LIGUVEITOSIDE A, A NEW TRITERPENOID SAPONIN FROM LIGULARIA VEITCHIANA

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Key words Ligularia veitchiana, Compositae, Triterpenoid saponin, Liguveitoside A, Liguveitol

In our previous paper, we reported two new eremophilane derivatives from Ligularia veitchiana. Further research to the polar section of this plant led to the isolation of a new triterpenoid saponin, named Liguveitoside A. Its structure was determined on the basis of the spectral and chemical methods.

Liguveitoside A (1) was obtained as colorless needles, with a m. p. at 220 — 221°C, from the n-BuOH soluble part of the EtOH extract of the plant. Comparison of the ¹³C NMR spectrum of 1 with those of the reported saponins revealed that Liguveitoside A was an oleanane-type monodesmoside. The molecular formula of 1 (C₃₆H₅₆O₈) was concluded from the peak at m/z 617 [M+H]+ in the positive FAB mass spectrum, while its fragment ion peaks were exhibited at m/z 439 [M—COOH]+ and 423 [M—OGlcUA]+, suggested the presence of a glucuronic acid piece in the molecule. Acid hydrolysis of 1 gave glucuronic acid (detected by PC), and the aglycone (2).

Compound 2 was analysed for seven tertiary methyls (δ0.73—1.16, 21H, 7 x Me), one —CH₂O— group (an AB system at δ3.13 and 4.11, 1H each, a pair of doublets, JAB = 10.8 Hz), one olefinic proton (δ5.13, t, J = 3.5 Hz) and two oxygen-bearing methine protons (δ3.17, dd, J = 10.0, 3.7 Hz; δ 4.24, ddd, J = 9.9, 2.4, 1.7 Hz). The EI mass spectrum of 2 showed a series of diagnostically important mass peaks at m/z 207, 189(207—H₂O), 232 and the base peak at m/z 201 (232—CH₂OH), which were typically attributed to a retro Diels—Alder fragmentation of an olean—12—en derivative bearing one hydroxy group in rings A / B.

Furthermore, a double doublet at δ3.17 in the ¹H NMR spectrum of 2 with coupling constants at J = 1.0 Hz (axial—axial coupling) and J = 3.7 Hz (axial—equatorial coupling) corresponded to 3α—H(axial...
proton), showed the equatorial orientation of the hydroxy group at C-3. According to the unsaturated value of 2, another ring (named F ring) was most likely to exist in compound 2. This ring was finally deduced to be a four-membered ring, formed by connection of C-28 and C-16 through an ether link. This could be evidenced by the $^{13}$C NMR spectrum of 2, for the chemical shifts of C-28 and C-16 was somewhat upfield shifted (by $\gamma$-effects each other) when comparing with the $^{13}$C NMR spectra of the 16-hydroxy derivative and the 28-CH$_2$OH derivatives.

Moreover, one of the AB system protons (H-28) was found to be a double doublet ($J = 10.8, 2.4$Hz), while H-16 at $\delta 4.24$ exhibited as a ddd peak ($J = 9.9, 3.7, 2.4$Hz), suggested an long distance W-type coupling was present between H-16 and H-28. Shown by the demonstrating model, only an axial orientation of H-16 (16a-H) permits this W-type coupling.

In addition, no variation of C-14 and C-20 in the $^{13}$C NMR spectrum of 2 was found when comparing with oleanane-type triterpenoids, also supported the above-mentioned structure.

Liguveitoside A (1): C$_{39}$H$_{56}$O$_{2}$, colorless needles, mp $220 - 221^\circ$C (MeOH). FAB-MS (positive) (m / z): 617 [M+H]$^+$, 439(25), 423(87), 286(75), 273(100), 201(65), 176(84). $^{13}$C NMR (δ, CSDSN): 38.90(C-1), 26.31(C-2), 89.11(C-3), 40.26(C-4), 55.83(C-5), 18.53(C-6), 34.37(C-7), 41.11(C-8), 47.19(C-9), 36.86(C-10), 23.90(C-11), 122.66(C-12), 144.01(C-13), 43.96(C-14), 36.86(C-15), 66.80(C-16), 39.60(C-17), 44.62(C-18), 47.19(C-19), 31.10(C-20), 33.05(C-21), 26.67(C-22), 28.25(C-23), 16.99(C-24), 15.70(C-25), 16.99(C-26), 27.17(C-27), 69.08(C-28), 33.41(C-29), 24.14(C-30), 107.20(C-1'), 77.80(C-2'), 78.22(C-3'), 73.44(C-4'), 75.59(C-5'), 172.75(C-6').

