**Supplementary Material**

**Plant polyacetylenoids: Phytochemical, analytical and pharmacological updates**

**Jia-Xin Lai†,** **Su-Fang Dai†, Bian-Xia Xue, Li-Hua Zhang, Yanxu Chang, Wenzhi Yang, Hong-Hua Wu[[1]](#footnote-1)**

*State Key Laboratory of Component-based Chinese Medicine, Institute of Traditional Chinese Medicine, Tianjin University of Traditional Chinese Medicine, 10 Poyanghu Road, West Area, Tuanbo New Town, Jinghai District, Tianjin 301617, People's Republic of China*

|  |  |  |
| --- | --- | --- |
| **Table of contents** | | **Page** |
| **Table S1.** | Origins of the plant polyacetylenoids | 3 |
| **Table S2.** | Characteristic 1H NMR data of the representative polyacetylenoids with polyacetylenic terminal types of **t1**–**t14** | 8 |
| **Table S3.** | Characteristic 13C NMR data of the representative polyacetylenoids with polyacetylenic terminal types of **t1**–**t14** | 10 |

**Table S1** Origins of the plant polyacetylenoids.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Origin** | **Chinese name** | **Origin (raw data in references)** | **Species in ThePlantList** | **Status** | **Confidence level** |
| *Aciphylla scott-thomsonii* | – | *Aciphylla scott-thomsonii* Cockayne & Allan | *Aciphylla scott-thomsonii* Cockayne & Allan | Accepted | ★★ |
| *Acroptilon repens* | 苦蒿/顶羽菊 | *Acroptilon repens* (L.) DC. | *Acroptilon repens* (L.) DC. | Synonym | ★★ |
| *Ambrosia maritima* | – | *Ambrosia maritima* L. | *Ambrosia maritima* L. | Accepted | ★★ |
| *Angelica furcijuga* | 天使山人参 | *Angelica furcijuga* KITAGAWA | *Angelica furcijuga* Kitag. | Accepted | ★★ |
| *Angelica gigas* | 朝鲜当归 | *Angelica gigas* | *Angelica gigas* Nakai | Accepted | ★★ |
| *Anthriscus sylvestris* | 峨参 | *Anthriscus sylvestris* HOFFM. | *Anthriscus sylvestris* (L.) Hoffm. | Accepted | ★★ |
| *Apium graveolens* | 旱芹 | *Apium graVeolens* L. var. rapaceum (Mill.) Gaud | *Apium graveolens* L. | Accepted | ★ |
| *Aralia cordata* | 食用土当归 | *Aralia cordata* Thunb. | *Aralia cordata* Thunb. | Accepted | ★★★ |
| *Artemisia annua* | 黄花蒿 | *Artemisia annua* L. | *Artemisia annua* L. | Accepted | ★★ |
| *Artemisia capillaris* | 茵陈 | *Artemisia capillaris* Thunb. | *Artemisia capillaris* Thunb. | Accepted | ★★ |
| *Artemisia halodendron* | 盐蒿 | *Artemisia halodendron* Turcz. ex Bess. | *Artemisia halodendron* Turcz. ex Besser | Accepted | ★★ |
| *Artemisia lactiflora* | 白苞蒿 | *Artemisia lactiflora* | *Artemisia lactiflora* Wall. ex DC. | Accepted | ★★ |
| *Artemisia monosperma* | – | *Artemisia monosperma* | *Artemisia monosperma* | Accepted | ★★ |
| *Artemisia ordosica* | 油蒿 | *Artemisia ordosica* Krasch | *Artemisia ordosica* Krasch. | Accepted | ★★ |
| *Artemisia scoparia* | 猪毛蒿 | *Artemisia scoparia Waldst*. et Kit. | *Artemisia scoparia* Waldst. & Kitam. | Accepted | ★★ |
| *Artemisia selengensis* | 蒌蒿 | *Artemisia selengensis* Turcz. | *Artemisia selengensis* Turcz.\Artemisia selengensis Turcz. ex Besser | Accepted | ★★ |
| *Atractylodes japonica* | 关苍术 | *Atractylodes japonica* Koidz. ex Kitam | *Atractylodes japonica* Koidz. ex Kitam. | Accepted | ★ |
