SHORT REPORT

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Chemical Study of Calyxes and Roots of *Physalis solanaceus*

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Abstract: The sucrose esters **1** and **2** together with the flavonoid rutin (**3**) were isolated from the calyxes of *Physalis solanaceus* while 4,7-didehydrophysalin B (**4**) was obtained from the roots. The structural elucidation of the isolates was carried out by analysis of their spectroscopic data. Compound **4** was obtained as natural product for the first time.

Keywords: *Physalis solanaceus*; calyxes; roots; sucrose esters; flavonoid; physalin.

1. Plant Source

The genus *Physalis* (family Solanaceae) groups about 90 species which are easily recognized by its accrescent fruiting calyx that envelops the berry. This genus is native to America, however, Mexico, with over 70 species, mostly endemic, is considered the centre of diversity of *Physalis* [1].

Physalis solanaceus (Schltdl.) Axelius (section Angulatae) [2] was collected in Cerro del Azteca, state of Querétaro, Mexico, on August 2002. The plant was authenticated by Dr. M. Martínez and a voucher specimen (M. Martínez 6366) has been deposited at the Herbarium of the Universidad Autónoma de Querétaro, Mexico.

2. Previous Studies

Chemical studies of roots of *Physalis* species have shown that withasteroids (compounds with an ergostane skeleton) [3-5] as well as pyrrolidine and *nor*-tropane alkaloids [6,7] are the main secondary metabolites isolated. The calyxes have also been subjected to chemical studies, which indicated that withasteroids and flavonoids are the main compounds isolated so far [8,9]. In the case of *Physalis solanaceus* only the stems, leaves, and fruits have been studied chemically [10,11]. From the stems and leaves were reported several physalins which are a group of *seco*-withasteroids with a high degree of oxidation, and from fruits, sucrose esters and one physalin were described.

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3. Present Study

The dried calyxes (35.9 g) of *P. solanaceus* were consecutively extracted with EtOAc and MeOH. Evaporation of the solvents gave 7.3 and 9.0 g of EtOAc and MeOH extracts, respectively. EtOAc extract was fractionated by column chromatography (CC; silica gel 60 G, Macherey-Nagel) eluted with a gradient of MeOH in $CHCl_3$. Fractions eluted with $CHCl_3$-MeOH 98:2 were combined (400 mg) and subjected to a CC eluted with hexane-Me_2CO 1:1 to afford 96.6 mg of a complex mixture of physalins whose components could not be separated. Fractions eluted with $CHCl_3$-MeOH 94:6 were combined (1.35 g) and purified by flash CC (silica gel 60, 230-400 mesh, Macherey-Nagel) eluted with $CHCl_3$-MeOH 90:10 followed of several preparative RP-TLC (Sil RP-18W/UV_{254} plates of 1.0 mm thickness, Macherey-Nagel) eluted with MeOH-H_2O 70:30 (5 to 9 elutions) to yield 14.8 mg of solanose C (**1**) [11] and 35.6 mg of physordinose B (**2**) [12]. MeOH extract was purified by CC eluted with a gradient of MeOH in CH_2Cl_2. Eluates of CH_2Cl_2-MeOH 80:20 and 70:30 were combined (1.5 g) and purified by a Sephadex LH-20 column (25-100 μm; Amersham Pharmacia Biotech AB; eluent MeOH) followed of a CC eluted with $CHCl_3$-MeOH 75:25 to give 28.9 mg of rutin (**3**) [13].

