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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

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

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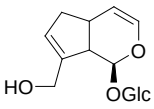

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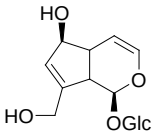

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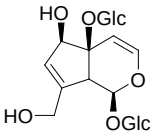

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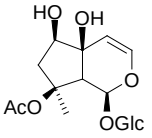

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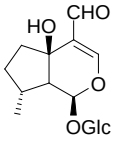

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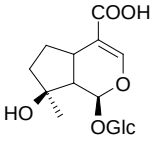

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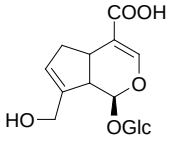

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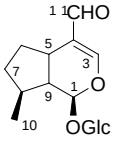

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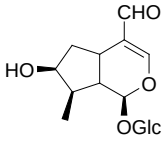

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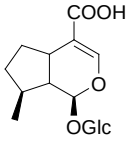

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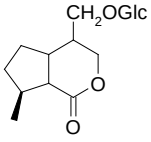

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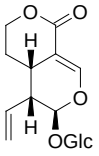

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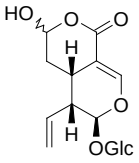

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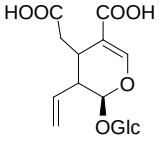

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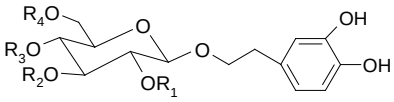
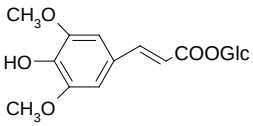


15 R_1=H, R_2=Rha, R_3=Caffeoyl, R_4=H
16 R_1=H, R_2=Rha, R_3=Caffeoyl, R_4=Glc
17 R_1=Ac, R_2=Rha, R_3=Caffeoyl, R_4=Glc
18 R_1=H, R_2=Rha, R_3=Caffeoyl, R_4=2-Ac-Ara



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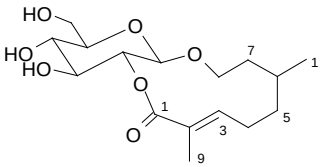

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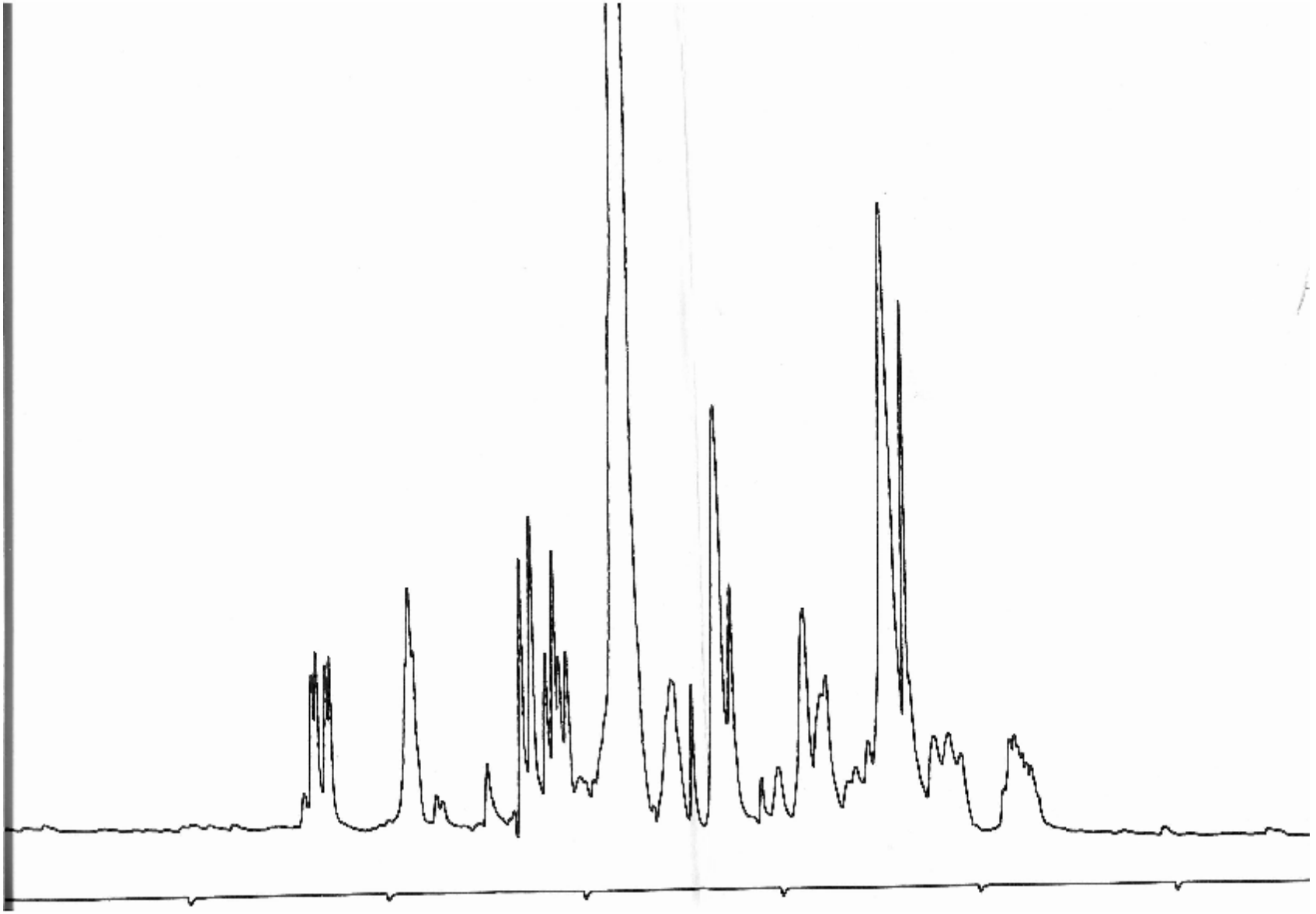
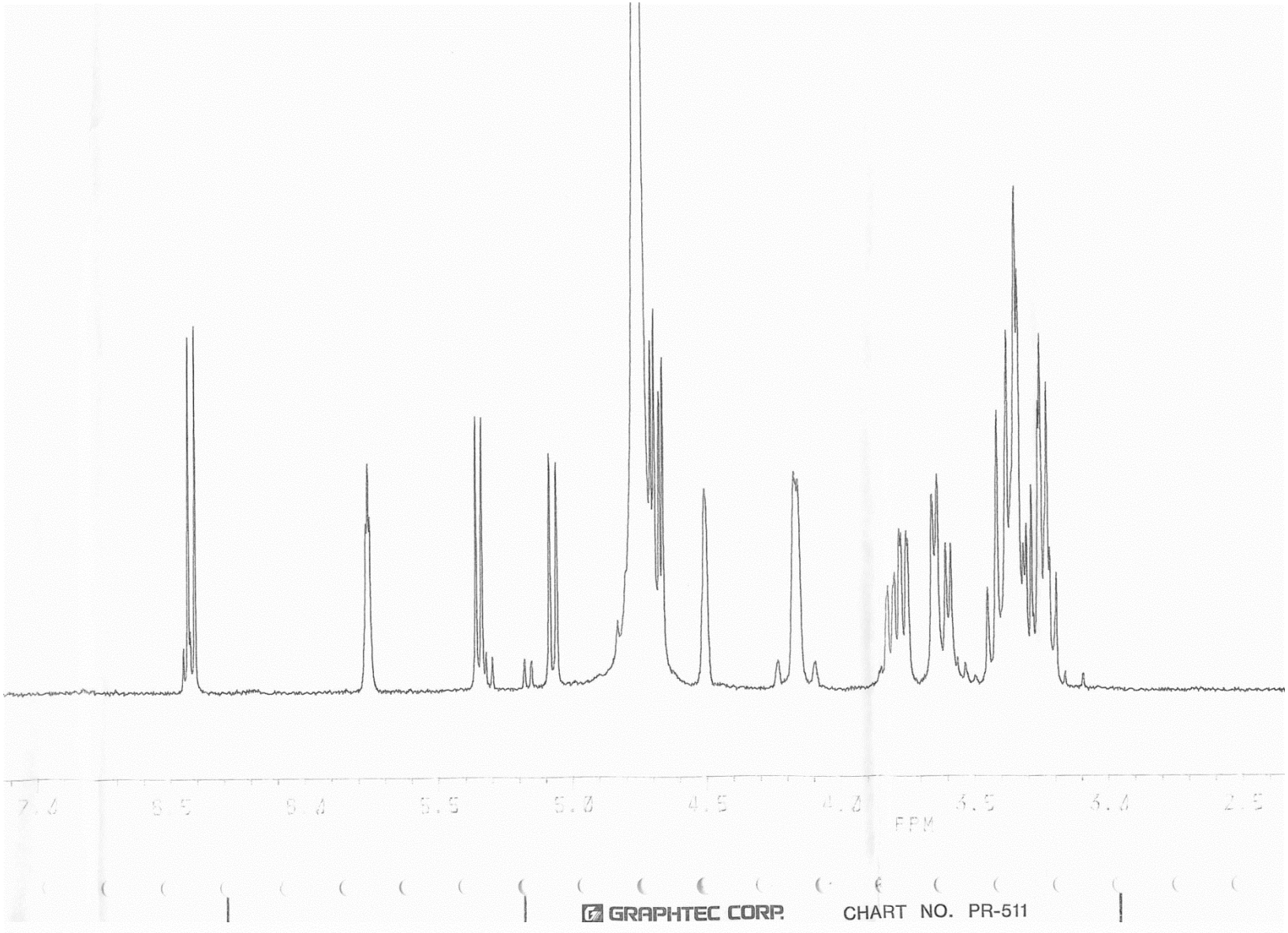
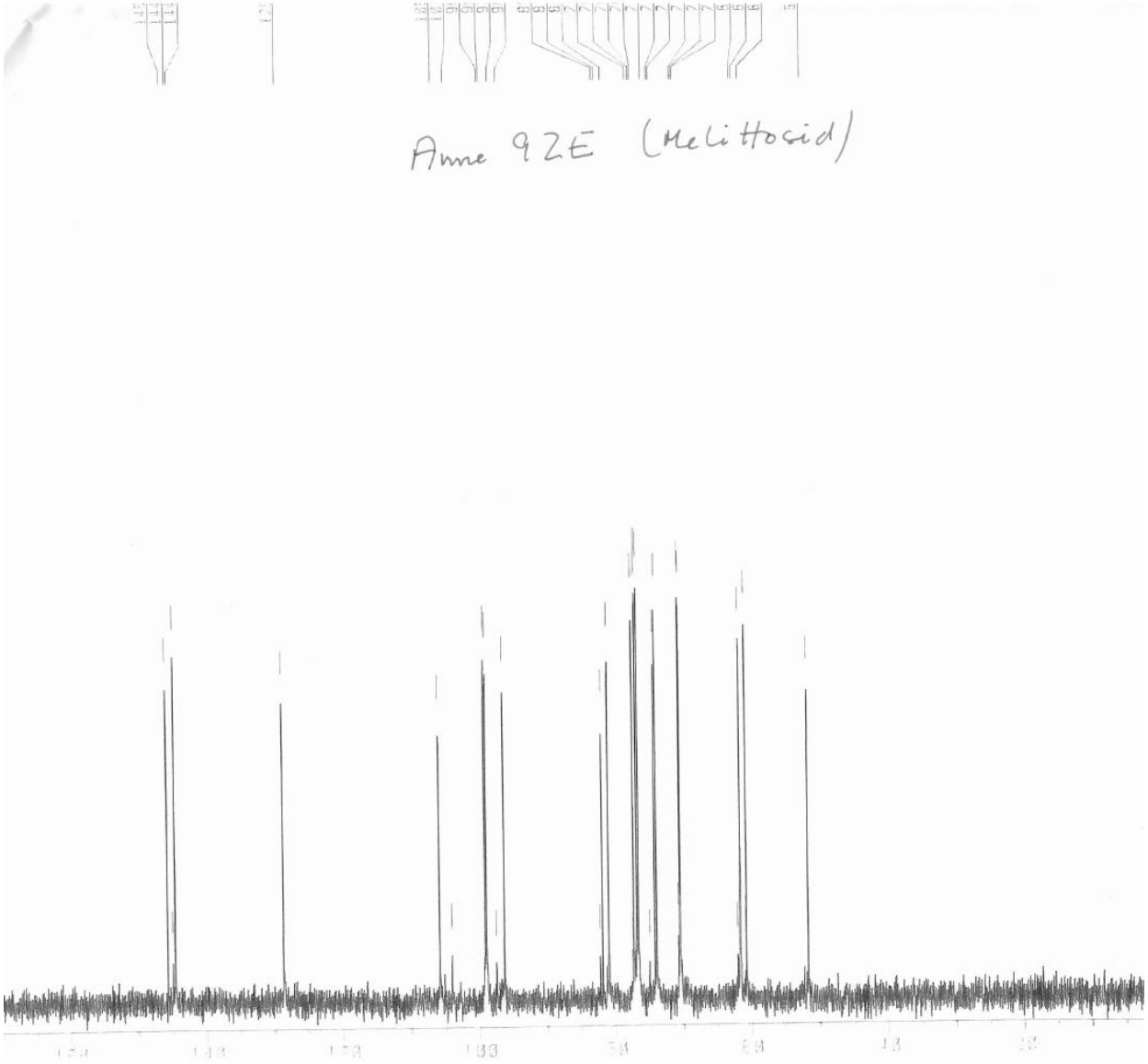
Sutera foetida (picture by Gry Bastholm)