Liguveitol (2): C$_{39}$H$_{48}$O$_{2}$, colorless gum, EIMS (m / z): 440[M]$^+$, 423(55), 232(57), 201(100). $^{13}$C
NMR (δ,C,D): 38.63(C-1), 26.21(C-2), 78.73(C-3), 39.78(C-4), 55.22(C-5), 18.32(C-6), 33.58(C-7), 40.11(C-8), 46.76(C-9), 38.77(C-10), 23.46(C-11), 122.30(C-12), 142.98(C-13), 43.67(C-14), 36.04(C-15), 67.52(C-16), 36.84(C-17), 44.72(C-18), 46.64(C-19), 30.73(C-20), 32.56(C-21), 27.18(C-22), 28.08(C-23), 15.52(C-24,25), 16.65(C-26), 26.76(C-27), 70.88(C-28), 33.06(C-29), 23.87(C-30).

参考文献


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Δα253-1.02(MeOH; c 0.164)表示。

10. NMR 表示为1H NMR 或13C NMR, 须注明仪器的频率,溶剂及内标物。化学位移以 δ 值(对TMS)表示,注明确形,如: 单峰(s),宽单峰(brs),双峰(d),双二重峰(dd),复峰(m)等。13C NMR 及1H NMR 数须注明所对应的碳和氢的位置,采用 IUPAC 定位,标为 C-1, C-2; H-1, H-2。例如: 13C NMR(21.15MHz, CDCl3): δ30.1(t, C-5), 74.1(d, C-6), 121.3(d, C-3), 144.2(s, C-4)。1H NMR(100MHz, CDCl3): δ5.801(3H, s, H-18), 174.000(H, d, J=6.0Hz, H-26 and H-27), 0.901(3H, d, J=5.0Hz, H-21), 4.342(1H, q, J6a, 7a = 4.5Hz, J6a, 7a = 2.0Hz, H-6), 4.211(1H, m, W,,,—18.0Hz, H-3a)。所用仪器频率及溶剂若在实验部分的总论中已注明,则以下皆可省略。

11. 质谱须注明所用的方法,如(EIMS, CIMS, GC-MS, FABMS 等)及高级能,只须给出分子离子峰及重要的特征碎片峰(相对强度), 如: EIMS(70eV m/z(%): 386[M+](36), 368[M-H2O]+(100), 275[M-111]+(35) 等。高分辨质谱(HRMS)若有必要可多给一些信息。

12. 紫外光谱表示法,如 UVEOHnm(lgc): 203(4.17)。

13. 紫外光谱表示法,如 UVmaxnm(lgc): 1740。官能团的指定放在圆括号内,如: 1740(>C=O)。若要标明吸收带的强度,则采用以下缩写符号: w(弱), m(中等), ν(可变), s(强), vs(很强)。

14. 有机化合物和无机化合物及有关的缩写符号须规范化(参考 CA), 如烷代溶剂 CDCl3, DMSO-d5, D2O, pyridine-d5,等。常见化学试剂在文中均以化学符号表示,如: MeOH, EtOH, n-BuOH, PrOH, iso-PrOH, PhOH(苯酚), petrol(石油醚), CHCl3, CCl4, C6H6, Et2O, Me2CO, HOAc, EtOAc, THF, Ac2O, NaOMe, CH3N2, HCO2H(甲酸), TCA(三氯乙酸), TFA(三氟乙酸), NaOAc, NaOH, HCl, H2SO4, CO2, H3BO3, NH3, N2,等。

15. 制备薄层须注明(1) 薄层厚度; (2) 样品的量; (3) 确定带的方法; (4) 溶剂及附吸剂上洗脱下化合物所用的溶剂。特殊 TLC 的吸附剂须注明,如: AgNO3—硅胶(1 : 9)。

16. 气相色谱(GC)须注明检测器(FID, EC 等), 载气及流速, 操作温度, 柱子情况等。

17. 高压液相(HPLC)须注明(1)柱子情况,如大小、型号; (2) 压力及溶剂; (3) 检测方法, 如 UV 或折射率。

18. X-衍射须给出立体结构图(最好有键长)及必要的数据,详细记录可指明在什么地方储存。