The dried and ground roots (144 g) were extracted with MeOH. Evaporation of the solvent gave 15.4 g of extract which was suspended in H_2O and partitioned with hexane and EtOAc. Hexane fraction (670 mg) was purified by CC (silica gel 60, 230-400 mesh, Macherey-Nagel) eluted with a gradient of EtOAc in hexane. Fractions obtained with hexane-EtOAc 95:5 gave 11.6 mg of β-sitosterol and stigmasterol as a mixture. Fractions obtained with hexane-EtOAc 30:70 and 0:100 yielded 17 mg of β-sitosteryl glucoside. Fraction soluble in EtOAc (1.7 g) was submitted to a CC using as eluent mixtures of hexane-EtOAc (60:40 → 0:100). Eluates of hexane-EtOAc 60:40 were combined (290 mg) and purified by CC (eluent hexane-EtOAc 75:25) followed of a preparative TLC (precoated Sil G-100UV_{254} plates, Macherey-Nagel; eluent $CHCl_3$-EtOAc 94:6, × 3) to afford 5.0 mg of 4,7-didehydrophysalin B (**4**) [14].

*4,7-Didehydrophysalin B (**4**):* Yellow amorphous solid. Optical rotation: $[\alpha]_D^{25}$- 75.5º (*c* 0.2, MeOH); UV (MeOH) λ_{max} nm (log ε): 215 (3.95), 326 (3.50); IR (KBr) ν_{max} cm^{-1}: 3259, 1776, 1738, 1711, 1653; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.83 (1H, dd, *J* = 10.0, 5.0 Hz, H-3), 6.35 (1H, dd, *J* = 10.0, 2.0 Hz, H-7), 6.25 (1H, ddd, *J* = 10.0, 3.0, 0.5 Hz, H-6), 5.87 (1H, d, *J* = 10.0 Hz, H-2), 5.85 (1H, d, *J* = 5.0 Hz, H-4), 4.63 (1H, dd, *J* = 13.5, 4.5 Hz, H-27a), 4.55 (1H, dd, *J* = 3.5, 2.5 Hz, H-22), 4.17 (1H, s, OH-13), 3.84 (1H, dd, *J* = 13.5, 1.5 Hz, H-27b), 3.22 (1H, dd, *J* = 11.0, 7.0 Hz, H-9), 2.88 (1H, bdt, *J* = 11.0, 2.0 Hz, H-8), 2.48 (1H, ddd, *J* = 17.0, 13.0, 5.5 Hz, H-12a), 2.47 (1H, bd, *J* = 4.5 Hz, H-25), 2.20 (1H, s, H-16), 2.17 (1H, m, H-11a), 2.08 (1H, dd, *J* = 14.5, 3.5 Hz, H-23a), 2.04 (1H, dd, *J* = 14.5, 2.5 Hz, H-23b), 1.96 (3H, s, H_3-21), 1.62 (1H, m, H-12b), 1.39 (3H, s, H_3-19), 1.29 (3H, s, H_3-28), 1.20 (1H, m H-11b); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 212.3 (C, C-1), 207.7 (C, C-15), 171.8 (C, C-18), 166.4 (C, C-26), 153.0 (C, C-5), 139.9 (CH, C-3), 129.4 (CH, C-7), 128.0 (CH, C-6), 124.2 (CH, C-2), 118.6 (CH, C-4), 106.4 (C, C-14), 81.0 (C, C-17), 80.8 (C, C-20), 80.2 (C, C-13), 77.0 (CH, C-22), 61.2 (CH_2, C-27), 55.6 (CH, C-16), 53.5 (C, C-10), 50.9 (CH, C-25), 45.4 (CH, C-8), 32.9 (CH_2, C-23), 31.7 (CH, C-9), 31.2 (C, C-24), 26.5 (CH_3, C-28), 25.9 (CH_2, C-12), 25.8 (CH_2, C-11), 21.4 (CH_3, C-21), 19.5 (CH_3, C-19); The ^{1}H and ^{13}C NMR data are supported on the COSY, DEPT, HSQC, HMBC, and NOESY spectra; HRFAB*: m/z* = 509.1813 $[M + H]^+$ (Calcd for $C_{28}H_{29}O_9$: 509.1812).

