

New 5-*O*-Caffeoylquinic Acid Derivatives in Fruit of the Wild Eggplant Relative *Solanum viarum*

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Fruit of the cultivated eggplant species *Solanum melongena*, *Solanum aethiopicum*, and *Solanum macrocarpon*, and wild relatives including *Solanum anguivi* and *Solanum incanum*, have a high content of hydroxycinnamic acid conjugates with potential human health benefits. Typically, caffeoylquinic acid esters predominate, and in particular 5-*O*-(*E*)-caffeoylquinic acid. By contrast, fruit from accession PI 319855 in the USDA eggplant core collection, unambiguously identified as *Solanum viarum* by morphological characters, were found to include several major, closely related hydroxycinnamic acid conjugates with much longer C₁₈-HPLC retention times than those of 5-*O*-(*E*)-caffeoylquinic acid and other monocaffeoylquinic acid isomers. Four of these compounds were isolated from methanolic extracts of lyophilized fruit tissues by C₁₈-HPLC, and structurally elucidated using ¹H and ¹³C NMR techniques and HR-TOF-MS. Isomeric compounds **1** and **2** are composed of 5-*O*-(*E*)-caffeoylquinic acid with a malonyl group on the 3- or 4-hydroxyl of quinic acid, respectively, plus a 6-*O*-sinapoylglucose group 1-*O*-β-D linked with the 4-hydroxyl on the phenyl ring of the caffeoyl moiety (1β,4β-dihydroxy-3β-carboxyacetoxyl- and 1β,3β-dihydroxy-4β-carboxyacetoxyl-5α-[[3-[4-[1β-(6-*O*-(*E*)-sinapoyl-β-D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic acid). Compound **3** has the same structure as **1** and **2** without malonation of quinic acid (1β,3β,4β-trihydroxy-5α-[[3-[4-[1β-(6-*O*-(*E*)-sinapoyl-β-D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic acid). Compound **4** differs from **3** by methylation of the carboxyl group on quinic acid (methyl 1β,3β,4β-trihydroxy-5α-[[3-[4-[1β-(6-*O*-(*E*)-sinapoyl-β-D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylate). Some features of these four new compounds, such as malonation and the specific linkages between caffeoyl, glucosyl, and sinapoyl moieties, are common in acylated and glycosylated phenylpropanoids, but have not previously been reported in complex derivatives of 5-*O*-(*E*)-caffeoylquinic acid.

KEYWORDS: Wild eggplant relative; *Solanum viarum*; fruit; caffeoylquinic acid; malonylquinic acid; glucosylcaffeic acid; sinapoylglucose

INTRODUCTION

A number of potential health-promoting benefits have been ascribed to plant phenolic phytochemicals consumed as constituents in fruits and vegetables (1–3). Phenolic acids as well as other phenylpropanoids are effective free radical scavengers (2,4), and it was once widely accepted that the antioxidant activity of these dietary phytochemicals is directly linked with their protective effects against diseases involving free-radical mediated lipid peroxidation and chronic inflammation (1, 2). In recent years, however, it has come to light that other, systemic modes of action are likely of much greater importance, particularly when the low level absorption and metabolic alteration of dietary phenolics are considered (1, 2). Two such modes of action supported by emerging evidence are modulation of cell signaling cascades

involved in regulation of vital functions (e.g., growth, proliferation, and apoptosis) and activation of endogenous antioxidant defenses (1–3).

Despite this shift in the health benefits of phenolic phytochemicals paradigm, the water-soluble antioxidant activity of fruit and vegetable extracts is generally a good measure of the levels of various phenylpropanoids (4, 5), although other compounds including ascorbic acid and glutathione also contribute. A study using four different assays to evaluate the antioxidant activity in 120 vegetables ranked eggplant among the top 10 for scavenging of superoxide (6). This is attributed to phenolic constituents in the fruit, and in particular a high content of hydroxycinnamic acid conjugates (6–8). Phenolic compounds extracted from eggplant fruit and administered orally to normal and cholesterol-fed rats had a significant hypolipidemic effect (9). In addition, eggplant extracts were found to inhibit protein-activated receptor 2 inflammation associated with atherosclerosis (10).

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Rapid advances in analytical instrumentation have enabled increasingly detailed profiling of food phenolics over the past decade, and results thus far indicate high variability, even within a given food (5, 7, 8, 11). Accurate quantitation, as well as knowledge of the complete profile of phenolic phytochemicals and their potential health benefits, is needed to establish future dietary guidelines for recommending phenolic-rich foods as modulators of disease (12). There is also considerable interest in identifying novel, biologically active phenolic compounds in crop species and their wild relatives, with the aims of nutraceutical enrichment (i.e., breeding of new functional foods) and development of new pharmaceuticals. With these aims in mind, we previously conducted an evaluation of phenolic constituents in eggplant fruit flesh from accessions in the USDA eggplant germplasm core collection (7).

