



## Iridoid glucosides in the genus *Sutera* (Scrophulariaceae) as chemotaxonomic markers in tribe Limoselleae

Gousiadou, Chryssoula; Kokubun, Tetsuo; Albach, Dirk C.; Gotfredsen, Charlotte Held; Jensen, Søren Rosendal

*Published in:*  
Phytochemistry

*Link to article, DOI:*  
[10.1016/j.phytochem.2018.10.021](https://doi.org/10.1016/j.phytochem.2018.10.021)

*Publication date:*  
2019

*Document Version*  
Other version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Gousiadou, C., Kokubun, T., Albach, D. C., Gotfredsen, C. H., & Jensen, S. R. (2019). Iridoid glucosides in the genus *Sutera* (Scrophulariaceae) as chemotaxonomic markers in tribe Limoselleae. *Phytochemistry*, 158, 149-155. <https://doi.org/10.1016/j.phytochem.2018.10.021>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# Iridoid glucosides in the genus *Sutera* (Scrophulariaceae) as chemotaxonomic markers in tribe Limoselleae

Chryssoula Gousiadou<sup>a</sup>, Tetsuo Kokubun<sup>b</sup>, Dirk Albach<sup>c</sup>, Charlotte H. Gotfredsen<sup>a</sup>, Søren Rosendal Jensen<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, The Technical University of Denmark, Build. 207, DK-2800 Lyngby, Denmark*

<sup>b</sup> *Royal Botanic Gardens, Kew, Richmond, Surrey TW9 3AB, UK*

<sup>c</sup> *Institut für Biologie und Umweltwissenschaften, Carl von Ossietzky-Universität Oldenburg, 26111 Oldenburg, Germany*

## A B S T R A C T

From two species of *Sutera* (*S. foetida* and *S. cordata*) (Scrophulariaceae tribe Limoselleae) were isolated four known secoiridoid glucosides secologanoside as well as three iridoid congeners, all biosynthetically derived from iridodial glucoside (and/or deoxyloganic acid). In addition, two previously unknown compounds were found, namely a terpenoid glucoside lactone (suterolide, **20**) and the phenylethanoid glycoside 2''''-acetyl-angoroside A (**18**) as well as verbascoside, echinacoside and tubuloside A. Two other species previously considered to belong to the same genus were shown to belong to two different genera, *Jamesbrittenia dissecta* and *Lyperia antirrhinoides*, respectively. Significantly, these two species contained iridoids derived from *epi*-iridodial (and epideoxyloganic acid), namely aucubin, melittoside and acetylharpagide. In addition we investigated *Melanospermum transvaalense*, *Lyperia tristis* and *Microdon dubius* likewise from Limoselleae and all of these contained iridoid glucosides from the latter pathway. Thus, secoiridoid distribution confirms the DNA-based circumscription of *Sutera* and its sister-group relationship with *Manulea*. In addition, the results show that this clade has a biosynthetic pathway to iridoids fundamentally different from the rest of the tribe and from the whole family Scrophulariaceae.

*Keywords:*

*Sutera foetida*

*Sutera cordata*

*Melanospermum transvaalense*

Scrophulariaceae

Secoiridoid glucosides

Iridoid glucosides

Phenylethanoid glycosides

Chemotaxonomy

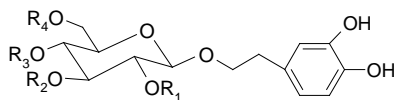
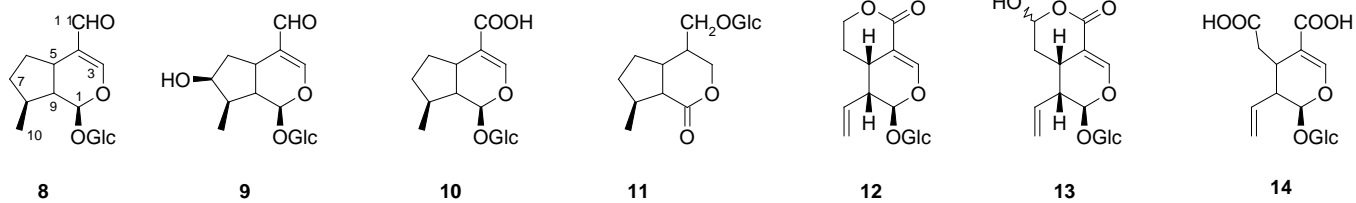
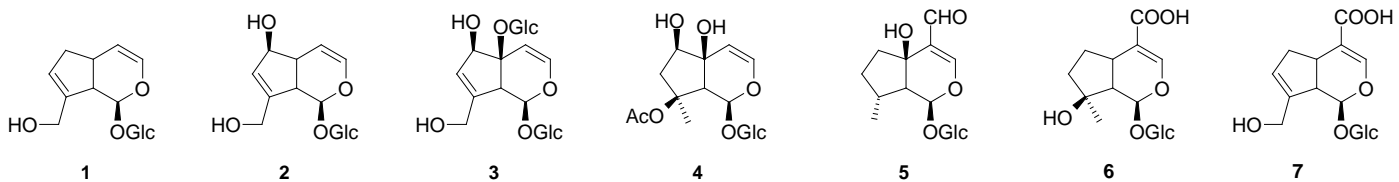
---

\* Corresponding author. Tel.: +45-20650984; fax: +45-45933968.

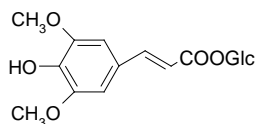
*E-mail address:* srj@kemi.dtu.dk (S.R. Jensen).

## Content:

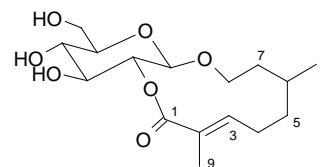
1. Formulas	3
2. Picture of <i>Sutera foetida</i>	4
3. <sup>1</sup> H NMR spectrum of aucubin from <i>Lyperia (Sutera) antirrhinoides</i>	5
4. <sup>1</sup> H NMR spectrum of melittoside from <i>Lyperia (Sutera) antirrhinoides</i>	6
5. <sup>13</sup> C NMR spectrum of melittoside from <i>Lyperia (Sutera) antirrhinoides</i>	7
6. <sup>1</sup> H NMR spectrum of 8- <i>O</i> -acetylharpagide from <i>Lyperia (Sutera) antirrhinoides</i>	8
7. <sup>13</sup> C NMR spectrum of 8- <i>O</i> -acetylharpagide from <i>Lyperia (Sutera) antirrhinoides</i>	9
8. <sup>1</sup> H NMR spectrum of suterolide ( <b>20</b> ) from <i>Sutera foetida</i>	10
9. <sup>13</sup> C NMR spectrum of suterolide ( <b>20</b> ) from <i>Sutera foetida</i>	11
10. <sup>1</sup> H NMR spectrum of secologanic acid ( <b>13</b> ) from <i>Sutera cordata</i>	12
11. <sup>13</sup> C NMR spectrum of secologanic acid ( <b>13</b> ) from <i>Sutera cordata</i>	13
12. Mass spectrum of secologanic acid ( <b>13</b> ) <i>Sutera cordata</i>	14
13. <sup>1</sup> H NMR spectrum of villoside ( <b>11</b> ) from <i>Sutera cordata</i>	15
14. <sup>13</sup> C NMR spectrum of villoside ( <b>11</b> ) from <i>Sutera cordata</i>	16
15. <sup>1</sup> H NMR spectrum of 2''''-Acetyl angoroside A ( <b>18</b> ) from <i>Sutera cordata</i>	17
16. <sup>13</sup> C NMR spectrum of 2''''-Acetyl angoroside A ( <b>18</b> ) from <i>Sutera cordata</i>	18
17. <sup>1</sup> H NMR spectra of crude aq. extract from <i>Lyperia tristis</i>	19
18. <sup>1</sup> H NMR spectra of crude aq. extract from <i>Microdon dubius</i>	20
19. Origin of ITS-sequences used in the phylogenetic analysis	21



- 15  $R_1=H$ ,  $R_2=Rha$ ,  $R_3=Caffeoyl$ ,  $R_4=H$   
 16  $R_1=H$ ,  $R_2=Rha$ ,  $R_3=Caffeoyl$ ,  $R_4=Glc$   
 17  $R_1=Ac$ ,  $R_2=Rha$ ,  $R_3=Caffeoyl$ ,  $R_4=Glc$   
 18  $R_1=H$ ,  $R_2=Rha$ ,  $R_3=Caffeoyl$ ,  $R_4=2-Ac-Ara$



