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CONFIGURATIONAL ASSIGNMENT BY NMR SPECTROSCOPY OF STEREOISOMERIC 2,6-DIMETHYL-TRICYCLO[5.2.1.$0^{2,6}$]DEC-3-ENES AND DECANES

ALBENE AND ISOALBENE

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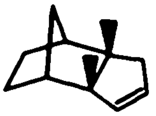
Abstract—By means of ^{13}C NMR spectroscopy a distinction is made between the two stereoisomeric 2,6-dimethyl-tricyclo[5.2.1.$0^{2,6}$]dec-3-enes 1 and 5. This corrects the previously proposed structure of the natural hydrocarbon "albene".

In 1962 Novotný *et al.*[1] first reported the isolation of an optically active tricyclic hydrocarbon $C_{12}H_{18}$ from *Petasites albus* (white pestilence weed). Ten years later Šorm's group[2] solved the structure of this compound (termed "albene") by degradation to and correlation with (−)-*endo*-camphane. In the same paper its absolute configuration had been established by an ORD examination.



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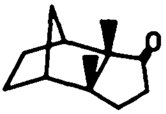

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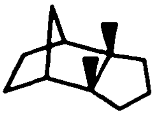
In the following year, Lansbury[3] confirmed constitution 1, which had been assigned to natural "albene", by synthesizing a tricyclic ketone to which he attributed structure 2 and which he identified as Šorm's degradation product.

We undertook a total synthesis of "albene" via the reported Diels–Alder addition of pyrocinchonic acid anhydride to cyclopentadiene[4] and obtained a racemic olefin (m.p. 150–154°) which had the constitution of 1, the properties of which, however, were not identical with those of the natural material. This is exemplified by the ^{1}H NMR spectra in Fig. 1.

Keeping in mind that ketone 2 had been correlated with natural "albene", we followed Lansbury's reaction sequence starting with (+)-camphenilone and obtained a second 2,6 - dimethyl - tricyclo[5.2.1.$0^{2,6}$]dec - 3 - ene (m.p. 113–115°), all the properties of which agreed with those of the natural product.

Thus the questions of the difference in the constitution of the two cycloalkenes and of the actual structure of "albene" arose. The two olefins were expected to be configurational isomers from the appearence of their ^{1}H NMR spectra and because of the well known synthetic procedures involved in their preparation. In order to decide whether the methyl groups are in a *cis*- or *trans*-orientation, the products of both syntheses were subjected to catalytic hydrogenation furnishing dihydro derivatives of m.p. 182–186° and 125–130°, respectively.

The ^{13}C NMR spectrum of the higher melting compound consisted of seven signals while the lower melting one showed only six lines because of accidental degeneracy. Consequently, both dihydro compounds possess a plane of symmetry which is only compatible with a *cis*-arrangement of the methyl groups. Thus only structures 3 and 4 are possible for the 2,6 - dimethyl - tricyclo[5.2.1.$0^{2,6}$]decanes and, similarly, the problem of the configurational assignment of the parent olefins is reduced to a distinction between formulas 1 and 5.



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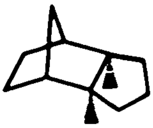

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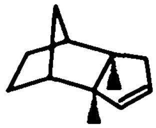

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The relative configurations of the olefins and their hydrogenation products were determined on the basis of their ^{13}C NMR spectra. As a result, constitution 1, which had been claimed for natural "albene", must be attributed to the synthetic product with m.p. 150–154° whereas the material melting at 110–115° is represented by formula 5. The ^{13}C chemical shifts of "albene" 5, "isoalbene" 1 and their saturated derivatives 4 and 3, respectively, are reported in Table 1 and correlated in Fig. 2.

