

CORRESPONDENCE

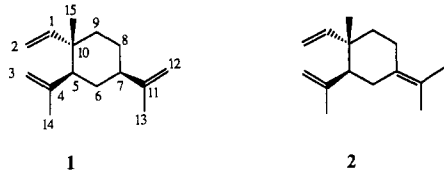
Comment on Sesquiterpene Composition of Basil Oil. Assignment of the ^1H and ^{13}C NMR Spectra of β -Elemene with Two-Dimensional NMR

Sir: This letter concerns the ^1H and ^{13}C assignments of β -elemene (1) published by Gadou et al. (1989). We would like to point out the incorrect assignments of four of the carbon atoms of 1, as well as some inconsistent reasoning leading to incorrect assignments of the ^1H NMR signals.

Our spectra were very similar to those published by Gaydou et al. (1989), except that our sample did not contain the impurity causing the additional ^1H methyl signal at ca. 1.1 ppm. Other differences will be mentioned as they arise. The most striking error in Gaydou et al. (1989) is the observation of a "zigzag coupling" between H-2a and H-5 in the ^1H NMR spectrum [The numbering of elemene in Gaydou et al. (1989) is consistent neither with cyclohexane rules nor with sesquiterpene convention. We have numbered them as secoeudesmanes.] which led them to postulate a trans orientation of the vinyl group at C-10 and the proton at C-5. These groups are in fact cis oriented in the generally accepted formula of elemene [cf. Ganter and Keller-Wojtkiewicz (1971) and Thomas et al. (1973)], and there seems no reason to expect any coupling between H-2 and H-5; indeed, we did not see any.

The key to interpretation of the ^1H NMR spectrum of β -elemene (1) lies in the couplings of the signals centered on 1.94 and 2.01 ppm (Gaydou et al. give 1.91 for the first of these). The signal at higher field is a complex multiplet, while the signal at 2.01 ppm shows some higher order double-doublet with approximately 5.5- and 8-Hz couplings and must therefore be assigned to the proton at C-5 (coupled with the two C-6 protons). Consequently, the signal at 1.94 ppm is that of the proton at C-7, coupling with two protons at C-6 and two at C-8. The proton at 1.94 ppm is coupled with one of the protons of a methylene group at 4.72 ppm (the other proton of this group is at 4.70 ppm), and this methylene group is associated with the methyl group at 1.75 ppm, these signals thus accounting for the isopropenyl group at C-7. Similarly, the proton at 2.01 ppm is coupled with one proton (4.59 ppm) of a methylene group, the other proton of which is at 4.82 ppm, these being associated with the methyl group at 1.71 ppm. Attribution of the cyclohexane methylene groups is indeed not possible using only the COSY spectrum. Nevertheless, the proton at 1.94 ppm can be seen to couple with two sets of protons; of these two sets, the one at lower field is also coupled with the proton at 2.01 ppm and must therefore be attributed to the CH_2 group at C-6, the other set being at C-8. The ^1H - ^{13}C correlation spectrum then allows attribution of the ^{13}C signals to these groups as 26.9 (C-8) and 33.0 (C-6), values more in line with similarly substituted cyclohexanes than the attributions of Gaydou et al. Our attributions are shown in Table I, together with comparative figures for γ -elemene (2). The similarity of the attributions of the ^{13}C signals for all carbon atoms except those of the iso-

Table I



		^{13}C		^1H	
		1	2	1	2
C-1	(7) ^a	150.4	150.0	5.82	5.79
C-2	(8)	109.9	110.0	4.90, 4.91	4.90, 4.91
C-3	(10)	112.1	111.9	4.59, 4.82	4.62, 4.83
C-4	(9)	147.7	148.0		
C-5	(6)	52.9	53.1	2.01	2.07
C-6	(5)	33.0	31.4	~1.58	1.95, 2.42
C-7	(4)	45.6	131.0	1.94	
C-8	(3)	26.9	25.5	~1.46	1.91, 2.05
C-9	(2)	40.0	40.1		1.42
C-10	(1)	39.8	39.9		
C-11	(12)	150.4	121.0		
C-12	(13)	108.3	19.9 ^b	4.70, 4.72	
C-13	(14)	21.1	20.0 ^b	1.75	1.67
C-14	(11)	24.8	24.7	1.71	1.75
C-15	(15)	16.7	17.0	1.01	1.07

^a Numbers in parentheses refer to numbering used by Gaydou et al. (1989). ^b May be interchanged.

propylidene group support the attributions for β -elemene (1).

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