| *Atractylodes lancea* | 苍术 | *Atractylodes lancea*\*Atractylodes lancea* (Thunb.) DC. | *Atractylodes lancea* (Thunb.) DC. | Accepted | ★★★ |
| *Atractylodes macrocephala* | 白术 | *Atractylodes macrocephala* Koidz. | *Atractylis macrocephala* (Koidz.) Hand.-Mazz. | Synonym | ★★ |
| *Bidens bipinnata* | 鬼针草/婆婆针 | *Bidens bipinnata* L. | *Bidens bipinnata* L. | Accepted | ★★ |
| *Bidens frondosa* | 大狼杷草 | *Bidens frondosa* (L.) | *Bidens frondosa* L. | Accepted | ★★ |
| *Bidens gardneri* | – | *Bidens gardneri* Bak. | *Bidens gardneri* Baker | Accepted | ★★ |
| *Bidens parviflora* | 小花鬼针草 | *Bidens parviflora* Willd.\*Bidens parviflora* WILLD. | *Bidens parviflora* Willd. | Accepted | ★★ |
| *Bidens pilosa* | 三叶鬼针草 | *Bidens pilosa*\*Bidens pilosa* L. | *Bidens pilosa* L. | Accepted | ★★ |
| *Bupleurum chinense* | 柴胡/北柴胡 | *Bupleurum chinense* DC. | *Bupleurum chinense* DC. | Accepted | ★★ |
| *Bupleurum fruticosum* | – | *Bupleurum fruticosum* | *Bupleurum fruticosum* L. | Unresolved | ★ |
| *Bupleurum longiradiatum* | 大叶柴胡 | *Bupleurum longiradiatum* | *Bupleurum longiradiatum* Turcz. | Accepted | ★★ |
| *Bupleurum scorzonerifolium* | 红柴胡/南柴胡 | *Bupleurum scorzonerifolium* | *Bupleurum scorzonerifolium* Willd. | Accepted | ★★ |
| *Carlina acaulis* | 无茎刺苞菊 | *Carlina acaulis* | *Carlina acaulis* L. | Accepted | ★★ |
| *Carthamus tinctorius* | 红花 | *Carthamus tinctorius* L. | *Carthamus tinctorius* L. | Accepted | ★★ |
| *Centella asiatica* | 积雪草 | *Centella asiatica* (L.) Urb. | *Centella asiatica* (L.) Urb. | Accepted | ★★ |
| *Chaerophyllum aureum* | – | *Chaerophyllum aureum* L. | *Chaerophyllum aureum* L. | Accepted | ★★ |
| *Chrysanthemum indicum* | 野菊花 | *Chrysanthemum indicum* | *Chrysanthemum indicum* L. | Accepted | ★ |
| *Chrysanthemum morifolium* | 菊花 | *Dendranthema morifolium* (Ramat.) kitam. | *Chrysanthemum morifolium* Ramat. | Accepted | ★★ |
| *Chrysanthemum zawadskii* | 紫花野菊 | *Dendranthema zawadskii* var. latilobum Kitamura | *Chrysanthemum zawadskii* var. latilobum (Maxim.) Kitam. | Synonym | ★ |
| *Cicuta maculata* | – | *Cicuta maculata* | *Cicuta maculata* L. | Accepted | ★★ |
| *Cirsium japonicum* | 大蓟 | *Cirsium japonicum* var. ussuriense (Regel) Kitam. Ex Ohwi | *Cirsium japonicum* var. ussuriense (Regel) Kitam. ex Ohwi | Synonym | ★ |
| *Cirsium rhinoceros* | – | *Cirsium rhinoceros* Nakai | *Cirsium rhinoceros* (H.Lév. & Vaniot) Nakai | Accepted | ★★ |
| *Cnidium officinale* | 日本川芎 | *Cnidium officinale* Makino | *Cnidium officinale* Makino | Synonym | ★ |
| *Codonopsis cordifolioidea* | 心叶党参 | *Codonopsis cordifolioidea* | *Codonopsis cordifolioidea* P.C.Tsoong | Accepted | ★★★ |
| *Codonopsis lanceolata* | 羊乳/轮叶党参 | *Codonopsis lanceolata* Trautv. | *Codonopsis lanceolata* (Siebold & Zucc.) Benth. & Hook.f. ex Trautv. | Accepted | ★★★ |
| *Codonopsis pilosula* | 党参 | *Codonopsis pilosula* (Franch.) Nannf. | *Codonopsis pilosula* (Franch.) Nannf. | Accepted | ★★★ |
| *Codonopsis tangshen* | 川党参 | *Codonopsis tangshen* Oliv. | *Codonopsis tangshen* Oliv. | Synonym | ★★★ |
