

A NEW DIENOIC ACID OF *Capsicum annuum* var. *fasciculatum*

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A new dienoic acid, paprikadienoic acid (1) was isolated from the stems of Capsicum annuum var. fasciculatum (Sturtev.) Irish (Solanaceae). The structure of the new dienoic acid was elucidated by chemical and physical evidence.

Keywords: *Capsicum annuum* var. *fasciculatum* (Sturtev.) Irish, Solanaceae, dienoic acid.

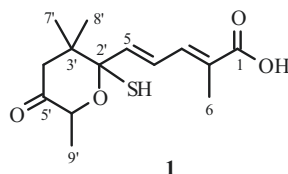
Red pepper, *Capsicum annuum* L. (Solanaceae), is used as a spice all over the world. Red pepper is studied actively because its pungent principal component, capsaicin, has a dietary effect, analgesic activity, and antioxidant activity [1]. The pungent principal component of red peppers is a group of acid amides of vanillylamine and C8–C13 fatty acids, known generally as capsaicin [2]. More than 16 other capsaicinoids have been found as minor components [3]. Although numerous studies have been done on the red pepper fruit, there are few studies on stems [2–4]. This study shows the isolation from the stems of *C. annuum* var. *fasciculatum* (Sturtev.) Irish. To understand more about the chemotaxonomy and to continue searching for biologically and chemically novel agents from *Solanaceous* plants, the stems of *C. annuum* var. *fasciculatum* were chosen for further phytochemical investigation. In this paper, we report on the isolation and structural elucidation of this new dienoic acid.

Paprikadienoic acid (**1**) was obtained as a white amorphous powder from CH₂Cl₂. Its molecular formula was deduced as C₁₄H₂₀O₄S by HR-ESI-MS *m/z* 307.0984 [M + Na]⁺ (calcd 307.0980). The UV spectrum of paprikadienoic acid (**1**) contained absorption bands typical of dienoic acid [5]. The IR spectrum of **1** showed characteristic absorption bands due to the presence of hydroxyl (3500 cm⁻¹), mercapto (2530 cm⁻¹), carbonyl (1660 cm⁻¹) groups. The ¹H NMR spectrum of **1** contained three ethylenic protons indicated by two doublets each for ¹H at δ 5.75 (1H, d, J = 16.0 Hz), 5.84 (1H, d, J = 16.0 Hz), and 5.88 (1H, br.q, J = 1.2 Hz), their spin coupling pattern indicates the presence of two *trans*-di-substituted ethylene moiety in the molecule, which is further confirmed by the Overhauser effect from methyl C-6 to H-4. It also represented an oxymethine at δ 4.32 (1H, br.q, J = 6.4 Hz), and one methylene at δ 2.16 (1H, dd, J = 16.8, 1.0 Hz) and 2.48 (1H, d, J = 16.8 Hz). Additionally, the compound illustrated four methyl groups for 12 protons at δ 1.02 (3H, s), 1.04 (3H, s), 1.25 (3H, d, J = 6.4 Hz), and 1.92 (3H, br.d, J = 1.2 Hz). The ¹³C NMR and DEPT experiments of **1** showed 14 resonance lines consisting of four methyls, one methylene, four methines, and five quaternary carbons. Structure **1** was confirmed by 2D NMR experiments. A COSY correlation was observed between the H-3, H-4, and H-5 and between the H-6' and H-9'. The HETCOR experiment showed that the carbon signals at δ 50.7 for C-4', 68.6 for C-6', 127.1 for C-4, 129.9 for C-5 and 136.9 for C-3 were correlated to the proton signals at δ 2.16/2.48 for H-4', δ 4.32 for H-6', δ 5.84 for H-4, δ 5.75 for H-5 and δ 5.88 for H-3, respectively. Thus, the structure of **1** was a new dienoic acid, which was further confirmed by NOESY and HMBC experiments (Table 1).

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TABLE 1. ^1H (400 MHz) and ^{13}C (100 MHz) NMR Data of **1** (CD_3OD , δ , ppm, J/Hz)

C atom	δ_{H}	δ_{C}	HMBC ($^1\text{H} \rightarrow ^{13}\text{C}$)
1	–	167.6	–
2	–	130.0	–
3	5.88 (br.q, J = 1.2)	136.9	C-1, 2, 4, 5, 6
4	5.84 (d, J = 16.0)	127.1	C-2, 3, 5, 2'
5	5.75 (d, J = 16.0)	129.9	C-3, 4, 2', 3'
6	1.92 (br.d, J = 1.2)	19.6	C-1, 2, 3, 4
2'	–	80.1	–
3'	–	42.2	–
4'	2.16 (dd, J = 16.8, 1.0) 2.48 (d, J = 16.8)	50.7	C-2', 3', 5', 6', 7', 8'
5'	–	201.4	–
6'	4.32 (br.q, J = 6.4)	68.6	C-2', 4', 5', 9'
7'	1.02 (s)	23.4	C-2', 3', 4', 8'
8'	1.04 (s)	23.8	C-2', 3', 4', 7'
9'	1.25 (d, J = 6.4)	24.5	C-5', 6'



EXPERIMENTAL

General. UV spectra were obtained in MeCN, IR spectra were measured on a Hitachi 260-30 spectrophotometer. ^1H NMR (400 MHz, CD_3OD) and NOESY spectra were obtained on a Varian (Unity Plus) NMR spectrometer. Low-resolution ESI-MS spectra were obtained on an API 3000 (Applied Biosystems) and high-resolution ESI-MS spectra on a Bruker Daltonics APEX II 30e spectrometer. Silica gel 60 (Merck, 70–230 mesh, 230–400 mesh) was used for column chromatography. Precoated Silica gel plates (Merck, Kieselgel 60 F-254), 0.20 mm and 0.50 mm, were used for analytical TLC and preparative TLC, respectively, visualized with 50% H_2SO_4 .

Plant Material. The specimen of *C. annuum* var. *fasciculatum* (Sturtev.) Irish was collected from Chiayi County, Taiwan in June, 2014. A voucher specimen was characterized by Dr. Jin-Cherng Huang of Department of Forest Products Science and Furniture Engineering, National Chiayi University, Chiayi, Taiwan and deposited in the School of Medical and Health Sciences, Fooyin University, Kaohsiung, Taiwan.

Extraction and Isolation. The air-dried stems of *C. annuum* var. *fasciculatum* (7.7 kg) were extracted with MeOH (10 L \times 5) at room temperature and the MeOH extract (236.2 g) was obtained upon concentration under reduced pressure. The MeOH extract was chromatographed over silica gel using CH_2Cl_2 –MeOH as eluent to produce 10 fractions. Part of Fr. 8 (12.8 g) was subjected to silica gel chromatography by eluting with CH_2Cl_2 –MeOH (100:1), enriched with MeOH to furnish five subfractions (8-1–8-5). Subfraction 8-4 (2.6 g) eluted with CH_2Cl_2 –MeOH (80:1) was further purified using silica gel column chromatography using the same solvent system to give paprikadienoic acid (**1**) (12 mg).

Paprikadienoic acid (1), white amorphous powder. UV (MeCN, λ_{max} , nm) (log ϵ): 402 (3.11). IR (neat, ν_{max} , cm^{-1}): 3500 (br, OH), 2530 (SH), 1660 (C=O). ESI-MS m/z 307 [$\text{M} + \text{Na}$] $^+$; HR-ESI-MS m/z 307.0984 [$\text{M} + \text{Na}$] $^+$ (calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{SNa}$, 307.0980). ^1H and ^{13}C NMR, see Table 1.

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