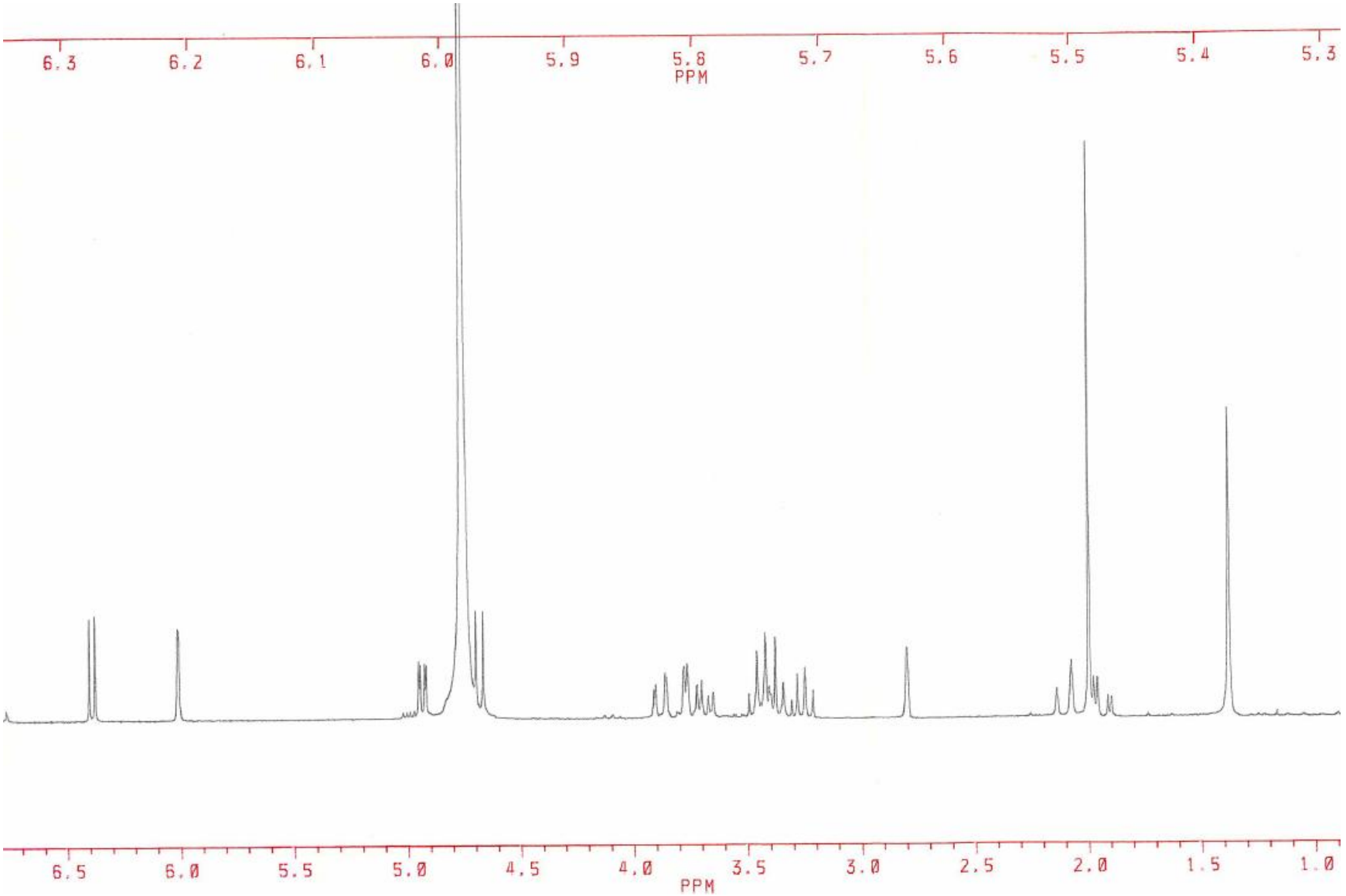
3. ^{1}H NMR spectrum (60 MHz, D_2O) of aucubin (**2**) from *Lyperia (Sutera) antirrhinoides*.