| *Coreopsis lanceolata* | 剑叶金鸡菊 | *Coreopsis lanceolata* | *Coreopsis lanceolata* L. | Accepted | ★★ |
| *Coreopsis tinctoria* | 两色金鸡菊 | *Coreopsis tinctoria* Nutt. | *Coreopsis tinctoria* Nutt. | Accepted | ★★ |
| *Crithmum maritimum* | 海茴香 | *Crithmum maritimum* L. | *Crithmum maritimum* L. | Unresolved | ★ |
| *Cussonia barteri* | – | *Cussonia barteri* | *Cussonia barteri* Seem. | Synonym | ★★★ |
| *Cussonia zimmermannii* | – | *Cussonia zimmermannii* Harms | *Cussonia zimmermannii* Harms | Accepted | ★★★ |
| *Daucus carota* | 野胡萝卜 | *Daucus carota* cv. Nantes\*Daucus carota* ssp. carota \*Daucus carota*, cv. Bolero | *Daucus carota* L. | Accepted | ★★ |
| *Dendropanax morbiferus* | 黄漆木 | *Dendropanax morbifera* Leveille | *Dendropanax morbiferus*H.Lév. | Accepted | ★★★ |
| *Desmanthodium guatemalense* | – | *Desmanthodium guatemalense* Hemsl. | *Desmanthodium guatemalense*Hemsl. | Accepted | ★★ |
| *Echinacea pallida* | 苍白松果菊 | *Echinacea pallida* (Nutt.) Nutt. | *Echinacea pallida* (Nutt.) Nutt. | Accepted | ★★ |
| *Echinacea purpurea* | 松果菊 | *Echinacea purpurea* (L.) Moench | *Echinacea purpurea* (L.) Moench | Accepted | ★★ |
| *Echinophora cinerea* | – | *Echinophora cinerea* (Boiss.) Hedge et Lamond | *Echinophora cinerea* (Boiss.) Hedge & Lamond | Accepted | ★★ |
| *Echinophora platyloba* | – | *Echinophora platyloba* DC. | *Echinophora platyloba* DC. | Accepted | ★★ |
| *Echinops ritro* | 硬叶蓝刺头 | *Echinops ritro* L. | *Echinops ritro* L. | Accepted | ★★ |
| *Echinops transiliensis* | – | *Echinops transiliensis* | *Echinops transiliensis* Golosk. | Accepted | ★★ |
| *Eclipta prostrata* | 鳢肠 | *Eclipta prostrata* | *Eclipta prostrata* (L.) L. | Accepted | ★★ |
| *Eryngium tricuspidatum* | – | *Eryngium tricuspidatum* L. | *Eryngium tricuspidatum* L. | Accepted | ★★ |
| *Eryngium triquetrum* | – | *Eryngium triquetrum* Vahl | *Eryngium triquetrum* Vahl | Accepted | ★★ |
| *Eryngium yuccifolium* | 丝兰叶剌芹 | *Eryngium yuccifolium* Michaux. | *Eryngium yuccifolium* Michx. | Accepted | ★★ |
| *Eurycoma longifolia* | 东革阿里 | *Eurycoma longifolia* | *Eurycoma longifolia* Jack | Accepted | ★★ |
| *Ferulago campestris* | – | *Ferulago campestris* (Besser) Grecescu | *Ferulago campestris* (Besser) Grecescu | Synonym | ★★ |
| *Glehnia littoralis* | 珊瑚菜 | *Glehnia littoralis* F. Schmidt ex Miquel \ Glehnia littoralis Fr.Schmidt. ex Miq. | *Glehnia littoralis* F.Schmidt ex Miq. | Accepted | ★★ |
| *Gymnaster koraiensis* | – | *Gymnaster koraiensis* | *Gymnaster koraiensis* (Nakai) Kitam. | Synonym | ★ |
| *Hedera rhombea* | 菱叶常春藤 | *Hedera rhombea* Bean | *Hedera rhombea* (Miq.) Siebold ex Bean | Accepted | ★★★ |
| *Helianthus annuus* | 向日葵 | *Helianthus annuus* L. cv. Russia | *Helianthus annuus* L. | Accepted | ★★ |
| *Helichrysum aureonitens* | – | *Helichrysum aureonitens* | *Helichrysum auronitens* Sch.Bip. | Accepted | ★★ |
| *Heracleum dissectum* | 兴安独活 | *Heracleum dissectum* Ledeb. | *Heracleum dissectum* Ledeb. | Synonym | ★★ |
| *Heracleum maximum* | 川白芷 | *Heracleum maximum* | *Heracleum maximum* W. Bartram | Accepted | ★★ |
