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

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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

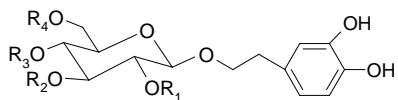
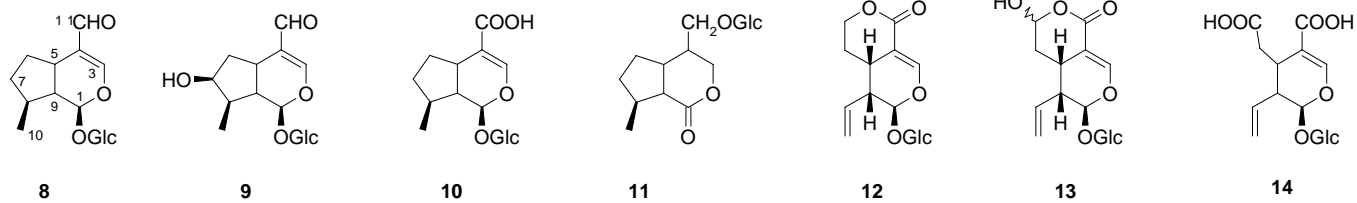
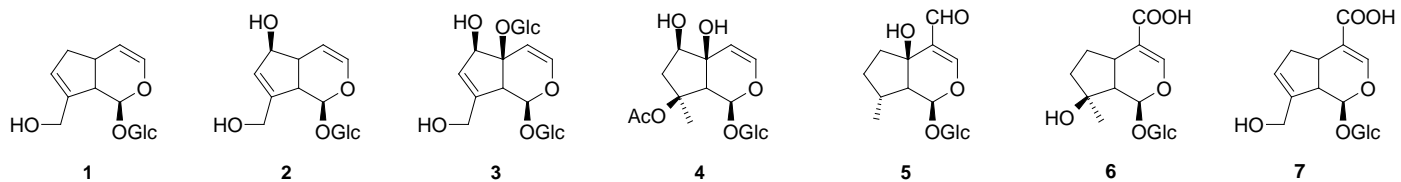
Chemotaxonomy

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

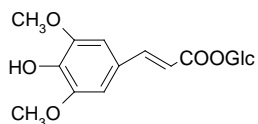
E-mail address: srj@kemi.dtu.dk (S.R. Jensen).

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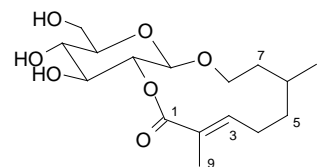
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- 15 $R_1=H$, $R_2=Rha$, $R_3=Caffeoyl$, $R_4=H$
 16 $R_1=H$, $R_2=Rha$, $R_3=Caffeoyl$, $R_4=Glc$
 17 $R_1=Ac$, $R_2=Rha$, $R_3=Caffeoyl$, $R_4=Glc$
 18 $R_1=H$, $R_2=Rha$, $R_3=Caffeoyl$, $R_4=2-Ac-Ara$