The USDA eggplant core subset, maintained by the ARS Plant Genetic Resources Conservation Unit in Griffin, GA, includes 101 accessions of the widely cultivated eggplant species *Solanum melongena*, plus 14 accessions representing related cultivated and wild species. Among the relatives of *S. melongena*, there are 10 accessions of *Solanum aethiopicum* and one of *Solanum macrocarpon* (species cultivated in Africa), as well as two of *Solanum anguivi* and one of *Solanum incanum* (wild African species). Our prior survey of the hydroxycinnamic acid conjugate profiles of fruit tissues from all 115 core collection accessions found that the vast majority included predominantly monocaffeoylquinic acid esters, with 5-*O*-(*E*)-caffeoylquinic acid composing about 75–90% of the total hydroxycinnamic acid conjugates (7). The two marked exceptions were accessions of *S. incanum* (PI 500922) and purportedly *S. anguivi* (PI 319855). In extracts of fruit tissues from PI 319855, a group of closely related compounds with primary UV absorbance maxima ranging from 318–320 nm was noted to elute much later than 5-*O*-(*E*)-caffeoylquinic acid on C₁₈-HPLC, and together they accounted for >36% of the total hydroxycinnamic acid conjugates (7). We recently determined that the plants grown from seed of accession PI 319855 were *Solanum viarum*, and it was fruit of this species that yielded the unusual hydroxycinnamic acid conjugates. Here we report isolation of the four most abundant of these compounds by C₁₈-HPLC, and their structural elucidation using various ¹H- and ¹³C NMR and HR-ESI-MS techniques.

MATERIALS AND METHODS

Plant Material and Cultural Methods. Seed of eggplant core collection accession PI 319855 were obtained from the USDA, ARS, Plant Genetic Resources Conservation Unit, in Griffin, GA. Although this accession is designated as *Solanum anguivi* Lam. in the USDA, ARS GRIN database (13), it was found to include a mixed population predominated by *Solanum viarum* Dunal. Identification of this species was confirmed by an expert in *Solanum* taxonomy, Dr. Michael Nee at the New York Botanical Garden, after examination of photos of whole plants, leaves, shoots, flowers, and immature fruit. After seed germination, seedlings were raised in a greenhouse using standard production practices. Six 7-week old plants were transplanted to a field plot at the Beltsville Agricultural Research Center, Beltsville, MD, into Keyport fine loam soil using standard horticultural practices for eggplant production in Maryland (14). Plants were spaced at 0.45 m intervals in single rows on polyethylene covered raised beds, with beds positioned on 1.5 m centers. Fertilizer and supplemental water were supplied using trickle irrigation.

Three fruit from each of three plants were harvested from about 35–40 days postanthesis, when they had reached full size but the seeds had not yet fully developed. The small, round fruit were pale green with dark green veins, and ranged from about 2.0 to 4.0 cm in diameter and from 5.6 to 8.8 g fresh weight. After removal of the peduncle, the fruit were washed with tap water and blotted dry. They were then quickly diced, and the tissues were frozen in liquid N₂ and lyophilized. The pooled freeze-dried

tissue from the nine fruit (6.2 g total) was pulverized and stored as a single sample in a small Ziplock bag at –80 °C until used.

Extraction of Total Hydroxycinnamic Acid Conjugates from Fruit Tissues. Total phenolics were extracted from three 2.0 g samples of the lyophilized, powdered tissue by sonicating for 15 min in 30 mL of methanol containing 0.5% butylated hydroxytoluene (BHT). The first methanol extract was decanted after centrifugation and the tissue sample extracted a second time with 30 mL of methanol plus BHT. The two extracts were combined, vacuum filtered through a glass fiber disk inserted in a sintered glass funnel, and then reduced to about 30 mL under a stream of N₂ while heated at 40 °C. An equal volume of 0.1% (10 mM) aqueous phosphoric acid was added, followed by vortexing for 20 s and cooling on ice for 15 min to precipitate the BHT. Extracts were then centrifuged 3 min at 2000g to pellet the precipitate, decanted, and vacuum filtered as before. The filtered supernatants (3 × 60 mL) were each extracted twice with 10 mL of hexane to remove pigments, lipids, and residual BHT. They were then reduced to 20 mL volume under a stream of N₂ while heated at 40 °C prior to extraction three times with 20 mL of ethyl acetate. The three combined ethyl acetate extracts (60 mL each) including >90% of the total hydroxycinnamic acid conjugates (evaluated using a spectrophotometer) were individually N₂ evaporated. The residue from each was then dissolved in 4 mL of methanol, which was transferred to a 6 mL amber vial. The vials were flushed with N₂, sealed with a Teflon-lined screw cap, and stored at –80 °C until the extracts were fractionated.

