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Four lignans from *Portulaca oleracea* L. and its antioxidant activities

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ABSTRACT

A new lignan, named oleralignan (**1**) and three known compounds (+)-syringaresinol (**2**), (+)-lirioresinol A (**3**) and monomethyl 3,30,4,40-tetrahydroxy- δ -truxinate (**4**) were isolated from the *P. oleracea* for the first time. The compound (**1**) were identified by 1D, 2D NMR spectroscopic methods and high resolution electrospray ionization time-of-flight mass spectrometry. In addition, it was found that the four lignans presented the scavenging activities in 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical quenching assay more than that of hydroxyl anisole (BHA).

KEYWORDS

Portulaca oleracea L.; lignans; antioxidant activity

1. Introduction

Portulaca oleracea L. belonging to the family of Portulacaceae, was widely used as a potherb in the Mediterranean, Central European and Asian countries, which was listed in the World Health Organization as one of the most used medicinal plants and has been given the term 'Global Panacea' (Wu et al. 2012). As a traditional Chinese medicine, it is well-known for the function of removing heat, counteracting toxicity, cooling blood, hemostasia and antidiarrhoea (The Pharmacopoeia Commission of PRC 2015). At the same time, it also exhibits a wide range of pharmacological effects, such as antiinflammatory (Meng et al. 2016), antibacterial (Chan et al. 2015), antioxidant (Dkhil et al. 2011), wound-healing activities (Rashed et al. 2003), antitumor (Shen et al. 2013) attributing to its components, i.e., alkaloids (Li et al. 2017; Xu et al. 2017; Zhao et al. 2018; Jiang et al. 2018; Xiu et al. 2018), flavonoids (Yang et al. 2018), phenolic acids (Erkan 2012), terpenoids (Acedo et al. 2012), coumarins (Awad 1994), α -linolenic acid, β -carotenoid (Liu et al. 2000) and trace elements (Petropoulos et al. 2015) etc. Recently, the lignans

was found from the *Portulaca oleracea* L. for the first time in our laboratory including a new lignan, together with 3 known lignans isolated from the *Portulaca oleracea* L. for the first time (Figure 1). Lignans and norlignans constitute abundant classes of phenylpropanoids, and these compounds have received widespread interest, mainly because they have various clinically important biological activities (Suzuki and Umezawa 2007), such as antitumour, antioxidant, antimitotic, antiviral activity and etc. (Raghavendra et al. 2015). Therefore, its antioxidant activities against DPPH free radical-scavenging was investigated, and butylated hydroxyanisole (BHA) is being as the antioxidant that is similar to lignans with the phenolic hydroxyl groups as a free radical absorbents (Rahmatzadeh et al. 2017).

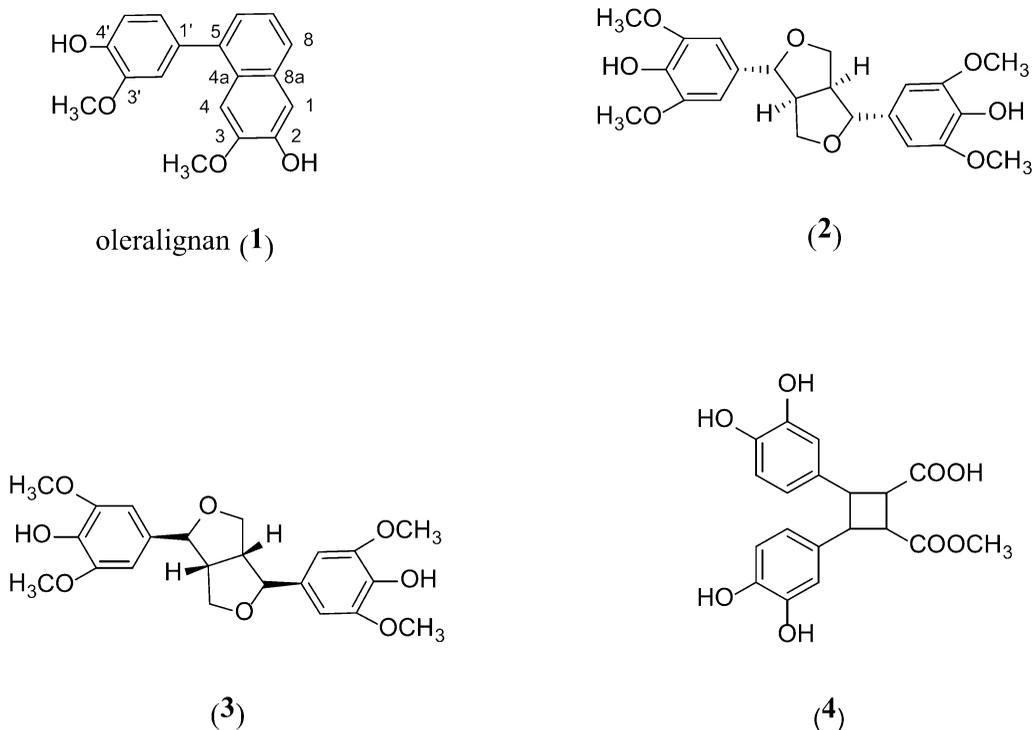


Figure 1. Structure of compounds 1–4.

