



ELSEVIER

Contents lists available at ScienceDirect

Data in brief

journal homepage: www.elsevier.com/locate/dib

Data Article

NMR data for the hydroxyl groups detected by NOESY spectra in sesquiterpene lactones

Jaromir Budzianowski^{a,*}, Joanna Nawrot^b, Gerard Nowak^b^a Department of Pharmaceutical Botany and Plant Biotechnology, Poznań University of Medical Sciences, Św. Marii Magdaleny Str. 14, 61-861 Poznań, Poland^b Department of Medicinal and Cosmetic Natural Products, Poznań University of Medical Sciences, Mazowiecka Str. 33, 60-623 Poznań, Poland

ARTICLE INFO

Article history:

Received 31 December 2018

Received in revised form 1 July 2019

Accepted 8 July 2019

Available online 12 July 2019

Keywords:

Hydroxyl groups detection

NOESY spectra

NMR spectra

Sesquiterpene lactones

ABSTRACT

In this article we present the correlations observed in the NOESY spectra, which provide direct and unequivocal detection of hydroxyl groups occurring in the chemical structures of three sesquiterpene lactones - a germacranolide (8 α -(E)-4'-hydroxy-seneciocyloxy-9 α -hydroxyparthenolide) and two guaianolides (cynaropicrin and desacylcynaropicrin 8 α -(Z)-(4'-hydroxy-2'-methyl)butenoate). The NOESY spectra and other NMR spectra, which served for the structural determination, are also presented. The data provided in this article are associated with the research article "Phytochemical profiles of the leaves of *Stizolophus balsamita* and *Psephellus sibiricus* and their chemotaxonomic implications" Nawrot et al., 2019.

© 2019 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Data

In the course of our investigations [1], it emerged that hydroxyl groups (OH) are best detected in the NOESY spectrum, which usually serves for the stereochemical studies (e.g. [2–4]). In this type 2D NMR spectrum the OH signals are recognized by the chemical exchange cross-peaks with the solvent

DOI of original article: <https://doi.org/10.1016/j.phytochem.2018.12.022>.

* Corresponding author.

E-mail address: jbudzian@ump.edu.pl (J. Budzianowski).

<https://doi.org/10.1016/j.dib.2019.104246>

2352-3409/© 2019 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Specifications table

Subject area	Phytochemistry
More specific subject area	Natural products research; structural characterization
Type of data	NMR spectra figures, structural formulae with NMR correlations arrows
How data was acquired	NMR spectra of sesquiterpene lactones acquired a Bruker Avance 600 spectrometer
Data format	Raw and analyzed
Experimental factors	First, the samples were isolated from CH ₂ Cl ₂ fractions of <i>Psephellus sibiricus</i> or <i>Stizolophus balsamita</i> leaf MeOH extracts. Then the samples were dissolved in aprotic solvents, like CDCl ₃ and/or DMSO- <i>d</i> ₆ before NMR studies.
Experimental features	Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 instrument using 600 MHz and 150 MHz frequencies for hydrogen nuclei (¹ H) and carbon nuclei (¹³ C), respectively, and tetramethylsilane (TMS) as internal standard. The aprotic solvents used contained residual water. The NOESY spectra were edited with different colours for the cross-peaks with different sign (negative, positive) to differentiate dipolar and chemical exchange interactions.
Data source location	Department of Medicinal and Cosmetic Natural Products, Poznań University of Medical Sciences, Mazowiecka Str. 33, 60–623 Poznań, Poland
Data accessibility	Data is provided in the article
Related research article	Nawrot J, Budzianowski J, Nowak G. Phytochemical profiles of the leaves of <i>Stizolophus balsamita</i> and <i>Psephellus sibiricus</i> and their chemotaxonomic implications. <i>Phytochemistry</i> 159 (2019) 172–178 [1].

Value of the data

- The data are useful because they show that hydroxyl groups in sesquiterpene lactones can be detected directly by the use of a NOESY spectrum.
- Researchers can benefit from this data during the structural elucidation of sesquiterpene lactones containing hydroxyl groups.
- The data can be used whenever the NOESY spectra are utilized in the structural elucidation.
- The additional value of the data is that in the case of NMR spectra recorded in CDCl₃, the challenging detection of hydroxyl groups is avoided.

residual water signal. Those peaks have the same phase as diagonal (positive) but opposite to all other resonances with dipolar couplings (negative) [5]. The correlations (Fig. 1) observed in the NOESY spectra (Figs. 2–5) and other 2D NMR spectra for the signals of the OH groups occurring in three sesquiterpene lactones: a germacranolide (8 α -(*E*)-4'-hydroxyseneciolyoxy-9 α -hydroxypartenolide) (**5**) and two guaianolides (cynaropicrin and desacylcynaropicrin 8 α -(*Z*)-(4'-hydroxy-2'-methyl)butenoate) (**12**, **13**), are presented. The set of 1D and 2D NMR spectra of compound **5** recorded in CDCl₃ (Figs. 6–10) and in DMSO-*d*₆ (Figs. 11–16) and those of compounds **12** (Figs. 17–22) and **13** (Figs. 23–28) recorded in DMSO-*d*₆, is also provided in this article. The typical NMR data for these compounds, including OH resonances, like chemical shifts, multiplicity and coupling constants, are reported in the main article [1]. Generally, as can be seen in the case of compound **5**, two OH groups resonated much more downfield in DMSO-*d*₆ (range 5.2–5.8 ppm) than in CDCl₃ (range 2.0–2.6 ppm). The chemical exchange cross-peaks between those OH groups were also observed.

2. Experimental design, materials and methods

The NMR spectra were recorded on a Bruker Avance 600 instrument using 600 MHz and 150 MHz frequencies for hydrogen nuclei (¹H) and carbon nuclei (¹³C), respectively, and tetramethylsilane (TMS) as internal standard. The spectra were obtained for CDCl₃ or DMSO-*d*₆ solutions at 298 K. No special pulse programmes were used. It should be emphasized, that NMR measurements were made in aprotic solvents without the addition of solvents causing deuterium exchange, like CD₃OD, D₂O or TFA-*d* (CF₃COOD), but containing residual water, what is crucial for the hydroxyl group detection in the NOESY spectra. Therefore, those solvents must not be dried to remove the mentioned water completely. To recognize the ¹H signals of hydroxyl groups two approaches were utilized – the direct

