.0\mu\text{s}$ was used to aid in the acquisition of the slower relaxing carbons. The total time delay between pulses was 1.3 sec. The proton-decoupled spectra were obtained using a square-wave modulated noise band centred in the proton spectrum. All samples were prepared as 0.3 M CDCl_3 solns in 12 mm sample tubes. The probe temp. in each case was 37°. Chemical shifts are accurate to ± 0.05 ppm.

Compounds 3 to 8 have been previously described [21,22], whilst diterpenes 1 and 2 were obtained from compounds 3 and 4, respectively, by literature methods [23].



- 1 R = H
2 R = OH



	R ¹	R ²	R ³
3	H ₂	Ac	Ac
4	H AcO	Ac	Ac
5	H AcO	H	H
6	H HO	CMe ₂	
7	HO H	CMe ₂	
8	O	CMe ₂	

Table 1. ^{13}C NMR chemical shifts (in ppm from TMS) of compounds 1-8

	1	2	3	4	5	6	7	8
C-1	26.5	30.8	26.5	30.4	30.4	30.8	25.7	28.9
C-2	21.9	22.4	21.9	22.3	22.3	22.4	21.8	21.8
C-3	40.8	40.9	40.7	40.7	40.7	40.9	40.7	40.9
C-4	36.3	36.3	36.5	36.3	36.3	36.3†	35.9	36.2
C-5	145.7	146.6	145.6	146.1	146.2	146.6	145.7	146.2
C-6	116.2	115.6	116.0	115.5	115.5	115.4	115.4	114.4
C-7	30.2*	29.4*	29.3	29.0	29.2	29.4	30.5	28.9
C-8	36.1	36.3	35.6	35.8	35.9	35.7	29.4	37.7†
C-9	34.7†	40.5	34.6	39.3	39.4	40.5	38.7	49.1
C-10	47.3*	47.1*	47.1	46.0	46.1	46.9	38.0	38.5†
C-11	34.3	77.9	33.6	78.3	80.2*	77.6	72.2	214.7
C-12	32.4	38.6	30.2	34.8	34.6	35.5	34.7	43.7*
C-13	35.8†	37.3	35.8	37.3	37.5	36.4†	34.7	40.9
C-14	39.1	42.5	36.2	35.8	35.8	38.7	36.5	35.7
C-15	151.3	149.8	79.2	79.2	80.2	84.0	84.8	82.8
C-16	108.4	108.9	63.0	62.7	62.3	64.4	64.3	64.3
C-17	22.4	23.7	18.5	19.6	19.8	20.0	22.5	20.2
C-18	29.3‡	28.6†	29.1†	28.4†	28.4†	28.5‡	29.6†	28.7‡
C-19	29.7‡	30.0†	29.7†	29.9†	29.9†	30.0‡	29.7†	29.6‡
C-20	12.4*	5.9*	12.3*	7.2*	7.2	5.9	12.8*	12.2
11-OAc	—	—	—	170.1	170.5	—	—	—
	—	—	—	21.6*	21.7*	—	—	—
15-OAc	—	—	170.6‡	170.3‡	—	—	—	—
	—	—	20.9§	20.8§	—	—	—	—
16-OAc	—	—	170.3‡	170.1‡	—	—	—	—
	—	—	20.8§	20.7§	—	—	—	—
—CMe ₂ —	—	—	—	—	—	108.5	108.5	108.8
	—	—	—	—	—	26.2	26.2*	26.2*
	—	—	—	—	—	25.0	25.1*	25.0*

* These assignments have been confirmed by selective decoupling experiments.

†, ‡, § Values in any vertical column may be interchanged, but those given here are considered to be most likely.

ent-Rosa-5,15-diene (1). Thick oil, n_D^{10} 1.5137, $[\alpha]_D^{21} -42.4^\circ$ (c 1.33, CHCl_3). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3090, 3050, 1640, 915, 870, 830, 820, 805. ^1H NMR (CDCl_3) δ H-15 and 2H-16 as an ABX system: $\delta_A = 4.93$, $\delta_B = 5.00$, $\delta_X = 5.95$ ($J_{AB} = 2.6$, $J_{AX} = 10.6$, $J_{BX} = 18$ Hz), 5.60 (1H, m, $W_1 = 7$ Hz, H-6), C-Me singlets at 1.09 (3H), 1.05 (6H) and 0.69 (3H). (Found: C, 88.27; H, 11.56. $\text{C}_{20}\text{H}_{32}$ requires: C, 88.16; H, 11.84%).

ent-11 β -Hydroxy-rosa-5,15-diene (2). Mp 99–102° (n-hexane), $[\alpha]_D^{21} -45.4^\circ$ (c 0.68, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3290, 3095, 3060, 1640, 1020, 915, 825, 805. ^1H NMR (CDCl_3) δ H-15 and 2H-16 as an ABX system: $\delta_A = 4.91$, $\delta_B = 4.96$, $\delta_X = 5.88$ ($J_{AB} = 2.6$, $J_{AX} = 10.6$, $J_{BX} = 18$ Hz), 5.60 (1H, m, $W_1 = 7$ Hz, H-6), 3.77 (1H, q, $J_{aa'} = 9.3$ Hz, $J_{ae} = 6.6$ Hz, H-11), C-Me singlets at 1.07 (6H), 1.05 (3H) and 0.70 (3H). (Found: C, 83.31; H, 11.27. $\text{C}_{20}\text{H}_{32}\text{O}$ requires: C, 83.27; H, 11.18%).

Acknowledgements—We thank Miss M. D. Casado and Miss M. Plaza for recording the ^{13}C and ^1H NMR spectra and Mr. J. Prieto for elemental analyses. This work was supported in part by the Comisión Asesora de Investigación Científica y Técnica.

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