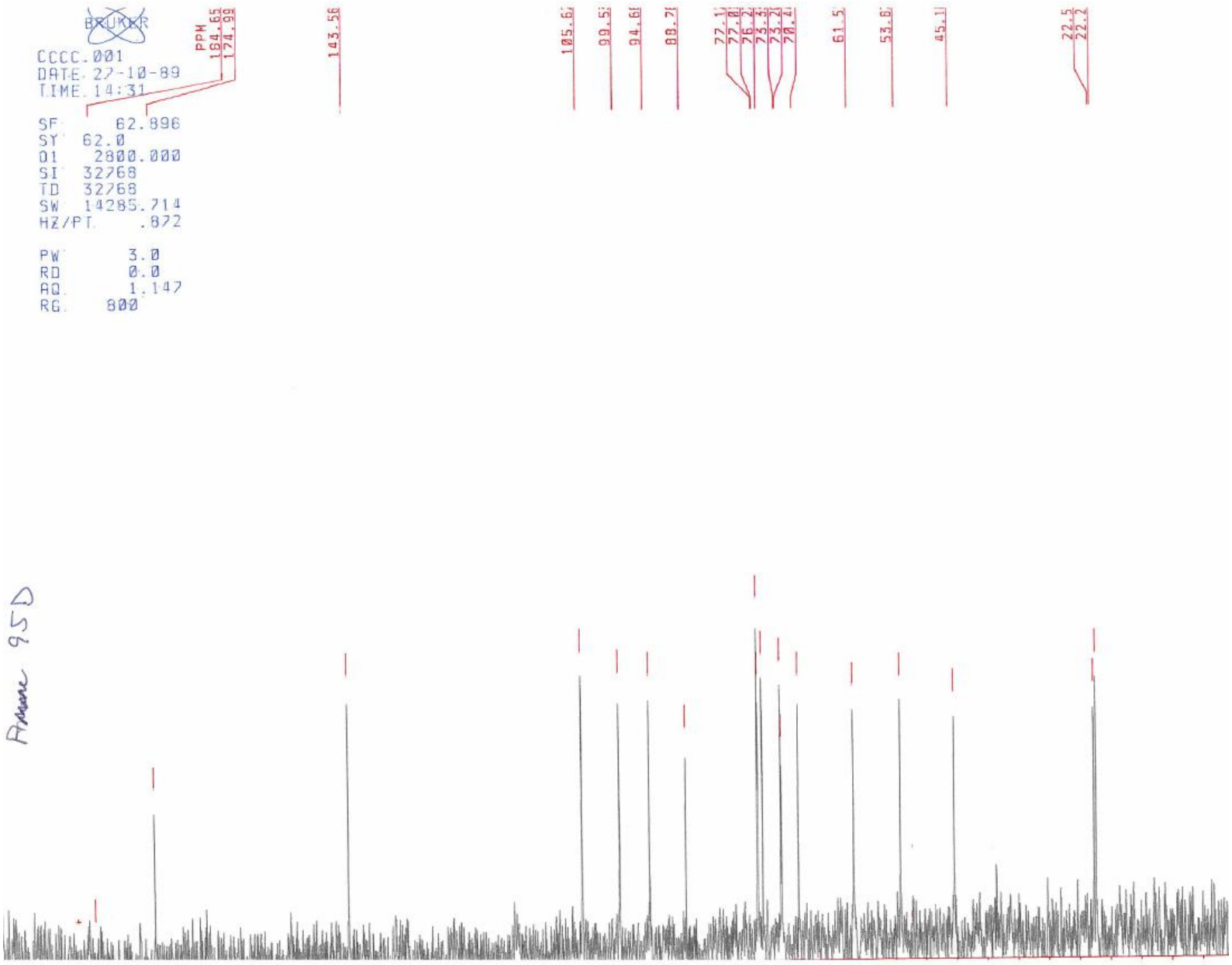
4. ^{1}H NMR spectrum (200 MHz, D_2O) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.



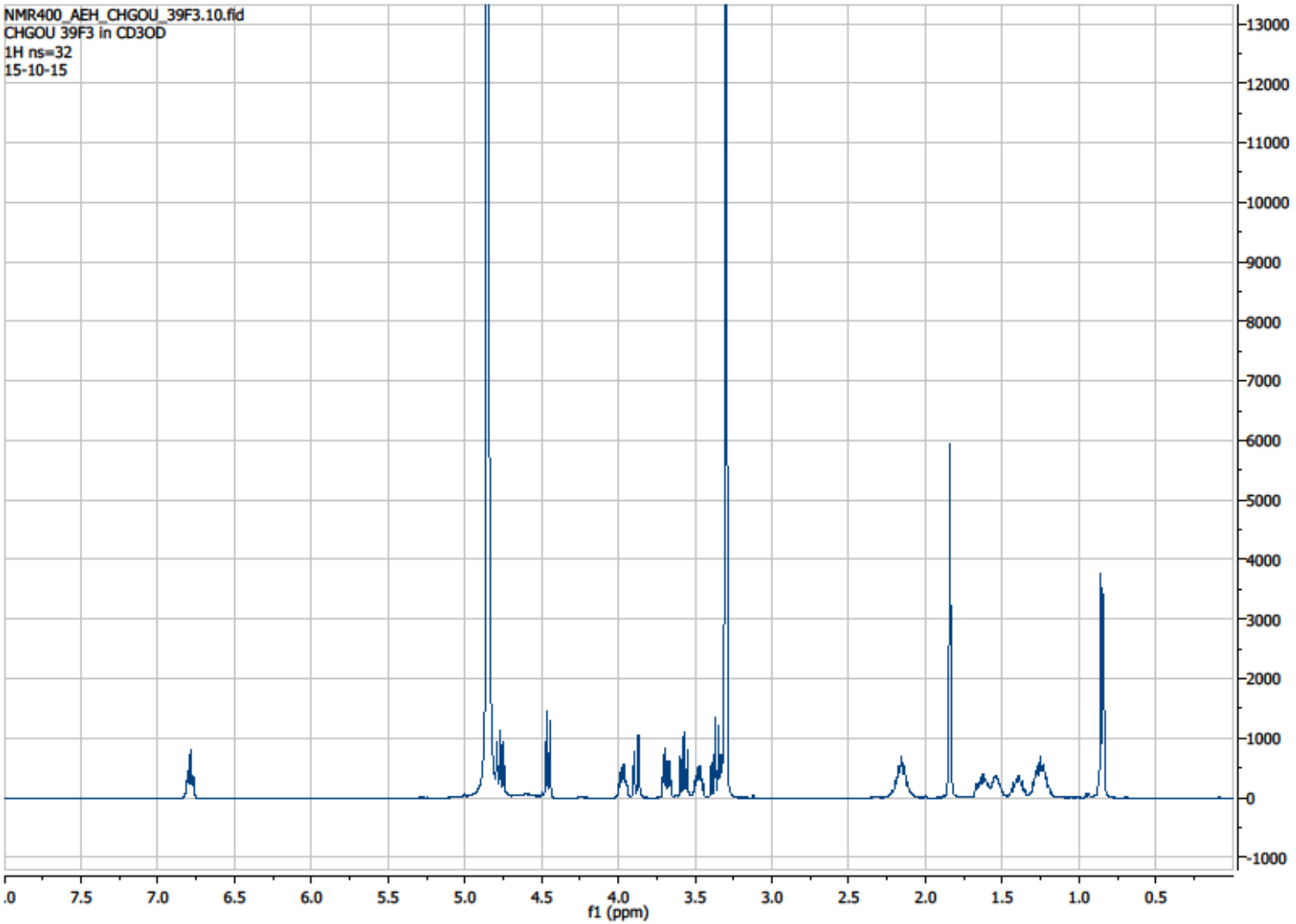
5. ^{13}C NMR spectrum (50 MHz, D_2O) of melittoside (**3**) from *Lyperia (Sutera) antirrhinoides*.