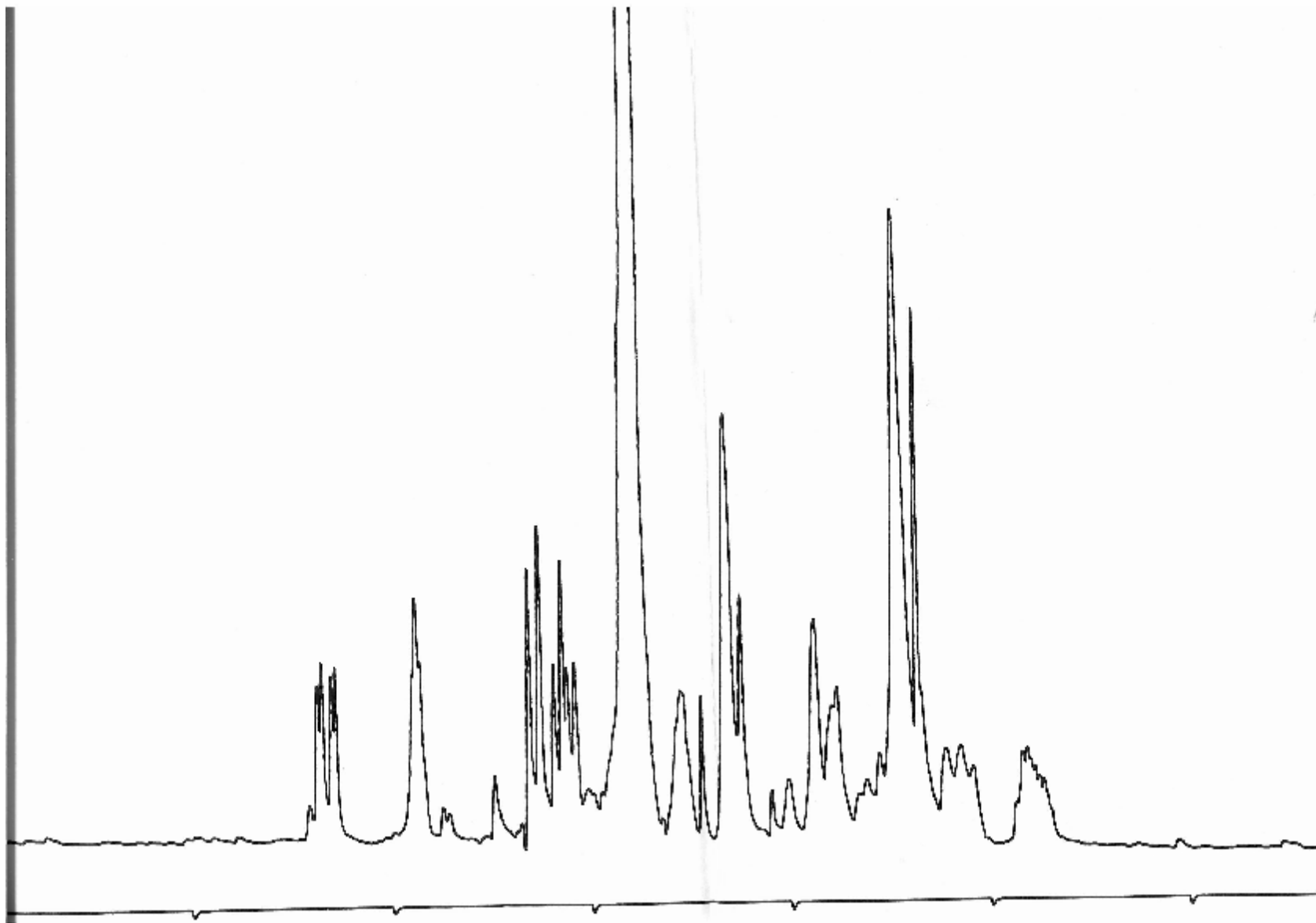
19



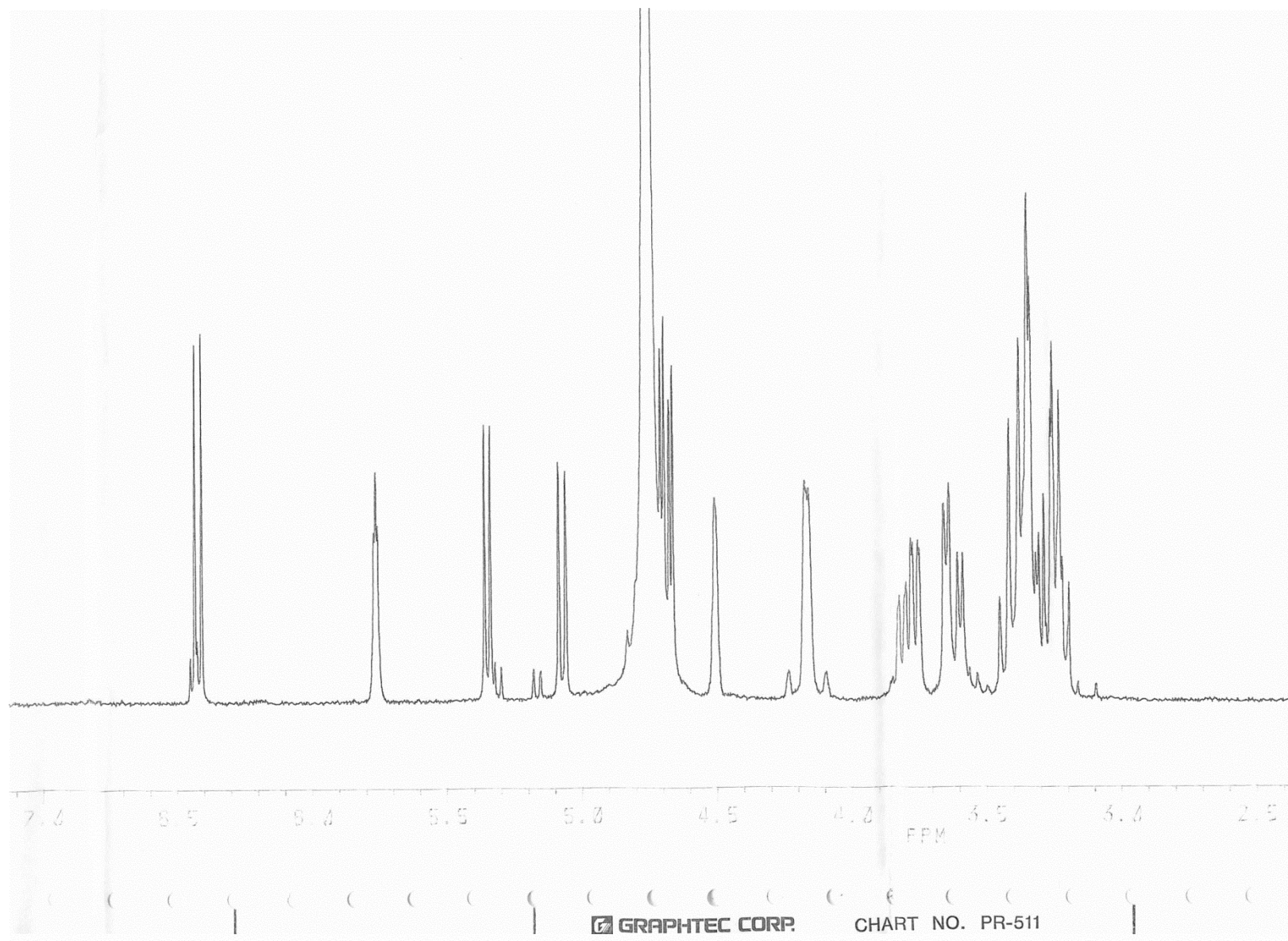
20



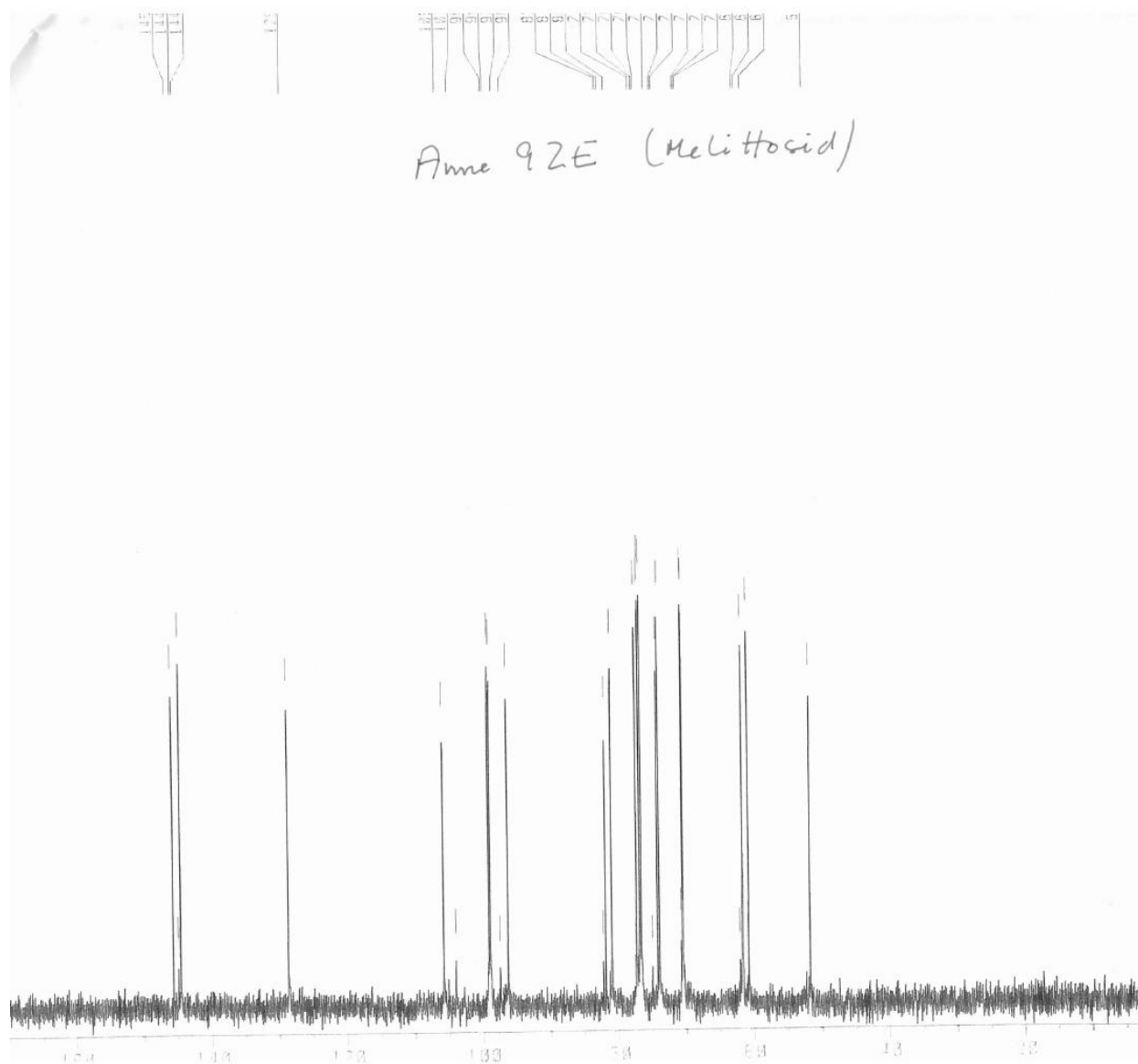
*Sutera foetida* (picture by Gry Bastholm)



3.  $^1\text{H}$  NMR spectrum (60 MHz,  $\text{D}_2\text{O}$ ) of aucubin (2) from *Lyperia (Sutera) antirrhinoides*.