| *Herpetospermum caudigerum* | 波棱瓜 | *Herpetospermum caudigerum* Wall. | *Herpetospermum caudigerum* Wall. ex Chakrav. | Synonym | ★ |
| *Launaea capitata* | – | *Launaea capitata* | *Launaea capitata* (Spreng.) Dandy | Accepted | ★★ |
| *Leontopodium alpinum* | 雪绒花/高山火绒草 | *Leontopodium alpinum* Cass. | *Leontopodium alpinum* Colm. ex Cass. | Accepted | ★★ |
| *Leuzea carthamoides/Rhaponticum carthamoides* | 鹿草 | *Rhaponticum carthamoides*/*Leuzea carthamoides* (Willd.) DC. | *Leuzea carthamoides* Willd. | Accepted | ★★ |
| *Levisticum officinale* | 欧当归 | *Levisticum officinale* L. | *Levisticum officinale* W.D.J.Koch | Accepted | ★★ |
| *Ligusticum mutellina* | – | *Ligusticum mutellina* (L.) CRANTZ | *Ligusticum mutellina* (L.) Crantz | Accepted | ★ |
| *Ligusticum tenuissimum* | 细叶藁本 | *Ligusticum tenuissimum* KITAGAWA | *Ligusticum tenuissimum* (Nakai) Kitag. | Accepted | ★★ |
| *Lobelia chinensis* | 半边莲 | *Lobelia chinensis* | *Lobelia chinensis* Lour. | Accepted | ★★★ |
| *Lobelia inflata* | 北美山梗菜 | *Lobelia inflata* L. | *Lobelia inflata* L. | Accepted | ★★★ |
| *Matricaria chamomilla* | 洋甘菊 | *Matricaria chamomilla* | *Matricaria chamomilla* L. | Accepted | ★★ |
| *Mitrephora glabra* | – | *Mitrephora glabra* Scheff. | *Mitrephora glabra* Scheff. | Accepted | ★★ |
| *Mitrephora tomentosa* | 银钩花 | *Mitrephora tomentosa* Hook. f. & Thomson | *Mitrephora tomentosa* Hook. f. & Thomson | Accepted | ★★ |
| *Niphogeton ternata* | – | *Niphogeton ternata* WILLD.ex SCHLTR | *Niphogeton ternata* (Willd. ex Schult.) Mathias & Constance | Accepted | ★★ |
| *Notopterygium incisum* | 羌活 | *Notopterygium incisum* Ting ex H.T.Chang | *Notopterygium incisum* K.C.Ting ex H.T.Chang | Accepted | ★★ |
| *Ochanostachys amentacea* | 皮塔林树 | *Ochanostachys amentacea* Mast. | *Ochanostachys amentacea* Mast. | Unresolved | ★ |
| *Oenanthe fistulosa* | 空茎水芹 | *Oenanthe fistulosa* | *Oenanthe fistulosa* L. | Accepted | ★★ |
| *Ongokea gore* | – | *Ongokea gore* (Hua) Pierre | *Ongokea gore* (Hua) Pierre | Accepted | ★★ |
| *Oplopanax elatus* | 刺人参 | *Oplopanax elatus* NAKAI | *Oplopanax elatus* (Nakai) Nakai | Accepted | ★★★ |
| *Oplopanax horridus* | 北美刺人参 | *Oplopanax horridus* (Sm.) Miq.\Oplopanax horridus | *Oplopanax horridus* (Sm.) Miq. | Accepted | ★★★ |
| *Panax ginseng* | 人参 | *Panax ginseng* C. A. Meyer\Panax ginseng | *Panax ginseng* C.A.Mey. | Accepted | ★★★ |
| *Panax japonicus* | 竹节参 | *Panax japonicus* C.A. Meyer | *Panax japonicus* (T.Nees) C.A.Mey. | Accepted | ★★★ |
| *Panax pseudoginseng* | 假人参 | *Panax pseudo-ginseng* subsp. pseudo-ginseng | *Panax pseudoginseng* var. pseudoginseng | Synonym | ★ |
| *Panax quinquefolius* | 西洋参 | *Panax quinquefolius* L. | *Panax quinquefolius* L. | Accepted | ★★★ |
| *Panax stipuleanatus* | 屏边三七 | *Panax stipuleanatus* H. T. Tsai & K. M. Feng | *Panax stipuleanatus* H.T.Tsai & K.M.Feng | Accepted | ★★★ |
| *Pastinaca sativa* | 欧防风 | *Pastinaca sativa* cv. Gladiator\Pastinaca sativa L. | *Pastinaca sativa* L. | Accepted | ★★ |
| *Peucedanum praeruptorum* | 前胡 | *Peucedanum praeruptorum* Dunn | *Peucedanum praeruptorum* Dunn | Accepted | ★★ |