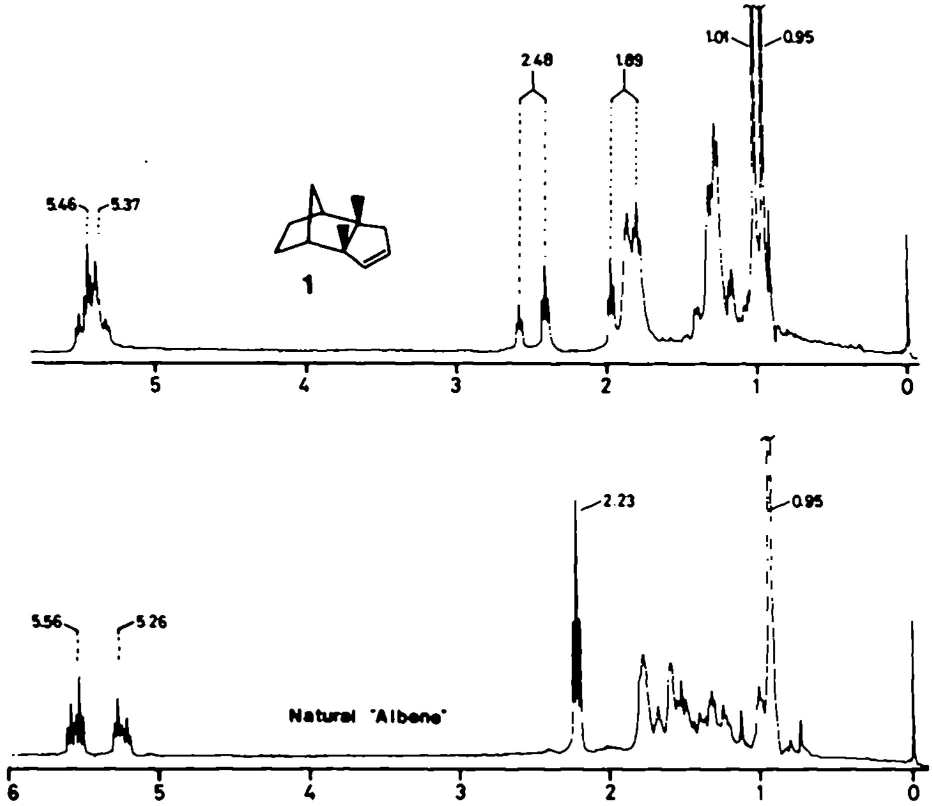

Fig. 1. 100 MHz-^{1}H NMR spectra of 1 (top) and of natural "albene" (bottom) in $CDCl_3$ solution, standard: internal TMS.

Table 1. ^{13}C Chemical shifts of 2,6-dimethyl-*endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene 1, 2,6-dimethyl-*exo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene 5, 2,6-dimethyl-*endo*-tricyclo[5.2.1.0^{2,6}]decane 3 and 2,6-dimethyl-*exo*-tricyclo[5.2.1.0^{2,6}]decane 4[a,b,c]

Carbon	1	5	3	4
1	49.39^{+}	50.36^{+}	50.71	47.75
2	58.38	56.38	50.89	48.86
3	139.19	139.65	38.45	43.58
4	126.24	128.34	26.22	23.03
5	43.00	51.83	38.45	43.58
6	49.37	46.61	50.89	48.86
7	47.25^{+}	47.13^{+}	50.71	47.75
8	23.71^{++}	23.83	24.86	23.03
9	26.76^{++}	23.83	24.86	23.03
10	36.67	34.23	39.48	34.10
11	22.30	18.09	25.68	20.58
12	24.81	20.67	25.68	20.58

[a] Chemical shifts of $CDCl_3$ solutions relative to internal tetramethyl silane (δ = 0.00) for **1**, **5** and **3** and relative to $CDCl_3$ (δ = 77.02) for **4**; spectra recorded on a Varian XL-100 spectrometer at 25.16 MHz.

[b] Chemical shifts marked with $^{+}$ or $^{++}$ are interchangeable within the same column.

[c] The signal multiplicities in the single frequency ^{1}H off-resonance decoupled spectra agree with the expectations.

