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NMR Studies of 3-Acylcamphor

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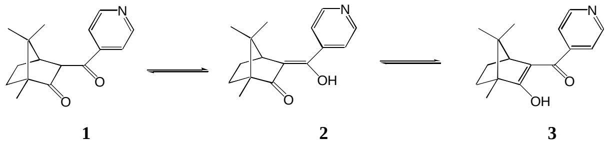
Abstract: NMR studies of some chiral 3-acyclcamphor were conducted. A complete assignment was given to 3-(4-pyridyl)carbonylcamphor by the 2D NMR technology. Assignments were also given to other β-diketones. The results showed that those 3-acylcamphors exist in the enol forms, while 2-benzoyl menthone exists in diketon form.

Keywords: NMR, 3-(4-pyridyl)carbonylcamphor, acylcamphor, β-diketone.

β-Diketones are useful chelating agents with many metal ions. Chiral β-diketones, especially chiral 3-acylcamphors as an outstanding representation, have even more extensive applications as stationary phases in chromatograpy and as ligands of chemical shifting reagents in NMR spectroscopy for determining the enantiomeric excess of chrial compounds[1,2]. Furthermore, they can be used as ligands in asymmetric catalysis[3-6]. Much work has been done for the synthesis of 3-acylcamphors due to their broad uses, but few efforts have been focused on their NMR data. Most NMR data of β-diketones only contain a part of information about their structures instead of total assignments[5-8]. In this paper, we attempted to give the NMR data of 3-(4-pyridyl)carbonyl camphor **1**, a typical β -diketones, a total assignment using the 2D NMR technology, and using the same method we also gave assignments to the NMR data of compound **4**, **5**, and **6**.

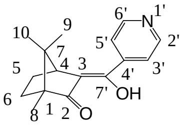
β -Diketones were synthesized by the condensation of d-camphor with alkyl carboxylate as described elsewhere[9]. Through recrystallization, pure compounds were obtained as indicated by TLC. However, they isomerized and other isomers were found in the solution after a period of time. For the 3-(4-pyridyl)carbonylcamphor, three isomers, **1**, **2** and **3** are possible in the solution. Among these isomers, compound **2** has the lowest heat of formation according to thermodynamic calculation. It shows that perhaps compound **2** is the main isomer in the solution.

The ^1H NMR and ^{13}C NMR spectra of the 3-(4-pyridyl)carbonylcamphor in $CDCl_3$ were recorded on a Bruker DRX-400NMR spectrometer with a BBI probe. TMS was taken as the reference of chemical shifts. ^1H NMR showed that the diketone exists in two forms: 93.2% in form **2**, and 6.8% in form **1**. No NMR spectral lines of compound **3** were observed. Therefore, the spectra of **2** were studied in detail by 1D and 2D NMR technology.



1 **2** **3**

The complete ^1H NMR and ^{13}C NMR data of the 3-(4-pyridylcarbonyl)camphor were assigned[10].



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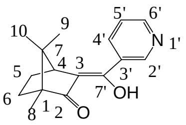

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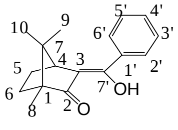

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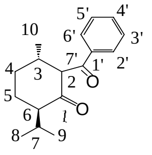

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With the same method, NMR spectra of compounds **4**, **5**, and **6** were assigned[11], too.

From the data of the NMR spectra of compounds **2**, **4**, **5**, and **6**, it is easy to see that the former three 3-acylcamphors exist in the enol form, while the last one, having a framework of menthone, exists in the diketone form.