| *Platycodon grandiflorus* | 桔梗 | *Platycodon grandiflorum* A. DC\*Platycodon grandiflorum* (Jacq.) A. DC. | *Platycodon grandiflorus* (Jacq.) A.DC. | Accepted | ★★★ |
| *Polyalthia debilis* | 弱小暗罗(拟) | *Polyalthia debilis* (Piere) Finet & ganep | *Polyalthia debilis* Finet & Gagnep. | Unresolved | ★ |
| *Pratia nummularia* | 铜锤玉带草 | *Pratia nummularia* (Lam.) A. Br. et Asch | *Pratia nummularia* (Lam.) A.Braun & Asch. | Synonym | ★★★ |
| *Pyrethrum tatsienense* | 川西小黄菊 | *Pyrethrum tatsienense* | *Pyrethrum tatsienense* (Bureau & Franch.) Ling ex C.Shih | Accepted | ★★ |
| *Saposhnikovia divaricata* | 防风 | *Saposhnikovia divaricata* (Turcz.) Schischk | *Saposhnikovia divaricata* (Turcz.) Schischk. | Accepted | ★ |
| *Schefflera taiwaniana* | 台湾鹅掌柴 | *Schefflera taiwaniana* | *Schefflera taiwaniana* (Nakai) Kaneh. | Accepted | ★★★ |
| *Selinum tenuifolium* | – | *Selinum tenuifolium* Wall. | *Selinum tenuifolium* Salisb. | Synonym | ★★ |
| *Sinodielsia yunnanensis* | 滇芹 | *Sinodielsia yunnanensis* WOLFF | *Sinodielsia yunnanensis* H. Wolff | Synonym | ★★ |
| *Swietenia macrophylla* | 大叶桃花心木 | *Swietenia macrophylla* | *Swietenia macrophylla* King | Accepted | ★★ |
| *Tanacetum vulgare* | 菊蒿 | *Tanacetum vulgare* L. | *Tanacetum vulgare* L. | Accepted | ★★ |
| *Toona sinensis* | 香椿 | *Toona sinensis* (A. Juss.) Roem. | *Toona sinensis* (Juss.) M.Roem. | Accepted | ★★ |
| *Torricellia angulata* | 齿裂鞘柄木 | *Torricellia angulata* var intermedia (Harms). | *Torricellia angulata* var. intermedia (Harms) Hu | Unresolved | ★ |
| *Tridax procumbens* | 羽芒菊 | *Tridax procumbens* | *Tridax procumbens*(L.) L. | Accepted | ★★ |
| *Vernonia scorpioides* | – | *Vernonia scorpioides* (Lam.) Pers. | *Vernonia scorpioides* (Lam.) Pers. | Synonym | ★★ |

**Table S2** Characteristic 1H NMR data of the representative polyacetylenoids with polyacetylenic terminal types of **t1**–**t14**.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Types** | **Representative compounds** | **Solvent** | **Positions started from the polyacetylenic terminal (*δ*H, *J* in Hz)** | | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 |
| 3*α-*Hydroxyl **t1** | **12**, **20**, **22**, **24**, **26** | CDCl3 | 5.46–5.47, br d (1H, >17.0); 5.24–5.26, br d (1H, >10.0) | 5.93–5.94, br dd (1H, >17.0, >10.0) | 4.93–4.97, br t (1H, 5.4) or br s |  |  |  |
| 3*β-*Hydroxyl **t1** | **1**, **19**, **51** | CDCl3 | 5.44–5.47, br d (1H, >17.0); 5.21–5.26, br d (1H, >10.0) | 5.91–5.94, br dd (1H, >17.0, >10.0) | 4.90–4.92, br t (1H, 5.4) or br s |  |  |  |
| 3*β-*OS1 **t1** | **32**, **60**, **65**, **202** | CDCl3 | 5.47–5.55, br d (1H, >16.0); 5.28–5.35, br d (1H, >9.5) | 5.79–5.91, m (1H) | 5.83–5.91, m (1H) |  |  |  |
| 3-Oxo **t1** | **43**, **45** | CDCl3 | 6.55–6.56, br d (1H, >17.0); 6.19–6.24, br d (1H, >10) | 6.40–6.41, dd (1H, >17.0, >10.0) |  |  |  |  |
| **t2** | **306**, **309** | CDCl3 | 1.83, dd (3H, 6.9, <2.0) | 6.34–6.36, dq (1H, >15.5, <7.2) | 5.52–5.58, br d (1H, >15.0) |  |  |  |
| 1-Hydroxyl **t2** | **114**, **266** | CDCl3 | 4.24–4.29, m (2H) | 6.41–6.46, dt (1H, >15.5, <5.0) | 5.82–5.86, br d (1H, >15.5) |  |  |  |