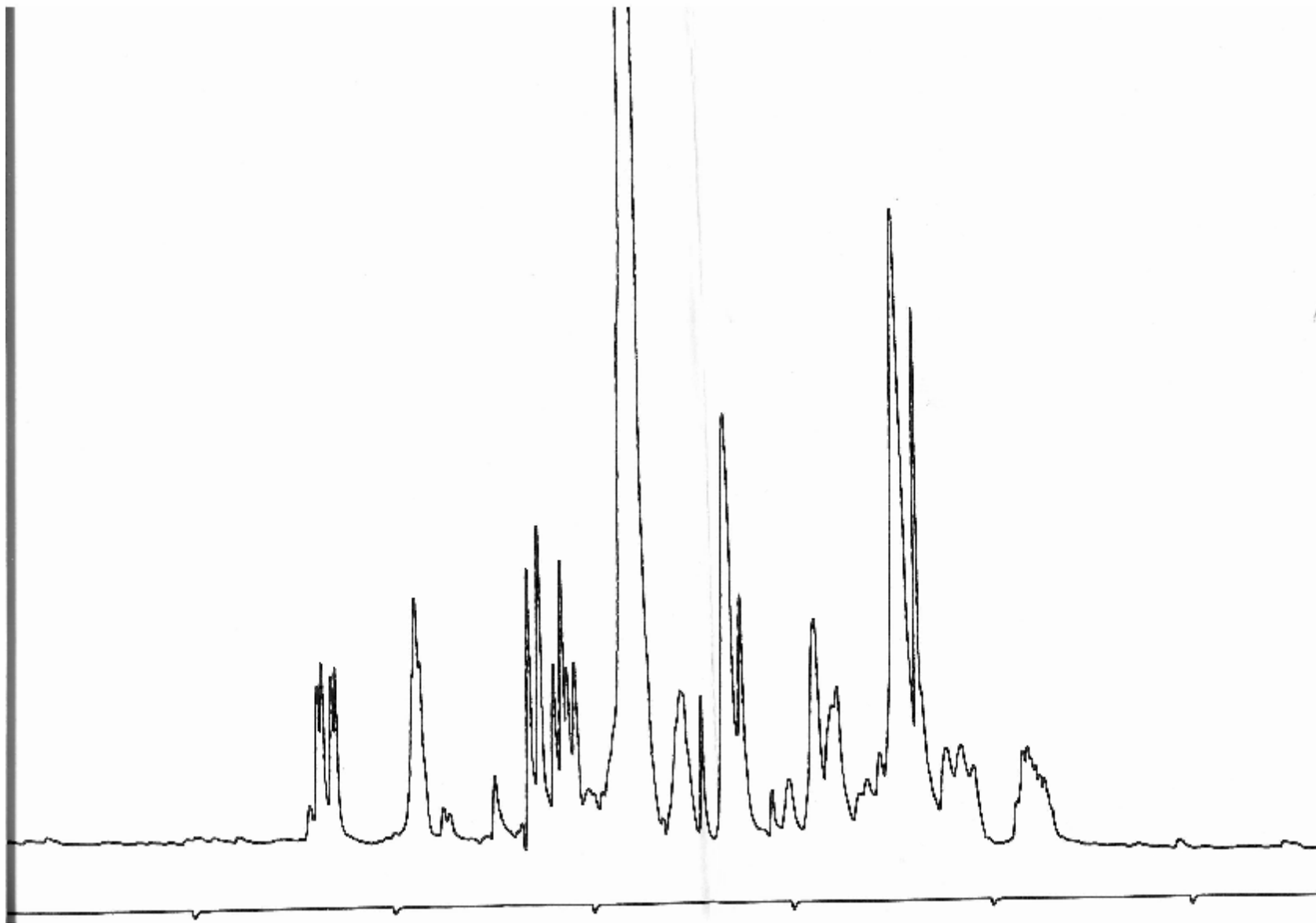
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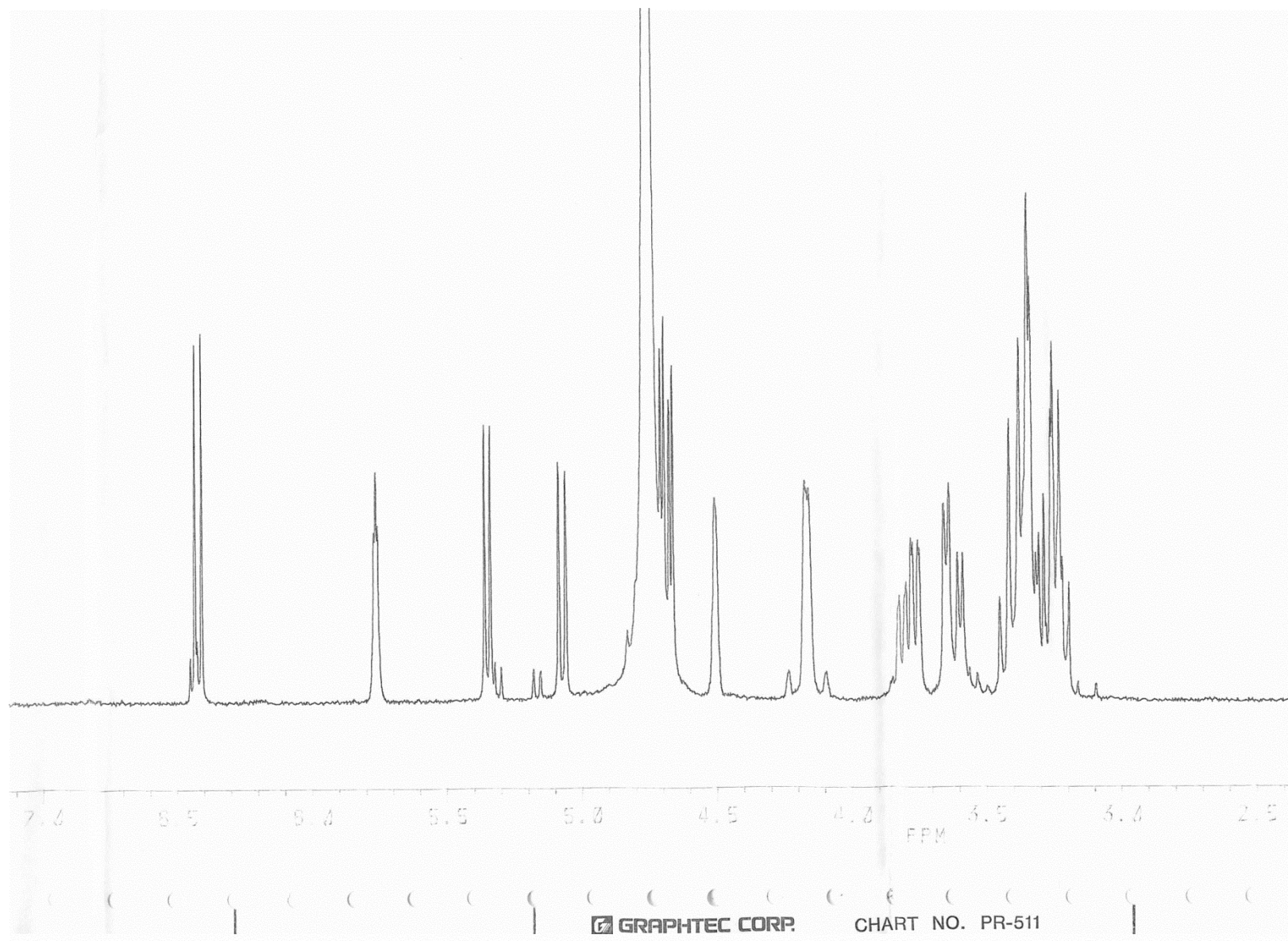
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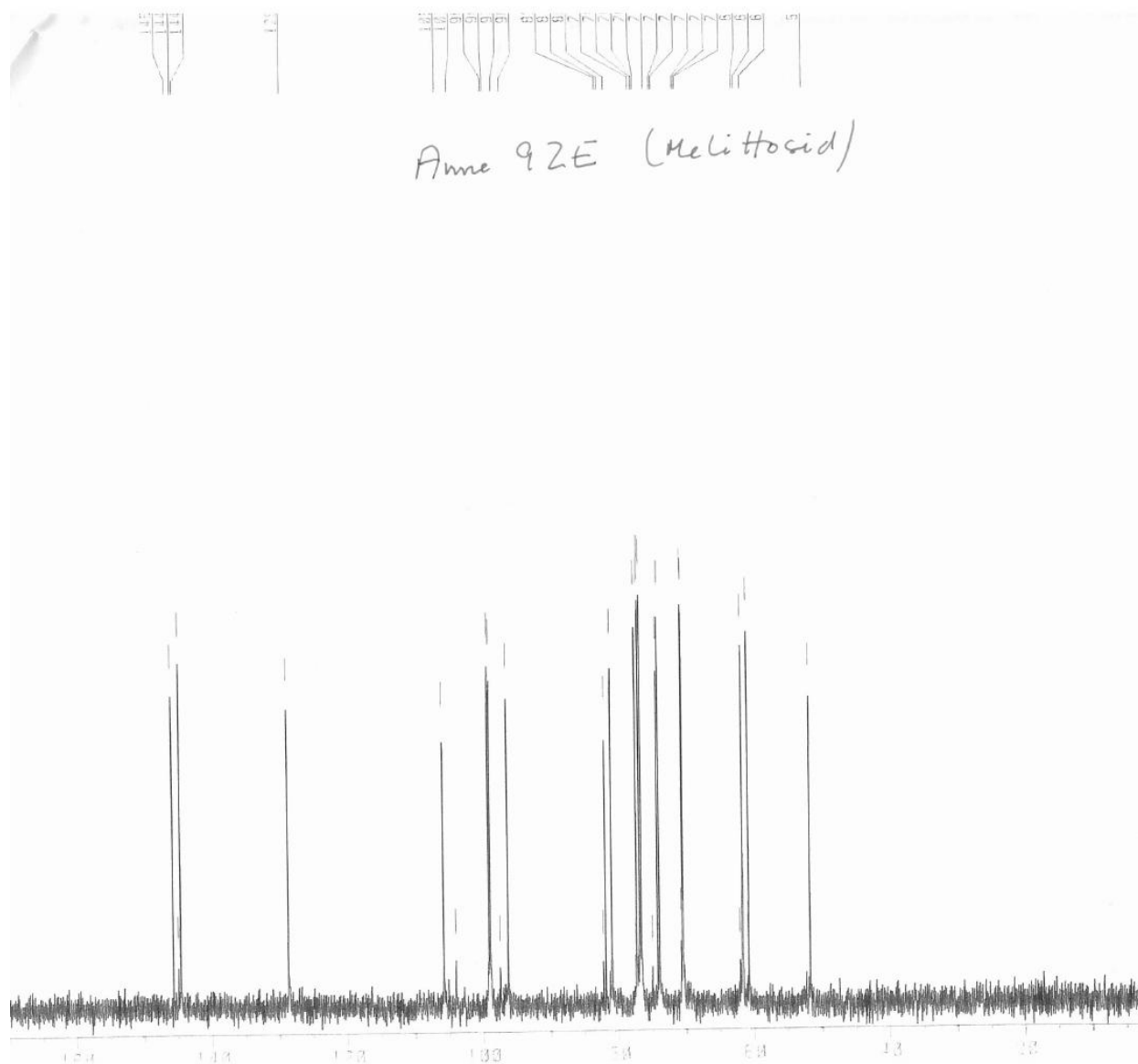
Sutera foetida (picture by Gry Bastholm)