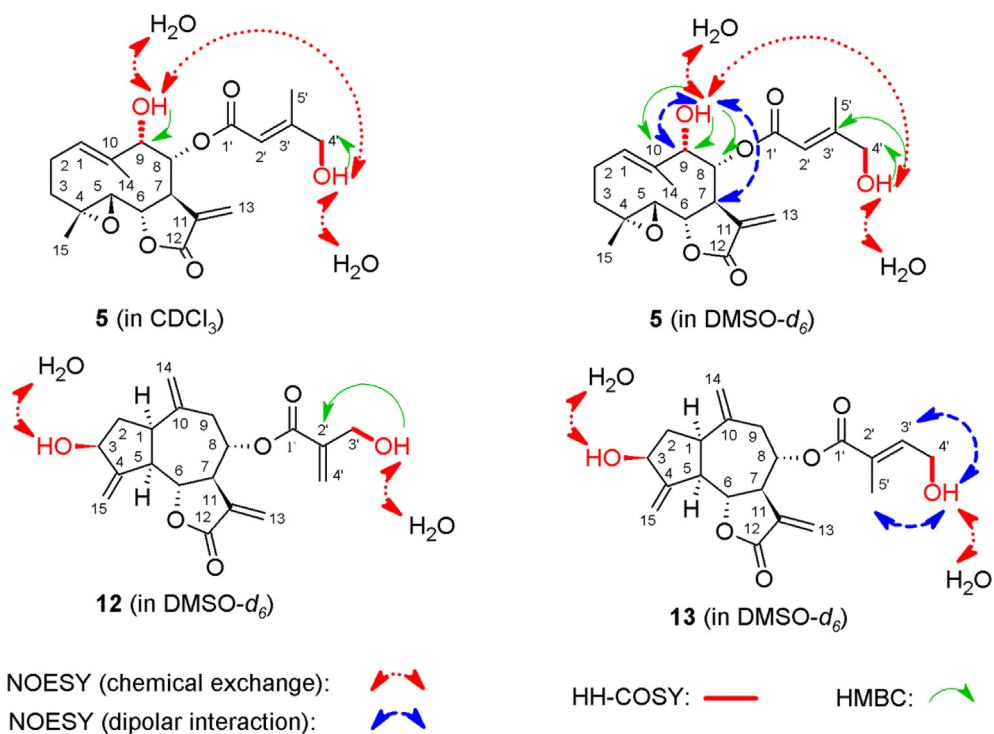


Fig. 1. 2D NMR - NOESY (dotted double arrows), HH-COSY (bold bonds) and HMBC (arrows) correlations observed for the hydroxyl groups signals of a germacranolide - 8α -(*E*)-4'-hydroxyseneciolyloxy-9 α -hydroxyparthenolide (compound **5**) and guaianolides – cynaropicrin (compound **12**) and desacylcynaropicrin 8α -(*Z*)-(4'-hydroxy-2'-methyl)butenoate (=cebellin F) (compound **13**). H_2O refers to the solvent residual water. HSQC correlations are never observed.

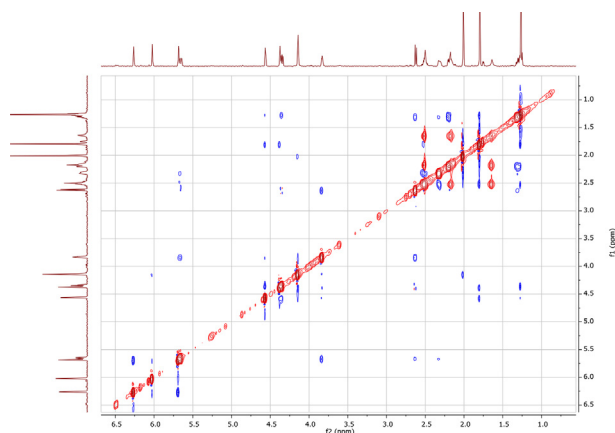


Fig. 2. NOESY spectrum of compound **5** recorded in CDCl_3 . The red cross-peaks indicate signals of hydroxyl groups.

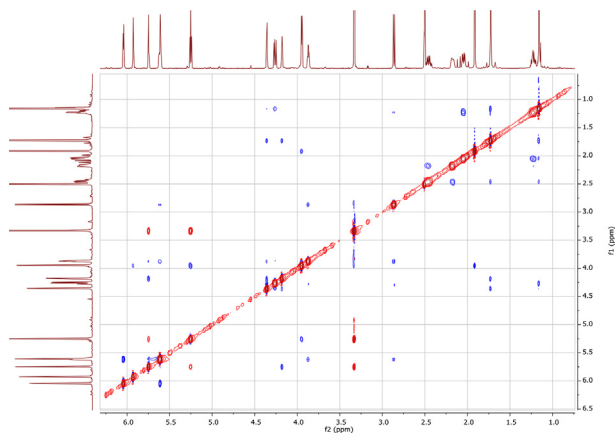


Fig. 3. NOESY spectrum of compound **5** recorded in DMSO- d_6 . The red cross-peaks indicate signals of hydroxyl groups.

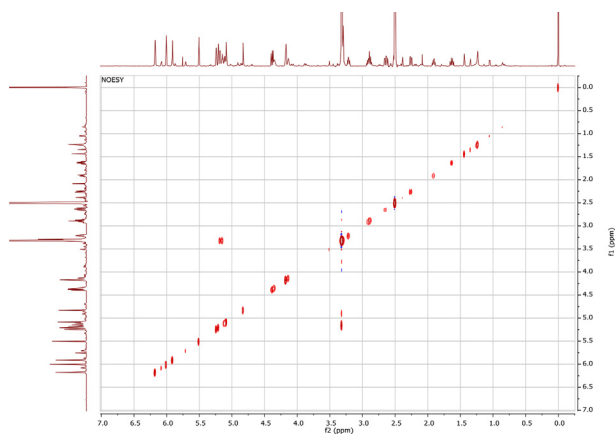


Fig. 4. NOESY spectrum of compound **12** recorded in DMSO- d_6 . The intensity of the spectrum was tuned to show the chemical exchange cross-peaks (red) of the hydroxyl groups only.

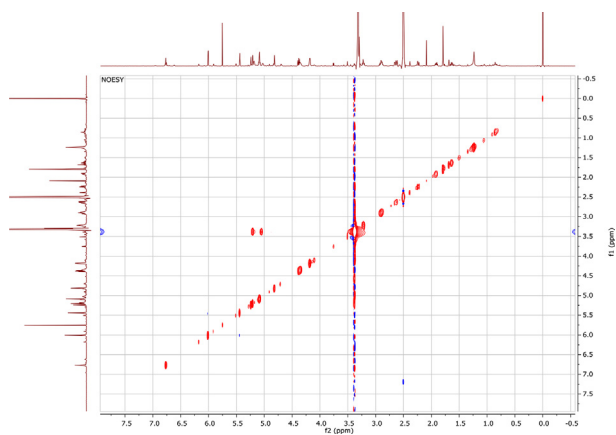


Fig. 5. NOESY spectrum of compound **13** recorded in DMSO- d_6 . The intensity of the spectrum was tuned to show the chemical exchange cross-peaks (red) of the hydroxyl groups only.