Isolation of Unknown Hydroxycinnamic Acid Conjugates 1–4 by SPE and HPLC. The hydroxycinnamic acid conjugate extracts were fractionated on 500 mg Strata-X polymer solid phase extraction (SPE) tubes (Phenomenex, Torrance, CA). First, the 4 mL methanolic samples were reduced to 2 mL by N₂ evaporation and diluted to 10 mL with deionized water (1:4, v/v). After washing the Strata-X bed with 10 mL methanol and 10 mL water, the 10 mL sample (in 20% methanol) was loaded and passed through the sorbent under gentle N₂ pressure to achieve a dropwise flow. The tube was then similarly eluted with successive 10 mL volumes of 25, 40, 50, and 90% aqueous methanol, which were collected as separate fractions. Examination of aliquots of the SPE fractions by UV spectrophotometry (Shimadzu UV160U) and C₁₈-HPLC-DAD showed that the 20 and 25% methanol eluates included mainly 5-*O*-(*E*)-caffeoylquinic acid and other monocaffeoyl conjugates, while the remaining fractions, in particular the 50% methanol eluate, were enriched in one or more of the unknown hydroxycinnamic acid conjugates of interest. Solvent was N₂ evaporated from the 40, 50, and 90% methanol fractions at 40 °C with addition of methanol as needed. Residue from each of the 40 and 50% fractions was dissolved in 1.5 mL of aqueous 20% methanol including 0.02% phosphoric acid, and the solutions were transferred to 2 mL amber HPLC vials in preparation for HPLC separation of the four major unknown hydroxycinnamic acid conjugates. Residue from the 90% fraction was dissolved in 1 mL of 20% aqueous methanol including 50 mM HCl and further fractionated on a 60 mg Strata-X-C SPE tube by stepwise elution with 4 mL volumes of 50 mM HCl in 20% methanol, 50% aqueous methanol, and 5% NH₄OH in methanol. The 50% methanol eluate was highly enriched in unknown compound 4, and was prepared for HPLC separation in 1 mL of 20% methanol plus 0.02% phosphoric acid.

HPLC isolation and purification of hydroxycinnamic acid conjugates 1–4 was performed using an HP 1100 Series instrument with a quaternary pump, autosampler, and photodiode array detector (Agilent Technologies). Data were acquired and analyzed with Agilent ChemStation software. A method was developed to achieve optimal separation of the four compounds on a 250 mm × 4.6 mm i.d., 5 μm, Luna C18(2) analytical column (Phenomenex) within 30 min. A binary mobile phase gradient of methanol in 0.01% aqueous phosphoric acid was used as follows: 0–10 min, linear increase from 20–25% methanol, 1.0 mL/min; 10–20 min, linear increase from 25–50% methanol, 1.0 mL/min; 20–26 min, linear increase from 50–75% methanol, 1.0 mL/min; 26–28 min, 75% methanol, linear increase from 1.0–1.2 mL/min; 28–31 min, linear decrease from 75–20% methanol, 1.2 mL/min; 31–34 min, 20% methanol, linear decrease from 1.2–1.0 mL/min. Order of elution of the four unknowns was 3:1:2:4 at 22.7, 23.5, 24.0, and 24.4 min, respectively. The injection volume varied from 50 to 80 μL, depending on sample concentration, to achieve an optimal balance of column loading and peak separation. Pooled fractions from the first round of collection of individual compounds 1–4 were N₂ evaporated to about 2 mL (largely aqueous). They

Table 1. ^1H and ^{13}C NMR Data for Compounds 1–4 Isolated from All Tissues of *S. viarum* Fruit^a