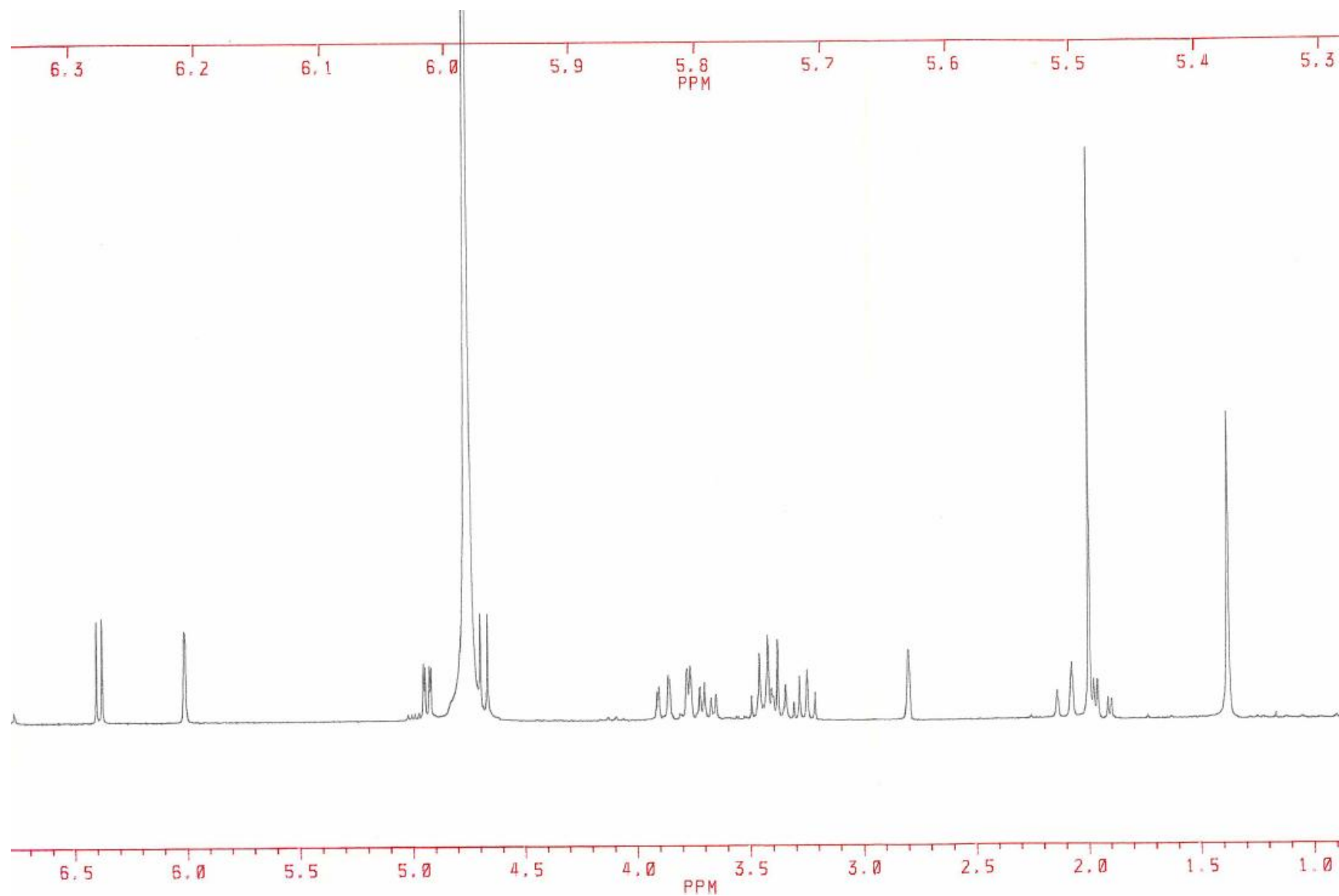


4.  $^1\text{H}$  NMR spectrum (200 MHz,  $\text{D}_2\text{O}$ ) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.

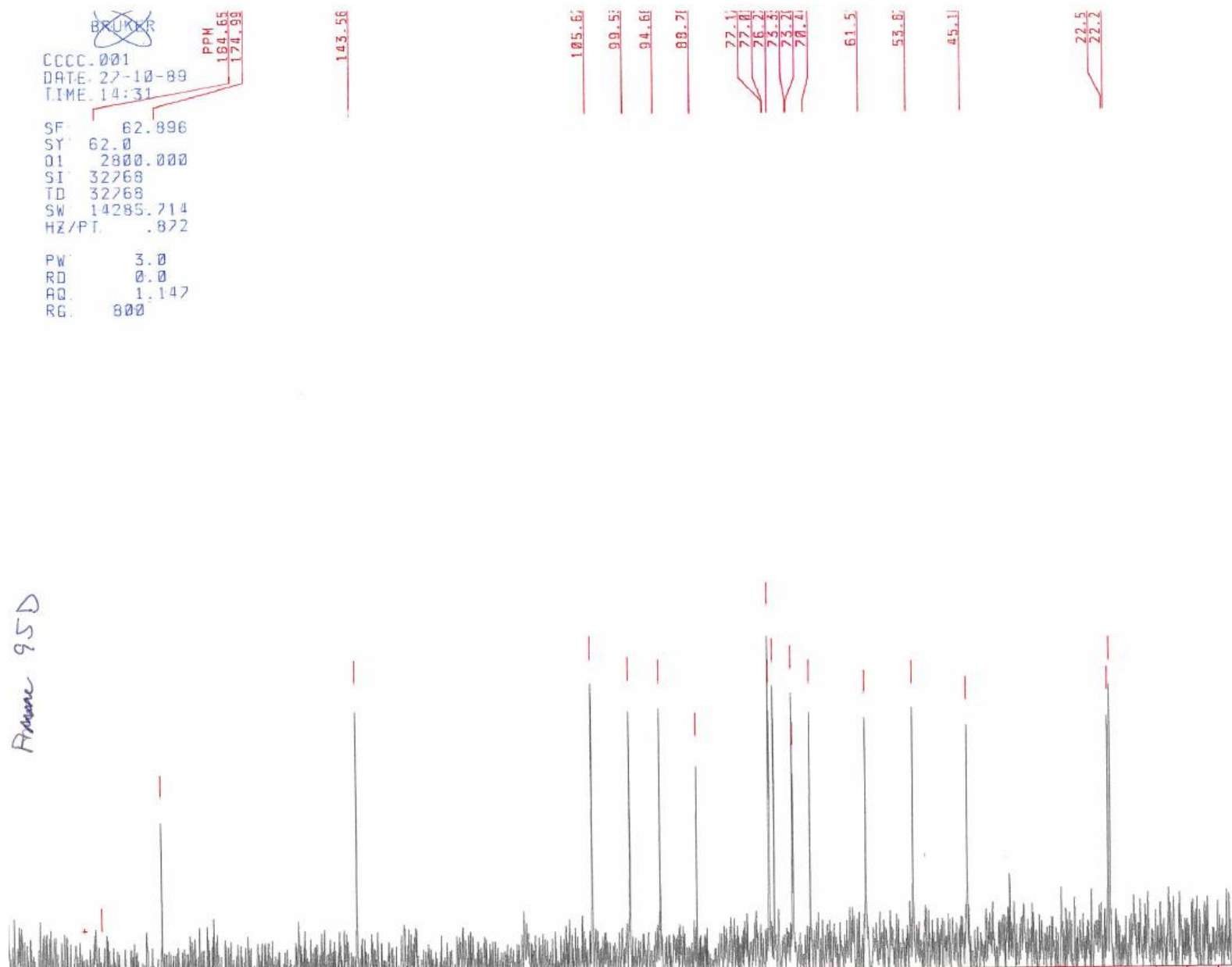


5.  $^{13}\text{C}$  NMR spectrum (50 MHz,  $\text{D}_2\text{O}$ ) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.