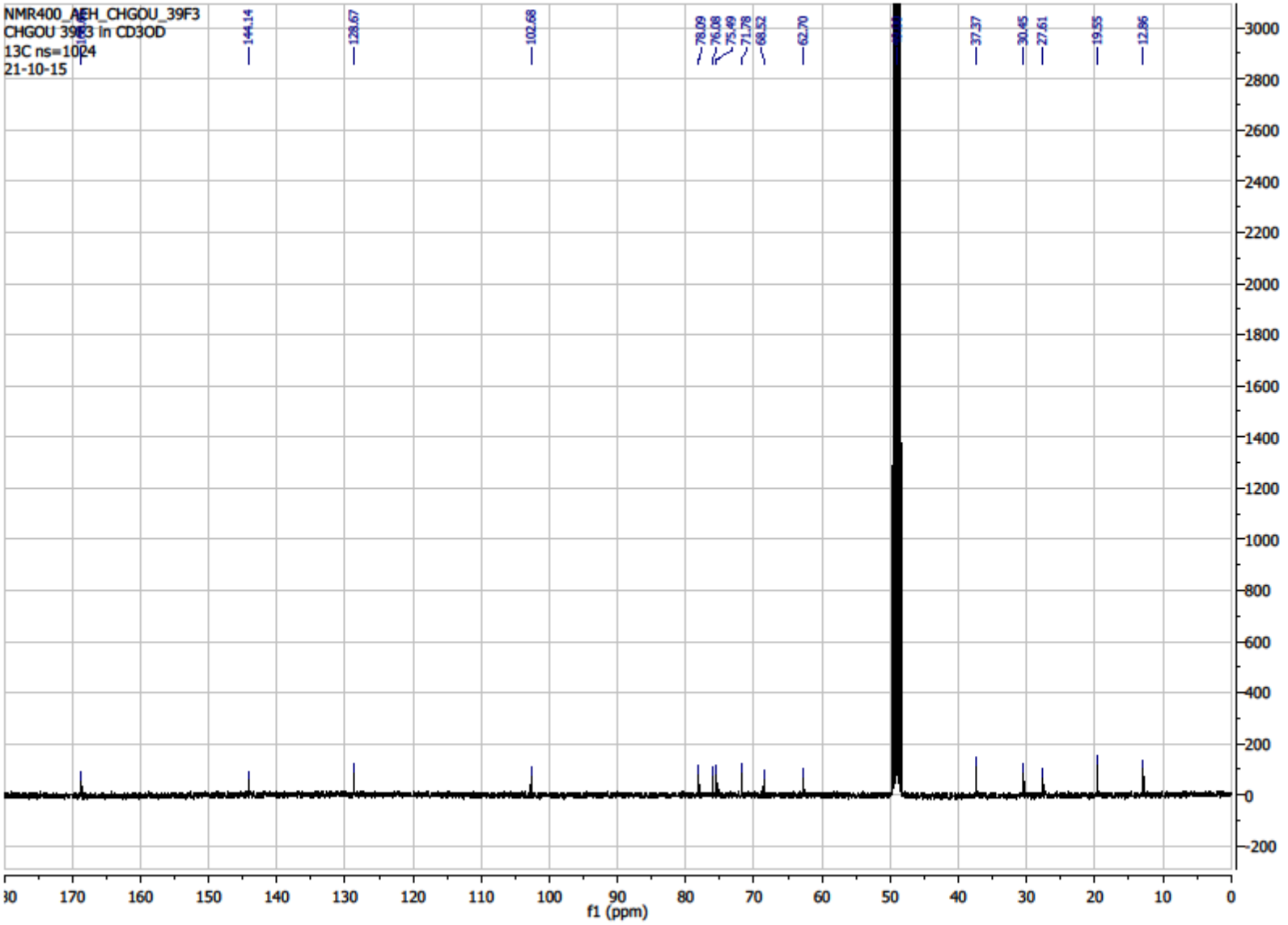
6. ^{1}H NMR spectrum (200 MHz, D_2O) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



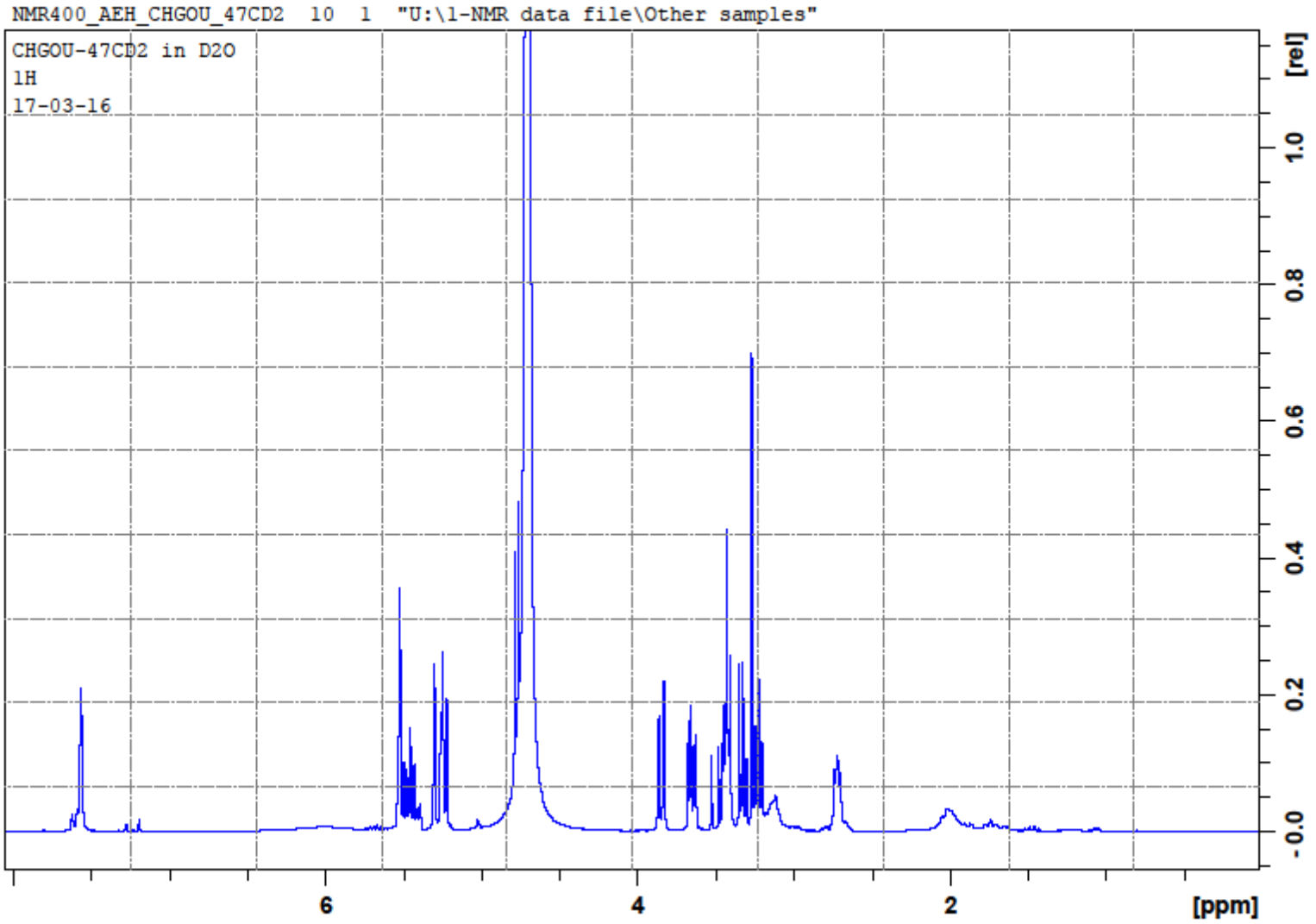
7. ^{13}C NMR spectrum (50 MHz, D_2O) of acetylharpagide (**4**) from *Lyperia (Sutera) antirrhinoides*.



