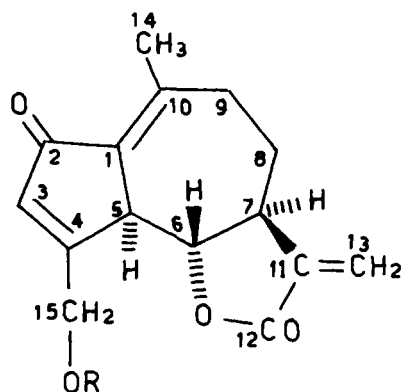


HIGH RESOLUTION NMR DATA OF 8-DEOXY-LACTUCIN

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A recent paper (1) by Bohlmann *et al.* prompts us to report additional nmr data about the sesquiterpene 8-deoxy-lactucin **1** isolated from the same species described by Bohlmann as *Picris echioides* L. (Compositae) and known by us as the synonymous (2) *Helminthia echioides* Gaertn.



- 1 R = H
2 R = Ac

Our material, collected in Sicily on the hills around Palermo (voucher in the Herbarium of the Botanic Garden, University of Palermo), was particularly rich in 8-deoxy-lactucin, whereas it contained only traces of jacquilenin and/or 11-epi-jacquilenin and some lupeol.

The guaiazulene lactone 8-deoxy-lactucin had been extracted previously by Pyrek (3) from *Lactuca serriola* L. (Compositae) and its absolute stereostructure exhaustively elucidated as **1**. Physical and spectroscopic data reported by Pyrek (3) and by Bohlmann (1) are in agreement with those found for our product. As we had the opportunity of registering a 400 MHz ^1H -nmr spectrum of **1** and a ^{13}C -nmr spectrum of the acetate **2**, we report the related data in tables 1 and 2. We wish also to correct a misprint in the 100 MHz ^1H -nmr reported (3) spectrum of acetate **2**. The chemical shift of H-13a is 5.50 and not 5.10 δ ; moreover, the signal of H-7 was clearly observed by us at 2.84 δ even at 90 MHz.

All assignments and coupling constants reported in table 1 were confirmed by spin decoupling experiments. Protons on C-8 and C-9 are indicated as H-8 ax, H-8 eq, H-9 ax and H-9 eq because the doubly condensed cycloheptene ring can assume two conformations ($8\beta,9\alpha$ -diaxial, or, less probably, $8\alpha,9\beta$ -diaxial).

Assignments in table 2 were confirmed by single frequency off-resonance decoupling and compared with literature data on guaianolides.

TABLE 1. Chemical shifts δ of [1] ^1H -nmr spectrum (CDCl_3 , 400 MHz).

H-3	6.44	dt	$J_{3,5\alpha}$ 1.5 Hz	$J_{3,15}$ 1.5 Hz		
H-5 α	3.70	d (br)	$J_{5\alpha,6\beta}$ 10 Hz	$J_{5\alpha,3}$ 1.5 Hz		
H-6 β	3.61	t	$J_{6\beta,5\alpha}$ 10 Hz	$J_{6\beta,7\alpha}$ 10 Hz		
H-7 α	2.89	m	$J_{7\alpha,6\beta}$ 10 Hz	$J_{7\alpha,13}$ 3 Hz	$J_{7\alpha,8ax}$ 11 Hz	$J_{7\alpha,8eq}$ 1 Hz
H-8 ax	1.46	m	$J_{8ax,7\alpha}$ 11 Hz	J_{gem} 13 Hz	$J_{8ax,9ax}$ 13 Hz	$J_{8ax,9eq}$ 2.5 Hz
H-8 eq	2.22	m	$J_{8:q,7\alpha}$ 1 Hz	J_{gem} 13 Hz	$J_{8eq,9eq}$ 6 Hz	$J_{8eq,9ax}$ 2.5 Hz
H-9 eq	2.40	m	$J_{9eq,8ax}$ 2.5 Hz	J_{gem} 13 Hz	$J_{9eq,8eq}$ 6 Hz	
H-9 ax	2.53	m	$J_{9ax,8ax}$ 13 Hz	J_{gem} 13 Hz	$J_{9ax,8eq}$ 2.5 Hz	
H-13 a	5.49	d	$J_{13a,7\alpha}$ 3 Hz			
H-13 b	6.19	d	$J_{13b,7\alpha}$ 3 Hz			
3H-14	2.46	s				
H-15 a	4.57	d (br)	J_{gem} 17 Hz	$J_{15a,3}$ 1.5 Hz		
H-15 b	4.90	d (br)	J_{gem} 17 Hz	$J_{15b,3}$ 1.5 Hz		

TABLE 2. Chemical shifts ppm of [2] ^{13}C -nmr spectrum (CDCl_3 , 25.1 MHz).

C-1	130.8 s	C-10	153.4 s
C-2	194.2 s	C-11	138.4 s
C-3	133.6 d	C-12	168.2 s**
C-4	165.9 s	C-13	118.9 t
C-5	52.7 d*	C-14	22.0 q ⁺
C-6	83.5 d	C-15	63.2 t
C-7	50.6 d*	CO acetyl	169.8 s**
C-8	24.3 t	CH ₂ "	20.6 q ⁺
C-9	37.4 t		

*, **, +Interchangeable assignments.

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