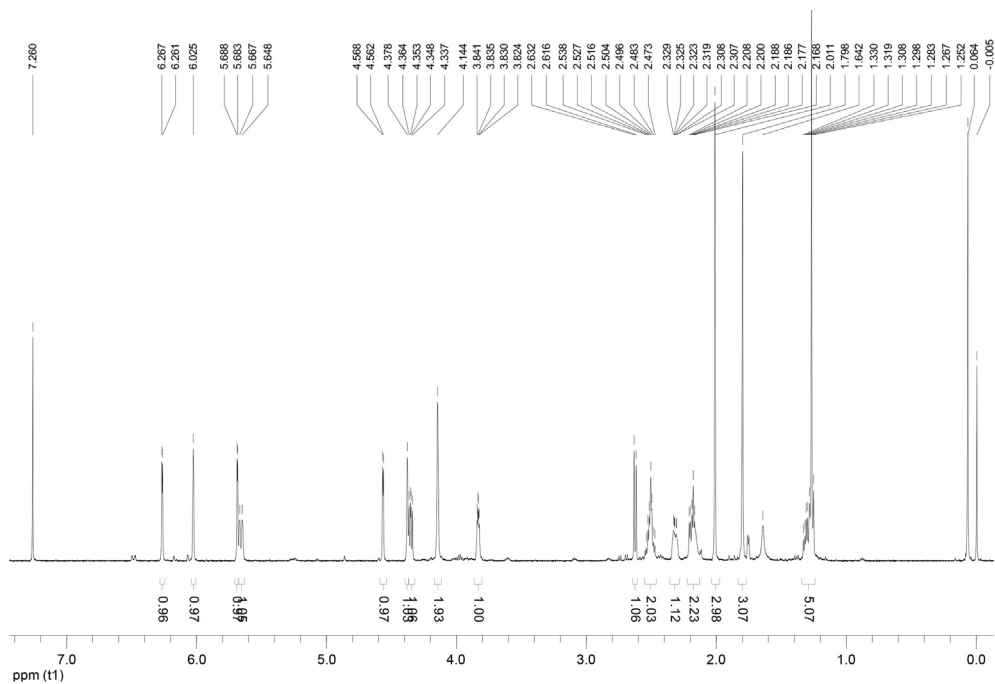


Fig. 6. ^1H NMR (CDCl_3) spectrum of compound 5.

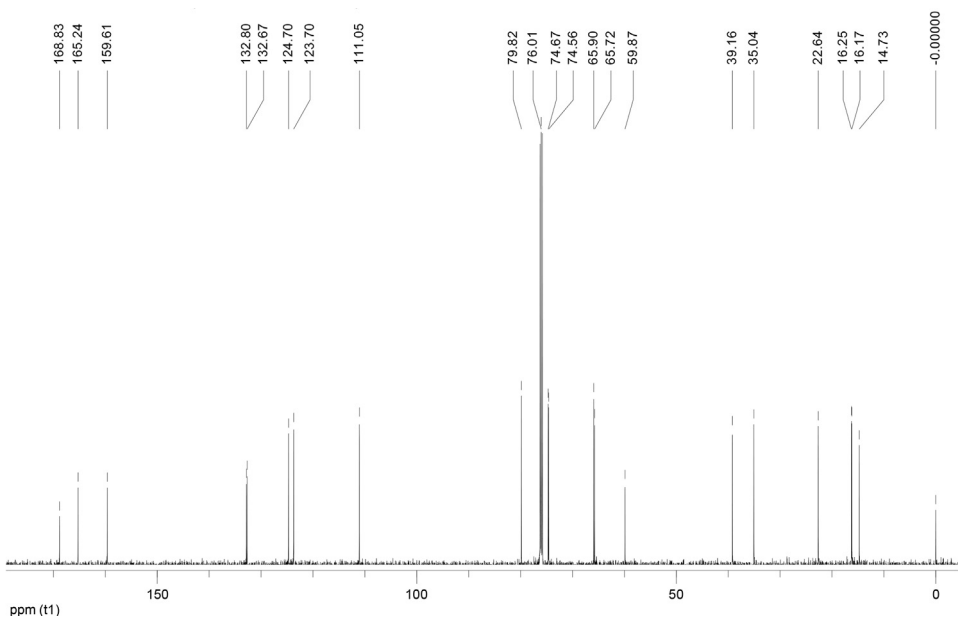


Fig. 7. ^{13}C NMR (CDCl_3) spectrum of compound 5.

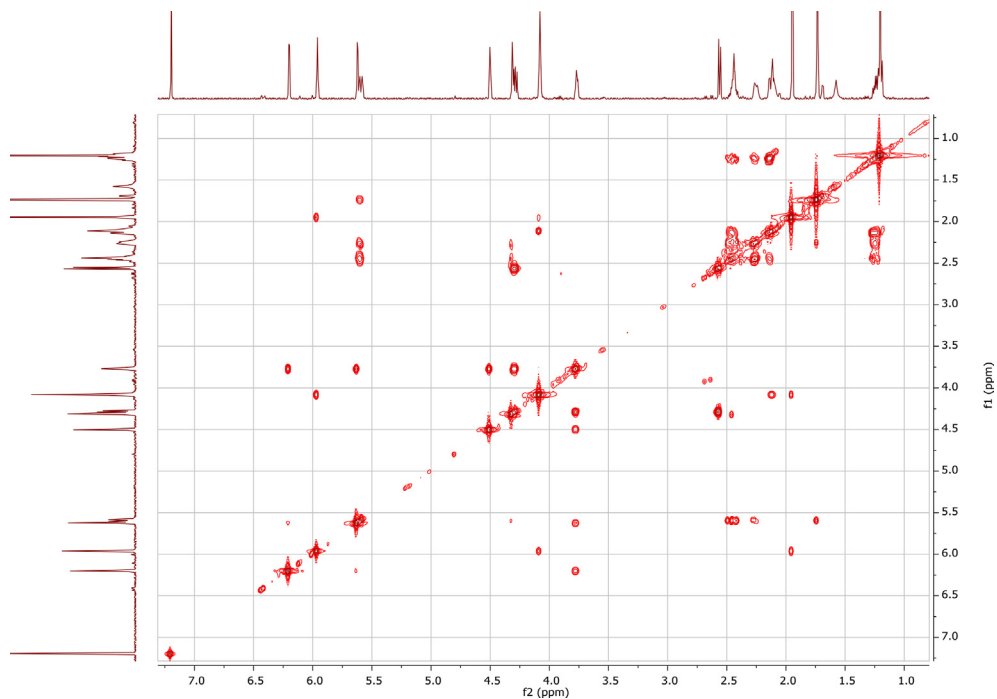


Fig. 8. HH-COSY (CDCl_3) spectrum of compound 5.