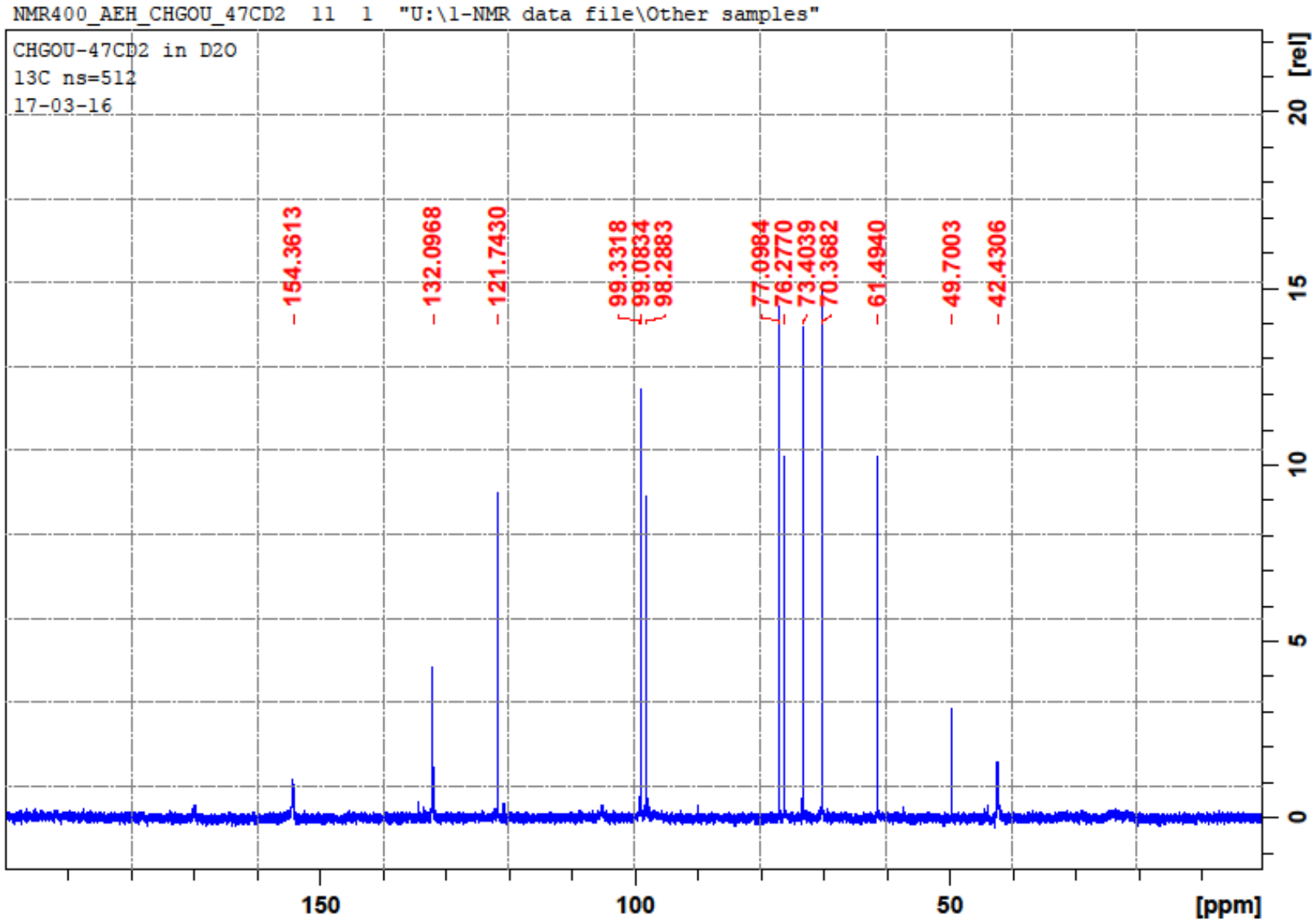
8. ^{1}H NMR spectrum (400 MHz, d_4-Methanol) of suterolide (**20**) from *Sutera foetida*.



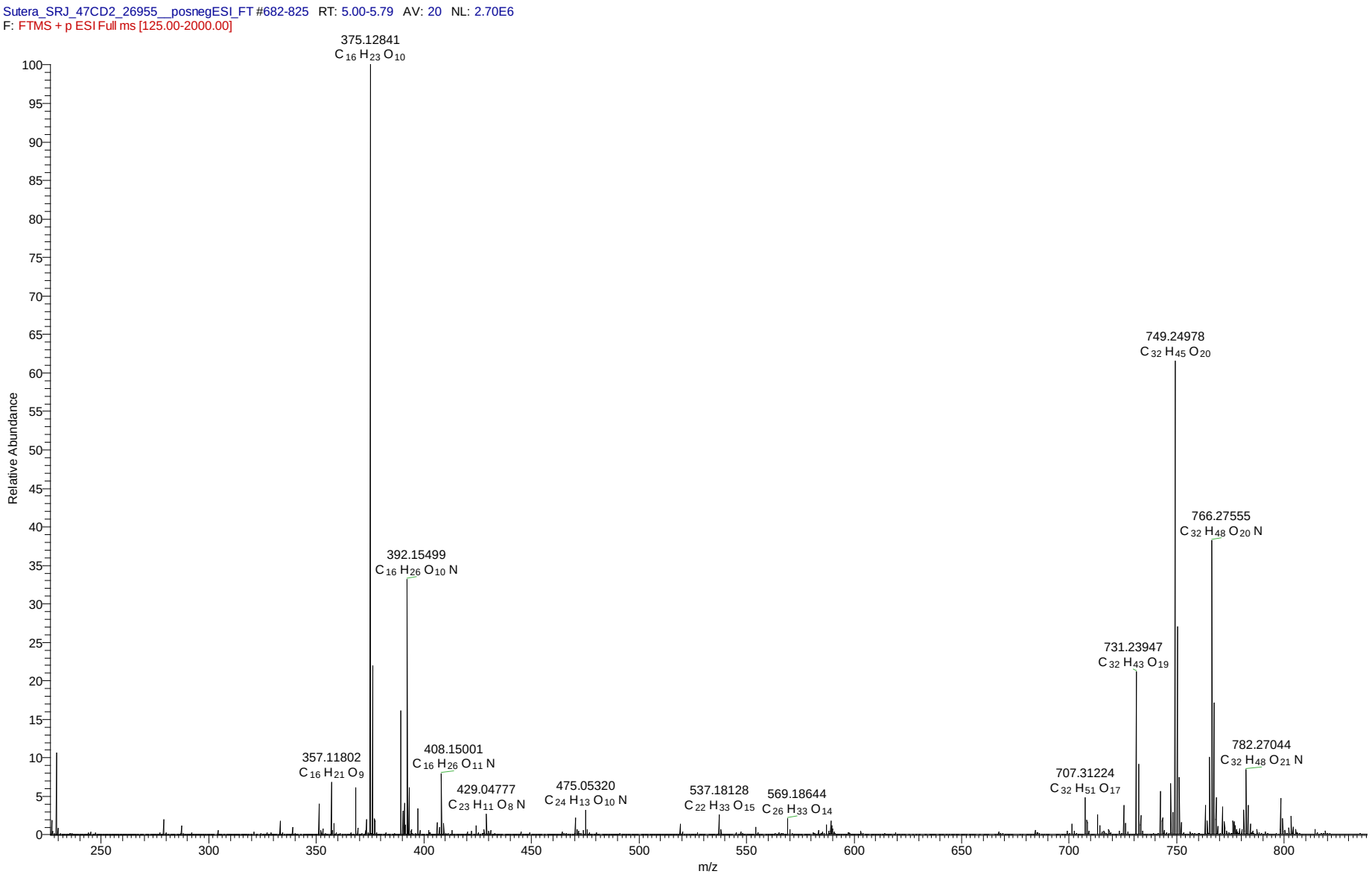
9. ^{13}C NMR spectrum (100 MHz, d_4-Methanol) of suterolide (**20**) from *Sutera foetida*.