| 1-Hydroxyl **t2** | **263** | DMSO-*d*6 | 4.07, br s (2H) | 6.53, dt (1H, 16.0, 4.0) | 5.89, d (1H, 16.0) |  |  |  |
| 1-OG4 **t2** | **269**, **282** | DMSO-*d*6 | 4.33–4.36, m (1H); 4.17–4.18, br d (1H, >15.5, <5.0) | 6.40–6.48, dt (1H, >15.5, <5.0) | 6.03–6.06, br d (1H, 16.0) |  |  |  |
| **t3** | **87**, **88**, **90** | CDCl3 | 0.99–1.01, t (3H, 7.4) | 1.57–1.60, m (2H) | 2.27–2.35, t (2H, 7.0) |  |  |  |
| 1-Methoxyl, 3-oxo **t3** | **85** | CDCl3 | 3.71, t (2H, 6.1) | 2.81, t (2H, 6.1) |  |  |  |  |
| 3-Hydroxyl **t3** | **67**, **68**, **69** | CDCl3 | 1.03, t (3H, 7.4) | 1.77, m (2H) | 4.43–4.44, t (1H, 6.4) |  |  |  |
| 3-OS1 **t3** | **65** | CDCl3 | 1.02, t (3H, 7.4) | 1.80, m (2H) | 5.35, t (1H, 6.5) |  |  |  |
| 1,3-Dihydroxyl **t3** | **83** | CDCl3 | 4.02, ddd (1H, 10.8, 7.9, 3.7); 3.88 (1H, ddd, 10.8, 6.3, 4.3) | 2.04, m (1H); 1.95, m (1H) | 4.72, dd (1H, 6.3, 4.8) |  |  |  |
| 2,3-Dihydroxyl **t3** | **94**, **95** | CDCl3 | 1.30–1.38, d (3H, 6.3) | 3.93–4.06, dq (1H, 6.3, 4.0) | 4.38–4.62, d (1H, 4.0) |  |  |  |
| 1,2,3-Trihydroxyl **t3** | **74**, **75**, **81** | CD3OD | 3.67–3.72, m (1H); 3.58–3.60, m (1H) | 3.61–3.64, m (1H) | 4.39–4.44, d (1H, 5.2) |  |  |  |
| **t4** | **101**, **102**, **103** | CDCl3 | 1.92–1.93, d (3H, 7.0) | 6.16–6.19, dq (1H, 10.8, 7.0) | 5.51–5.52, d (1H, 10.8) |  |  |  |
| **t4** | **197**, **271** | CD3OD | 1.86–1.90, d (3H, 6.7) | 6.13–6.22, dq (1H, 11.0, 7.0) | 5.49–5.55, d (1H, 11.0) |  |  |  |
| 1-Hydroxyl **t4** | **100**, **104**, **112** | CDCl3 | 4.43–4.62, br d (2H, 6.4) | 6.21–6.31, dt (1H, 10.5, 7.0) | 5.60–5.70, d (1H, 11.0) |  |  |  |
| 1-OS1 **t4** | **111** | CDCl3 | 4.84 dd (2H, 6.5, 1.5) | 6.14, m (1H, overlapped) | 5.76, d (1H, 11.0) |  |  |  |
| 1-OG4 **t4** | **195**, **196** | DMSO-*d*6 | 4.45–4.46, m (1H); 4.30–4.35, m (1H) | 6.31–6.33, m (1H) | 5.83–5.86, d (1H, 11.0) |  |  |  |
| 1-OG4 **t4** | **279** | CD3OD | 4.56, ddd (1H, 13.8, 6.0, 1.8); 4.48, ddd (1H, 13.8, 7.2, 1.8) | 6.28, ddd (1H, 10.8, 7.2, 6.0) | 5.68, d (1H, 10.8) |  |  |  |
| **t5** | **181**, **185**, **186**, **187**, **188**, **297**, **313** | CDCl3,  CD3OD,  DMSO-*d*6 | 1.93–2.06, s (3H) |  |  |  |  |  |
| **t6** | **315** | CD3OD | 1.85, dd (3H, 7.2, 1.8) | 6.47, dq (1H, 15.6, 7.2) | 5.65, dd (1H, 15.6, 1, 8) |  |  |  |
| 1-Hydroxyl **t6** | **319**, **320** | CD3OD | 4.17–4.66, m (2H) | 6.43–6.54, dt (1H, 16.0, 5.0) | 5.85–5.90, dt (1H, 16.0, 1.7) |  |  |  |
| 1-Hydroxyl **t7** | **119**, **120**, **237**, **238** | CDCl3 | 4.21–4.62 br d (2H, 6.0) | 5.80–5.88, dt (1H, 15.2, 6.0) | 6.28–6.33, dd (1H, 15.2, 11.0) | 6.50–6.53 dd (1H, 15.6, 11.0) | 5.60–5.79, d (1H, 15.6) |  |
| **t8** | **190**–**194** | CDCl3 | 2.00–2.46, s (1H) |  |  |  |  |  |
| **t9** | **345**, **346** | CDCl3 | 2.01–2.07, s (3H) |  |  |  |  |  |
| **t10** | **233** | CD3OD | 5.09, dd (1H, 17.0, 1.5); 5.04, dd (1H, 10.0, 1.5) | 5.83, m (1H) | 2.27, dd (2H, 13.9, 7.0) | 2.39, t (2H, 7.0) |  |  |