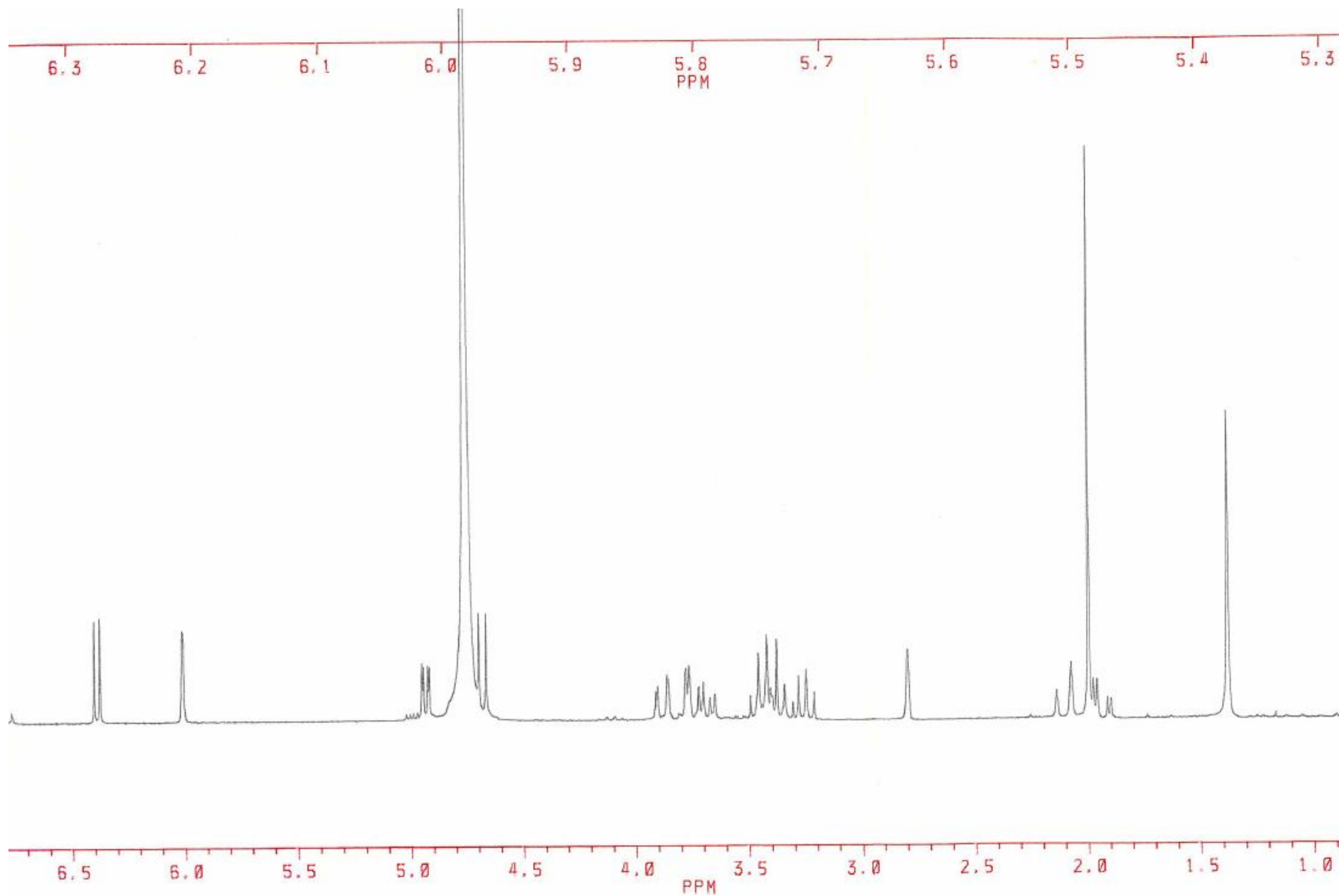
3. ^1H NMR spectrum (60 MHz, D_2O) of aucubin (2) from *Lyperia (Sutera) antirrhinoides*.



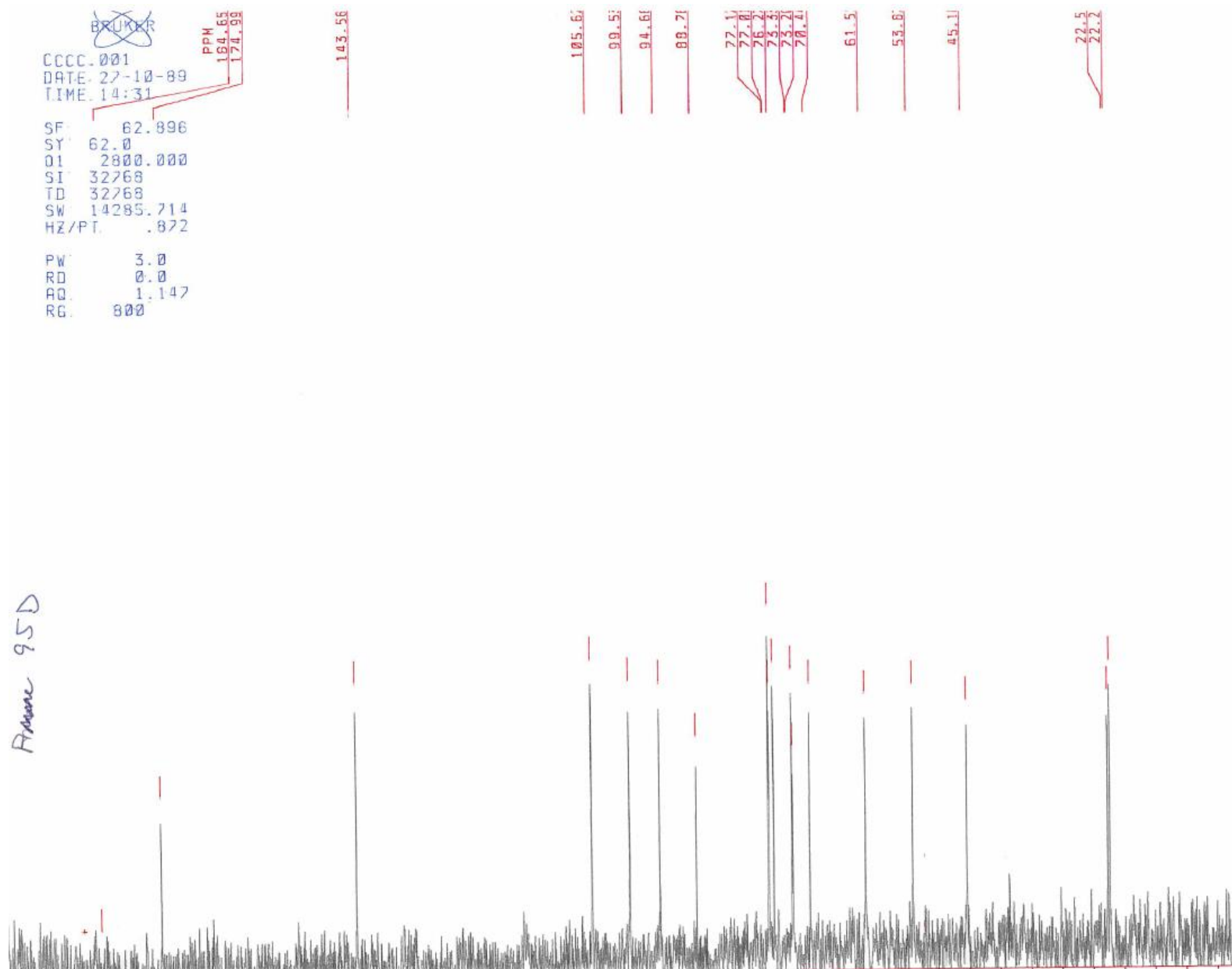
4. ^1H NMR spectrum (200 MHz, D_2O) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.



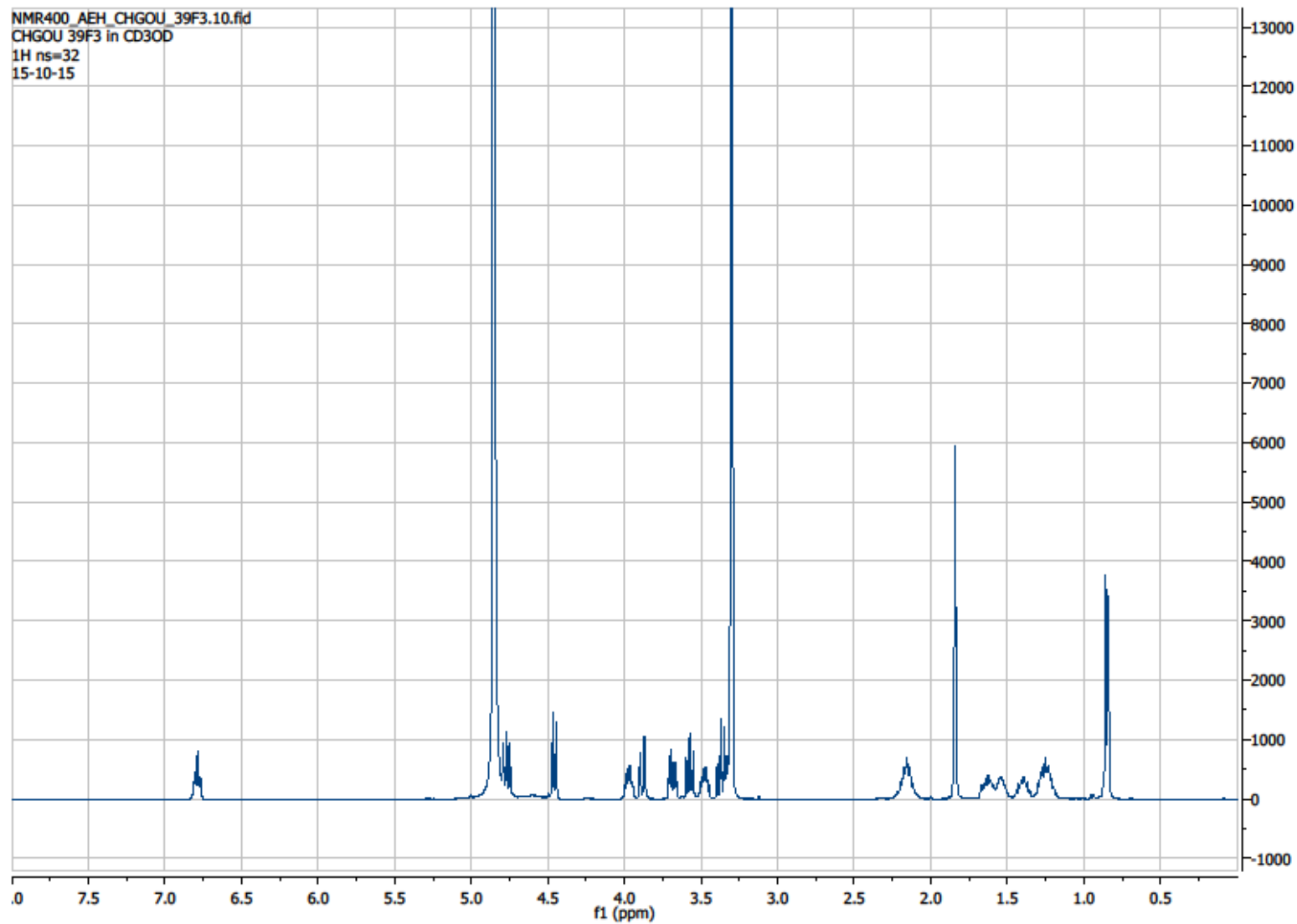
5. ^{13}C NMR spectrum (50 MHz, D_2O) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.