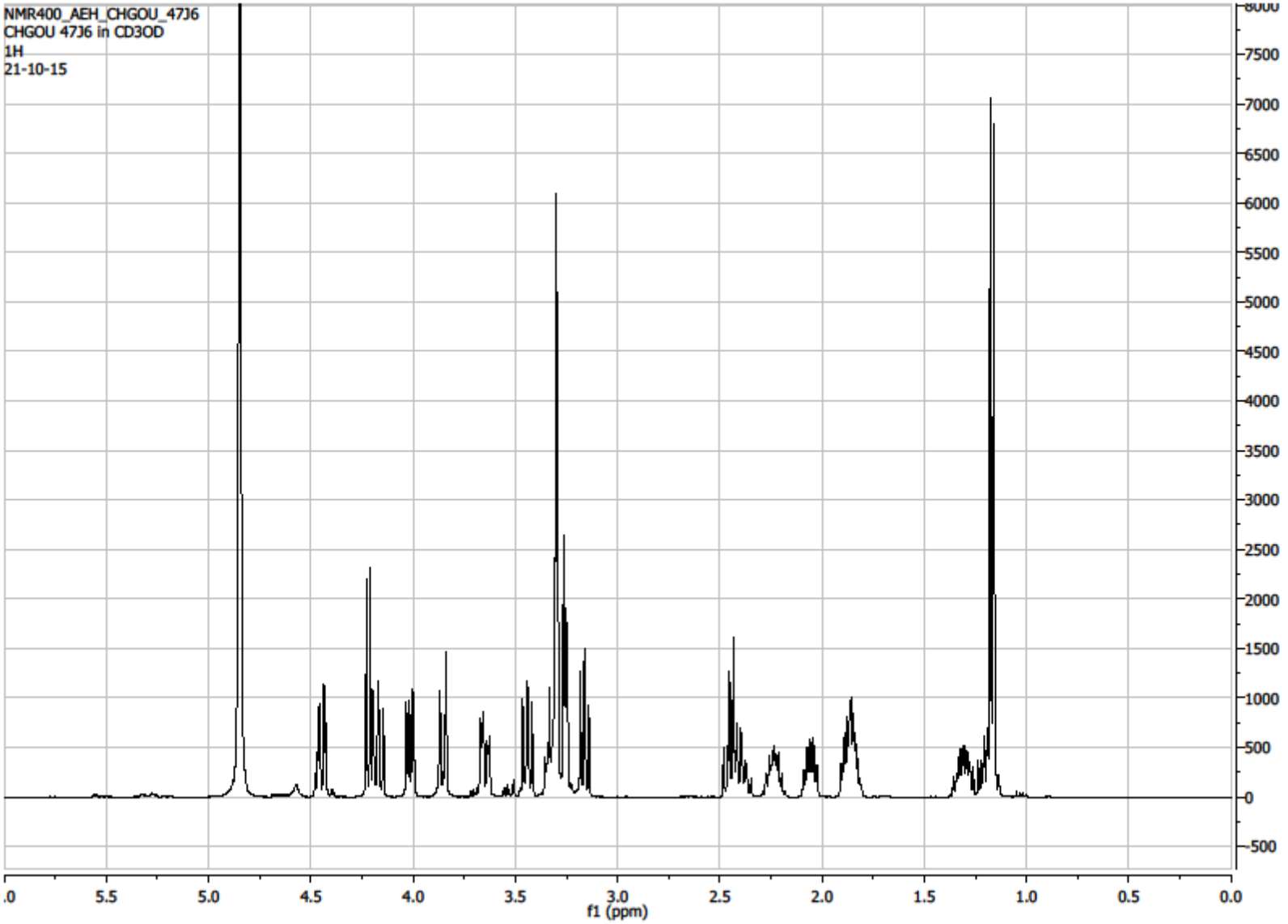
10. ^{1}H NMR spectrum (400 MHz, D_2O) of secologanic acid (**13**).



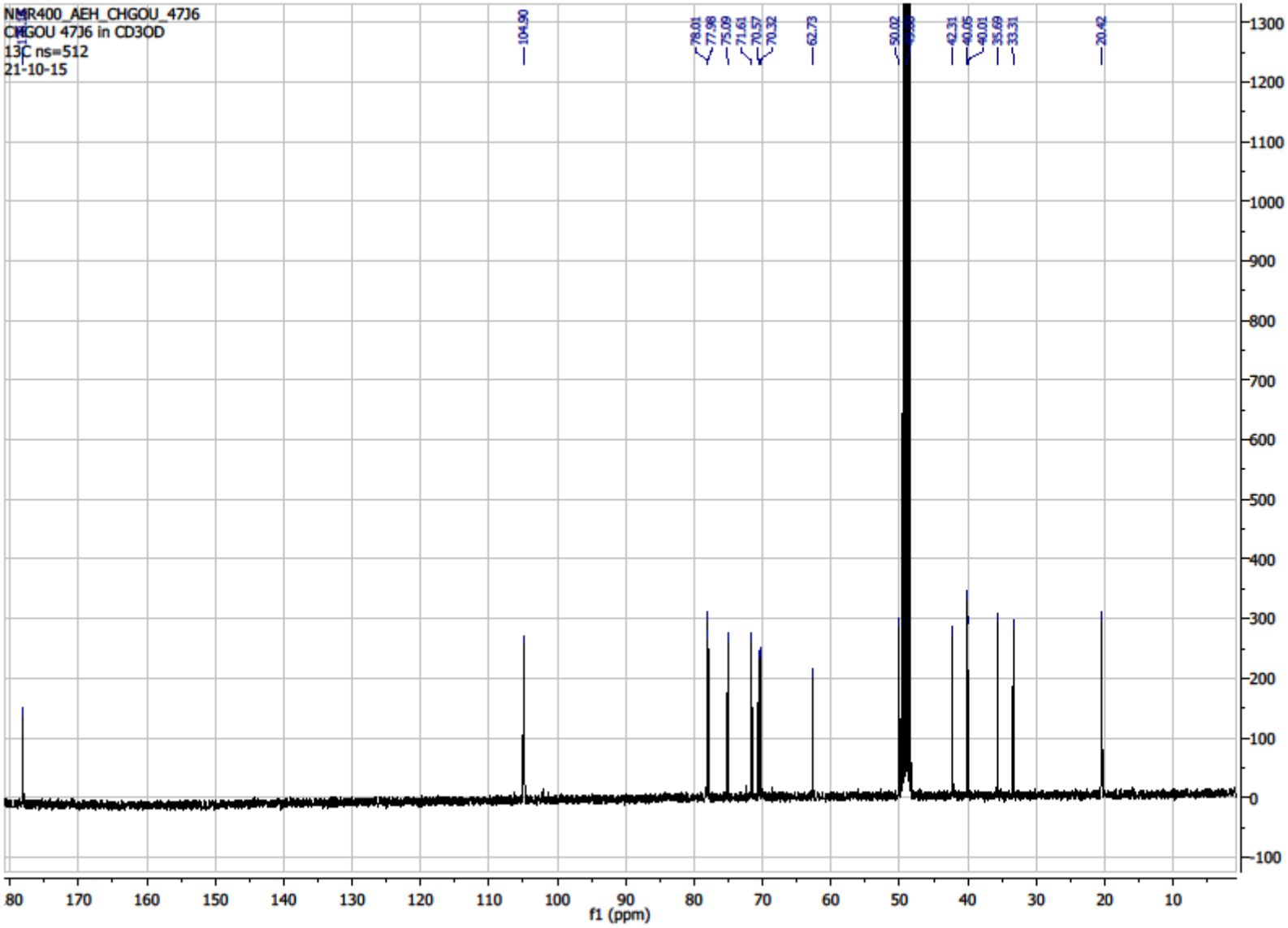
11. ^{13}C NMR spectrum (100 MHz, D_2O) of secologanic acid (**13**).