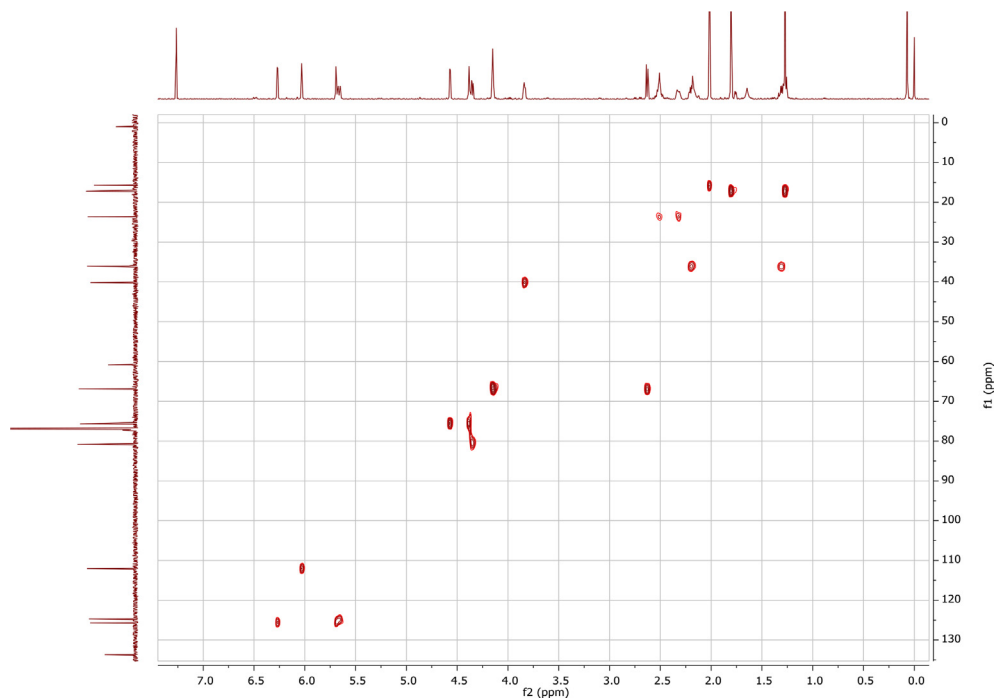


Fig. 9. HSQC (CDCl_3) spectrum of compound 5.

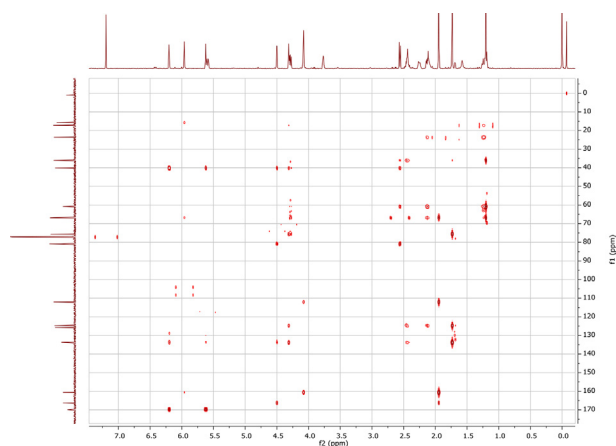


Fig. 10. HMBC (CDCl_3) spectrum of compound 5.

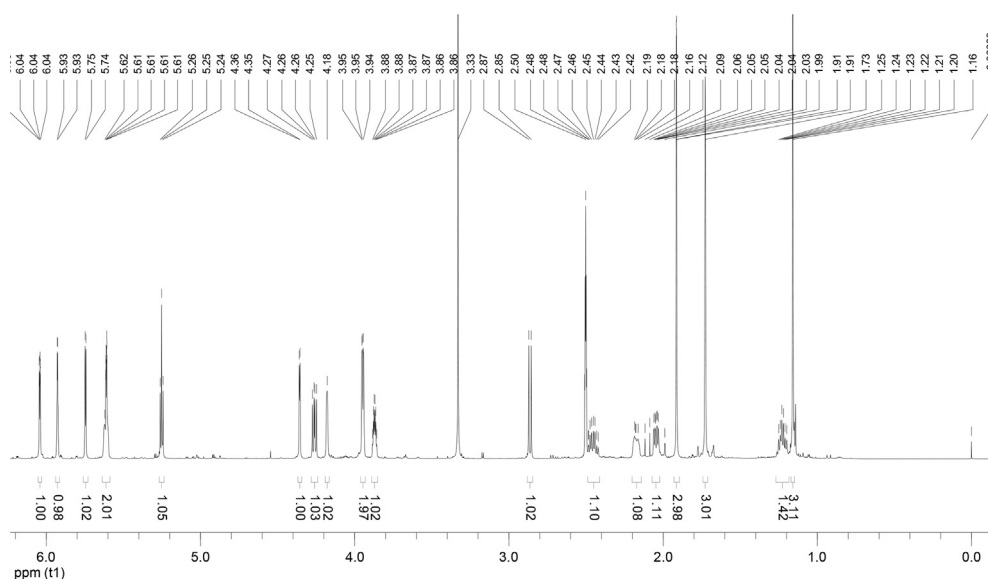


Fig. 11. ^1H NMR ($\text{DMSO}-d_6$) spectrum of compound 5.

and indirect one. In the direct approach the NOESY spectrum was examined for the presence of proton signals exhibiting cross-peaks with the residual water signal. In the indirect approach, the HSQC spectrum was examined for the ^1H signals lacking cross-peaks with carbon atom signals, i.e. without one-bond $^1\text{H}-^{13}\text{C}$ couplings.

