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化感植物向日葵叶化学成分的研究

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摘　要:从向日葵(*Helianthus annuus* L.)叶子的甲醇提取物中分离得到了8个已知化合物,其结构经波谱解析分别确定为:(－)-kaur-16-en-19-oic acid (**1**)、(6*R*,10*R*)-6,10,14-三甲基-十五烷-2-酮(**2**)、维生素 E(**3**)、dehydrocostus lactone(**4**)、(－)-α-tocospirone(**5**)、angeloygrandifloric acid(**6**)、*trans*-phytol(**7**)及 3(20)-phytene-1、2-diol(**8**)。其中化合物 **2**,**5** 和 **8** 为首次从该植物中分离得到。

关键词:向日葵;叶;化学成分

中图分类号:Q946-33　　**文献标识码**:A

Chemical Component from Allelopathic Cultivar Sunflower Leaves

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Abstract: The methanol extracts of the leaves of cultivar sunflower (*Helianthus annuus* L.) afforded eight known compounds (**1**～**8**), by spectroscopic analysis, their structures were elucidated as (－)-kaur-16-en-19-oic acid(**1**), (6*R*,10*R*)-6,10,14- trimethyl-2-pentadecanone(**2**), α-tocopherol(**3**), dehydrocostus lactone (**4**), (－)-α-tocospirone(**5**), angeloygrandifloric acid(**6**), *trans*-phytol(**7**), and 3(20)phytene-1,2-diol(**8**). Compound **2**,**5** and **8** were isolated from this plant for the first time.

Key words: sunflower; leaves; constituents

Our indiscriminate use of synthetic chemicals for herbicides and pest control poses a serious threat to our health and environment[1]. One way to overcome such problem is to find natural phytotoxins which is degradable and safe for agricultural production and human beings *via* isolation, identification and synthesis of active compounds from phytotoxic plant species[2]. Sunflower (*Helianthus annuus* L.), a well-known allelopathic plant, produced a variety of secondary metabolites, some of which possess significant allelopathic property[3]. To search for bioactive natural products from medicinal plants, the chemical component of cultivar sunflower were carried out. In this paper, we herein described the isolation and characterization of compounds **1**～**8** (Fig. 1) from sunflower leaves.

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1 Experimental

1.1 General

Melting points were obtained on a XRC-1 apparatus and uncorrected. Optical rotations were measured on a Horiba SEPA-300 polarimeter. NMR spectra were recorded on Bruker AV-400 and DRX-500 spectrometers with TMS as an internal standard. δ in 10^{-6}, J in Hz. IR spectra were obtained with a Bruker Tensor 27 FT-IR with KBr pellets. UV spectrum was measured on a Shimadzu double-beam 210A spectrometer. MS (EI, FAB) were recorded with a VG Autospec-3000 spectrometer, m/z(rel. int.). ESI and HR-ESI-MS was recorded with an API QSTAR Pulsar 1 spectrometer. Column chromatography (CC) was carried out on silica gel (200~300 mesh, Qingdao Marine Chemical Ltd., Qingdao, P. R. China) and Sephadex LH-20 (Amersham Biosciences, Uppsala, Sweden).

1.2 Plant material

Leaves of *Helianthus annuus* L. were collected in September 2003 in Wuzhong City, Ningxia, China and were identified by Mr. Wu Z H, at Northwest Institute of Botany, Yangling, Shaanxi, and were deposited at Natural Medicine Chemistry Research Centre, College of Sciences, Northwest A & F University.

1.3 Extraction and isolation

The dried and powdered leaves (20 kg) were extracted three times with MeOH at room temperature. The combined extracts were concentrated *in vacuo* to give a deep green gum (2 230 g), which was partitioned between $CHCl_3$ and H_2O. After removal of the organic solvent under reduced pressure, the resulting residue (498 g) was subjected to CC on silica gel eluting with $CHCl_3$/MeOH mixtures of increasing polarity to yield 8 fractions (frs 1~8) according to TLC analysis.