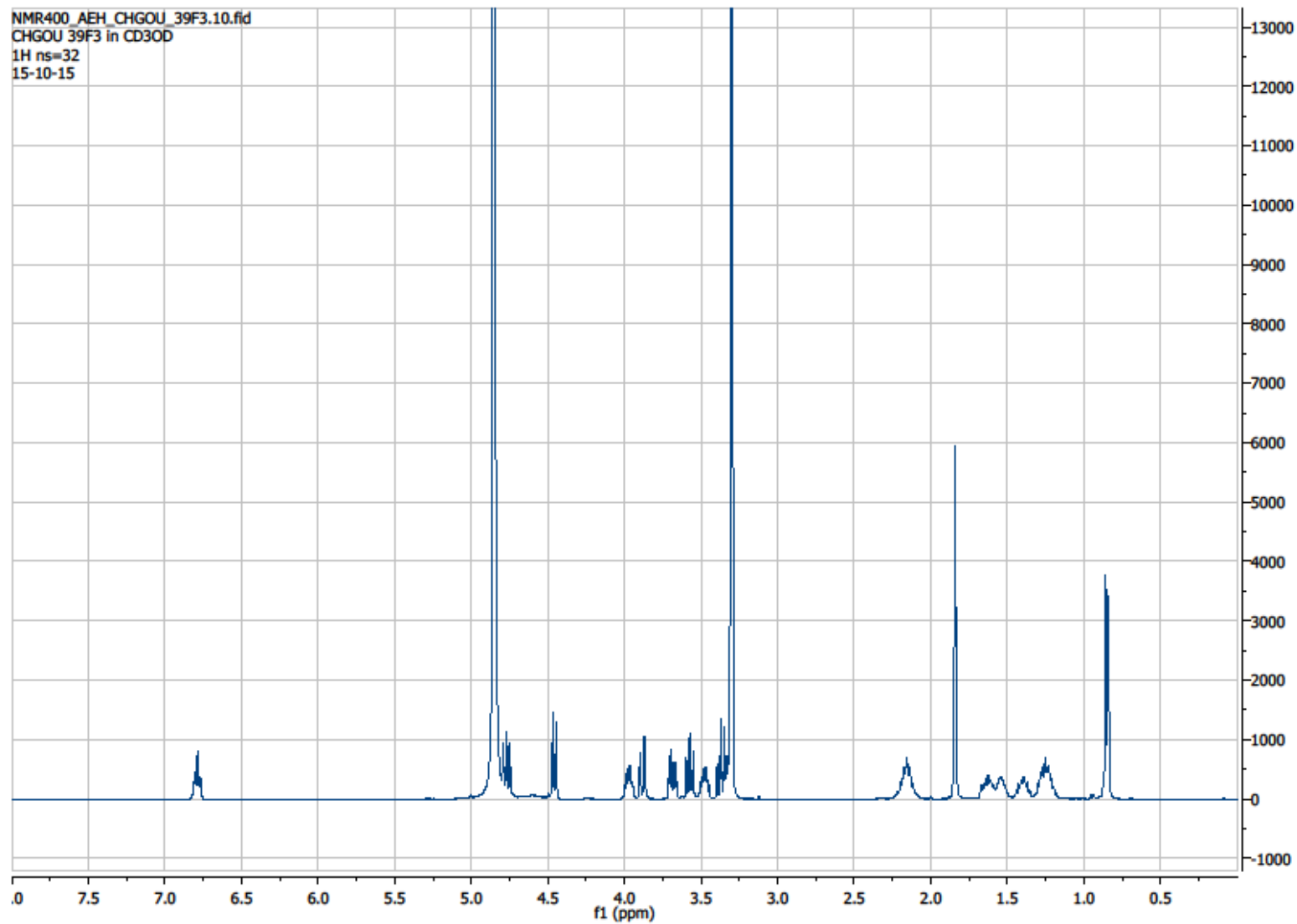




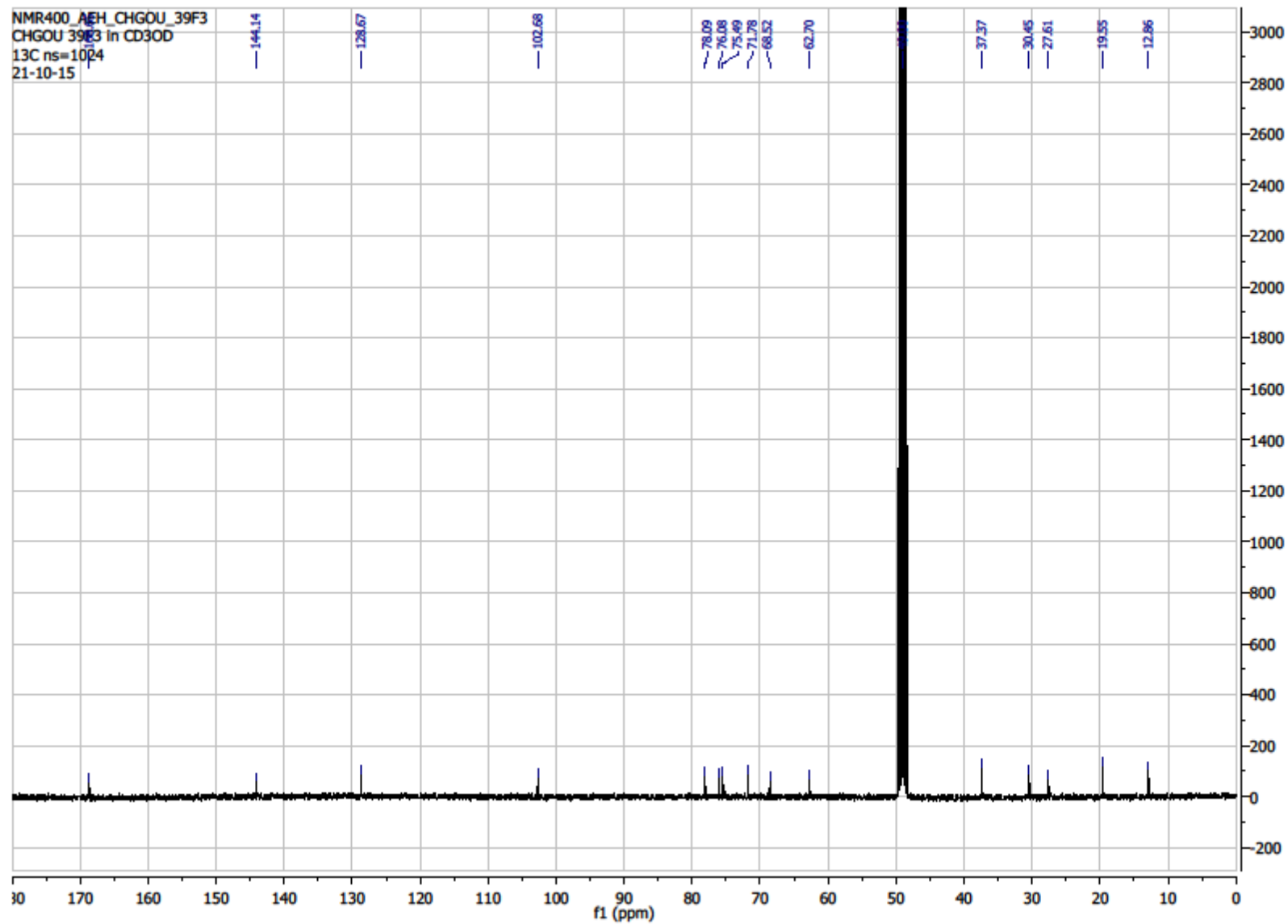
6.  $^1\text{H}$  NMR spectrum (200 MHz,  $\text{D}_2\text{O}$ ) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



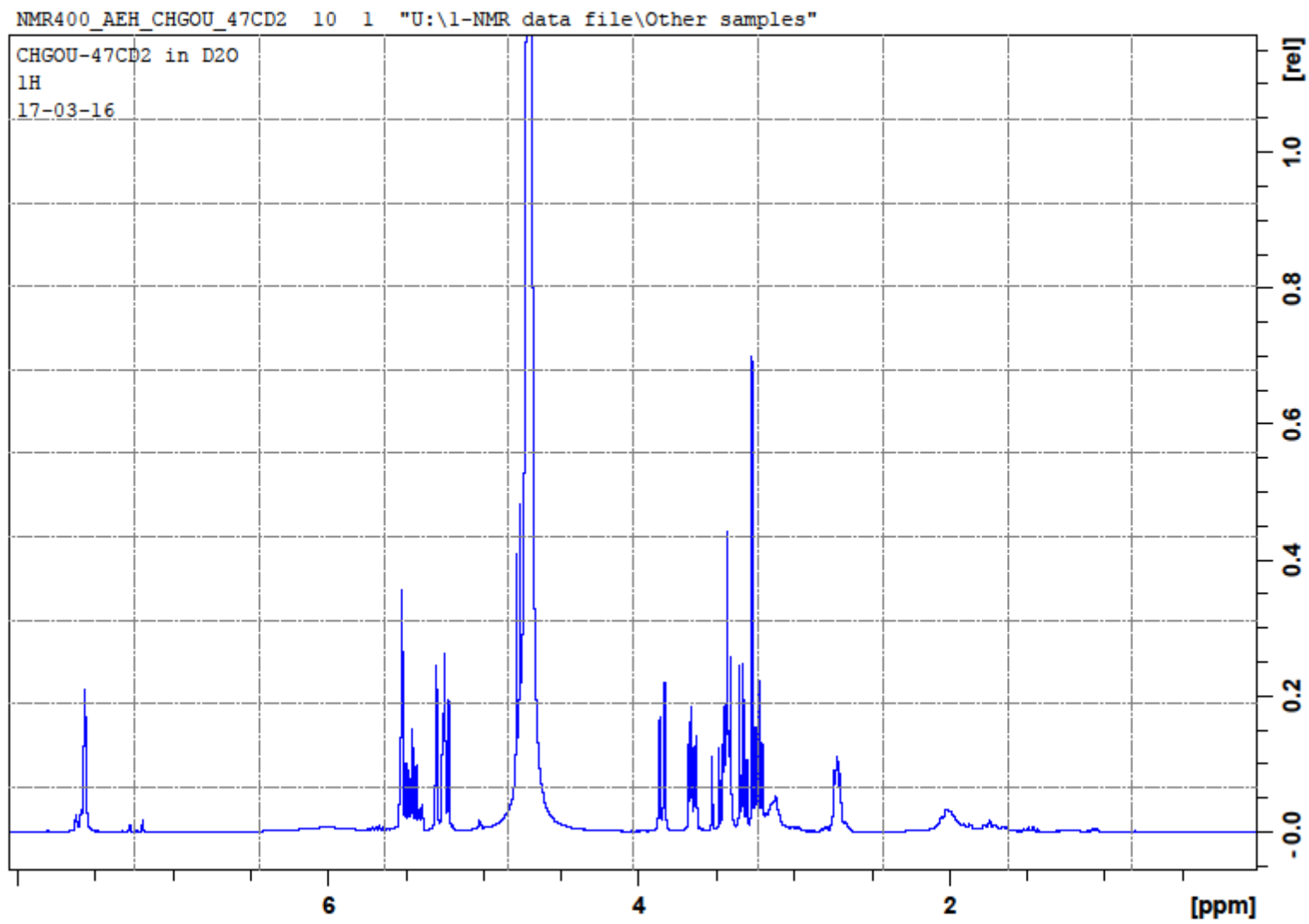
7.  $^{13}\text{C}$  NMR spectrum (50 MHz,  $\text{D}_2\text{O}$ ) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