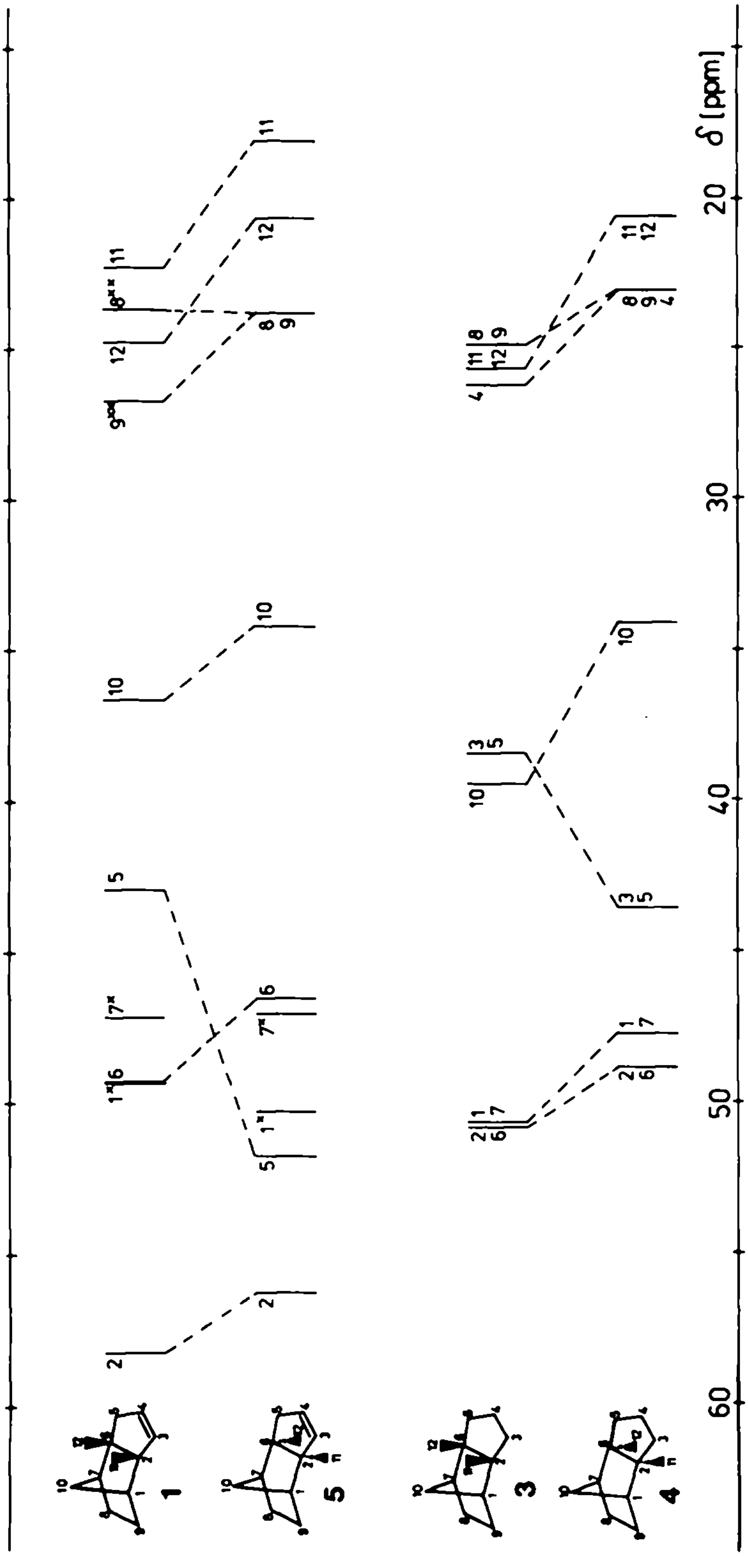

Fig. 2. Schematic representation of the ^{13}C NMR spectra of 1, 5, 3 and 4 in $CDCl_3$ solution.