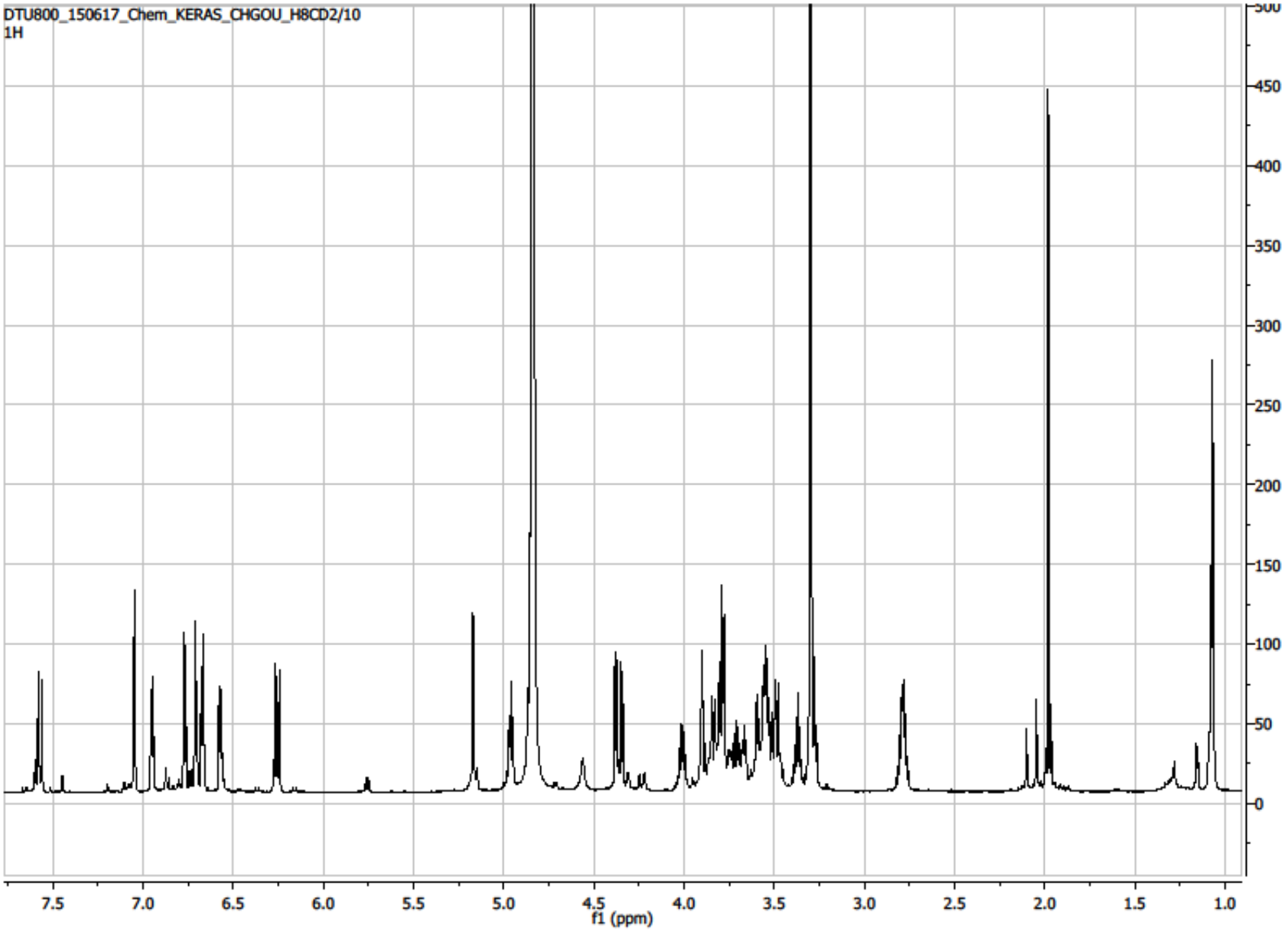
12. Mass spectrum of secologanic acid (**13**) expansion showing [M+H]+, $[M+NH_4]^+$, $[2M+H]^+$ and $[2M+NH_4]^+$



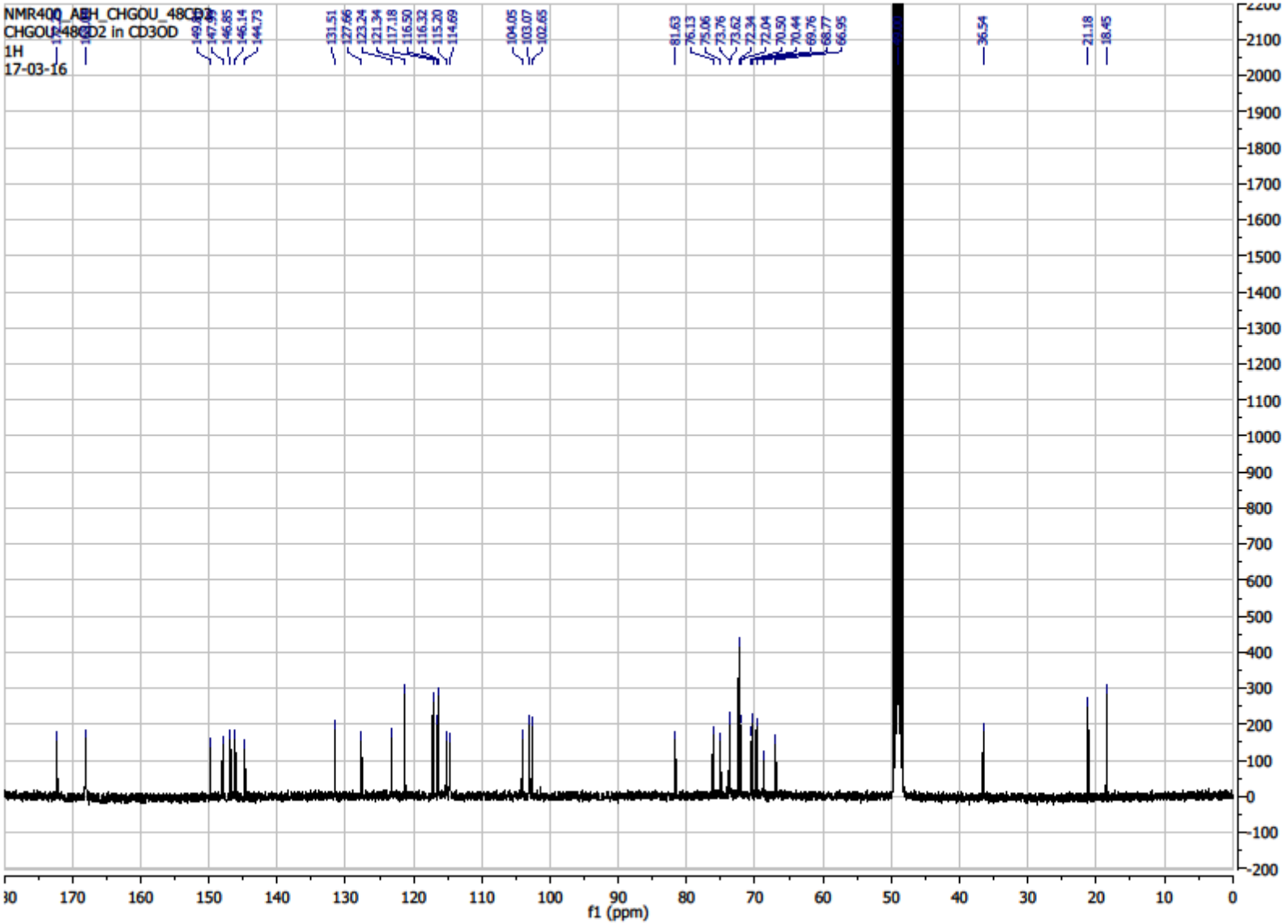
13. ^{1}H NMR spectrum (400 MHz, d_4-Methanol) of villoside (**11**) from *Sutera cordata*.