| **t10** | **234**, **235**, **236** | CDCl3 | 5.08–5.10, dd (1H, >16.0, <2.0); 5.04, dd (1H, >10.5, <2.0) | 5.81–5.84, m (1H) | 2.28–2.29, m (2H) | 2.37–2.38, m (2H) |  |  |
| **t11** | **230**, **231**, **232**, **229** | CDCl3 | 5.01–5.03, dd (1H, 17.0, <2.0); 4.97–4.99, dd (1H, <11.0, <2.0) | 5.75–5.78, ddt (1H, 17.0, 10.5, <7.0) | 2.14–2.16, m (2H) | 2.19–2.22, m (2H) | 6.25–6.28, dt (1H, <16.0, <7.0) | 5.49–5.51, d (1H, 16.0) |
| **t12** | **342**, **343**, **344** | CDCl3 | 1.87–1.95, d (3H, <7.0) | 5.91–6.10, dq (1H, <11.0, <7.0) | 5.47–5.69 d (1H, <11.0) |  |  |  |
| 2-Hydroxyl **t13** | **242** | CDCl3 | 1.49, d (3H, 6.8) | 4.59, q (1H, 6.7) |  |  |  |  |
| 2-Hydroxyl **t13** | **243** | C6D6 | 0.92, d (3H, 6.9) | 3.83, m (1H) |  |  |  |  |
| **t14** | **325**, **326**, **329** | CDCl3, CD3OD | 2.00–2.01, s (3H) |  |  |  |  |  |

**Table S3** Characteristic 13C NMR data of the representative polyacetylenoids with polyacetylenic terminal types of **t1**–**t14**.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Types** | **Representative compounds** | **Solvent** | **Positions started from the polyacetylenic terminal (*δ*C)** | | | | | | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 3*α-*Hydroxyl **t1** | **12**, **20**, **22**, **24**, **26** | CDCl3 | 117.3–117.4 | 135.7–136.2 | 63.5–63.7 | 77.5–80.4 | 70.3–70.0 | 67.8–73.5 |  |  |  |  |
| 3*β-*Hydroxyl **t1** | **1**, **19**, **51** | CDCl3 | 116.9–117.4 | 136.0–136.2 | 63.5–63.7 | 74.2–74.9 | 70.9–71.3 | 64.0–66.7 |  |  |  |  |
| 3*β-*OS1 **t1** | **32**, **60**, **65**, **202** | CDCl3 | 119.7–119.8 | 131.8–132.1 | 64.4–64.6 | 74.4–75.0 | 70.7–71.0 | 68.5–69.0 |  |  |  |  |
| 3-Oxo **t1** | **43**, **45** | CDCl3 | 134.1–137.8 | 137.8–138.1 | 177.3–177.8 | 74.6–88.1 | 70.6–75.6 | 63.6–68.3 |  |  |  |  |
| **t2** | **306**, **309** | CDCl3 | 19.0 | 144.2–145.0 | 109.3–109.7 | 71.3–81.4 | 71.9 | 74.5–76.2 |  |  |  |  |
| 1-Hydroxyl **t2** | **114**, **266** | CDCl3 | 62.6 | 145.7–145.8 | 108.6 | 76.7–77.3 | 73.8 | 69.5 |  |  |  |  |
| 1-Hydroxyl **t2** | **263** | DMSO-*d*6 | 60.8 | 149.9 | 105.9 | 82.3 | 73 | 79.1 |  |  |  |  |
| 1-OG4 **t2** | **269**, **282** | DMSO-*d*6 | 67.4 | 144.7–145.5 | 108.1–108.7 | 77.2–78.7 | 73.3–77.8 | 69.9–73.8 |  |  |  |  |
| **t3** | **87**, **88**, **90** | CDCl3 | 13.4–13.5 | 21.4–21.7 | 21.2–21.6 | 82.3–91.0 | 64.0–65.1 | 72.1–80.5 |  |  |  |  |
| 1-Methoxyl, 3-oxo **t3** | **85** | CDCl3 | 66.8 | 45.4 | 184.2 | 74.5 | 75.5 | 68.2 |  |  |  |  |
| 3-Hydroxyl **t3** | **67**, **68**, **69** | CDCl3 | 9.5 | 30.8–30.9 | 64.4–64.5 | 84.1–84.4 | 69.5–69.7 | 78.0–78.5 |  |  |  |  |
| 3-OS1 **t3** | **65** | CDCl3 | 9.3 | 27.8 | 65.3 | 76.7 | 69.3 | 68.8 |  |  |  |  |
| 1,3-Dihydroxyl **t3** | **83** | CDCl3 | 60.4 | 38.4 | 62.1 | 79.5 | 68.7 | 69.4 |  |  |  |  |
| 2,3-Dihydroxyl **t3** | **94**, **95** | CDCl3 | 18.6–19.2 | 70.6–71.0 | 54.9–67.8 | 74.2–77.4 | 71.0–72.4 | 68.3–69.0 |  |  |  |  |
| 1,2,3-Trihydroxyl **t3** | **74**, **75**, **81** | CD3OD | 63.7–64.0 | 75.9–76.1 | 64.5–65.2 | 79.8–82.4 | 70.2–74.4 | 68.9–70.7 |  |  |  |  |
| **t4** | **101**, **102**, **103** | CDCl3 | 16.5–16.9 | 143.7–144.0 | 108.6–108.7 | 76.0–76.5 | 77.2 | 71.3–80.0 |  |  |  |  |