The assignment of the ^{13}C signals was carried out as follows. The degree of substitution of the C atoms was determined from single frequency off-resonance ^{1}H-decoupled spectra. Among the methylene C signals of the tricyclodecanes, those of C-3/C-5 and C-8/C-9 could be distinguished from those of C-4 and C-10 by considering the different signal intensities caused by the molecular symmetry. In these compounds the large chemical shift differences between C-3/C-5 and C-8/C-9 permit assignment of the individual resonances by comparison with literature data of suitably substituted norbornane[5-7] and cyclopentane derivatives.[8] Similarly, one can distinguish between C-4 and C-10. In the tricyclodecenes, the deshielding of C-2 by the α,β-double bond[9] allows one to distinguish this carbon from C-6. Assignment within the pairs of signals for C-1 and C-7 in **1** and **5** and for C-8 and C-9 in **1** were not attempted. Although the characteristic shift of C-10[5] seemed sufficient to differentiate it from C-5, experimental proof was obtained by selective $^{13}C\{^{1}H\}$ double resonance: Irradiation at $\delta_{5\text{-}H} = 2.23$ ppm decoupled the ^{13}C signal at $\delta = 51.83$ ppm. In each of **1** and **5**, one methyl carbon experiences a chemical shift ($\delta = 24.81$ and 20.67 ppm, respectively) very similar to that of the corresponding methyl carbon in the saturated derivatives **3** and **4** ($\delta = 25.68$ and 20.58 ppm, respectively). This is probably the 12-Me group, the immediate surroundings of which are not changed by hydrogenation (in contrast to the 11-Me groups). The shielding of C-11 relative to C-12, inferred by this assignment, fits with the model of Beierbeck and Saunders[10] in which the shielding of a particular C atom increases with a decrease of the number of β-hydrogens.

The ^{13}C spectra thus assigned (Fig. 2) show the presence of the plane of symmetry in the hydrogenation products **3** and **4**, thereby demonstrating that the chirality of the parent olefins **1** and **5** is caused merely by the presence of the double bond. Furthermore, comparison of the spectrum of **1** with that of **5** and of the spectrum of **3** with that of **4** (Fig. 2) indicates the *endo*- or *exo*-orientation of the substituents at C-2/C-6. The high-field shifts by 4.1–5.1 ppm of the Me signals in **5** and **4** relative to **1** and **3** point to the *endo*-arrangement of the Me groups in the former compounds. These shift differences correspond to those between 2-*exo*,3-*exo*- and 2-*endo*,3-*endo*-dimethylnorbornane derivatives.[11,12] The shielding of the Me carbons in the *endo*- relative to the *exo*-configuration parallels the fact that larger steric interactions exist between C-11 (C-12) and the γ-carbon C-9 (C-8) in the *endo*-orientation (dihedral angle $\Phi_{endo} \sim 40°$)[†] than exist in the *exo*-orientation between C-11 (C-12) and the γ-carbon C-10 ($\Phi_{exo} \sim 80°$).[†] The derived configuration is confirmed by the deshielding that C-5 experiences in going from **1** to **5** (8.8 ppm) and that C-3/C-5 experience in going from **3** to **4**. On account of these latter findings, the C-3, C-4, C-5 bridge is *exo*-oriented in **4** and **5**. An additional indication of the configuration is given by the fact that C-8 and C-9 have identical chemical shifts in **5**, where they are in similar environments, and that they show separate signals in **1**, where their surroundings are different.

Summarizing, we conclude that the constitution that Šorm derived for natural "albene" has to be changed to **5**. Moreover, the tricyclodecanone synthesized by Lansbury does not possess the relative configuration of **2**. Finally, the corrected structural formula of "albene" demands a reinterpretation of the correlation that Šorm carried out in the determination of the absolute configuration. The conclusions described above are independently confirmed by the result of an X-ray structural analysis of a derivative of **1**.[13]

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[†] Estimated from Dreiding models.