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2 D-NMR of Natural Products. Part VII* Assignment of Carbonylresonances of Glutathion by Heteronuclear Shift Correlation

Short Communication

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The CO-resonances of glutathion were unambiguously assigned by means of heteronuclear 2 D-^{1}H-^{13}C-shift correlation.

(Keywords: Nuclear magnetic resonance; Peptides)

2D-NMR von Naturstoffen, 7. Mitt.: Zuordnung der Carbonyl-Resonanzen von Glutathion mittels heteronuklearer Shiftkorrelation (Kurze Mitteilung)

Durch heteronukleare 2 D-^{1}H-^{13}C-Shiftkorrelation wird die eindeutige Zuordnung der CO-Resonanzen von Glutathion getroffen.

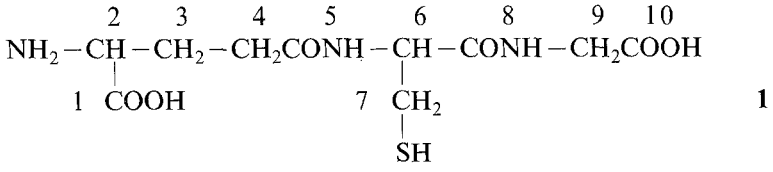
The assignment of carbon resonances via long range couplings is of great practical interest in determining three bond ^{1}H-^{13}C connectivities. Especially in peptides the unambiguous assignment of carbonylresonances can be achieved by using those couplings. Two-dimensional heteronuclear shift correlation[1–4] and selective INEPT[5] experiments have been developed using polarisation transfer via long range coupling. A shortcoming of these methods are the long delays, which must be used for very small J_{CH}. These delays cause loss of magnetization due to relaxation. Recently a new improved pulse sequence for shift correlation has been described which reduces these delays[6].

Using the $^{2}J_{HC}$ which is in the order of 4–7 Hz and the $^{2}J_{^{1}H^{13}CO}$ which

* For part VI see Ref.[9].

is 3–5 Hz[7] one can in favorable cases gain information about the amino acid sequence of small peptides[6].

We have performed a conventional heteronuclear shift correlation experiment to assign the carbonyl resonances of glutathion (**1**).



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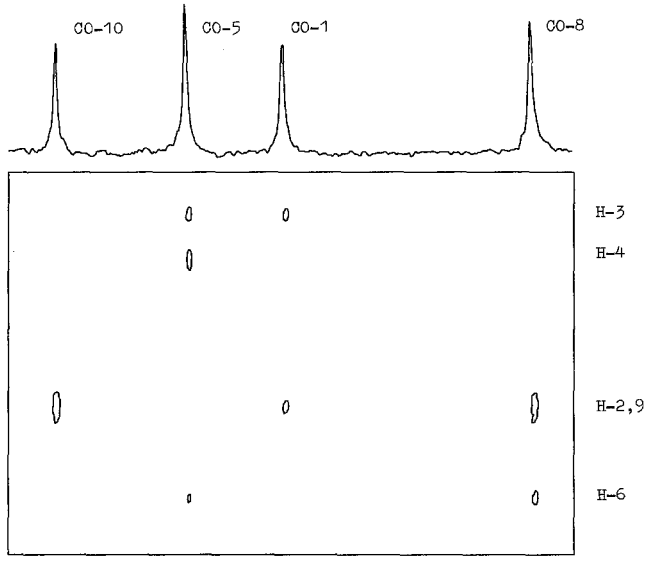

Fig. 1. Contour plot for the CO-resonances of **1**

Since the 2D experiment yields an assignment different from that described in the literature[8] we want to report these results (see Table 1).

Table 1. *Chemical shifts of the* CO*-resonances in* D_2O, pH = 3.5 *of* **1**

CO	(ppm)
1	173.7
5	174.3
8	172.3
10	175.0

Fig. 1 shows a contour plot of the carbonyl resonances. In addition to the correlation via the $^2J_{^1H^{13}CO}$ one can also see correlation signals produced by the $^3J_{^1H-C-C^{13}CO}$ which can be as large as 9 Hz[7].

In *Glu* this leads to a correlation signal between CO-5 and the protons in position 3. No such correlation has been found to CO-1.

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References

[1] *Mondsley A. A., Ernst R. R.*, Chem. Phys. Lett. **50**, 368 (1977).
[2] *Bodenhousen G., Freeman R.*, J. Magn. Reson. **28**, 471 (1977).
[3] *Mondsley A. A., Müller L., Ernst R. R.*, J. Magn. Reson. **28**, 463 (1977).
[4] *Binst G. v., Wynants C., Hallenga K., Michel A., Zanen J.*, J. Magn. Reson. **57**, 93 (1984).
[5] *Bax A. D.*, J. Magn. Reson. **57**, 314 (1984).
[6] *Kessler H., Griesinger C., Zarbock J., Loosli H. R.*, J. Magn. Reson. **57**, 331 (1984).
[7] *Bystrow V. F.*, Progress in NMR Spectroscopy, Vol. 10, p. 41 (1976).
[8] *Jung G., Breitmaier E., Voelter W.*, Eur. J. Biochem. **24**, 438 (1972).
[9] *Buchbauer G., Fischlmayr A., Haslinger E., Robien W., Völlenkle H., Wassmann C.*, Monatsh. Chem. **115**, 739 (1984).