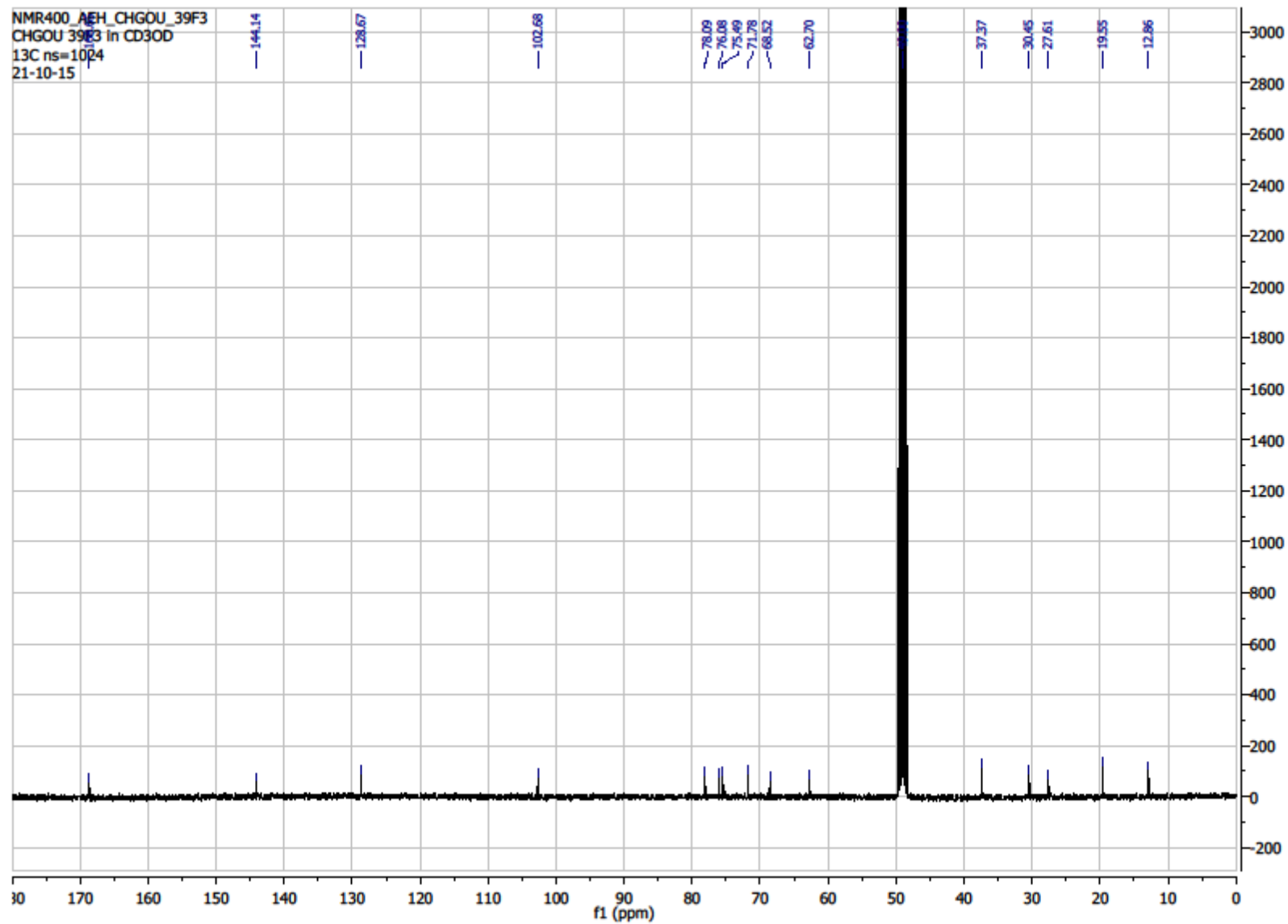
6. ^1H NMR spectrum (200 MHz, D_2O) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



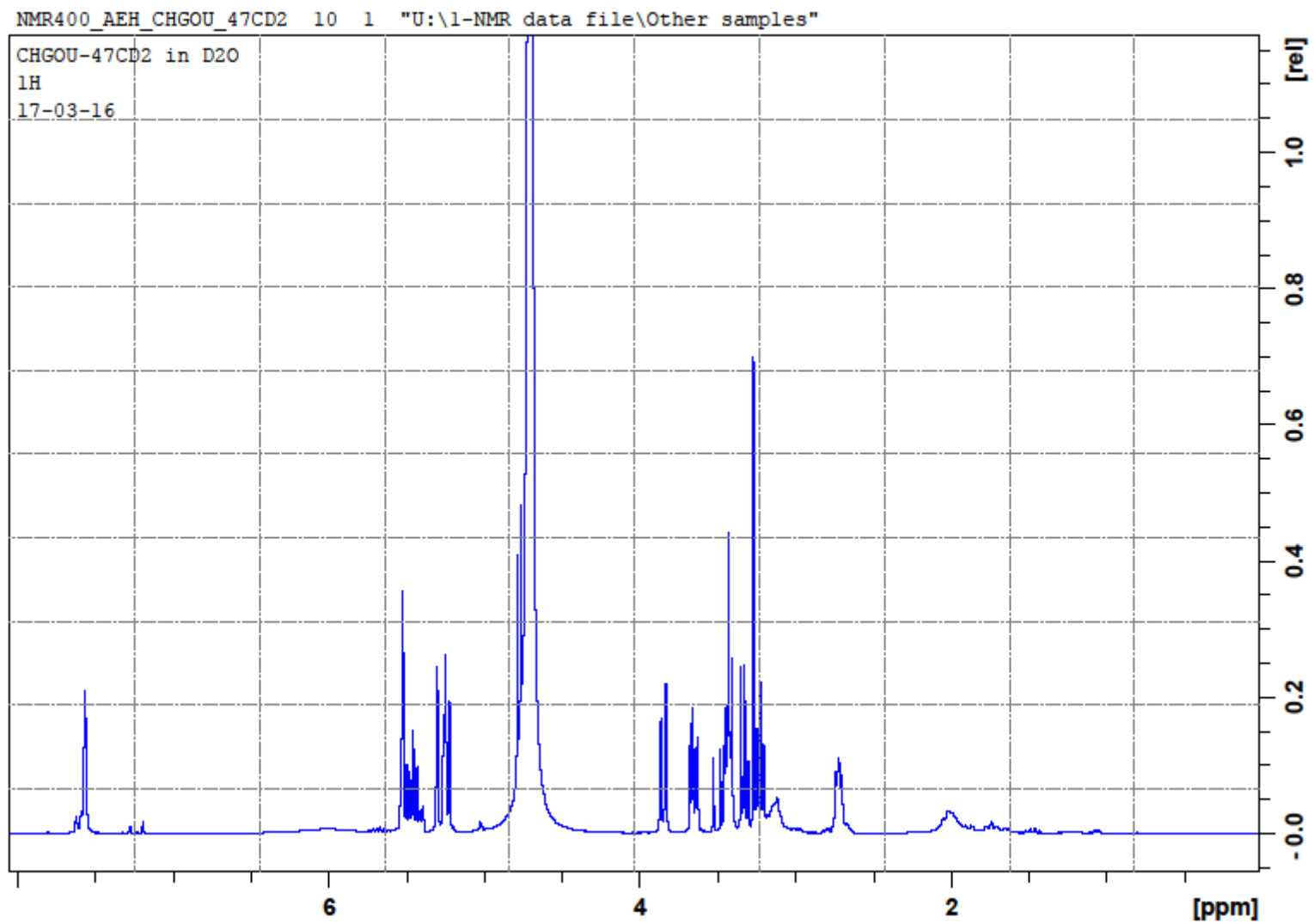
7. ^{13}C NMR spectrum (50 MHz, D_2O) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