positions	1		2		3		4	
	δ_{H} (int, multi <i>J</i> in Hz)	δ_{C}	δ_{H} (int, multi <i>J</i> in Hz)	δ_{C}	δ_{H} (int, multi <i>J</i> in Hz)	δ_{C}	δ_{H} (int, multi <i>J</i> in Hz)	δ_{C}
Caffeoyl Group								
1		131.2s		131.1s		131.2s		130.8s
2	6.96 (1H, d, 2.0)	116.5d	6.97 (1H, d, 1.9)	116.1d	6.95 (1H, d, 1.7)	116.5d	6.98 (1H, d, 2.1)	116.3d
3		148.8s		148.8s		148.6s		148.8s
4		148.6s		148.5s		148.7s		148.4s
5	7.03 (1H, d, 8.4)	118.2d	7.03 (1H, d, 8.8)	118.1d	7.03 (1H, d, 8.3)	118.3d	7.06 (1H, d, 8.1)	117.9d
6	6.78 (1H, dd, 8.4, 1.9)	122.1d	6.79 (1H, dd, 8.7, 2.3)	122.3d	6.75 (1H, dd, 8.5, 1.6)	121.9d	6.79 (1H, dd, 8.5, 2.2)	122.0d
7	7.34 (1H, d, 15.7)	146.3d	7.31 (1H, d, 15.9)	146.5d	7.33 (1H, d, 16.1)	146.1d	7.34 (1H, d, 15.2)	146.2d
8	6.02 (1H, d, 15.6)	117.4d	6.00 (1H, d, 16.3)	117.1d	6.02 (1H, d, 15.8)	117.6d	6.02 (1H, d, 15.8)	117.2d
9		167.9s		167.7s		168.3s		167.8s
Sinapoyl Group								
1'		126.8s		126.7s		126.7s		126.6s
2'/6'	6.82 (2H, s)	107.1d	6.81 (2H, s)	107.1d	6.82 (2H, s)	107.1d	6.85 (2H, s)	106.7d
3'/5'		149.7s		149.7s		149.9s		149.6s
4'		139.9s		139.9s		139.9s		139.7s
7'	7.54 (1H, d, 15.7)	147.5d	7.54 (1H, d, 16.1)	147.6d	7.55 (1H, d, 15.8)	147.5d	7.57 (1H, d, 15.8)	147.6d
8'	6.33 (1H, d, 15.9)	115.9d	6.33 (1H, d, 15.8)	115.9d	6.34 (1H, d, 15.9)	115.9d	6.36 (1H, d, 15.9)	115.8d
9'		168.9s		168.9s		168.9s		168.8s
CH ₃	3.77 (6H, s)	57.1q	3.77 (6H, s)	57.1q	3.78 (6H, s)	57.1q	3.72 (6H, s)	56.9q
Quinic Acid Group								
1''		76.5s		75.9 s		76.6s		75.9 s
2''ax	2.21 (1H, dd, 14.2, 3.8)	36.1t	2.20 (1H, dd, 14.3, 2.9)	39.1t	2.25 (1H, m)	39.2t	2.17 (1H, m)	38.6t
2''eq	2.04 (1H, m)	36.1t	2.11 (1H, m)	39.1t	2.14 (1H, m)	39.2t	2.09 (1H, m)	38.6t
3''	5.28 (1H, dd, 5.8, 3.6)	74.1d	4.24 (1H, dd, 6.1, 3.3)	68.9d	4.07 (1H, dd, 7.2, 3.6)	71.8d	4.08 (1H, ddd, 6.4, 3.4, 3.2)	71.6d
4''	3.87 (1H, dd, 7.9, 3.6)	70.9d	4.99 (1H, dd, 8.9, 3.1)	76.5d	3.66 (1H, m)	73.8d	3.70 (1H, dd, 7.8, 3.0)	73.8d
5''	5.22 (1H, dd, 13.8, 6.2)	72.2d	5.41 (1H, dd, 15.3, 6.7)	69.1d	5.22 (1H, ddd, 8.4, 8.2, 4.6)	72.4d	5.23 (1H, ddd, 8.4, 8.0, 4.4)	72.3d
6''ax	2.02 (1H, m)	38.0t	1.96 (1H, dd, 14.5, 5.5)	38.3t	2.09 (1H, m)	38.5t	1.97 (1H, m)	38.0t
6''eq	2.05 (1H, m)	38.0t	2.11 (1H, m)	38.3t	2.23 (1H, m)	38.5t	2.11 (1H, m)	38.0t
7''		177.5s		177.5s		177.6s		175.5s
8''							3.62 (3H, s)	53.1q
Sugar Moiety								
1'''	4.76 (1H, d, 8.7)	103.4d	4.76 (1H, d, 8.7)	103.3d	4.76 (1H, d, 8.7)	103.4d	4.77 (1H, d, 7.3)	103.1d
2'''	3.43 (1H, m)	74.9d	3.43 (1H, m)	74.9d	3.44 (1H, m)	74.9d	3.42 (1H, m)	74.8d
3'''	3.41 (1H, m)	77.6d	3.41 (1H, m)	77.6d	3.42 (1H, m)	77.7d	3.40 (1H, m)	77.5d
4'''	3.32 (1H, m)	72.1d	3.33 (1H, m)	72.0d	3.33 (1H, m)	72.1d	3.32 (1H, m)	72.0d
5'''	3.66 (1H, m)	75.9d	3.66 (1H, m)	75.9d	3.65 (1H, m)	75.9d	3.67 (1H, m)	75.8d
6'''a	4.30 (1H, dd, 12.0, 7.6)	64.7t	4.30 (1H, dd, 11.7, 7.0)	64.7t	4.31 (1H, dd, 11.9, 7.4)	64.7t	4.34 (1H, dd, 11.9, 7.5)	64.6t
6'''b	4.46 (1H, dd, 11.6, 1.8)	64.7t	4.46 (1H, dd, 11.7, 2.0)	64.7t	4.46 (1H, dd, 11.9, 2.2)	64.7t	4.49 (1H, dd, 11.9, 2.2)	64.6t
Malonyl Group								
1''''		168.6s		168.3s				
2''''	3.22 (2H, s)	50.2t	3.24 (2H, s)	50.3t				
3''''		171.0s		170.9s				

^a Assignments were based on ^1H – ^1H COSY, HMQC, and HMBC experiments. Samples were in CD_3OD . ^1H and ^{13}C scans were at 300 and 75 MHz, respectively.

were then loaded on 200 mg Strata-X tubes, which were washed with 2 mL of water to rinse through phosphoric acid, followed by elution of the compounds with 3 mL of methanol. Solvent was N_2 evaporated, and the samples were prepared as described above for a second round of HPLC isolation to achieve additional separation and purification. A third and final round of HPLC isolation yielded compounds **1**, **2**, **3**, and **4** in the amounts 3.52, 2.34, 1.75, and 1.97 mg, and at purities of 92, 87, 96, and 96%, respectively.

