Triterpenoids from *Abies* species
18.* NMR spectra of abieslactone and its dehydro derivative

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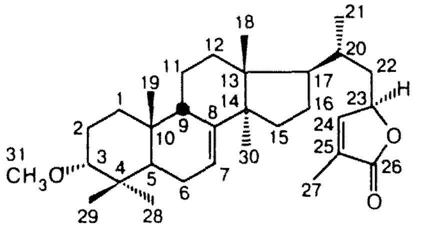
The contradictions in the interpretations of the ^{13}C NMR spectrum of a natural lanostanoid, abieslactone, and of the ^{1}H NMR spectrum of its 9,11-dehydro derivative reported in the literature were resolved by two-dimensional $^{1}H-^{1}H$ and $^{13}C-^{1}H$ (COSY) NMR spectroscopy.

Key words: triterpenoids, lanostanoids, two-dimensional NMR spectroscopy.

Abieslactone (**1**) is a representative of a large group of triterpenoids characteristic of conifers of the *Abies* Hill genus.[2–4] It has been known for about 25 years, but there are still some problems in its ^{13}C NMR spectrum.

The signals in the spectrum of compound **1** were first assigned[5] on the basis of comparison with the ^{13}C NMR spectrum of a holostane triterpenoid reported earlier. Two-dimensional $^{1}H-^{1}H$ (COSY) and $^{13}C-^{1}H$ (COSY, COLOC) spectroscopy was used in the study.[6] It should however be pointed out that the authors did not state that these methods were applied specifically to lactone **1**, as it was not the main object of the investigation. The interpretation of the spectrum differed from that described previously[5] only in the inverse assignment of the signals for the C(12) and C(15) atoms.



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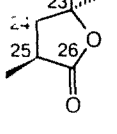

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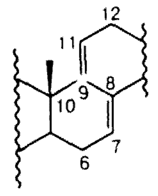

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Finally, one paper[7] reports the use of the method of LRJMD[8] and two-dimensional $^{13}C-^{1}H$ (COSY, COLOC) NMR spectroscopy. There the data of a study[6] concerning the signals of the C(12) and C(15) atoms were confirmed, but different assignments for the signals of the three other atoms, C(2), C(6), and C(11), were made (Table 2). No arguments in favor of the assignment of the C(2) and C(11) atoms were given. $CDCl_3$ was used for the registration of ^{13}C NMR spectra in Refs. 5, 6. Using a $CDCl_3-C_6D_6$ mixture (1 : 1 vol.)[7] did not result in significant differences in the chemical shifts of most of the signals of lactone **1**, except splitting of the signals of C(18) and C(29) that coincided in the case of $CDCl_3$ solution. Numbering of the carbon atoms of the methyl groups at C(4) in Ref. 7 differs from that commonly accepted, and their numbers should be changed, as we did in Table 1. It is also necessary to point out a mistake in the structural formula of lactone **1**: the Δ^7 double bond is not shown.

The problem of the correct assignment of the signals for the C(2), C(6), and C(11) atoms in the ^{13}C NMR spectrum of lactone **1** was resolved by an examination of the $^{1}H-^{1}H$ (COSY) and $^{13}C-^{1}H$ (COSY) NMR spectra. The following cross peaks were observed: H(3)/2 H(2), H(1β); H(7)/2 H(6), H(9); H(9)/2 H(11); C(2)/2 H(2); C(6)/2 H(6); and C(11)/2 H(11). The values of the chemical shifts for the C(2), C(6), and C(11) atoms in the ^{13}C NMR spectrum of lactone **1** correspond to those reported in Ref. 6 and thus confirm the correctness of that paper.

For additional proof of the erroneous assignment of the three atoms under consideration in Ref. 7, we recorded the NMR (^{1}H, ^{13}C) spectra and two-dimensional ($^{1}H-^{1}H$ (COSY) and $^{13}C-^{1}H$ (COSY, COLOC)) NMR spectra of (25*S*)-24,25-dihydroabieslactone **2** (reported in Ref. 9), which differs from lactone **1** only in the absence of the double bond in the lateral chain. The same $C_6D_6-CDCl_3$ mixture (1 : 1 vol.) as in the Ref. 7 was used for registration of the NMR spectrum. The data obtained (Table 1) testify that C_6D_6 has little influence on the position of the

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* For Part 17 see Ref. 1.