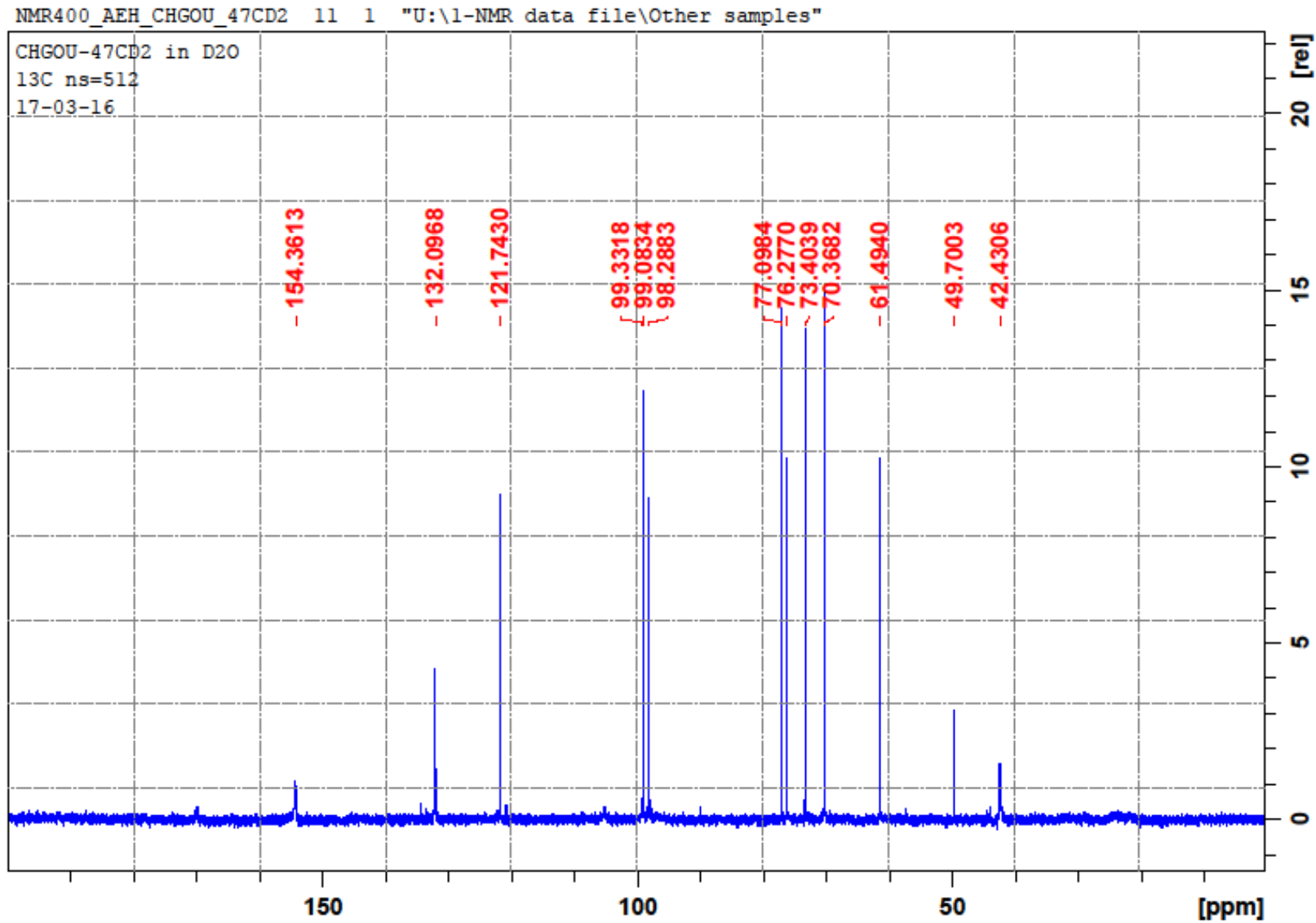
8. ^1H NMR spectrum (400 MHz, d_4 -Methanol) of suterolide (**20**) from *Sutera foetida*.



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

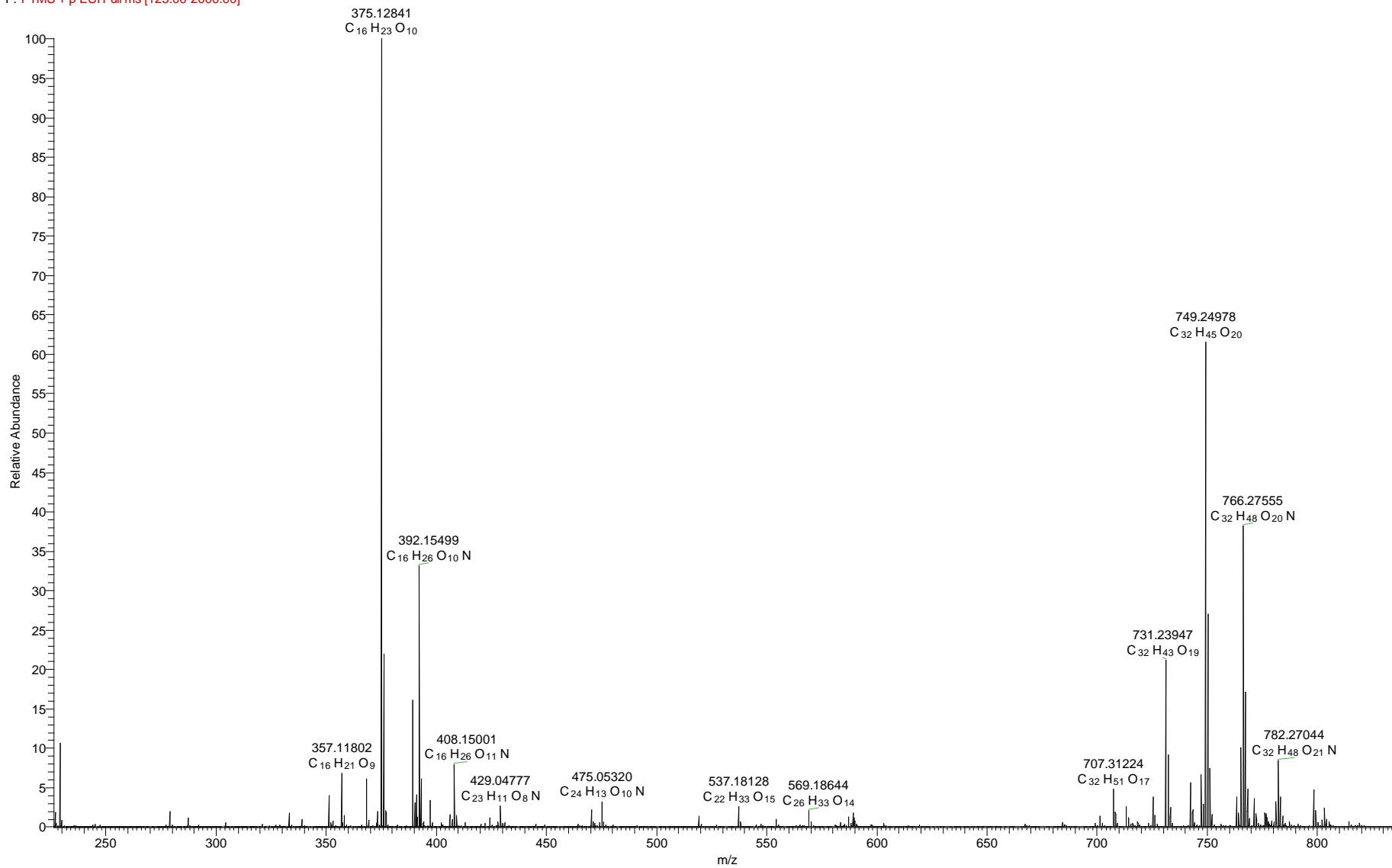


10. ^1H NMR spectrum (400 MHz, D_2O) of secologanic acid (**13**).