2. Results and discussion

2.1. Structure elucidation

Compound **1** was obtained as yellow green powder and turned cyan after spraying ferric chloride. Its molecular formula was identified as $C_{18}H_{16}O_4$ based on a molecular ion peak at m/z 297.1093 $[M+H]^+$ in the HR-ESI-TOF-MS (calcd. for $C_{18}H_{17}O_4$, 297.1121). The degrees of unsaturation of compound **1** were 11. Examination of 1H NMR, DEPT and HMQC led to conclude that compound **1** has 9 aromatic or olefinic CH and 2 singlet 1H signals corresponding to methoxy groups at δ_H 3.73 and 3.80 with carbons at δ_C 55.1 and 55.6,

respectively. Compound **1** also has 8 non-protonated carbons between δ 126.1 and 148.9. A 3-spin system defined based on proton coupling patterns and on the COSY experiment includes protons at δ 7.15 (H-6), 7.28 (H-7) and 7.58 (H-8) and defines a 1,2,3-trisubstituted phenyl ring. H-6 and H-8 both correlate with a carbon at δ 126.1 which must be attributed to C-4a. Quaternary carbons C-8a (δ 129.8) and C-5 (δ 138.2) can be assigned based on their HMBC correlation with H-7. Correlation H-8/C-1, correlations of H-1 with C-2, C-3, C-4a and C-8, and correlations of H-4 with C-2, C-3, C-5, C-8a define another tetrasubstituted fused aromatic ring. A methoxy group can be placed in C-3 based on MeO/C-3 correlation and the weak COSY correlation of the methyl group with H-4. The molecular formula and the carbon chemical shift indicate that C-2 bears a hydroxyl group. Another 3-spin system was found based on ^1H - ^1H coupling pattern and COSY experiment. It includes protons at δ 7.03 (H-2'), 6.91 (H-5') and 6.90 (H-6') and defines a 1,3,4-trisubstituted aromatic ring. A methoxy group was placed in C-3' based on correlation H-5'/C-3' and on the correlation of the methyl protons with C-3'. A hydroxyl substituent should therefore be in C-4'. Eventually, this additional phenyl ring was connected to C-5 based on the correlations H-6/C-1' and H-2'/C-5. As a result, compound **1** was identified as the 5-(4-hydroxy-3-methoxyphenyl)-3-methoxynaphthalen-2-ol and was given the trivial name oleralignan (**1**).

By comparison of the ^1H and ^{13}C NMR spectral data with literature, compounds **2–4** were identified as the (+)-syringaresinol (**2**) (Monthong et al. 2011), (+)-lirioresinol A (**3**) (Liu et al. 2013), monomethyl 3,3',4,4'-tetrahydroxy- δ -truxinate (**4**) (Liang et al. 2015), respectively.

2.2. Antioxidant activity

The DPPH radical scavenging method (Xiong et al. 1996) was used to determine the antioxidant activities of the compounds, which was improved to evaluate the four lignans isolated from *P. oleracea*. The results indicated that the four lignans presented higher antioxidant activity than that of BHA (Table S2 in supplementary material) because of its more phenolic hydroxyl group around the lignans framework playing an important role in scavenging DPPH radical (Miyake et al. 2005). Figure S17 showed that the antioxidant activities of the four lignans were dose-dependent.

3. Experimental

3.1. General experimental procedures

UV spectrum was obtained from a HITACHI U-3010 spectrophotometer (Hitachi Ltd, Tokyo, Japan), the IR spectrum and data obtained from IR200

spectrophotometer (Thermo Electron Corporation, Waltham, MA). The NMR spectra in DMSO- d_6 or MeOD was recorded by using an AVANCE 500 MHz instrument (Bruker Corporation, Switzerland). Relative molecular mass was recorded using a 6520 quadrupole-time-of-flight mass spectrometer (Agilent, Palo Alto, CA). Purity was detected on a Nexera X2 UHPLC LC-30A system (Shimadzu, Kyoto, Japan), using a Kromasil C18 column (150 mm x 4.6 mm, 5 mm, Dalian Johnsson Separation Science and Technology Corporation). In the separation process, column chromatography (CC) included silicagel (100–220 and 200–300 mesh, Qingdao Marine Chemical Co., Qingdao, China), polyamide resin (80–100 mesh, Taizhou Luqiao Sijia Biochemical Plastic Factory, Zhejiang, China) and ODS (20–40 μ m, GE Healthcare, Marlborough, MA). The TLC was prepared with silica gel GF254 (Qingdao Marine Chemical Co., Qingdao, China).

3.2. Plant materials and chemicals

The whole herbs of *P. oleracea* were collected in Shijiazhuang (Hebei, China) in June 2017, and identified by Prof. Xixiang Ying. The voucher specimen (No. 20171001) was displayed at Liaoning University of Traditional Chinese Medicine. 1,1-Diphenyl-2-picrylhydrazyl radical (DPPH) (purity \geq 99%) was purchased from Sigma Co. (USA). BHA (purity \geq 98%) was purchased from Shanghai Xiangrui Biological Technology Co., Ltd. (Shanghai, China). Methanol, acetonitrile and formic acid are all of HPLC grade provided by Damao Chemical

Reagent Plant (Tianjin, China, purity $\geq 99.9\%$). All other reagents were of analytical grade purchased from Jinfeng Chemical Factory (Tianjin, China), and the water was WAHAHA purified water (Shenyang, China).