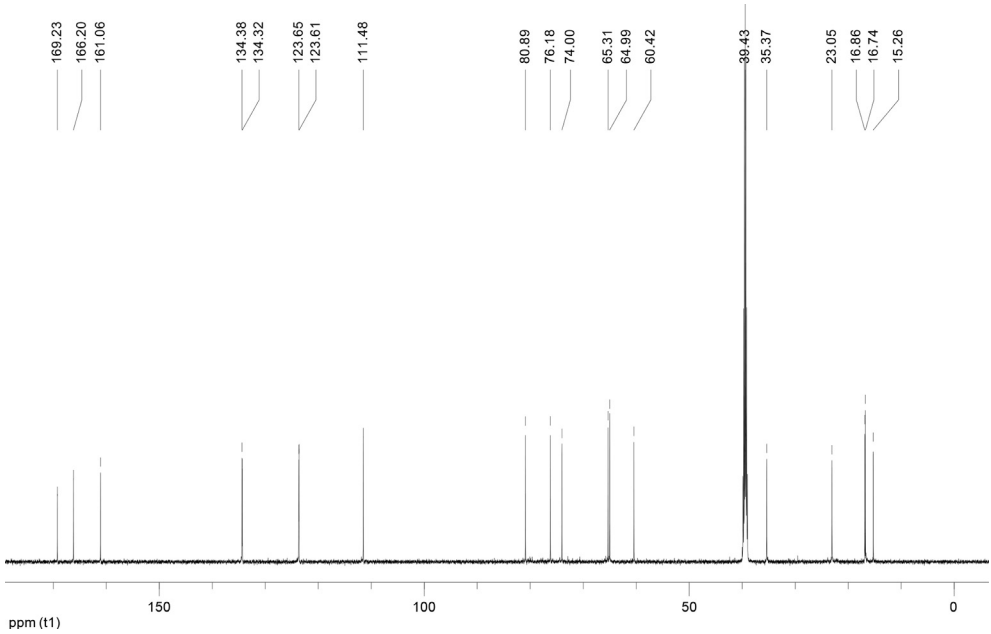


Fig. 12. ^{13}C NMR ($\text{DMSO}-d_6$) spectrum of compound 5.

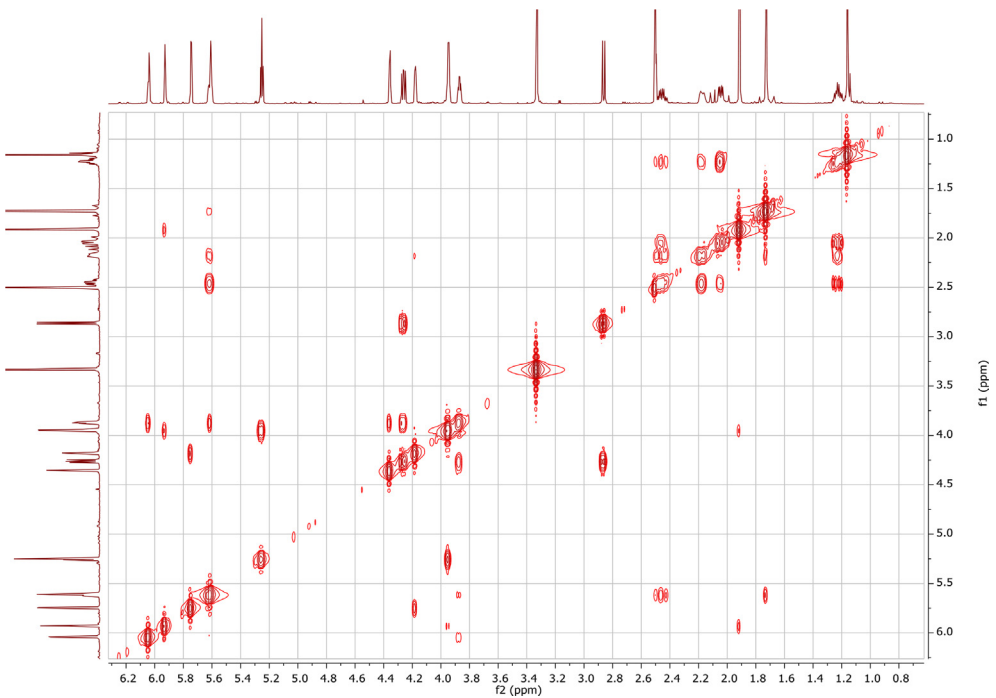


Fig. 13. HH-COSY ($\text{DMSO}-d_6$) spectrum of compound 5.

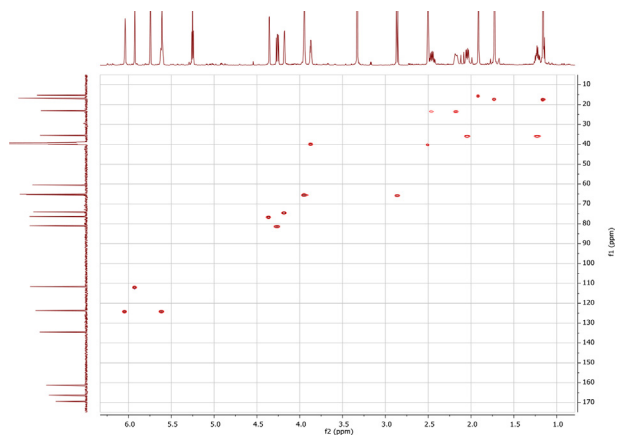


Fig. 14. HSQC NMR (DMSO- d_6) spectrum of compound **5**.

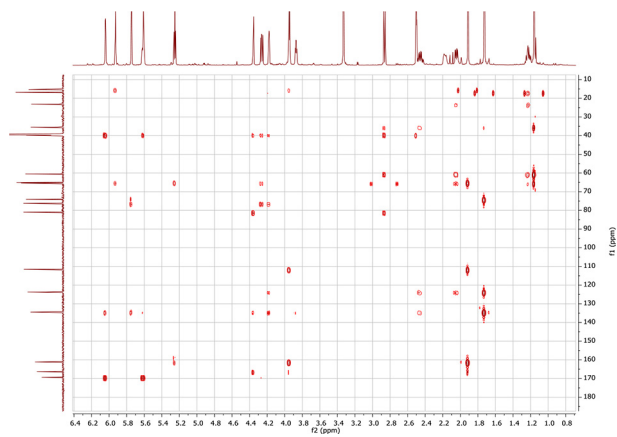


Fig. 15. HMBC (DMSO- d_6) spectrum of compound **5**.

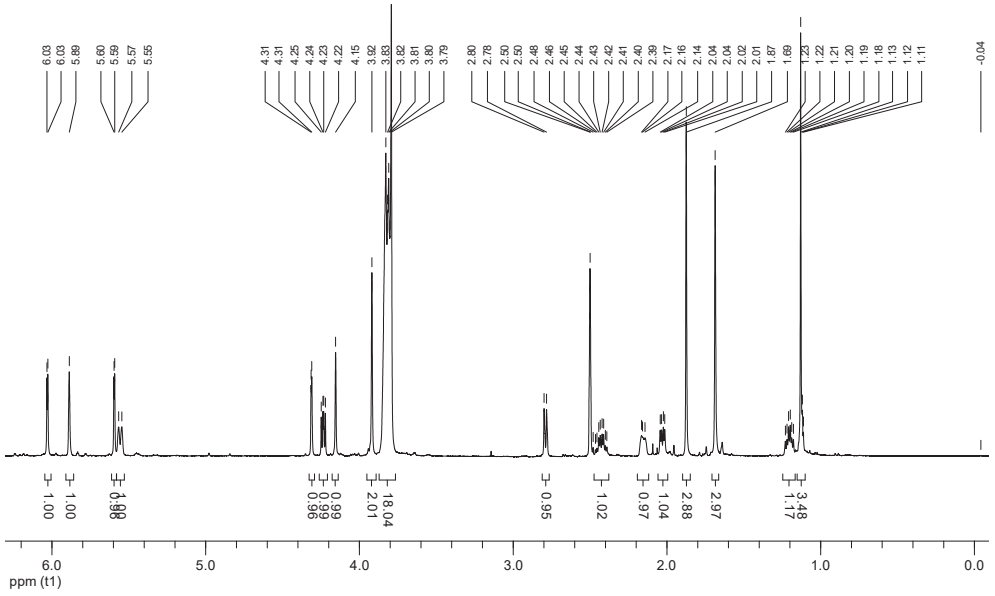


Fig. 16. ¹H NMR (DMSO-*d*₆+ D₂O) spectrum of compound 5.