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Table 1. ^{13}C NMR data for compounds **1**[6,7] and **2** and ^{1}H NMR data for compound **2**[a] (δ, ppm)

Atom number (*i*)	δC(*i*)			δH(*i*)
	1		**2**	**2**
	Data from Refs.			
	6	7		
1	30.10	30.041	29.95 t	1.05[b]; 1.80[b]
2	20.43	23.057	20.27 t	1.69[b] (2 H)
3	85.96	85.748	85.57 d	2.73 t
4	37.65	37.667	37.50 s	—
5	42.91	43.130	42.85 d	1.36[b]
6	23.10	22.791	22.93 t	1.87[b] (2 H)
7	121.64	121.754	121.58 d	5.58 m
8	148.51	148.446	148.36 s	—
9	48.61	48.736	48.54 d	2.28 m
10	35.71	35.736	35.55 s	—
11	22.87	20.535	22.78 t	1.52[b]; 1.76[b]
12	35.37	35.535	35.25 t	1.63[b]; 1.75[b]
13	43.70	43.766	43.49 s	—
14	52.88	52.837	52.73 s	—
15	33.27	33.293	33.16 t	1.54[b] (2 H)
16	28.64	28.455	28.46 t	1.28[b]; 1.87[b]
17	54.01	53.905	53.84 d	1.35[b]
18	23.83	23.524	23.56 q	0.942 s
19	24.54	24.383	24.33 q	1.029 s
20	33.47	33.364	33.18 d	1.73 m
21	18.41	18.258	18.09 q	0.87 d (J = 6.5 Hz)
28	28.71	28.535	28.58 q	1.013 s
29	23.83	23.450	23.49 q	0.890 s
30	30.91	30.564	30.64 q	1.026 s
31	56.88	56.492	56.42 q	3.182 s

[a] ^{1}H and ^{13}C NMR spectra for compound **2** are registered in C_6D_6—$CDCl_3$ (1 : 1 vol., c = 65 mg · mL^{-1}), chemical shifts δ for the atoms of the lateral chain of **1** and **2** are not included.

[b] The value is obtained from the two-dimensional ^{13}C—^{1}H (COSY) spectrum.

signals of the C(2), C(6), and C(11) atoms in the ^{13}C NMR spectrum and support the interpretation made in Ref. 6.

The 9,11-dehydro derivative of lactone **1**, dienolactone **3**, is a natural component of the extract from the bark of the fir of a Japanese species (*Abies veitchii*).[10] It was also obtained by treatment of lactone **1** with SeO_2 [10] and treatment of 7,8-epoxyabieslactone with H_2SO_4.[11] The assignment of the H(7) and H(11) protons in the ^{1}H NMR spectrum of dienolactone **3** in Ref. 10 is the reverse of that reported in Ref. 11. The validity of the latter interpretation[11] is indicated by the presence of all three signals of the atoms forming the H(5)—2 H(6)—H(7)—H(11)—2 H(12) chain (see Experimental) in the ^{1}H NMR spectrum of dienolactone **3**. Interestingly, the assignment of the signals of C(7) and C(11) in the ^{13}C NMR spectrum of **3** in Ref. 10 is correct in spite of the mistake in the assignment of the signals of the H(7) and H(11) protons in the ^{1}H NMR spectrum. This was verified in the two-dimensional ^{1}H—^{1}H (COSY) and ^{13}C—^{1}H (COSY) NMR spectra of this compound.

Experimental

Lactones 1 and 2 were obtained by procedures reported previously,[9] and dienolactone **3** was obtained as described in Ref. 11.

NMR spectra were registered on a Bruker AM-400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, δ-scale) at +30 °C HH-COSY (9 Hz), HC-COSY (125 Hz), and COLOC (5 Hz) Bruker standard programs were used for the registration of the two-dimensional NMR spectra.

Dienolactone 3. ^{1}H NMR ($CDCl_3$, δ, J/Hz): 1.48 (t, 1 H, H(5), $^3J_{5,6}$ = 8.0); 1.98 (dd, 2 H, ^3J = 8.0 and 4.0, 2 H(6)); 2.08 (dd, 1 H, H(12a), ^2J = 17, $^3J_{12a,11}$ = 6.0); 2.19 (br. d, 1 H, H(12b), ^2J = 17); 5.29 (ddd, 1 H, H(11), $^3J_{11,12a}$ = 6.0, $^3J_{11,12b}$ = $^5J_{11,7}$ = 2); 5.43 (br. t, 1 H, H(7), $^3J_{7,6}$ = 4.0). Other signals correspond to those reported in Ref. 11.

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