Fr. 2 was subjected to CC on silica gel eluting with petroleum ether/EtOAc (50 : 1 to 10 : 1) to provide four subfractions (A~D). Subfraction A was separated by silica gel CC using petroleum ether/EtOAc (40 : 1) to afford compound **1** (3.15 g). Subfraction B was rechromatographed over silica gel CC with petroleum ether/$CHCl_3$ (6 : 1), and Sephadex LH-20 column ($CHCl_3$/MeOH 1 : 1), followed by Prep-TLC (petroleum ether/ether, 7 : 1) to give compound **2** (13 mg). Subfraction C was rechromatographed over silica gel column using petroleum ether/EtOAc (50 : 1), then Sephadex LH-20 column ($CHCl_3$/MeOH, 1 : 1) to furnish compound **3** (14 mg). Subfraction D was rechromatographed over silica gel column eluting with petroleum ether/$CHCl_3$ (1 : 2.5), followed by Sephadex LH-20 column ($CHCl_3$/MeOH, 1 : 1), and Prep-TLC (petroleum ether/ether, 2.5 : 1), yielding compound **4** (12 mg). Four fractions (E~G) were obtained from fr. 3 by CC on silica gel eluted with petroleum ether/EtOAc mixtures of increasing polarity (20 : 1, 10 : 1, 3 : 1). Fraction E was rechromatographed over silica gel column using petroleum ether/acetone (60 : 1), and on Sephadex LH-20 column ($CHCl_3$/MeOH, 1 : 1), and further purified by Prep-TLC (petroleum ether/EtOAc, 5 : 1), yielding **5** (17 mg). Fraction F was chromatographed over silica gel eluting with petroleum ether/EtOAc (15 : 1) to afford a mixture containing compound **6** (258 mg), which was further purified by recrystallization in petroleum ether/$CHCl_3$. Fraction G was chromatographed over silica gel column using petroleum ether/$CHCl_3$ (3 : 2), followed by Sephadex LH-20 column ($CHCl_3$/MeOH, 1 : 1) to give compounds **7** (91 mg) and **8** (18 mg).

2 Results and discussion

A chloroform-soluble fraction of the methanolic extract of the leaves of sunflower was subjected to repeated silica gel column chromatography, followed by Sephadex LH-20 to give compounds **1**~**8**.

(−)-Kaur-16-en-19-oic acid (**1**) $C_{20}H_{30}O_2$, colorless crystals, mp. 179~180℃; $[\alpha]_D^{24.5}$ -111° (c 1.6, $CHCl_3$); +TOF-MS m/z: 303$[M+1]^+$. The ^1H NMR and ^{13}C NMR data were identical to those recorded for an authentic specimen of (−)-kaur-16-en-19-oic acid[4,5].

(6*R*,10*R*)-6,10,14-Trimethyl-2-pentadecanone (**2**) $C_{18}H_{36}O$, FAB+MS m/z: 269$[M]^+$ (100);

^{1}H NMR(400 MHz, $CDCl_3$): δ2.41(2H, m), 2.13 (3H, s, H-1), 0.86(6H, d, J=6.6 Hz, H-15 and H-18), 0.85(3H, d, J=6.8 Hz), 0.83(3H, d, J=6.8 Hz), 1.60～1.00(19H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ29.9 (q, C-1), 209.5 (s, C-2), 44.2 (t, C-3), 21.4 (t, C-4), 36.5 (t, C-5), 32.6 (d, C-6), 37.2 (t, C-7), 24.4 (t, C-8), 37.2 (t, C-9), 32.8 (d, C-10), 37.4 (t, C-11), 24.8 (t, C-12), 39.4 (t, C-13), 28.0 (d, C-14), 22.6 (q, C-15), 19.6 (q, C-16), 19.7(q, C-17), 22.7(q, C-18). These data were identical to those recorded for an authentic specimen of (6*R*, 10*R*)-6, 10, 14-Trimethyl-2-pentadecanone [6]. The data of 1H NMR were assigned after comparison by those data of (－)-α-tocospirone[10] and 3(20)phytene-1, 2-diol[12].