Analytical Procedures and Instrumentation. Optical rotations were determined on an AUTOPOL III polarimeter (Rudolph Research Analytical, Hackettstown, NJ) equipped with a sodium lamp (589 nm) and a 10 cm microcell. UV and IR spectra were obtained on a UV-2450 spectrometer (Shimadzu, Japan) and a Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA), respectively. A Bruker Avance 300 NMR spectrometer, equipped with bbi (for ^1H and 2D) and bbo (for ^{13}C) probes, was operated at 300.1312 MHz for ^1H and at 75.4753 MHz for ^{13}C NMR

experiments. More than 200, 26624, 200, and 416 scans, respectively, were used in the ^1H NMR, ^{13}C NMR, HSQC, and HMBC experiments for each compound. For the two-dimensional NMR experiments, resolutions of 128 and 2048 data points (HMBC), and 256 and 2048 data points (HSQC), were used in the F1 and F2 dimensions, respectively. These large numbers of data points greatly enhanced resolution of the TD spectra. High resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed using a LCT premier XE TOF mass spectrometer (Waters, Milford, MA) equipped with an ESI interface and controlled by MassLynx V4.1 software. Full mass and collision-induced dissociation (CID) MS/MS spectra were acquired in the negative mode over the range m/z 100–1000. The capillary voltage was set to 2800 V, and the cone voltage was 20 V. Nitrogen gas was used both for the nebulizer and in desolvation. The desolvation and cone gas flow rates were 600 and 20 L/h, respectively. The desolvation temperature was 400 °C, and the source temperature was 120 °C. A lock-mass of leucine enkephalin infused by a secondary

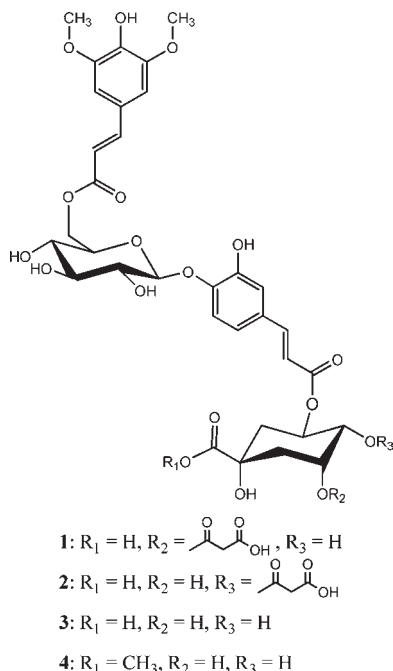


Figure 1. Structures of new 5-*O*-caffeoylquinic acid derivatives 1–4 isolated from fruit tissues of *Solanum viarum*. All four compounds have the same backbone composed of 5-*O*-(*E*)-caffeoylquinic acid with a 6-*O*-(*E*)-sinapoylglucose group 1-*O*- β -D linked to the 4-hydroxyl on the phenyl ring of caffeic acid, and identical to **3**. Isomeric **1** and **2** differ from **3** by malonation of the 3- or 4-hydroxyl, respectively, on quinic acid, whereas **4** differs from **3** by methylation of the 1-carboxyl on quinic acid.

reference probe at 200 pg/mL in acetonitrile/water, 1:1, containing 0.1% formic acid was used for the negative ion mode ($[M - H]^-$, m/z 554.2615). The reference mass was scanned once every two scans during data collection. ESI⁻ data were collected using a scan time of 0.5 s. For full mass spectra, the aperture 1 voltage was held at 0 V, while for MS/MS spectra, it was set at 60 V for compounds 1–3 and 50 V for compound 4.

Acid Hydrolysis and Determination of the Sugar Moiety in 1–4. Each compound (0.1 mg) was refluxed in 2 M HCl (5 mL) for 3 h. The solvent was evaporated under a stream of N₂, the residue was dissolved in *n*-butanol (10 mL), and the *n*-butanol solution was then extracted three times with H₂O (10 mL). The combined aqueous extracts were evaporated to dryness under N₂, and the residue was dissolved in 2 mL of H₂O. Samples were passed through a Phenex RC 0.45 μ m filter prior to HPLC–TOF–MS analysis. Analytical HPLC was performed on a 150 mm \times 2.0 mm i.d., 3 μ m, Luna NH₂ column (Phenomenex) at 25 °C using the isocratic mobile phase CH₃CN/10 mM aqueous ammonium acetate, 75:25, at a flow rate of 0.2 mL/min. Peaks were detected with a LCT premier XE TOF mass spectrometer (Waters) equipped with an ESI interface, and their retention times were compared with those of authentic monosaccharide standards.