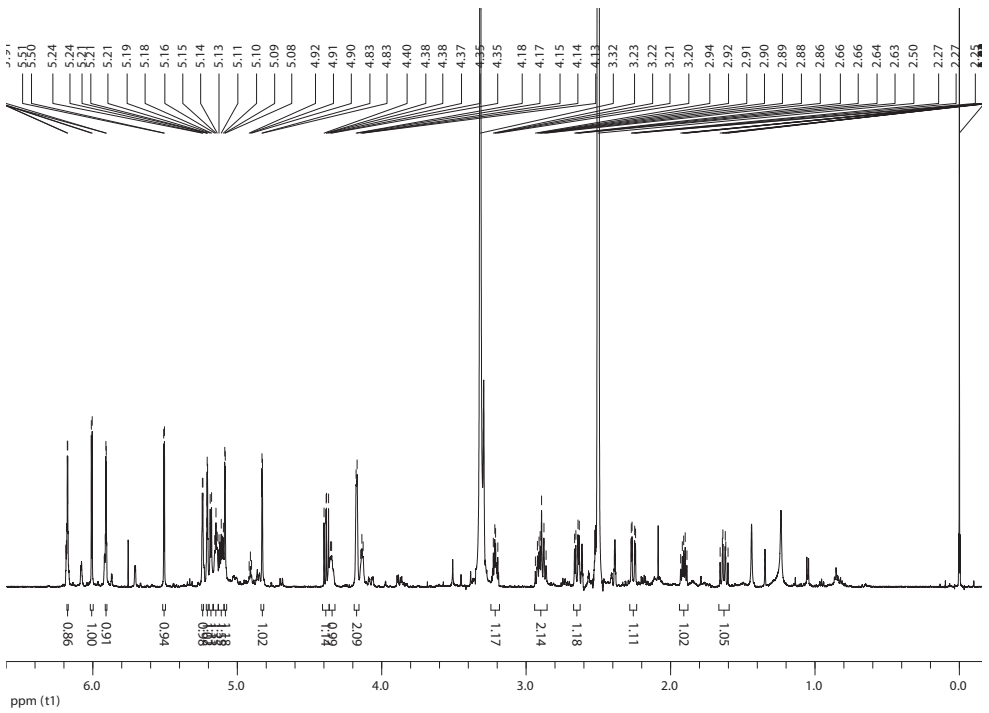


Fig. 17. ¹H NMR (DMSO-*d*₆) spectrum of compound 12.

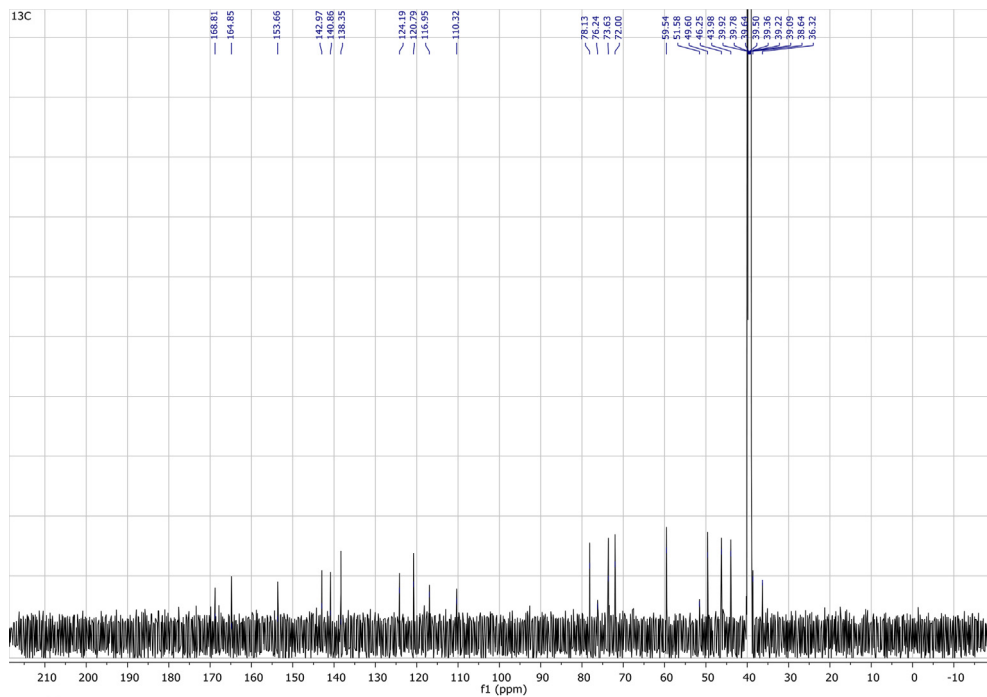


Fig. 18. ^{13}C NMR ($\text{DMSO}-d_6$) spectrum of compound 12.

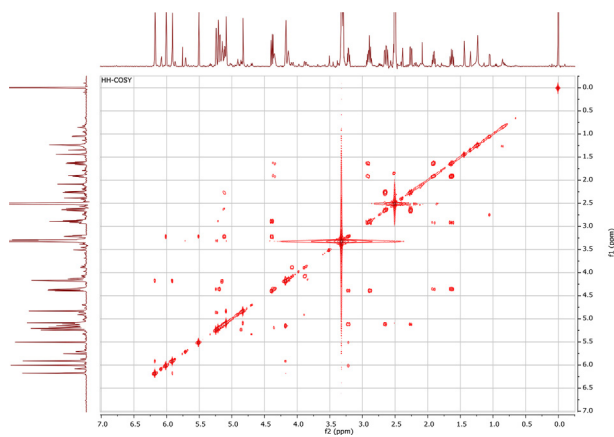


Fig. 19. HH-COSY ($\text{DMSO}-d_6$) spectrum of compound 12.