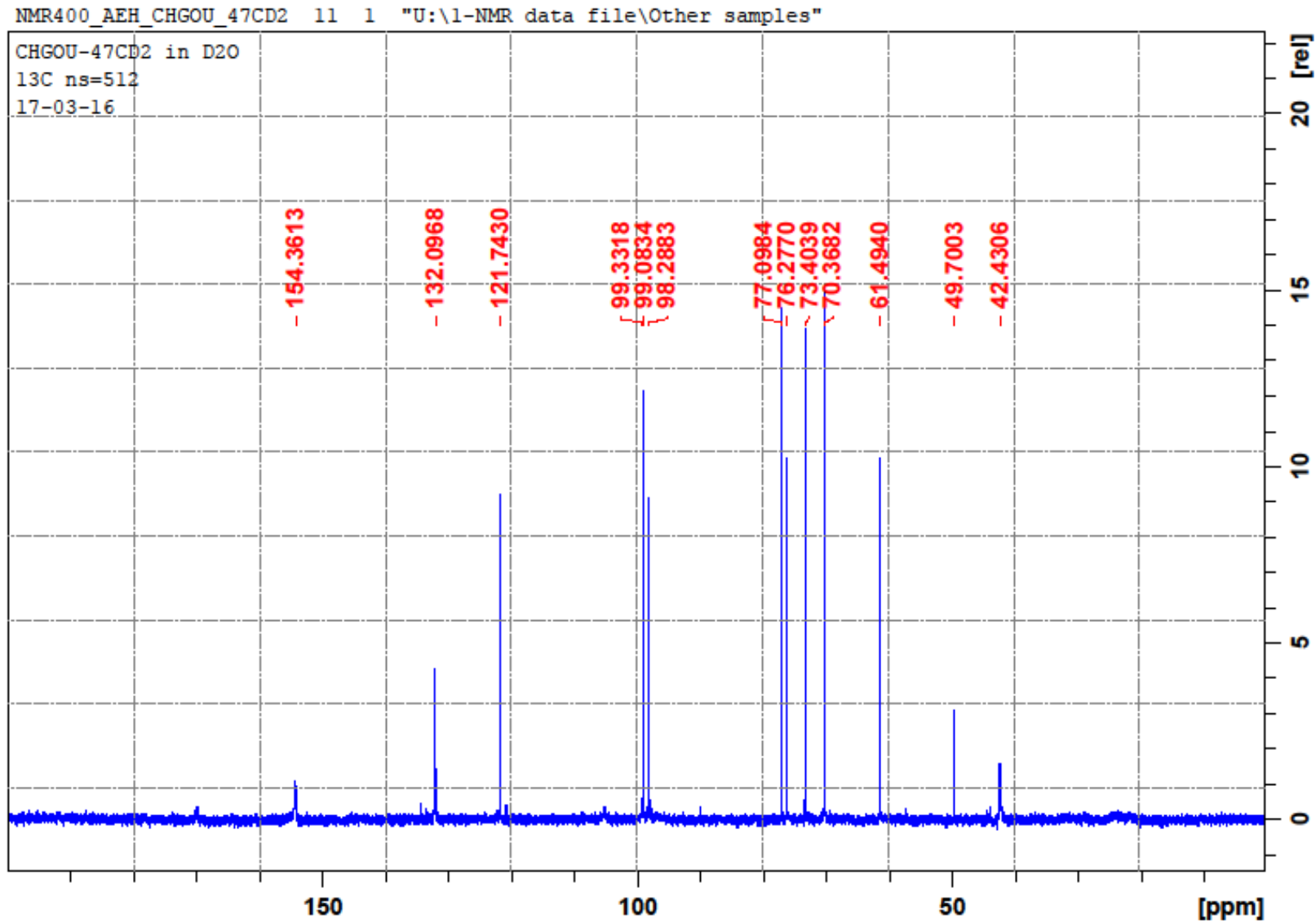
8.  $^1\text{H}$  NMR spectrum (400 MHz,  $d_4$ -Methanol) of suterolide (**20**) from *Sutera foetida*.



9.  $^{13}\text{C}$  NMR spectrum (100 MHz,  $d_4$ -Methanol) of suterolide (**20**) from *Sutera foetida*.

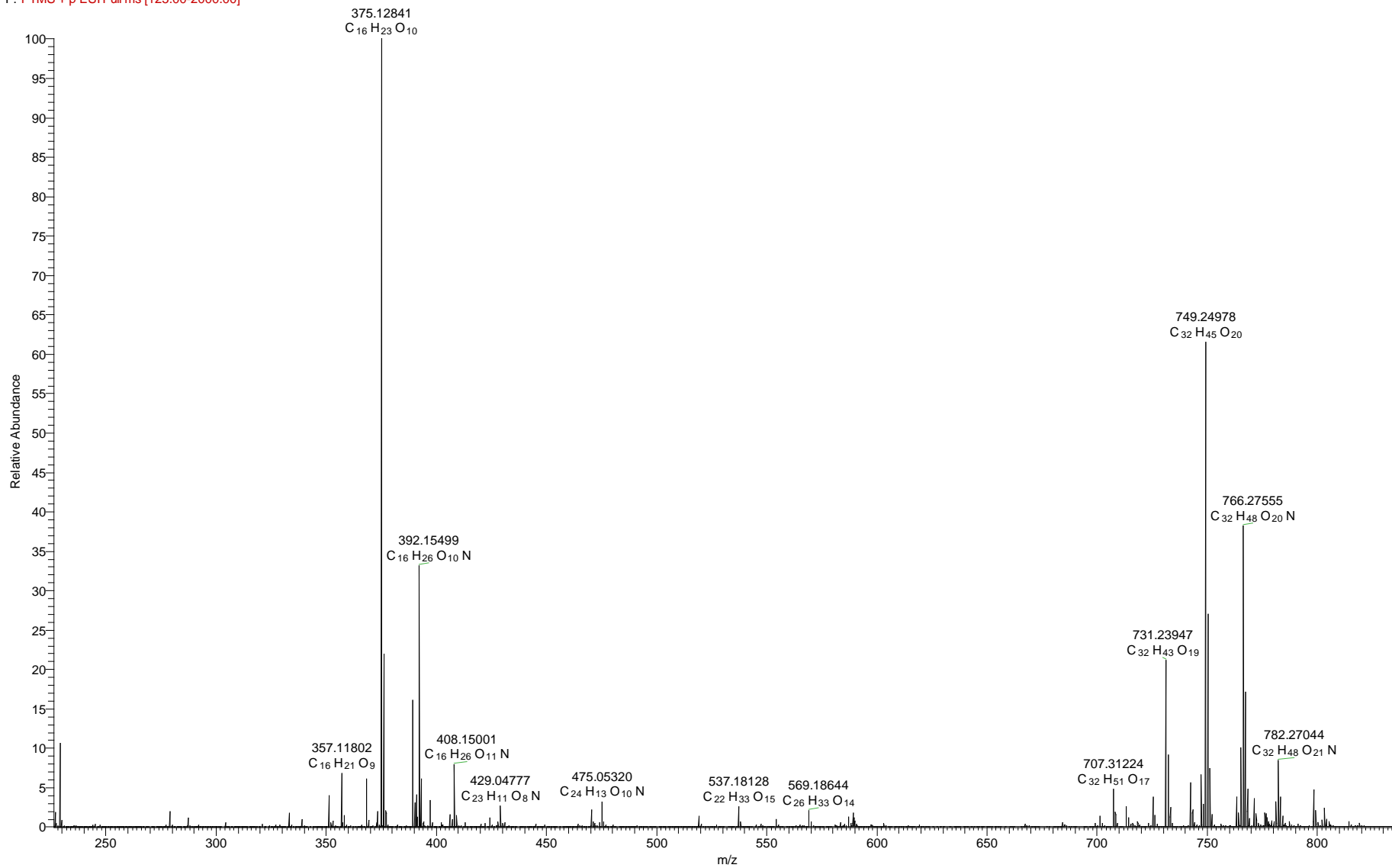


10.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ ) of secologanic acid (**13**).