Hydroxycinnamic Acid Conjugate (1): 1 β ,4 β -Dihydroxy-3 β -carboxyacetoxo-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)-oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic Acid (IUPAC Numbering). White amorphous powder: IR ν_{\max} cm⁻¹ 3363, 2958, 2927, 2359, 1727, 1600, 1457, 1270, 1120, 1072; UV (CH₃OH) λ_{\max} nm (log ϵ) 320 (4.48), 221 (4.62); $[\alpha]_D^{20} = -118.2^\circ$ (*c*, 0.00022, MeOH); ¹H NMR (CD₃OD, 300 MHz) and ¹³C NMR (CD₃OD, 75 MHz) data, see Table 1; HR-ESI-MS (negative mode) m/z 807.1953 ($[M - H]^-$ calcd for C₃₆H₃₉O₂₁, 807.1984).

Hydroxycinnamic Acid Conjugate (2): 1 β ,3 β -Dihydroxy-4 β -carboxyacetoxo-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)-oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic Acid. White amorphous powder: IR ν_{\max} cm⁻¹ 3387, 2958, 2928, 2358, 1727, 1599, 1462, 1272, 1122, 1073; UV (CH₃OH) λ_{\max} nm (log ϵ) 321 (4.42), 221 (4.59); $[\alpha]_D^{20} = -92.8^\circ$ (*c*, 0.00028, MeOH); ¹H NMR (CD₃OD, 300 MHz) and ¹³C NMR (CD₃OD, 75 MHz) data, see Table 1; HR-ESI-MS (negative mode) m/z 807.1957 ($[M - H]^-$ calcd for C₃₆H₃₉O₂₁, 807.1984).

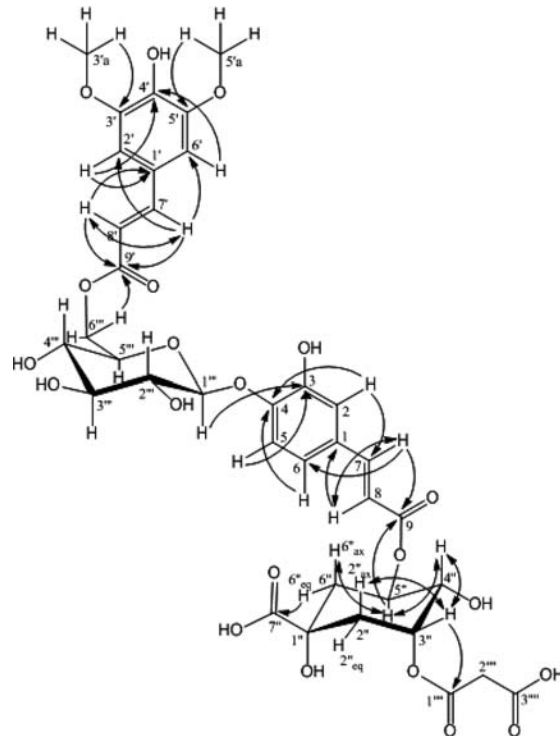


Figure 2. Selected HMBC (→) and H-H COSY (↔) NMR correlations used in structural elucidation of the complex 5-*O*-caffeoylquinic acid derivative **1** isolated from fruit tissues of *Solanum viarum*.

Hydroxycinnamic Acid Conjugate (3): 1 β ,3 β ,4 β -Trihydroxy-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)-oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic Acid. White amorphous powder: IR ν_{\max} cm⁻¹ 3305, 2959, 2929, 2358, 1728, 1600, 1462, 1273, 1122, 1072; UV (CH₃OH) λ_{\max} nm (log ϵ) 320 (4.39), 221 (4.62); $[\alpha]_D^{20} = -138.2^\circ$ (*c*, 0.00034, MeOH); ¹H NMR (CD₃OD, 300 MHz) and ¹³C NMR (CD₃OD, 75 MHz) data, see Table 1; HR-ESI-MS (negative mode) m/z 721.2002 ($[M - H]^-$ calcd for C₃₃H₃₇O₁₈, 721.1980).

Hydroxycinnamic Acid Conjugate (4): Methyl 1 β ,3 β ,4 β -Trihydroxy-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)-oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylate. White amorphous powder: IR ν_{\max} cm⁻¹ 3409, 2959, 2929, 2359, 1728, 1600, 1457, 1271, 1121, 1073; UV (CH₃OH) λ_{\max} nm (log ϵ) 320 (4.41), 219 (4.52); $[\alpha]_D^{20} = -82.5^\circ$ (*c*, 0.00040, MeOH); ¹H NMR (CD₃OD, 300 MHz) and ¹³C NMR (CD₃OD, 75 MHz) data, see Table 1; HR-ESI-MS (negative mode) m/z 735.2123 ($[M - H]^-$ calcd for C₃₄H₃₉O₁₈, 735.2136).

RESULTS AND DISCUSSION

A molecular formula of C₃₆H₄₀O₂₁ for compound **1** (Figure 1) was determined from the HR-ESI-MS molecular ion $[M - H]^-$. The UV spectrum of **1** showed absorption maxima at 320 and 221 nm.