References and Notes

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10 · ^{1}H NMR: 12.20 (br, 1H, OH), 8.75 (br, 2H, $H_{2'}$, $H_{6'}$), 7.55 (s, 2H, $H_{3'}$, $H_{4'}$), 2.88 (s, 1H, H_4), 2.20 (m, 1H, H_{4a}), 1.82 (m, 1H, H_{5a}), 1.63-1.54 (m, 2H, H_{5b}, H_{4b}), 1.03 (s, 3H, H_8), 0.97 (s, 3H, H_{10}), 0.83 (s, 3H, H_9);

^{13}C NMR: 213.2 (C_2), 157.9 ($C_{4'}$), 150.1 ($C_{2'}$, $C_{6'}$), 141.1 ($C_{4'}$), 120.9 ($C_{3'}$, $C_{5'}$), 117.0 (C_3), 57.7 (C_1), 48.6 (C_7), 47.9 (C_4), 30.2 (C_6), 26.6 (C_5), 20.0 (C_9), 18.3 (C_{10}), 8.47 (C_8).

11. **4** ^{1}H NMR：12.31 (br, s, 1H, OH), 8.91 (s, 1H, $H_{2'}$), 8.67 (s, 1H, $H_{6'}$), 7.99 (d, 1H, $H_{5'}$), 7.41 (d, 1H, $H_{6'}$), 2.85 (s, 1H, H_4), 2.18 (m, 1H, H_{6endo}), 1.82 (m, 1H, H_{5endo}), 1.62-1.54 (m, 2H, H_{5exo}, H_{6exo}), 1.03 (s, 3H, H_8), 0.96 (s, 3H, H_{10}), 0.84 (s, 3H, H_9);

^{13}C NMR：213.0 (C_2), 158.4 ($C_{7'}$), 116.2 (C_3), 57.6 (C_1), 48.7 (C_7), 30.3 (C_6), 26.9 (C_5), 20.1 (C_9), 18.7 (C_{10}), 8.6 (C_8).

5 ^{1}H NMR：76.1% 12.47 (1H, OH), 7.66 (2H), 7.26 (S, 3H), 2.84 (m, 1H, H_4), 2.14 (m, 1H, H_{5endo}), 1.80-1.74 (m, 1H, H_{6endo}), 1.67-1.51 (m, 2H, H_{5exo}, H_{6exo}), 1.02 (S, 3H, H_{10}), 0.92 (S, 3H, H_8), 0.81 (S, 3H, H_9);

^{13}C NMR：213.0 (C_2), 161.7 ($C_{7'}$), 136.2 ($C_{1'}$), 130.2 ($C_{4'}$), 128.2 ($C_{2'}$), 127.6 ($C_{2'}$), 15.2 (C_3), 54.3 (C_1), 49.9 (C_9), 48.2 (C_4), 30.4 (C_6), 26.9 (C_5), 20.1 (C_9), 18.6 (C_{10}), 8.7 (C_8).

6 ^{1}H NMR 7.67 (d, J=7.67 Hz, 2H, $H_{2'}$, $H_{6'}$), 7.52 (m, 1H, $H_{4'}$), 7.44 (d, J=7.44, 2H, $H_{3'}$, $H_{5'}$), 4.07 (d, J=11.5 Hz, 1H, H_2), 2.53 (m, 1H, H_3), 2.29 (m, 1H, H_6), 2.14 (m, 1H, H_{5e}), 2.10 (m, 1H, H_7), 2.02 (m, 1H, H_{4e}), 1.56 (m, 1H, H_{4a}), 1.49 (m, 1H, H_{5a}), 0.97 (d, J=6.3, 3H, H_{10}), 0.91 (d, J=6.8 Hz, 3H, H_8), 0.85 (d, J=6.8 Hz, 3H, H_9);

^{13}C NMR 208.9 (C_1), 198.0 (C_7), 137.8 ($C_{1'}$), 132.8 ($C_{4'}$), 128.4 (C_3, $C_{5'}$), 127.9 ($C_{2'}$, $C_{6'}$), 65.8 (C_2), 55.7 (C_6), 37.4 (C_3), 33.2 (C_4), 27.8 (C_5), 25.8 (C_7), 21.03 (C_{10}), 21.0 (C_8), 18.4 (C_9).

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