α-Tocopherol (3) $C_{20}H_{50}O_2$, colorless oil, UV λ_{max}^{MeOH}: 291 and 298 nm; EI-MS ^{1}H NMR, and ^{13}C NMR data were identical to those recorded for an authentic specimen of α-tocopherol[7,8], and the data of H-12′a, H-13′, H-4′a and H-8′a were assigned after comparison by those data of (－)-α-tocospirone[10] and 3(20)phytene-1, 2-diol[12].

Dehydrocostus lactone (4) $C_{15}H_{18}O_2$, colorless needles (EtOAc), mp. 49℃; IR V_{max} cm^{-1}: 1762, 1644; +TOF-MS m/z: 231[M+1]$^+$. The ^{1}H NMR and ^{13}C NMR data were identical to those recorded for an authentic specimen of dehydrocostus lactone[9].

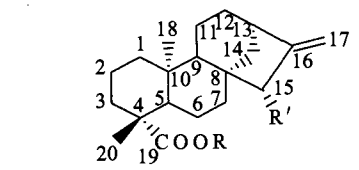
(－)-α-Tocospirone (5) $C_{29}H_{50}O_4$, colorless oil, UV λ_{max}^{MeOH}: 251.4 nm; IR V_{max} cm^{-1}: 3487 (OH), 1697, 1679(C=O), 1622; FAB+MS m/z: 463[M]$^+$ (100), 445[M + H-H_2O]$^+$ (35), 419 (85), 402 (15), 352 (8), 237[M-side chain]$^+$ (8), 167 (23); ^{1}H NMR (400 MHz, $CDCl_3$): δ0.83 (3H, d, J=6.8 Hz, H-17a), 0.84 (3H, d, J=6.8 Hz, H-13a), 0.85 (3H, d, J=6.8 Hz, H-21a), 0.86 (3H, d, J=6.8 Hz, H-22), 1.33 (3H, s, H-9a), 1.36 (3H, s, H-3a), 1.59 (1H, m, H-10a), 1.60 (1H, m, H-8a), 1.66 (1H, m, H-10b), 1.69 (1H, m, H-7a), 1.93 (1H, m, H-8b), 2.03 (1H, m, H-7b), 2.05 (3H, s, H-5a), 2.06 (3H, s, H-6a), 3.82 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ198.8 (s, C-1), 93.3 (s, C-2), 81.2 (s, C-3), 24.2 (q, C-3a), 201.7 (s, C-4), 142.0 (s, C-5), 13.0 (q, C-5a), 146.9 (s, C-6), 13.4 (q, C-6a), 32.0 (t, C-7), 36.4 (t, C-8), 87.0 (s, C-9), 25.7 (q, C-9a), 41.3 (t, C-10), 22.3 (t, C-11), 37.5 (t, C-12), 32.8 (d, C-13), 19.7 (q, C-13a), 37.5 (t, C-14), 24.8 (t, C-15), 37.4 (t, C-16), 32.7 (d, C-17), 19.7 (q, C-17a), 37.3 (t, C-18), 24.4 (t, C-19), 39.3 (t, C-20), 28.0 (d, C-21), 22.6 (q, C-21a), 22.7 (q, C-22). These data were identical to those recorded for an authentic specimen of (－)-α-tocospirone[10].