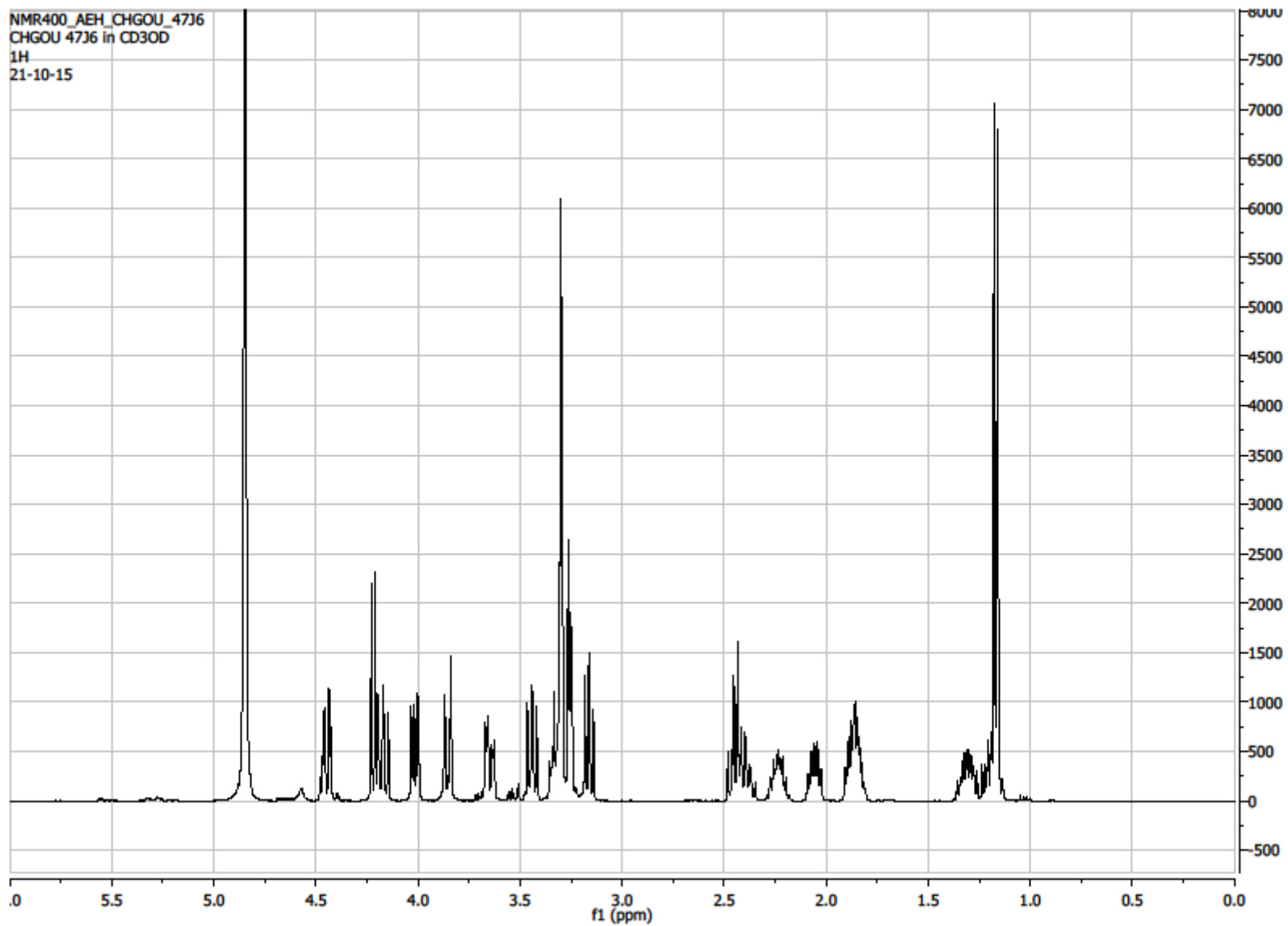


11. ^{13}C NMR spectrum (100 MHz, D_2O) of secologanic acid (**13**).

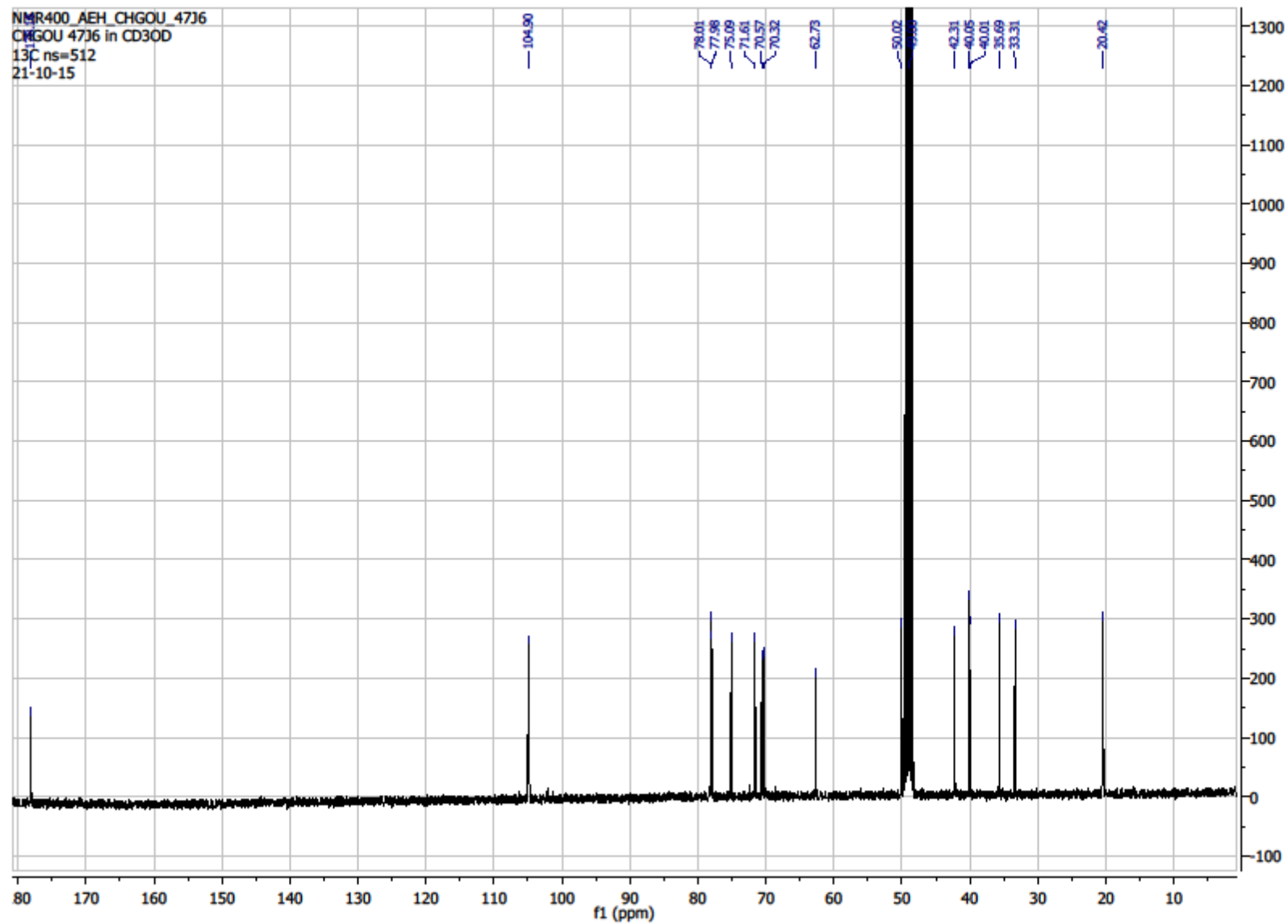
Sutera_SRJ_47CD2_26955_posnegESI_FT #682-825 RT: 5.00-5.79 AV: 20 NL: 2.70E6
F: FTMS + p ESI Full ms [125.00-2000.00]