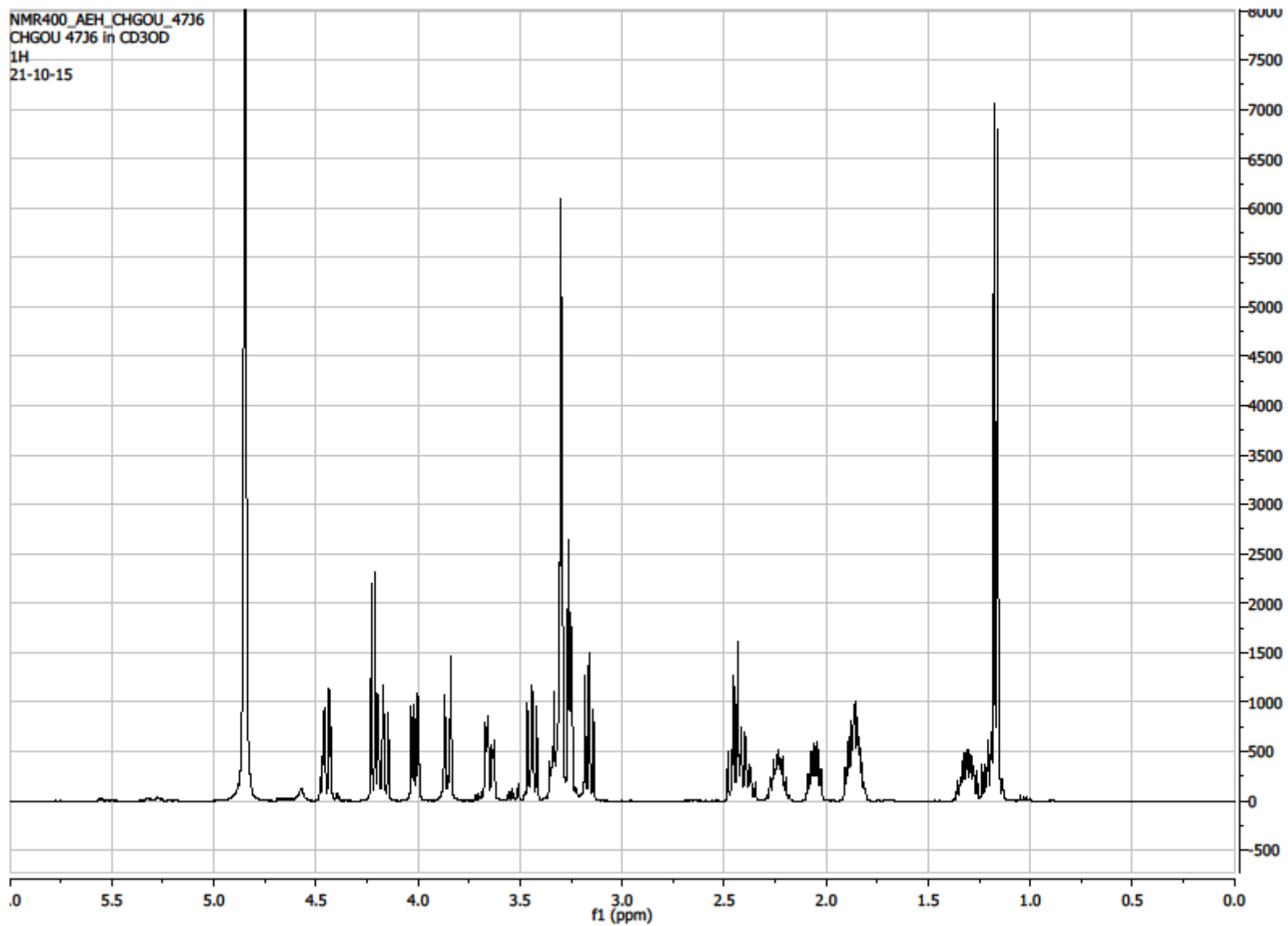


11.  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{D}_2\text{O}$ ) of secologanic acid (**13**).

Sutera\_SRJ\_47CD2\_26955\_posnegESI\_FT #682-825 RT: 5.00-5.79 AV: 20 NL: 2.70E6  
F: FTMS + p ESI Full ms [125.00-2000.00]

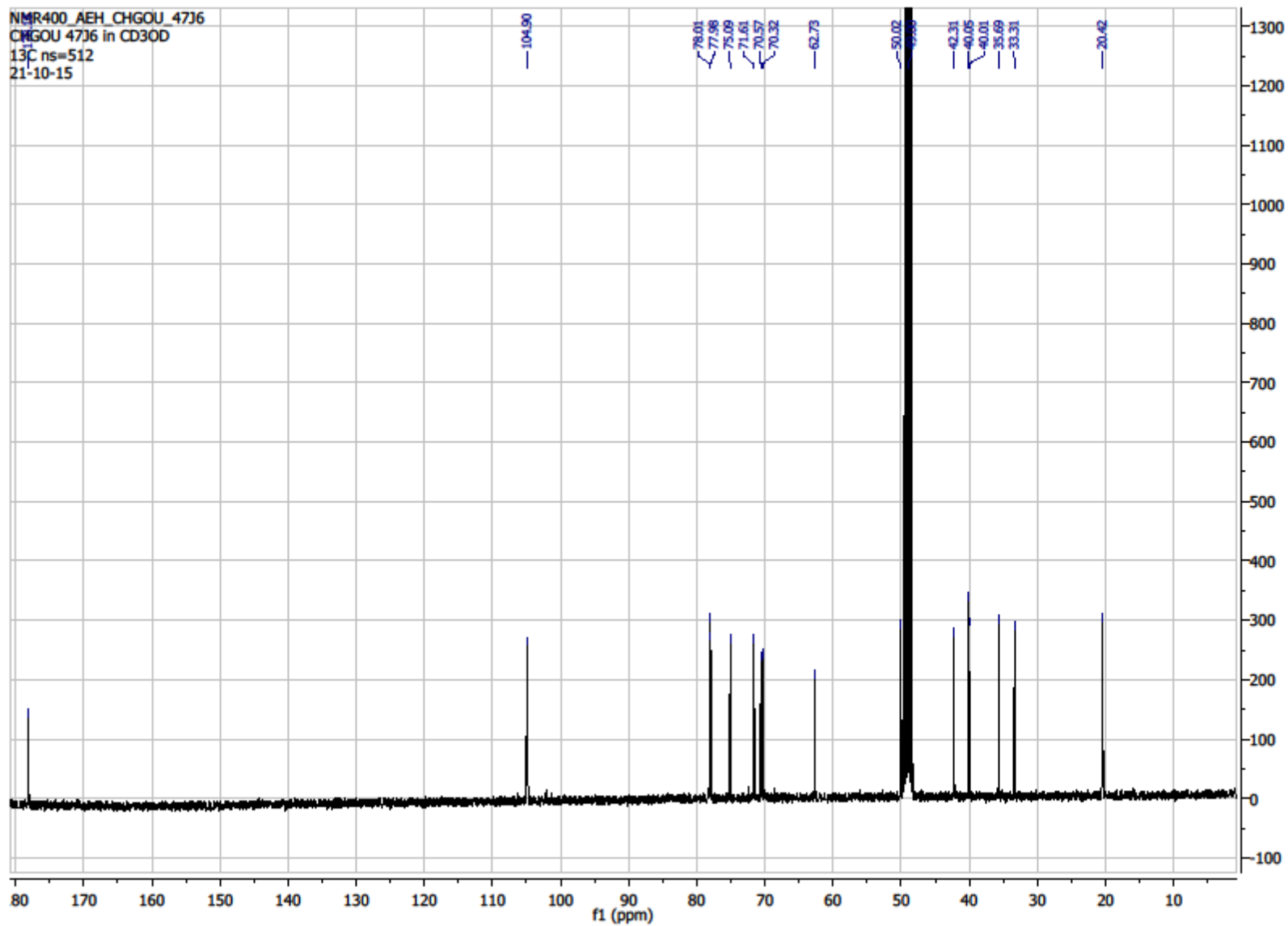


12. Mass spectrum of secologanic acid (13) expansion showing [M+H]<sup>+</sup>, [M+NH<sub>4</sub>]<sup>+</sup>, [2M+H]<sup>+</sup> and [2M+NH<sub>4</sub>]<sup>+</sup>