Structural elucidation of compounds **1**-**3** (Figure1), β-sitosterol and stigmasterol as mixture, and β-sitosteryl glucoside was carried out by analysis of their spectroscopic data which were compared with those described in the literature; additionally, compounds were compared with authentic samples. On the other hand, 4,7-didehydrophysalin B (**4**) (Figure 1) has only been described as a transformation product of the treatment of physalins A, D, E, G, H, I, K, and N [14-17] with concentrated acid (HCl, HCl-AcOH, AcOH, H_2SO_4) or with concentrated acid in Me_2CO, or with DDQ-MeOH for 10 min to 10 h at room temperature or under reflux. Since none of these procedures was used in the present work, compound **4** was obtained as natural product for the first time.

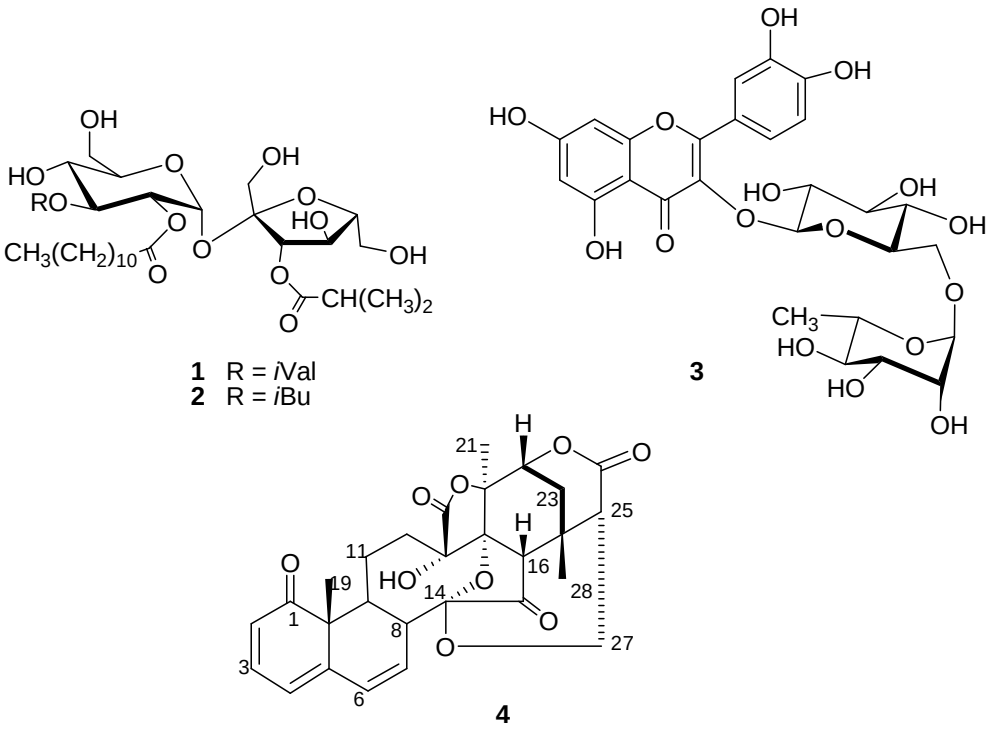

Figure 1. Structures of compounds **1**-**4** isolated from the roots and calyxes of *P. solanaceus.*

Physalis solanaceus along with ten other species form the section Angulatae (subgenus Rydbergis).[1] Although the section contains few species, only the calyxes of *P. ixocarpa* have been studied and four flavonoids, three of them quercetin glycosides, were isolated.[18] This fact agrees with the presence of rutin, a quercetin glycoside, in the calyxes of *P. solanaceus*. In the case of the roots, only those of three species of the section Angulatae, *P. angulata*, *P. ixocarpa*, and *P. philadelphica* have been analysed so far.[6,19] In these works the alkaloids phygrine and hygrine were reported. Quite different compounds, sterols and a physalin, were isolated of the roots of *P. solanaceus*. With these few data, a chemotaxonomic conclusion or a chemical profile of the calyxes and roots of the *Physalis* species, section Angulatae, is not possible.

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