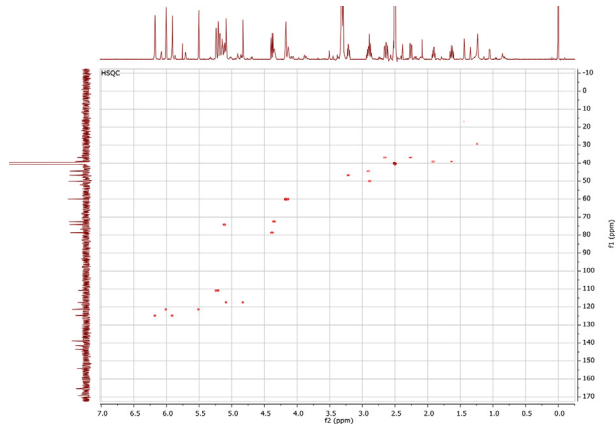


Fig. 20. HSQC (DMSO- d_6) spectrum of compound **12**.

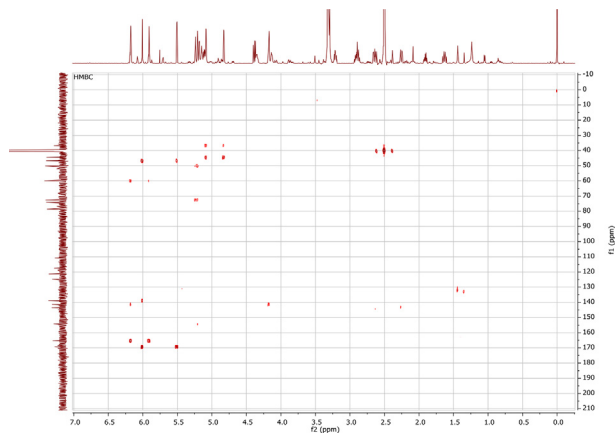


Fig. 21. HMBC (DMSO- d_6) spectrum of compound **12**.

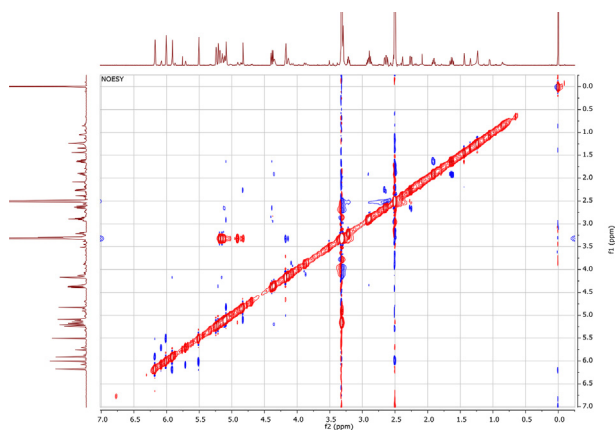


Fig. 22. NOESY (DMSO- d_6) spectrum of compound **12**. The intensity of the spectrum was tuned to show the cross-peaks due to the dipolar couplings (blue).

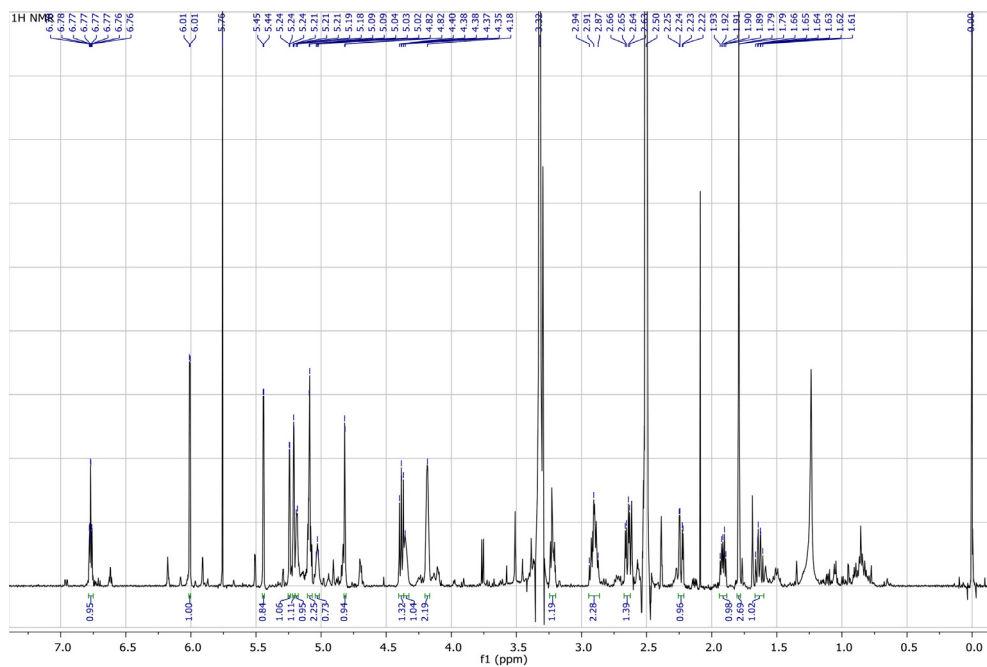


Fig. 23. ^1H NMR ($\text{DMSO}-d_6$) spectrum of compound 13.

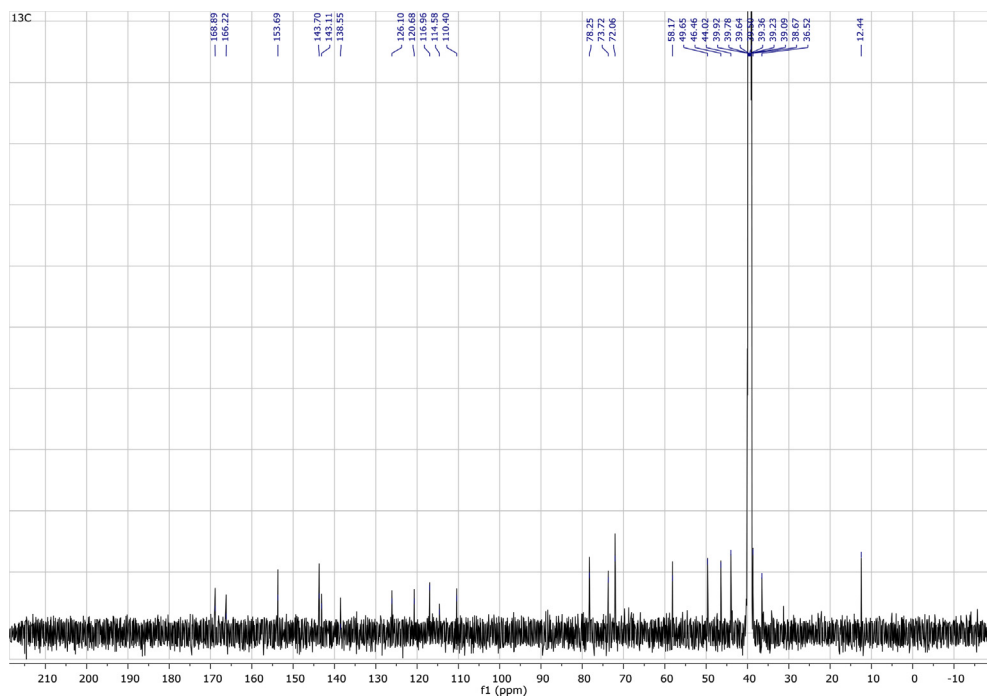


Fig. 24. ^{13}C NMR ($\text{DMSO}-d_6$) spectrum of compound 13.