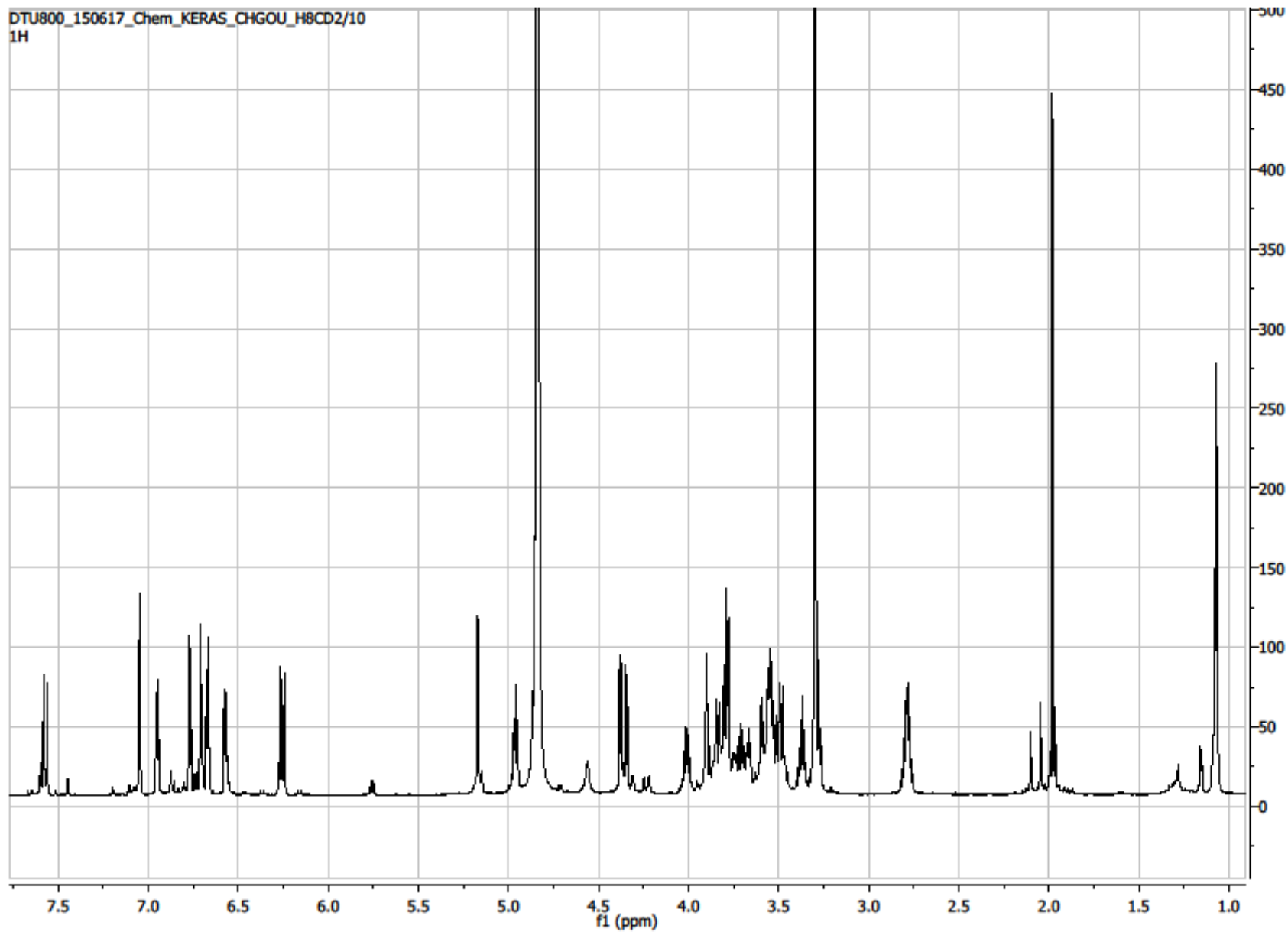


13.  $^1\text{H}$  NMR spectrum (400 MHz,  $d_4$ -Methanol) of villoside (**11**) from *Sutera cordata*.

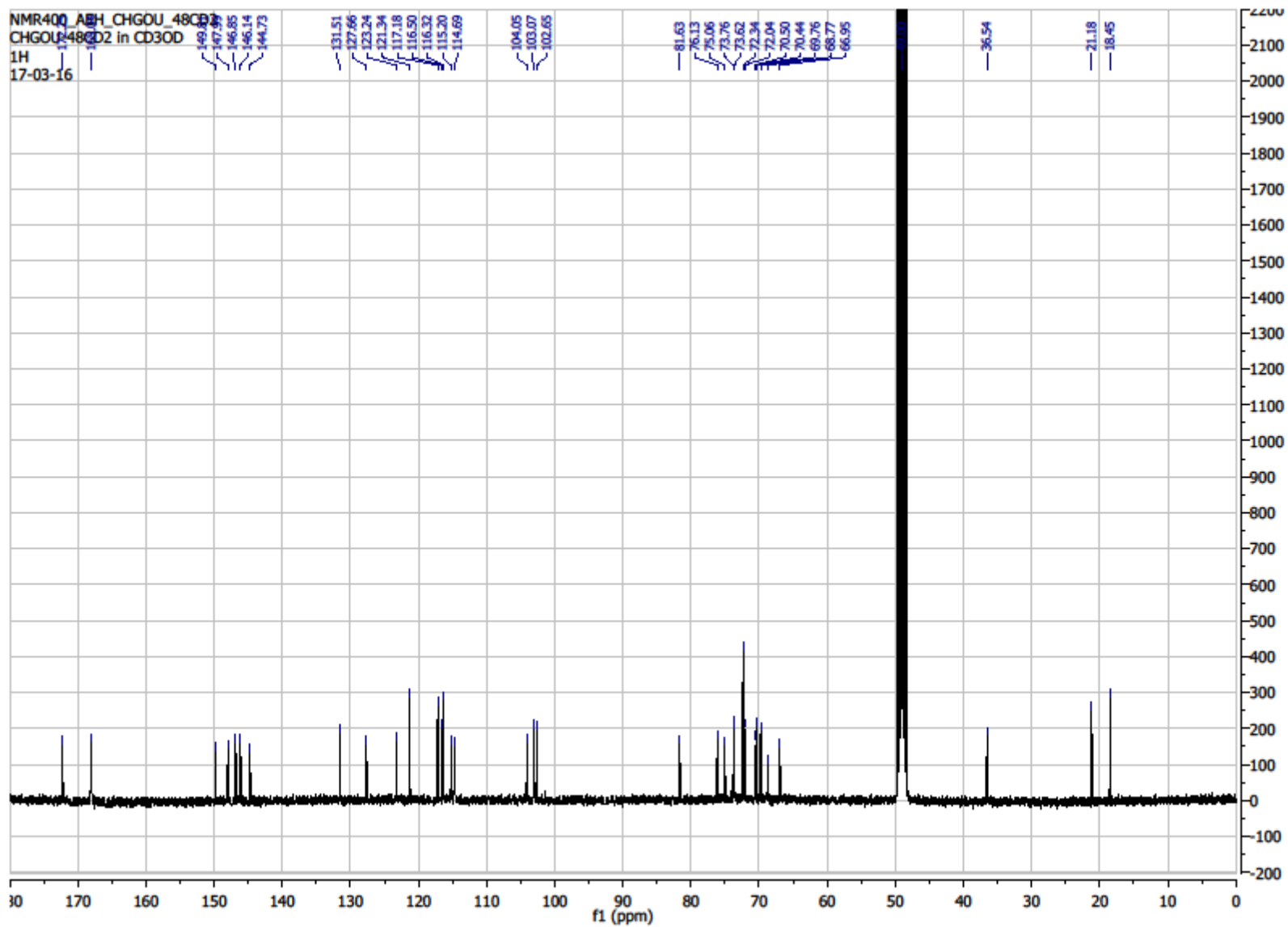




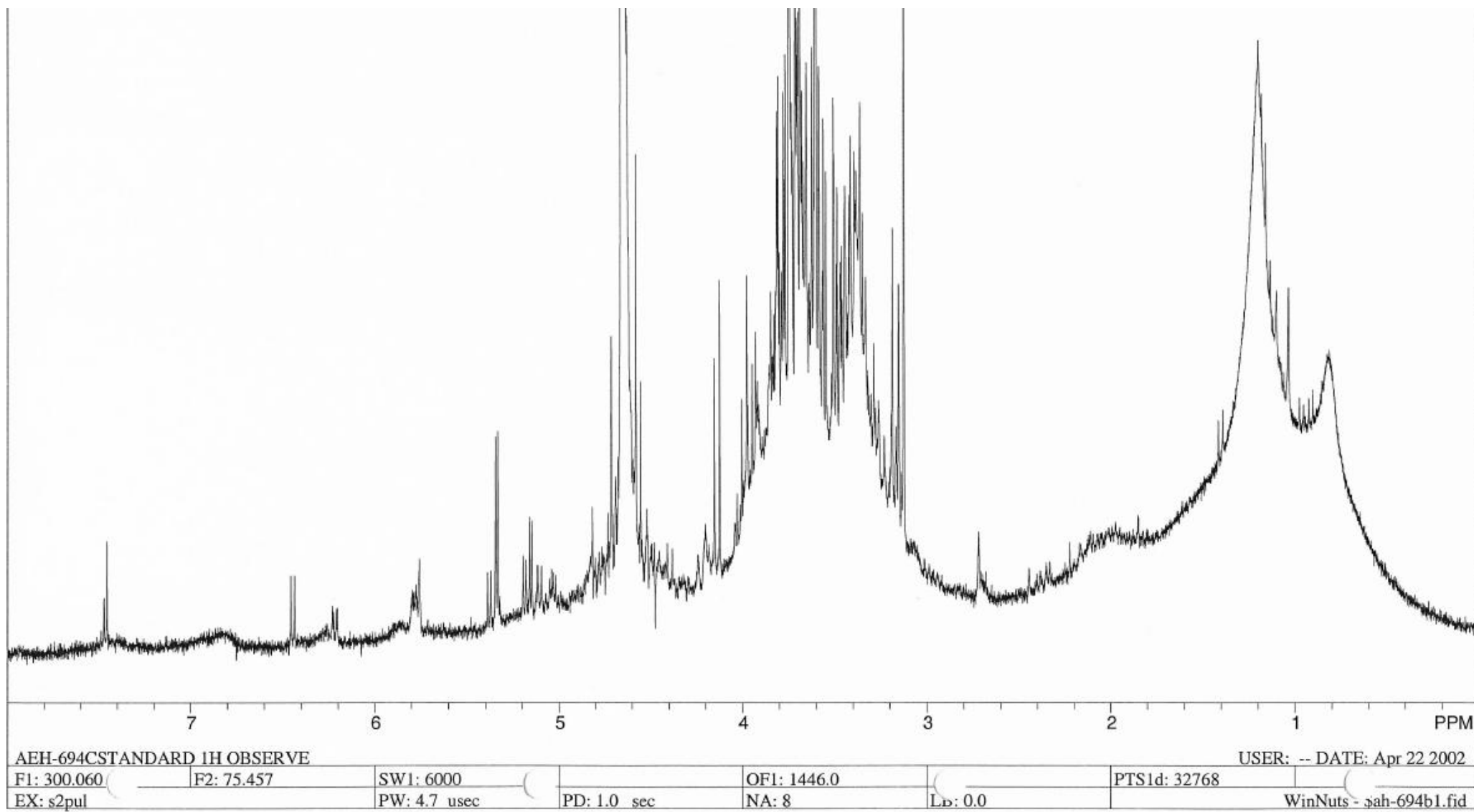
14.  $^{13}\text{C}$  NMR spectrum (100 MHz,  $d_4$ -Methanol) of villoside (**11**) from *Sutera cordata*.



