

C₁₂ STEREOCHEMISTRY OF α - AND β -LEVANTENOLIDE
CARBON-13 NMR SPECTRA OF LABDANOLIC DITERPENES

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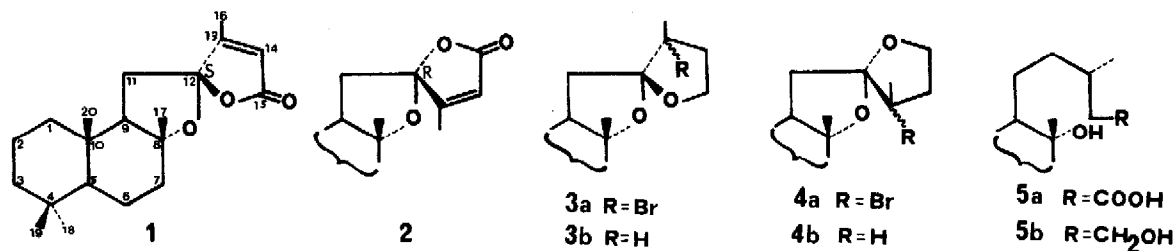
From Turkish tobacco Giles and Schumacher¹ isolated the two diterpene lactones β - and α -levantenolide, for which they proposed structures 1 and 2 respectively on the bases of chemical degradative work and spectral data.

As we show below, the stereochemistry of these compounds at C₁₂ must be revised in the light of spectroscopic studies.

The ¹H-decoupled natural abundance ¹³C FT NMR spectra of these and related labdanolic diterpenes have been examined in CDCl₃. Application of known chemical shift rules², SFORD and NORD experiments and comparison of the spectra of structurally related compounds led us to the ¹³C signal assignments shown in the Table. A survey of these values indicates that in the C₁₂ epimeric pairs 1 and 2, 3a and 4a, 3b and 4b, the C₉ carbon atom is shielded (4.5 - 2.5 ppm) in those isomers (2, 4a and 4b) in which the 12,15-epoxide oxygen and the axial hydrogen in C₉ are cis to one another. Moreover, a significant upfield shift (0.4 ppm) is observed in the C₅ carbon atom, induced by mutual compression of the H-C₉ and H-C₅. Analogues exemplifying this effect have been reported³.

In addition, a study of the LIS in the PMR spectra of 1 and 2, using Eu(fod)₃, was carried out, in which a similar deshielding was experienced by the H-C₁₄ in both isomers, and likewise by the Me-C₁₃, while the downfield shift of the Me-C₈ was stronger in 1 (12S) [slope(δ vs. [LSR]/[S]) = 2.7] than in 2 (12R) [slope = 1.6], as expected.

So, the C₁₂ stereochemistry of the α -levantenolide, $[\alpha]_D + 60.4^\circ$, should be changed to 12S and that of the β -levantenolide, $[\alpha]_D - 59.6^\circ$, to 12R.



T A B L E †

Carbon	1	2	3a	4a	3b	4b	5a	5b
1	40.0 [±]	39.9 [±]	40.0	39.9	40.0 [±]	39.9 [±]	39.8	39.8
2	18.3	18.3	18.4	18.4	18.4	18.4	18.5	18.5
3	42.4	42.2	42.5	42.5	42.6	42.5	42.1	42.1
4	33.2	33.2	33.1	33.1	33.1	33.1	33.3	33.3
5	57.3	56.9	57.2	56.8	57.2	56.8	56.1	56.2
6	20.6	20.9	20.5	20.9	20.5	21.0	20.5	20.6
7	39.7 [±]	40.1 [±]	40.0	41.2	39.9 [±]	40.6 [±]	40.6	40.9
8	85.4	86.2	84.0	84.7	81.6	81.9	75.0	74.4
9	62.4	58.1	61.8	58.8	61.3	58.8	62.1	62.5
10	36.6	36.7	36.3	36.3	36.2	36.1	39.2	39.2
11	32.4	32.8	31.5	32.7	32.2	32.1	23.9	24.0
12	114.1	114.1	116.0	116.4	114.3	116.4	43.9	44.3
13	165.8	165.5	73.4	72.4	32.8	30.0	31.3	30.6
14	117.1	119.0	41.7	42.3	42.6	41.9	41.6	39.8
15	170.6	170.0	64.7	64.6	65.6	65.1	177.7	60.3
16	12.3	12.7	26.6	26.9	13.5	16.6	20.0	20.1
17	22.4	23.7	22.9	23.9	23.0	23.0	23.1	23.2
18	33.5	33.5	33.5	33.5	33.5	33.5	33.4	33.5
19	21.0	21.4	21.1	21.3	21.1	21.0	21.5	21.5
20	15.0	15.8	14.9	15.6	14.9	15.4	15.5	15.5

† In ppm relative to TMS, using a Varian CFT-20. ± One of these assignments may be the more exact

R E F E R E N C E S

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