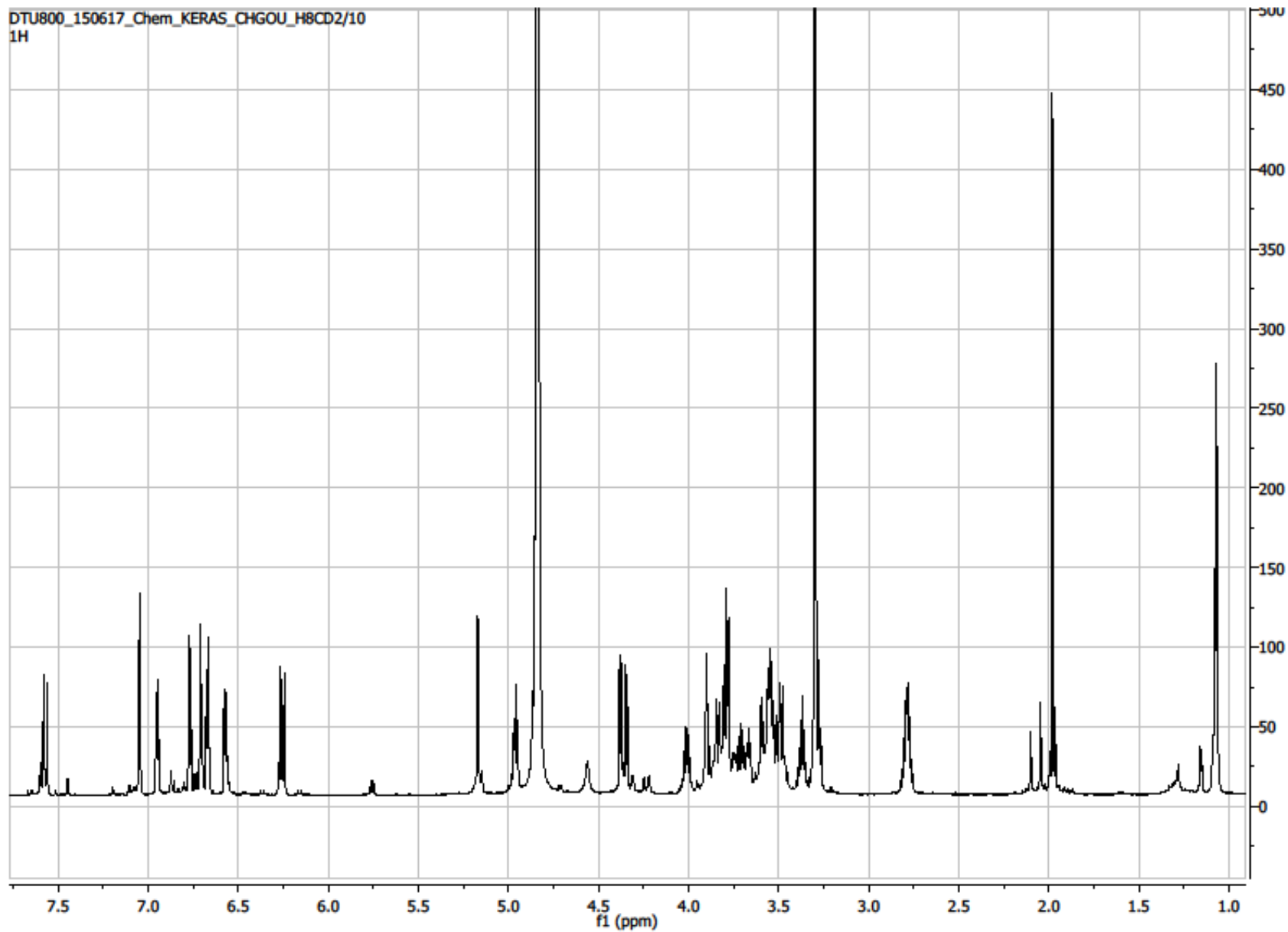
12. Mass spectrum of secologanic acid (**13**) expansion showing [M+H]⁺, [M+NH₄]⁺, [2M+H]⁺ and [2M+NH₄]⁺



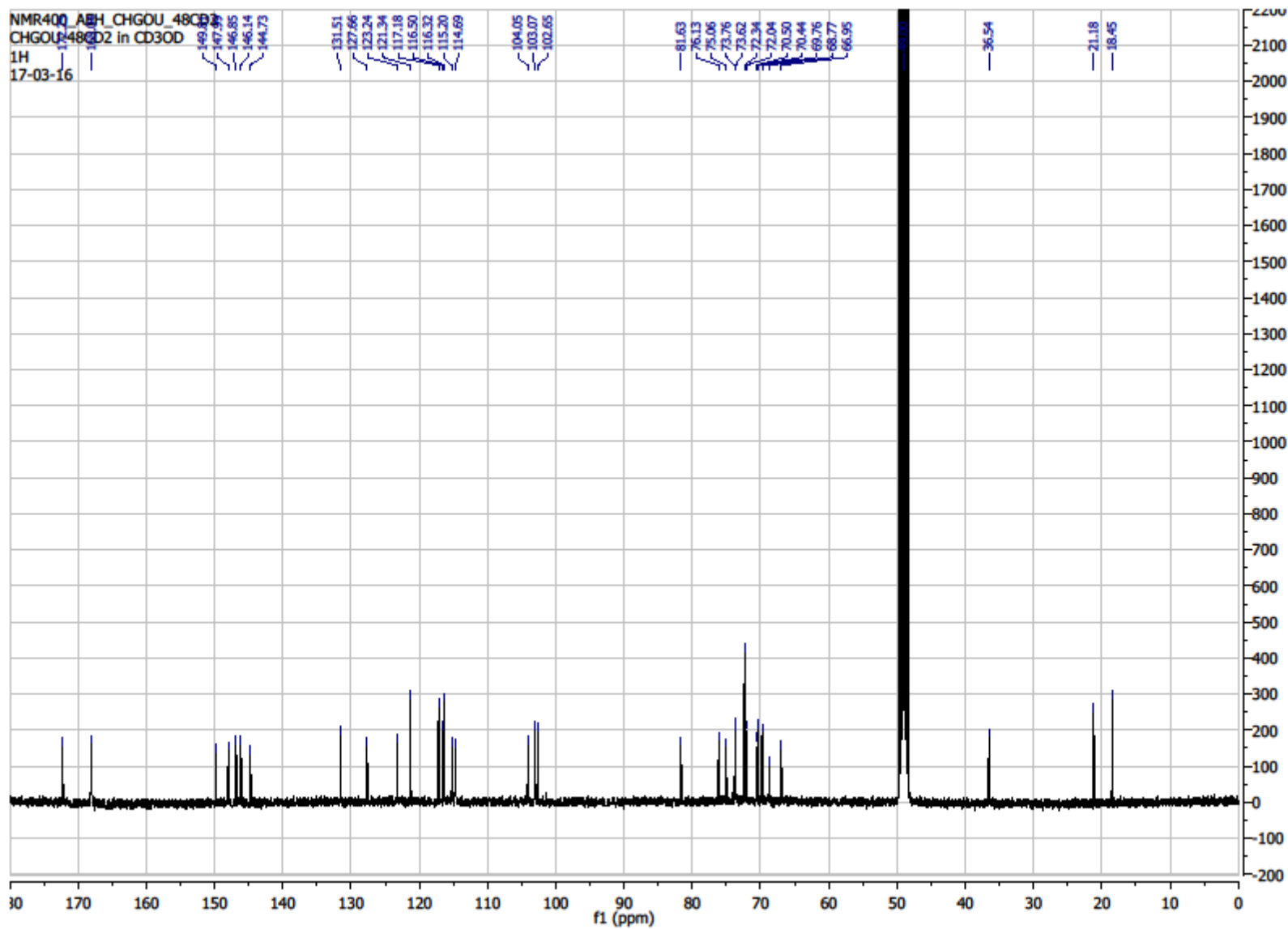
13. ^1H NMR spectrum (400 MHz, d_4 -Methanol) of villoside (**11**) from *Sutera cordata*.