The ¹H NMR signals at δ 7.03 (1H, d, $J = 8.4$ Hz, H-5), δ 6.96 (1H, d, $J = 2.0$ Hz, H-2) and δ 6.78 (1H, dd, $J = 8.4, 1.9$ Hz, H-6) suggested the presence of a set of aromatic ABX system protons. The ¹H NMR doublets at δ 7.34 (1H, d, $J = 15.7$ Hz, H-7), δ 6.02 (1H, d, $J = 15.6$ Hz, H-8) and the H–H COSY cross peak H-7/H-8 indicated two *trans* oriented olefinic protons (Figure 2). From the HMBC correlations H-7/C-6 (δ 122.1), C-9 (δ 167.9), H-8/C-1 (δ 131.2), H-2, H-6/C-4 (δ 148.6) and H-5/C-3 (δ 148.8) (Figure 2), a caffeoyl group was deduced in the structure. The ¹³C NMR signals at δ 118.2 (C-5), δ 116.5 (C-2), δ 122.1 (C-6), δ 146.3 (C-7), δ 117.4 (C-8) were assigned from HSQC data.

In the ¹H NMR spectrum, a two-proton singlet at δ 6.82 (2H, s, H-2' and H-6'), a 6H singlet at δ 3.77 (6H, s, H-3'a and H-5'a), two 1H doublets at δ 7.54 (1H, d, $J = 15.7$ Hz, H-7') and 6.33

Table 2. HR-ESI-MS Fragmental Analysis of Compounds 1–4

frag. ion no.	fragmental ions (<i>m/z</i>)				ion formulas	calcd mass	<i>mDa</i> difference	ppm difference	structures of fragments
	1	2	3	4					
1	807.1953	807.1957			C ₃₆ H ₃₉ O ₂₁	807.1984	-3.1 to -2.7	-3.8 to -3.3	[M (1 or 2) - H] ⁻
2	763.2096	763.2093			C ₃₅ H ₃₉ O ₁₉	763.2086	0.7-1.0	0.9-1.3	[M (1 or 2) - H - COO] ⁻
3				735.2123	C ₃₄ H ₃₉ O ₁₈	735.2136	-1.3	-1.8	[M (4) - H] ⁻
4	721.1990	721.1989	721.2002	721.2003	C ₃₃ H ₃₇ O ₁₈	721.1980	0.9-2.3	1.2-3.2	[M (1 or 2) - H - propanedioic acid group] ⁻ ; [M (3) - H] ⁻ ; [M (4) - H - CH ₃] ⁻
5	703.1880	703.1892			C ₃₃ H ₃₅ O ₁₇	703.1874	0.6-1.8	0.8-2.5	[M (1 or 2) - H - propanedioic acid group - H ₂ O] ⁻
6	547.1479	547.1492	547.1475	547.1547	C ₂₆ H ₂₇ O ₁₃	547.1452	-0.5-4.0	-0.9-7.3	[sinapoyl + glucosyl + caffeoyl groups] ⁻
7				529.1609	C ₂₃ H ₂₉ O ₁₄	529.1557	5.2	9.8	[glucosyl + caffeoyl + quinic acid groups + CH ₃] ⁻
8	515.1454	515.1429	515.1437		C ₂₂ H ₂₇ O ₁₄	515.1401	2.8-5.3	5.4-10.3	[glucosyl + caffeoyl + quinic acid groups] ⁻
9	409.1141	409.1188			C ₁₉ H ₂₁ O ₁₀	409.1135	0.6-5.3	1.5-12.9	[caffeoyl + quinic acid + propanedioic acid groups + CH ₃ - COO] ⁻
10	395.1010	395.1029			C ₁₈ H ₁₉ O ₁₀	395.0978	3.2-5.1	8.1-12.9	[caffeoyl + quinic acid + propanedioic acid groups - COO] ⁻
11	367.1057	367.1076	367.1042	367.1028	C ₁₇ H ₁₉ O ₉	367.1029	-0.1-4.7	-0.3-12.8	[sinapoyl + glucosyl groups] ⁻ for 1-3; [Caffeoyl + quinic acid + CH ₃ groups] ⁻ for 4
12	353.0905	353.0924	353.0887		C ₁₆ H ₁₇ O ₉	353.0873	1.4-5.1	3.9-14.4	[caffeoyl + quinic acid groups] ⁻
13	335.0749	335.0773	335.0819	335.0781	C ₁₆ H ₁₅ O ₈	335.0767	-1.8-5.2	-5.4-15.5	[caffeoyl + quinic acid groups - H ₂ O] ⁻
14	233.0633	233.0658			C ₉ H ₁₃ O ₇	233.0661	-2.8 to -0.3	-12.0 to -1.3	[quinic acid + propanedioic acid groups - COO - H] ⁻
15	223.0586	223.0602	223.0591	223.0563	C ₁₁ H ₁₁ O ₅	223.0606	-4.3 to -0.4	-19.3 to -1.8	[sinapic acid group - H] ⁻
16	191.0517	191.0537	191.0550	191.0546	C ₇ H ₁₁ O ₆	191.0556	-3.9 to -0.6	-20.4 to -3.1	[quinic acid group - H] ⁻
17	179.0313	179.0338	179.0335	179.0335	C ₉ H ₇ O ₇	179.0344	-3.1 to -0.6	-17.3 to -3.4	[caffeic acid group - H] ⁻