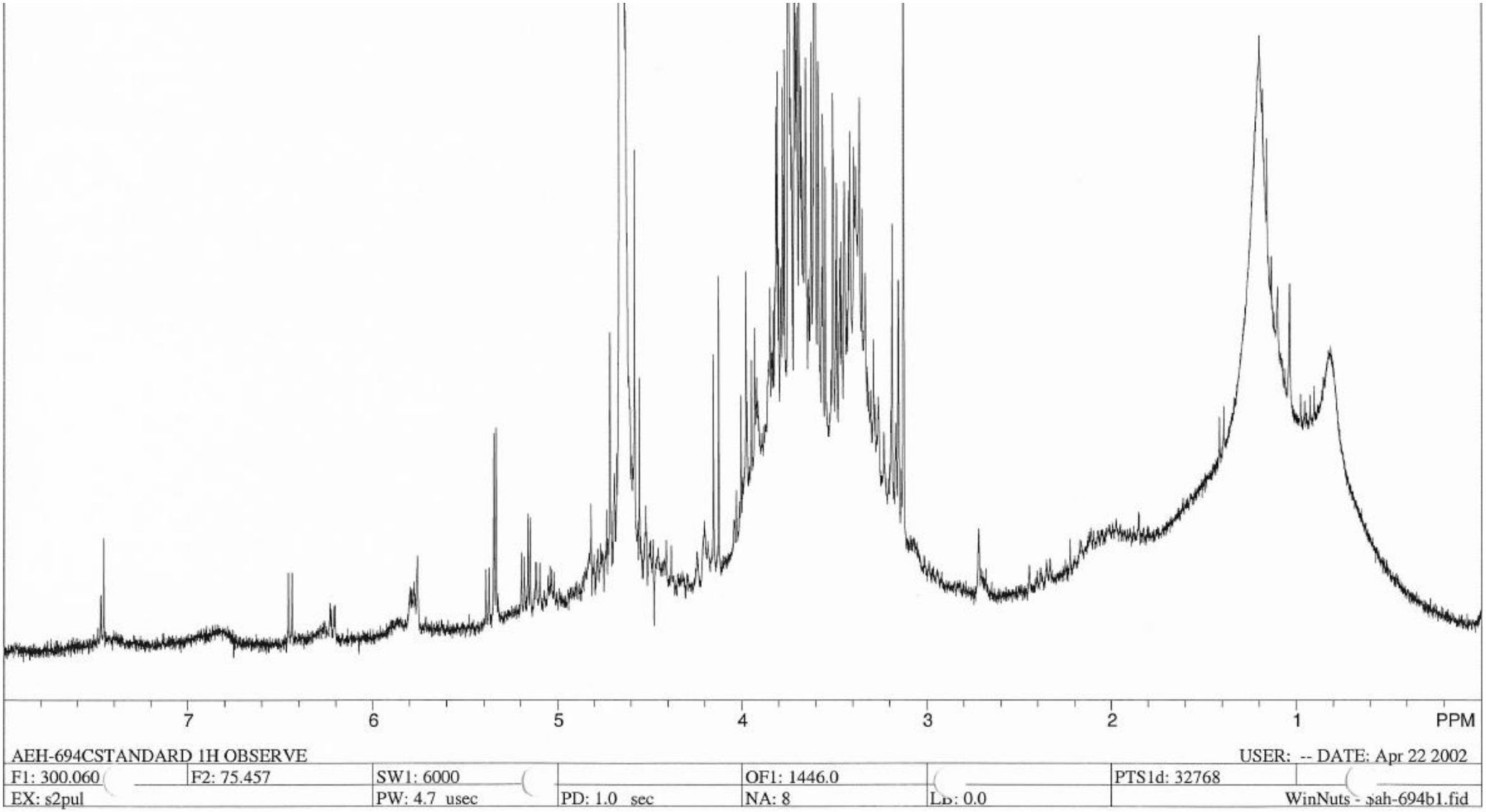
14. ^{13}C NMR spectrum (100 MHz, d_4-Methanol) of villoside (**11**) from *Sutera cordata*.



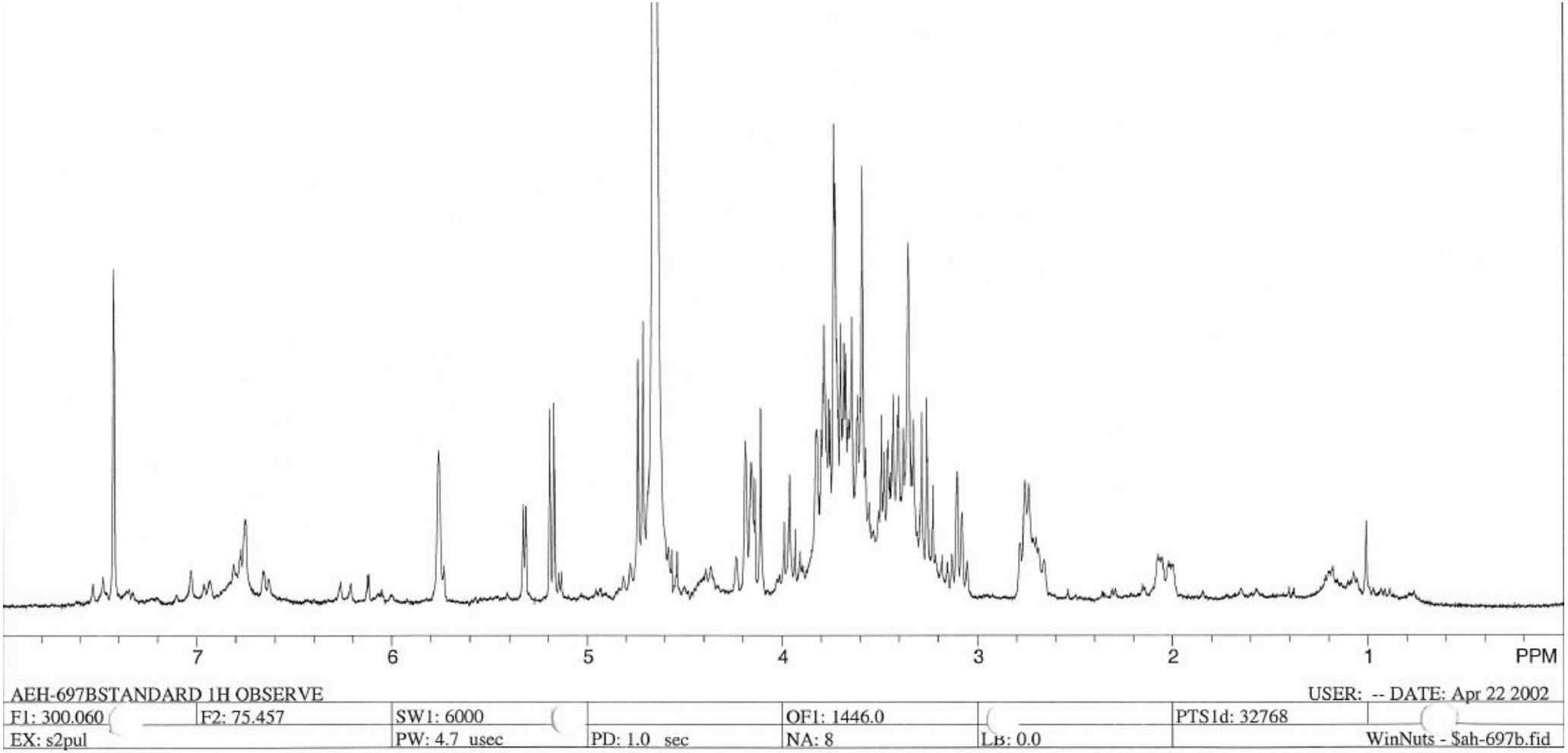
15. ^{1}H NMR spectrum (800 MHz, d_4-Methanol) of 2′′′′-Acetyl angoroside A (**18**) from *Sutera cordata*.



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



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



18. ^{1}H 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 rercurvifolia* 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*; Trieenea glutinosa* AJ584758*; Zaluzianskya capensis* AJ584822*; Zaluzianskya glareosa* AJ584816*; Zaluzianskya gracilis* AJ584820*; Zaluzianskya minima* AJ584751*; Zaluzianskya villosa* AJ584804*;*