| **t4** | **197**, **271** | CD3OD | 14.6–16.9 | 142.3–142.9 | 107.7–110.0 | 69.1–79.6 | 72.5–76.6 | 66.1–74.1 |  |  |  |  |
| 1-Hydroxyl **t4** | **100**, **104**, **112** | CDCl3 | 61.1–61.3 | 145.0–146.9 | 109.1–109.6 | 70.9–81.2 | 79.0–80.0 | 64.5–80.2 |  |  |  |  |
| 1-OS1 **t4** | **111** | CDCl3 | 62.4 | 139.5 | 111.8 | 77.1 | 80.6 | 75.3 |  |  |  |  |
| 1-OG4 **t4** | **195**, **196** | DMSO-*d*6 | 66.4–66.5 | 144.5 | 109.2 | 78.9–79.1 | 76.8–78.2 | 71.8–77.0 |  |  |  |  |
| 1-OG4 **t4** | **279** | CD3OD | 68.2 | 144.1 | 110.9 | 71.6 | 80.6 | 66.1 |  |  |  |  |
| **t5** | **187** | CDCl3 | 4.7 | 58.9*a* | 64.9*a* | 68.6*a* | 74.6*a* | 79.1*a* |  |  |  |  |
| **t5** | **185** | DMSO-*d*6 | 4.6 | 81.3 | 64.6 | 67.4 | 59 | 74 |  |  |  |  |
| **t5** | **181**, **186**, **188**, **297**, **313** | CD3OD | 3.7–4.5 | 59.4–81.3*a* | 64.8–76.0*a* | 61.4–76.3*a* | 60.1–77.2 | 64.1–71.4 |  |  |  |  |
| **t6** | **315** | CD3OD | 19.1 | 147.7 | 109.9 | 79.6 | 72.8 | 68.2 | 65.4 | 75.2 |  |  |
| 1-Hydroxyl **t6** | **319**, **320** | CD3OD | 62.7–63.5 | 143.0–151.0 | 107.6–110.2 | 76.4–77.3 | 65.3–74.5 | 63.9–74.5 | 66.0–73.9 | 65.9–72.1 |  |  |
| 1-Hydroxyl **t7** | **119**, **120**, **237**, **238** | CDCl3 | 63.1–64.4 | 128.0–130.4 | 133.3–133.7 | 139.3–139.8 | 112.1–113.3 | 79.1–90.6 |  |  |  |  |
| **t8** | **190**–**194** | CDCl3 | 64.9–66.0 | 68.0–68.4 | 64.5–74.1 |  |  |  |  |  |  |  |
| **t9** | **345**, **346** | CDCl3 | 4.4–4.8 | 80.1–84.9 | 64.2–64.3 | 71.5–75.1*a* |  |  |  |  |  |  |
| **t10** | **233** | CD3OD | 116.6 | 137.5 | 33.3 | 19.8 | 79.4 | 66.6 | 60.8 | 61.1 | 66.2 |  |
| **t10** | **234**, **235**, **236** | CDCl3 | 116.2–116.4 | 136.1–136.2 | 32.2–32.3 | 19.3–19.4 | 78.5–79.4 | 66.2–66.3 | 60.3–60.5 | 60.7–60.8 | 65.8–65.9 |  |
| **t11** | **230**, **231**, **232**, **229** | CDCl3 | 115.4–115.5 | 137.3–137.4 | 32.6–32.8 | 32.5–32.6 | 147.0–147.2 | 109.2–109.3 | 73.8–74.0 | 73.1–73.2 | 65.2–65.4 |  |
| **t12** | **342**, **343**, **344** | CDCl3 | 14.0–16.0 | 137.2–141.6 | 109.7–110.3 | 76.7–96.0 |  |  |  |  |  |  |
| 2-Hydroxyl **t13** | **242** | CDCl3 | 24.0 | 58.8 | 81.6 | 65.9 | 63.7 | 60.4 | 60.9 | 64.2 | 68.4 |  |
| 2-Hydroxyl **t13** | **243** | C6D6 | 23.3 | 58.4 | 80.5 | 60.9 | 61.0 | 64 | 64.8 | 66.3 | 69.2 |  |
| **t14** | **329** | CDCl3 | 4.7 | 59.7 | 60.7 | 60.9 | 63.9 | 64.9 | 64.9 | 67.4 | 74.9 | 75.3 |
| **t14** | **325**, **326** | CD3OD | 4.0 | 59.4–59.5 | 61.0–61.1 | 61.3–61.6 | 63.5–63.8 | 63.6–63.9 | 64.1–64.2 | 64.7 | 69.7 | 76.9–79.6 |

1. **Corresponding author:**

   Hong-Hua Wu, Institute of Traditional Chinese Medicine, Tianjin University of Traditional Chinese Medicine, 10 Poyanghu Road, West Area, Tuanbo New Town, Jinghai District, Tianjin, 301617, China

   Tel./fax: +86-022-59791833; E-mail address: wuhonghua2011@tjutcm.edu.cn.

   ORCID: https://orcid.org/0000-0002-3089-4282.

   **†Co-first authors:**

   J.-X. Lai and S-F. Dai contributed equally to this work and should be considered co-first authors. [↑](#footnote-ref-1)