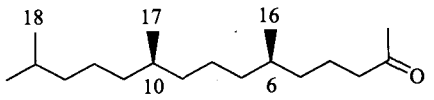
Angeloygrandifloric acid (6) $C_{25}H_{36}O_4$, colorless crystals, mp. 196～198℃; IR V_{max} cm^{-1}: 3 200～2 500, 1702, 1250, 1040, 1005 and 896; EI-MS m/z(%): 400[M]$^+$ (8), 300 (65), 285 (70), 272 (34), 255 (22), 83 (100); ^{1}H NMR (500 MHz, CD_3COCD_3): δ0.96 (3H, s, H-18), 1.23 (3H, s, H-20), 1.88 (3H, brs), 1.97 (1H, m), 2.80 (1H, m), 5.40 (1H, m), 5.08 (1H, brs), 5.13 (1H, m) and 6.07 (1H, m); ^{13}C NMR (125 MHz, CD_3COCD_3): δ40.6 (t, C-1), 19.0 (t, C-2), 35.1 (t, C-3), 43.8 (s, C-4), 56.6 (d, C-5), 20.9 (t, C-6), 37.4 (t, C-7), 47.6 (s, C-8), 53.0 (d, C-9), 39.9 (s, C-10), 20.7 (t, C-11), 32.7 (t, C-12), 42.6 (d, C-13), 37.7 (t, C-14), 82.6 (d, C-15), 155.6 (s, C-16), 109.9 (t, C-17), 28.9 (q, C-18), 184.0 (s, C-19), 15.8 (q, C-20), 168.1 (s, C-21), 128.3 (s, C-22), 137.3 (d, C-23), 15.8 (q, C-24), 18.5 (q, c-25). These data were identical to those recorded for an authentic specimen of angeloygrandifloric acid[4].

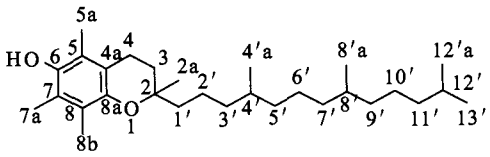
***trans*-Phytol (7)** $C_{20}H_{40}O$, EI-MS, ^{1}H NMR, and ^{13}C NMR data were identical to those reported for an authentic specimen of *trans*-phytol[11].

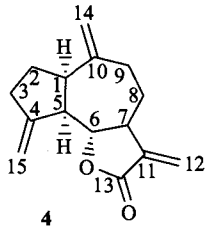
3(20)Phytene-1, 2-diol (8) $C_{20}H_{40}O_2$, colorless oil, IR V_{max} cm^{-1}: 3400, 1640 and 890; FAB+MS m/z: 313[M + 1]$^+$ (18), 295[M + 1 - H_2O] + (18), 277 (6), 83 (32); ^{1}H NMR (400 MHz, $CDCl_3$): δ4.98 (1H, s, H-20a), 5.13 (1H, s, H-20b), 4.21 (1H, dd, J=7.2, 3.2 Hz, H-2), 3.71 (1H, dd, J=11.2, 3.2 Hz, H-1a), 3.54 (1H, dd, J=11.2, 7.2 Hz, H-1b), 0.87 (6H, d, J=6.8 Hz, H-16 and H-17), 0.86 (3H, d, J=6.4 Hz, H-19), 0.84 (3H, d, J=6.4 Hz, H-18), 2.00 (2H, m, H-4), 1.60～1.00 (19H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ65.6 (t, C-1), 75.0 (d, C-2), 148.6 (s, C-3), 33.0 (t, C-4), 25.4 (t, C-5), 37.2 (t, C-6), 32.7 (d, C-7), 37.4 (t, C-8), 24.4 (t, C-9), 37.4 (t, C-

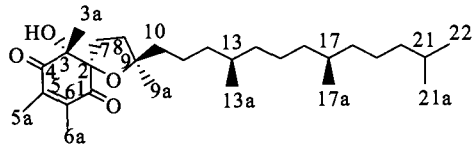
10),32.8 (d,C-11),37.3 (t,C-12),24.8 (t,C-13),39.3 (t,C-14,27.9 (d,C-15),22.6 (q,C-16),22.7 (q,C-17),19.7 (q,C-18),19.7 (q,C-19),110.5 (t,C-20). These data were identical to those recorded for an authentic specimen of 3(20)phytene-1,2-diol[11,12].

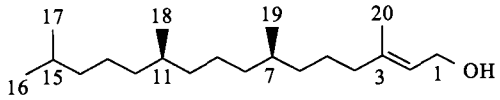












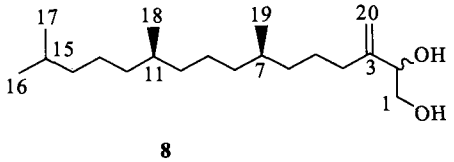


Fig. 1　Structures of compounds **1**～**8**

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