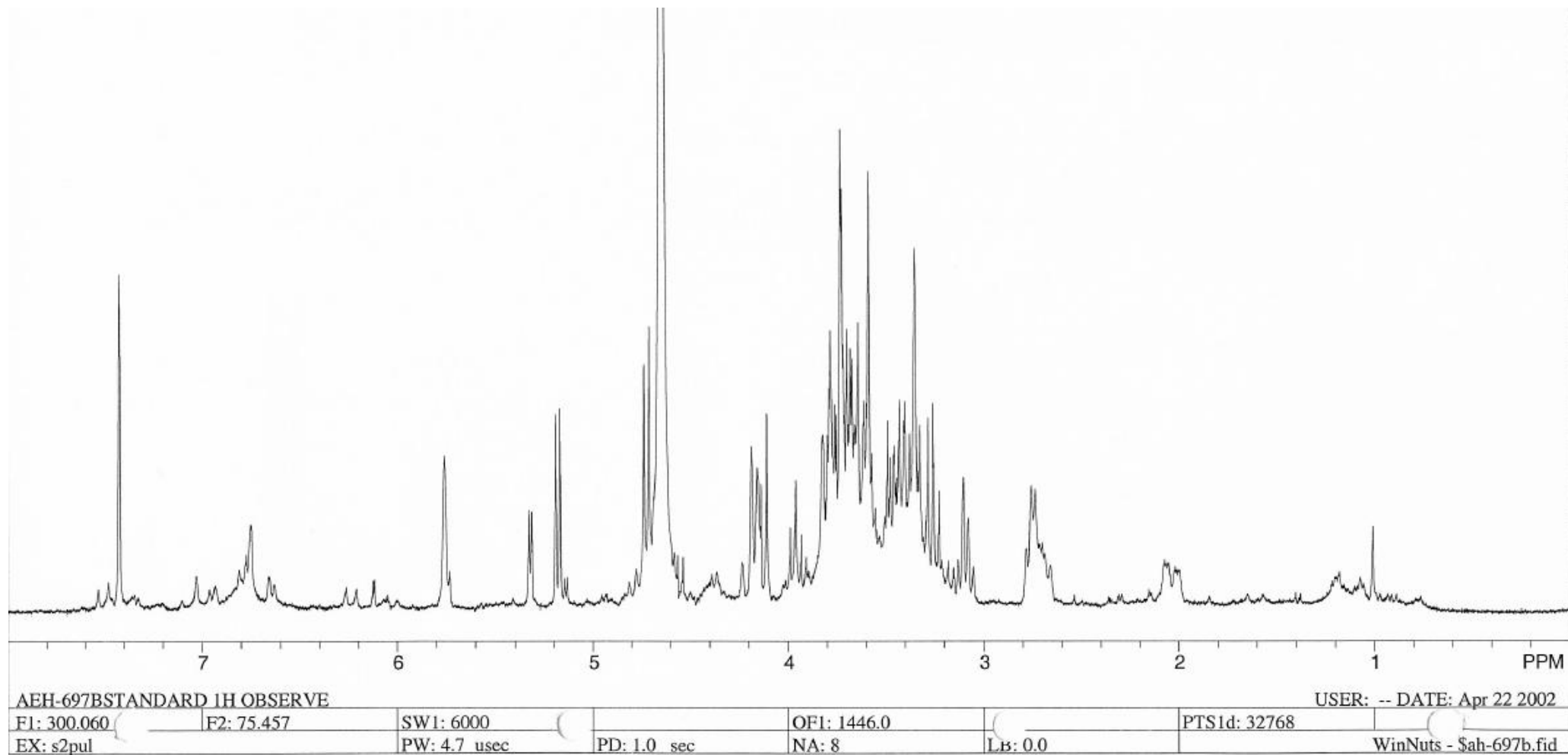
15.  $^1\text{H}$  NMR spectrum (800 MHz,  $d_4$ -Methanol) of 2'''-Acetyl angoroside A (**18**) from *Sutera cordata*.



16.  $^{13}\text{C}$  NMR spectrum (200 MHz,  $d_4$ -Methanol) of 2'''-Acetyl angoroside A (**18**) from *Sutera cordata*.



17.  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{D}_2\text{O}$ ) of a crude extract from *Lyperia tristis*.



18.  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{D}_2\text{O}$ ) of a crude extract from *Microdon dubius*.

## Origin of ITS-sequences used in the phylogenetic analysis

Outgroup: *Freylinia lanceolata* AF375147; *Teedia lucida* AF375148; *Buddleja saligna* AJ550578; *Camptoloma canariense* AJ550580; *Antherothamnus pearsonii* AJ550575; *Verbascum arcturus* AJ550615;

Limoselleae: *Barthlottia madagascariensis* AJ550576; *Chenopodiopsis retrorsa* AJ584757; *Cromidon decumbens* AJ584756; *Dichisma spicatum* AJ584823; *Glekia krebsiana* MG547586; *Glumicalyx flanaganii* AJ584815; *Glumicalyx flanaganii* AJ584752; *Glumicalyx goseloides* AJ584813; *Glumicalyx montanus* AJ584814; *Hebenstretia dentata* AJ584798; *Hebenstretia dura* AJ584821; *Hebenstretia integrifolia* AJ584797; *Hebenstretia lanceolata* AJ584825; *Hebenstretia parviflora* AJ584824; *Hebenstretia repens* AJ584818; *Jamesbrittenia adpressa* AY712577; *Jamesbrittenia megadenia* AJ550584; *Limosella aquatica* AJ550588; *Limosella africana* AJ550587; *Limosella grandiflora* LC133032; *Limosella sp* LC133033; *Limosella curdieana* LC133045; *Limosella subulata* LC133039; *Limosella australis* LC133036; *Limosella macrantha* AJ550586; *Limosella major* AJ550585; *Lyperia antirrhinoides* AJ616324; MG547585; *Lyperia tristis* AY712578; *Lyperia tristis* AJ550614; *Lyperia tristis* AJ550589; *Manulea annua* AJ550590; *Manulea bellidifolia* AJ550591; *Manulea calciphila* AJ550592; *Manulea caledonica* AJ550593; *Manulea cheiranthus* AJ550594; *Manulea chrysantha* AJ550595; *Manulea crassifolia* AJ550596; *Manulea dubia* AJ550597; *Manulea exigua* AJ550598; *Manulea glandulosa* AJ550599; *Manulea rubra* AJ550600; *Manulea schaeferi* AJ550601; *Manulea tomentosa* AJ550602; *Manulea dinterii* AJ616916; *Melanospermum foliosum* AJ584753; *Melanospermum transvaalense* AJ584759; MG547585; *Microdon dubius* AJ584792; *Microdon orbicularis* AJ584762; *Microdon polygaloides* AJ584770; *Phyllopodium dolomiticum* AJ584806; *Phyllopodium multifolium* AJ584802; *Polycarena batteniana* AJ584769; *Polycarena filiformis* AJ584807; *Polycarena formosa* AJ584754; *Polycarena pubescens* AJ584768; *Pseudoselago ascendens* AJ584812; *Pseudoselago bella* AJ584796; *Pseudoselago candida* AJ584819; *Pseudoselago densifolia* AJ584799; *Pseudoselago gracilis* AJ584800; *Pseudoselago langebergensis* AJ584817; *Pseudoselago recurvifolia* AJ584801; *Pseudoselago serrata* AJ584810; *Pseudoselago spuria* AJ584803; *Pseudoselago subglabra* AJ584811; *Reyemia chasmanthiflora* AJ584755; *Glekia krebsiana* 1468; *Selago alopecuroides* AJ584767; *Selago aspera* AJ584771; *Pseudoselago atherstonei* AJ584794; *Selago canescens* AJ584772; *Selago corymbosa* AJ550603; *Selago densiflora* AJ584793; *Selago dolichonema* AJ584760; *Selago dolosa* AJ584785; *Selago flanaganii* AJ584791; *Selago foliosa* AJ584786; *Selago fruticosa* AJ584773; *Selago geniculata* AJ584763; *Selago gracilis* AJ584782; *Selago hyssopifolia* AJ584764; *Selago impedita* AJ584784; *Selago levynsiae* AJ584780; *Selago longiflora* AJ584765; *Selago luxurians* AJ584774; *Selago myriophylla* AJ584775; *Selago myrtifolia* AJ584805; *Selago myrtifolia* AJ584829; *Selago nachtigalii* AJ584766; *Selago parvibractea* AJ584776; *Selago perplexa* AJ584779; *Selago pulchra* AJ584781; *Selago saxatilis* AJ584783; *Selago scabribractea* AJ584761; *Seago setulosa* AJ584828; *Selago setulosa* AJ584777; *Selago speciosa* AJ584787; *Selago spectabilis* AJ584788; *Selago tenuifolia* AJ584808; *Selago thomsonii* AJ584795; *Selago trauseldii* AJ584809; *Selago variicalyx* AJ584789; *Selago venosa* AJ584778; *Selago villosa* AJ584790; *Sutera caerulea* AJ550604; *Sutera calciphila* AJ550605; *Sutera campanulata* AJ550606; *Sutera cordata* AJ550607; *Sutera floribunda* AJ550608; *Sutera foetida* AJ550609; *Sutera foetida* AJ550611; *Sutera hispida* AY712583; *Sutera hispida* AJ550610; *Sutera patriotica* AJ550612; *Sutera revoluta* AJ550613; *Tetraselago longituba* AJ584826; *Tetraselago wilmsii* AJ584827; *Trieneea glutinosa* AJ584758; *Zaluzianskya capensis* AJ584822; *Zaluzianskya glareosa* AJ584816; *Zaluzianskya gracilis* AJ584820; *Zaluzianskya minima* AJ584751; *Zaluzianskya villosa* AJ584804;