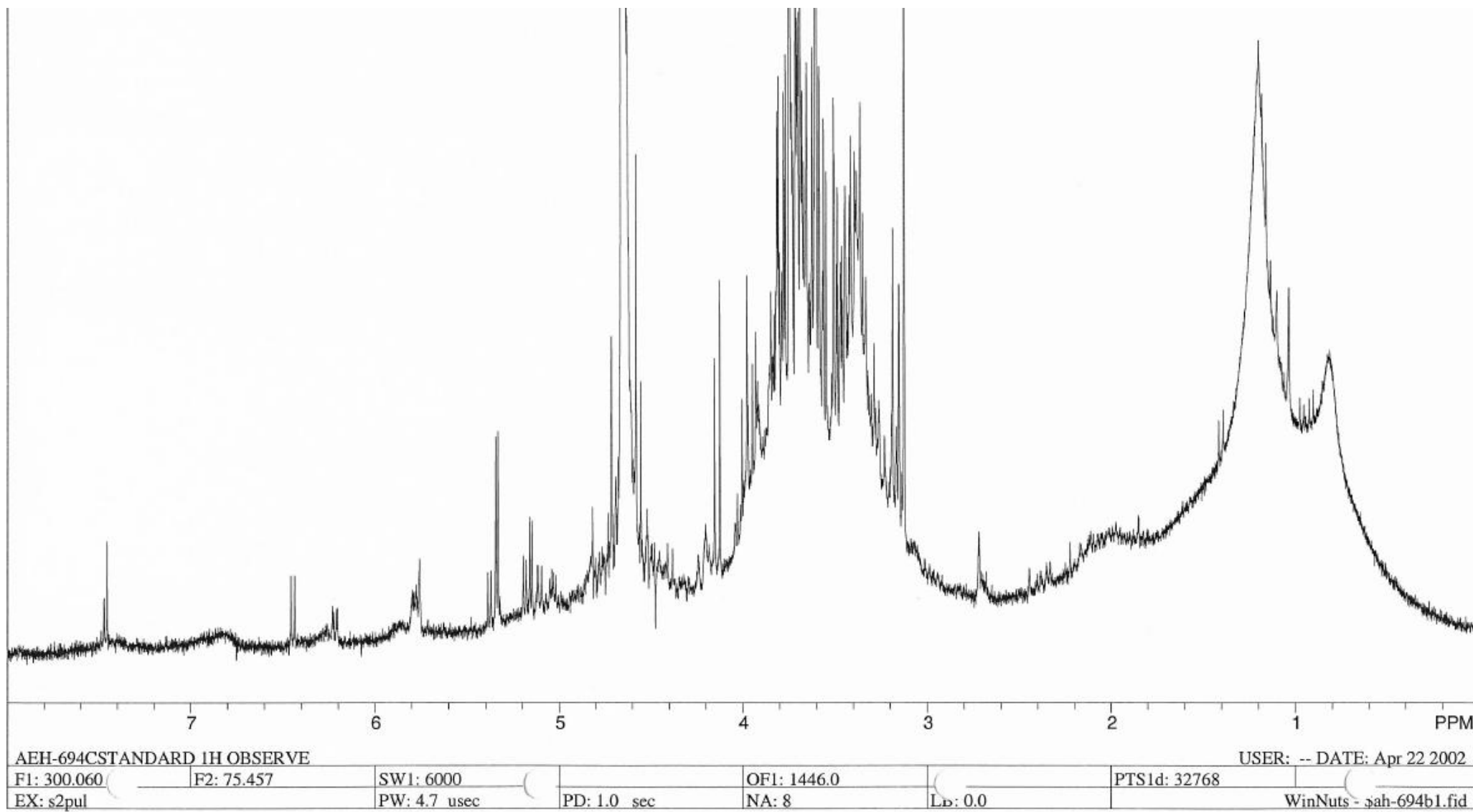
14. ^{13}C NMR spectrum (100 MHz, d_4 -Methanol) of villoside (**11**) from *Sutera cordata*.



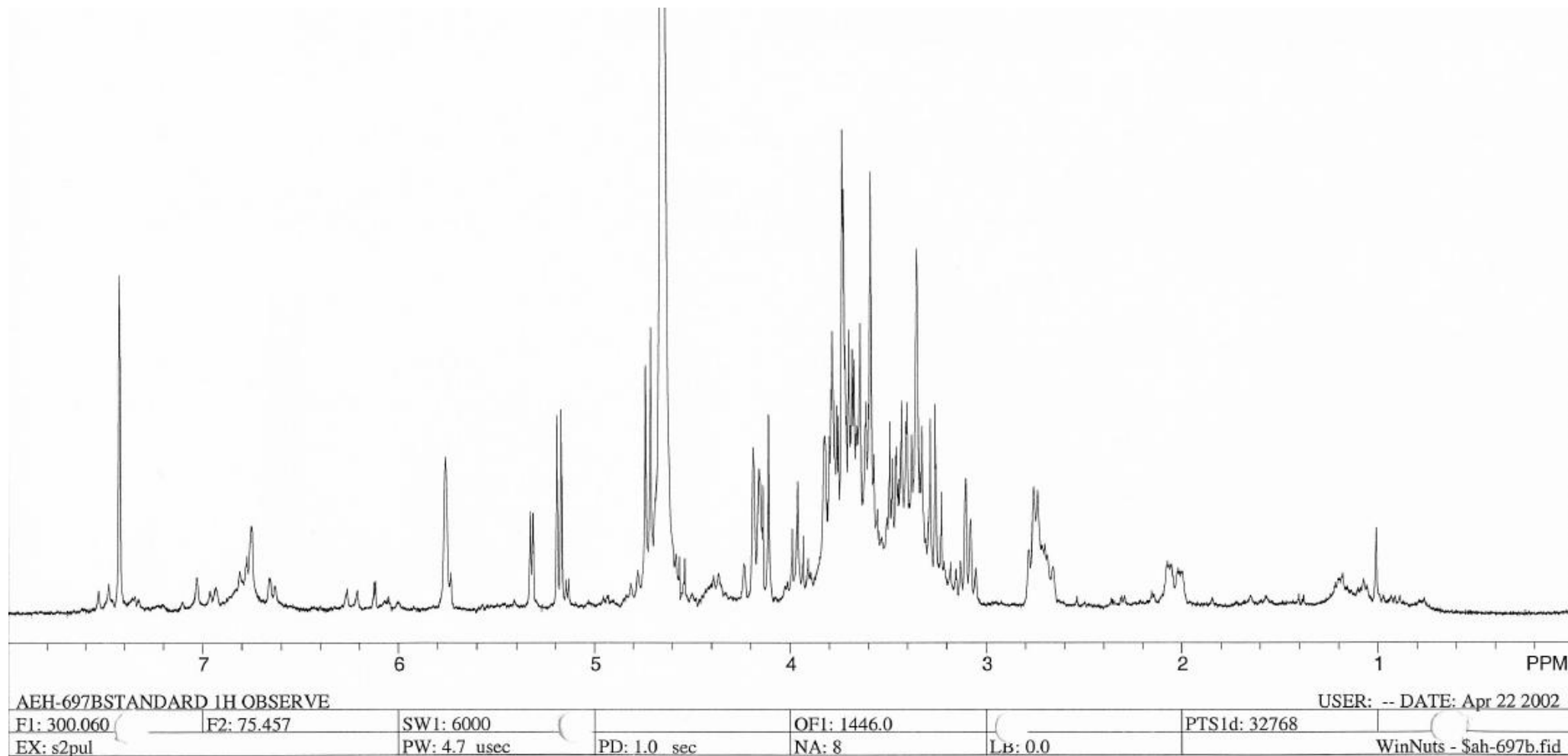
15. ^1H NMR spectrum (800 MHz, d_4 -Methanol) of 2'''-Acetyl angoroside A (**18**) from *Sutera cordata*.



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



17. ^1H NMR spectrum (300 MHz, D_2O) of a crude extract from *Lyperia tristis*.



18. ^1H NMR spectrum (300 MHz, D_2O) 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;