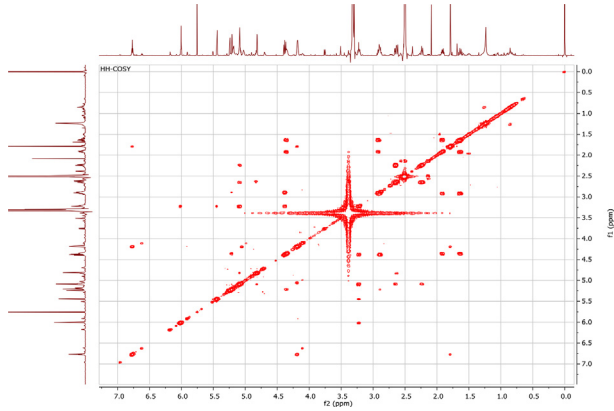


Fig. 25. HH-COSY (DMSO- d_6) spectrum of compound 13.

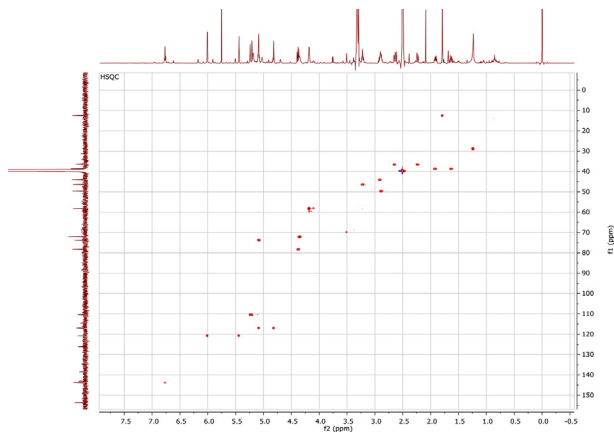


Fig. 26. HSQC (DMSO- d_6) spectrum of compound 13.

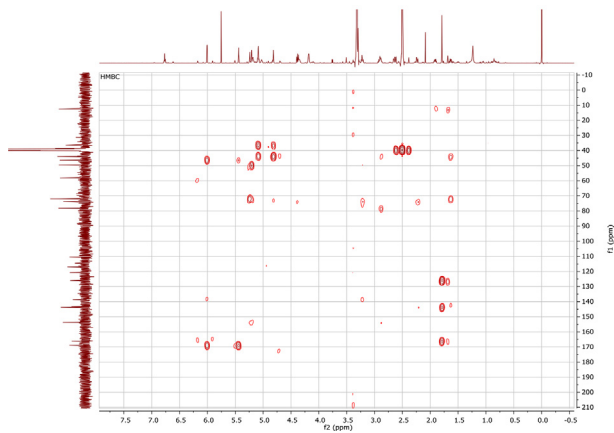


Fig. 27. HMBC (DMSO- d_6) spectrum of compound 13.

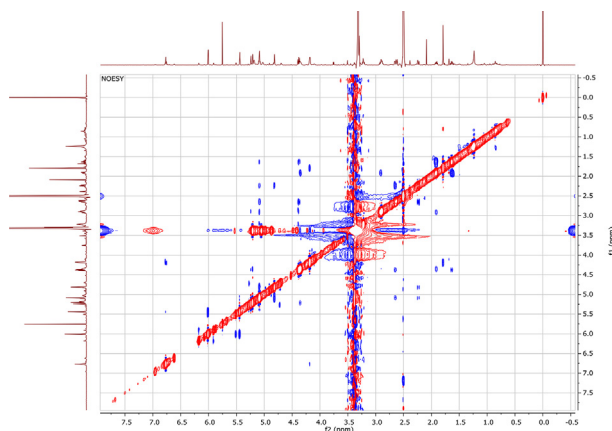


Fig. 28. NOESY (DMSO- d_6) spectrum of compound **13**. The intensity of the spectrum was tuned to show the cross-peaks due to the dipolar couplings (blue).

Acknowledgements

This study was supported by the Department of Medicinal and Cosmetic Natural Products, Poznań University of Medical Sciences, Poznań, Poland.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] J. Nawrot, J. Budzianowski, G. Nowak, Phytochemical profiles of the leaves of *Stizolophus balsamita* and *Psephellus sibiricus* and their chemotaxonomic implications, *Phytochemistry* 159 (2019) 172–178. <https://doi.org/10.1016/j.phytochem.2018.12.022>.
- [2] Y. Ren, U.M. Acuña, F. Jimenez, R. García, M. Mejía, H. Chai, J.C. Gallucci, N.R. Farnsworth, D.D. Soejarto, E.J. Carcache de Blanco, A.D. Kinghorn, Cytotoxic and NF- κ B inhibitory sesquiterpene lactones from *Piptocoma rufescens*, *Tetrahedron* 68 (2012) 2671–2678. <https://doi.org/10.1016/j.tet.2012.01.061>.
- [3] J.S. Chaves, D.C.R. de Oliveira, Sesquiterpene lactones and other chemical constituents of *Mikania hoehnii*, *R. J. Braz. Chem. Soc.* 14 (2003) 734–737. <https://doi.org/10.1590/S0103-50532003000500006>.
- [4] Y. Li, M.-L. Hang, B. Cong, S.-M. Wang, M. Dong, F. Sauriol, Ch.-H. Huo, Q.-W. Shi, Y.-Ch Gu, H. Kiyota, Achillinin A, a cytotoxic guaianolide from the flower of Yarrow, *Achillea millefolium*, *Biosci. Biotechnol. Biochem.* 75 (2011) 1554–1556. <https://doi.org/10.1271/bbb.110234>.
- [5] H. Kessler, H. Oschkinaf, H. Loosli, Two-dimensional NMR spectroscopy on the immunosuppressive peptide, cyclosporine A, in: W.R. Croasmun, R.M.K. Carlson (Eds.), *Two-dimensional NMR Spectroscopy. Applications for Chemists and Biochemists*, VCH, New York, 1987, pp. 259–298.