3.3. Isolation and identification

A sample (150 kg) of the air-dried aerial parts *P. oleracea* was treated twice with 10 volumes of water for 2 hours each time to afford a crude extract (21 kg). The extract was concentrated and subjected to a 100–200 mesh silica-gel column chromatography (61 x 55 cm, approximately, 150 kg) with a 2 volumes of ethyl acetate 3 times as the isocratic elution, affording the fraction evaporated (180 g). Then, the fraction eluted with water, 30%, 50%, 70% and pure ethanol was chromatographed respectively on a 80–100 mesh polyamide resin column (120 x 8 cm, approximately, 2.5 kg) to obtain five fractions (4 L each). The fraction of 50% extracting was condensed under the reflux to obtain the extract of 58 g, which was subjected to a 200–300 mesh silica-gel column (120 x 8 cm, approximately, 2.5 kg) for further purification with ethyl acetate, ethyl acetate and methanol (5:1, 2:1, 1:2, 1:4, v/v) as the gradient eluant, obtaining five fractions (Frs. 1–5, 500 mL each). The fractions (38 g), which turns cyan when exposed to ferric chloride reagent, were applied to an ODS column chromatography (20–40 μm , 150 g, Ultimate XB-C18, u_3 x 70 cm) and eluted with methanol (40%, 50%, 60%, 70%, respectively). At medium pressure, five fractions (A1–A5, 100 mL each) were obtained. A3 (0.46 g) was

changed to cyan when exposed to ferric chloride reagent, and then purified on a Sephadex LH-20 column (100 g, u2 x 150 cm) using methanol solvent to give fractions B1-B6, and then B3 was prepared by ultra-high performance liquid chromatography (UHPLC), using Acetonitrile-0.1% formic acid as the mobile phase, with flow rate of 1.0 mL/min, and obtained compound 1 (4 mg, purity of >99% with UHPLC, tR 9.606 min, Acetonitrile-0.1% formic acid, 40:60, v/v), compound 2 (5 mg, purity of >98% with UHPLC, tR 5.94 min, Acetonitrile-water, 30:70, v/v), compound 3 (7 mg, purity of >98% with UHPLC, tR 6.07 min, Acetonitrile-0.1% formic acid, 32:68, v/v), compound 4 (4 mg, purity of >97% with UHPLC, tR 28.23 min, MeOH-0.1% formic acid, 10:90, v/v).

Oleralignan (1): yellow-green powder; UV (CH₃OH) kmax 291, 236 nm; IR (KBr) νmax 3393, 2925, 2850, 1600, 1515, 1478, 1256, 1203, 1159, 1125, 1021, 859, 790, 762 cm⁻¹. ¹H and ¹³C NMR data (Table S1 in supplementary material); HR-ESI-TOF-MS m/z 297. 1093 [M+H]⁺ (calcd. for C₁₈H₁₇O₄, 297.1121).

3.4. Assay of scavenging DPPH radicals

Scavenging of DPPH free radical activity was the basis method of the antioxidative activities of determining the compounds (Sharma and Bhat 2009). Each compound has been diluted with methanol to five different concentrations ranging from 2.5 to 40 μM, and BHA as the positive control

was also diluted to the same concentrations. Thereafter, the different concentrations of sample and BHA (1 mL) was separately mixed with 80 μ M DPPH (1 mL) which dissolved in methanol. The methanol was used to zero the spectrophotometer. The mixtures were allowed to stand for 20 min, and measured at 517 nm at room temperature. The DPPH solution (1 mL) added to methanol (1 mL) were used as the blank group. The sample solution (1 mL) and methanol (1 mL) were used as the control group. Each sample was examined five times in parallel. Radical scavenging activity was expressed as the clearance percentage and calculated using the following formula (Mensor et al. 2001):

$$\text{DPPH radical scavenging effect (\%)} = (1 - (A_{\text{sample}} - A_{\text{control}}) / A_{\text{blank}}) \times 100\%$$

where, A_{control} is the absorbance of the control group, A_{sample} is the absorbance of the test compound, and A_{blank} is the absorbance of the blank group. The antioxidant capacities were evaluated by the values of IC_{50} , and values are expressed as the means \pm SD for $n = 5$.

4. Conclusion

In this study, the lignans was found in the *Portulaca oleracea* L. for the first time including a new lignans named oleralignan (**1**), together with three known compounds **2**, **3** and **4** isolated from the plant for the first time. The antioxidant activity assay indicated that the compound **1**, **2**, **3** and **4** showed more stronger activities of scavenging DPPH radical than that of BHA, with IC_{50}

value of 20.64, 17.34, 16.46 and 8.00 μM , respectively.

Disclosure statement

The authors have no conflicts of interest to disclose.

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