(1H, d, *J* = 15.9 Hz, H-8') with H-H COSY cross peak H-7'/H-8' and the HMBC correlations H-7', H-8'/C-9' (δ 168.9) were indicative of a sinapoyl group. This moiety was further confirmed by the HMBC correlations H-3'a (H-5'a)/C-3' (C-5', δ 149.7), H-2' (H-6')/C-4' (δ 139.9), H-7'/C-2' (C-6', δ 107.1) and H-8'/C-1' (δ 126.8) (Figure 2).

A quinic acid moiety was indicated by ¹H NMR resonances of three oxymethine protons at δ 5.22 (1H, dd, *J* = 13.8, 6.2 Hz, H-5''), 5.28 (1H, dd, *J* = 5.8, 3.6 Hz, H-3''), and 3.87 (1H, dd, *J* = 7.9, 3.6 Hz, H-4''), together with two pairs of sp³ methylene protons at δ 2.04 (1H, m, H-2''_{eq}), 2.21 (1H, m, H-2''_{ax}), and 2.02 (1H, m, H-6''_{ax})/2.05 (1H, m, H-6''_{eq}) as shown in Table 1. By inspection of the ¹³C NMR and DEPT spectra, these resonances were in agreement with three oxymethine resonances at δ 74.1 (C-3''), 72.2 (C-5''), 70.9 (C-4'') and two sp³ methylenes at δ 36.1 (C-2'') and 38.0 (C-6''). Their assignments were determined from HSQC data. Moreover, there were an oxygenated quaternary carbon at δ 76.5 (C-1'') and a carboxyl resonance at δ 177.5 (C-7'') in the ¹³C NMR spectrum, which are also characteristic of quinic acid. The assignments for the quinic acid nucleus were confirmed by analysis of the H-H COSY cross peaks H-2''_{ax}/H-3'', H-3''/H-4'', H-4''/H-5'' and H-5''/H-6 and HMBC correlation H-2''_{ax}/C-7'' (Figure 2). The deshielded resonances of two oxymethine protons in the quinic acid nucleus at δ 5.28 (H-3'') and 5.22 (H-5'') implied acylation of the hydroxyl groups at these positions as reported for other natural quinic acid derivatives (15, 16).

The chemical shifts of the six carbons at δ 103.4 (C-1'''), 74.9 (C-2'''), 77.6 (C-3'''), 72.1 (C-4'''), 75.9 (C-5'''), and 64.7 (C-6''') in the ¹³C NMR spectrum indicated a 1''',6'''-disubstituted hexose moiety. Acid hydrolysis of 1 with 2 M HCl afforded the component β -D-glucose, identified by HPLC-TOF-MS analysis and coelution with an authentic β -D-glucose standard (*t*_R, 6.53 min). The absolute configuration of the sugar residue was assumed to be D (dextro) based on the usual configuration of naturally occurring monosaccharides. An NMR coupling constant of 8.7 Hz for the anomeric protons indicated that the anomeric carbon configuration is β for the D-glucopyranosyl moiety. Linkages of D-glucose within the molecular structure were established by an HMBC experiment. The H-6''' glucose

proton at δ 4.30 (1H, dd, *J* = 12.04, 7.60 Hz, H-6''') correlated with the carbonyl carbon signal δ 168.9 (C-9') of the sinapoyl group, and the signal of the anomeric proton at δ 4.76 (1H, d, *J* = 8.70 Hz, H-1'') showed a ¹H-¹³C long-range correlation with a signal of the caffeoyl moiety at δ 148.6 (C-4), indicating the presence of caffeoyl and sinapoyl moieties at the C-1''' and 6''' positions of glucose, respectively (Figure 2).

All remaining signals, including δ 168.6 (C-1'''), 50.2 (C-2'''), and 171.0 (C-3''') in the ¹³C NMR spectrum and δ 3.22 (2H, s, H-2''') in the ¹H NMR spectrum, were attributed to a propanedioic acid (malonyl) group. The HMBC correlation between H-3''' and C-1''' demonstrated the propanedioic acid group to be attached to C-3''' of the quinic acid moiety.

The HR-ESI-MS fragmentation analysis data for 1 verified the structure assigned by NMR analyses. When the aperture 1 voltage of the MS detector was set at 60 V, TOF/TOF MS/MS yielded the fragments *m/z* 763.2096 [C₃₅H₃₉O₁₉, (M - H) - COO]⁻, 721.1990 [C₃₃H₃₇O₁₈, (M - H) - C₃H₂O₃ (propanedioic acid)]⁻, 547.1479 [C₂₆H₂₇O₁₃, (M - H) - C₃H₂O₃ (propanedioic acid) - C₇H₁₀O₅ (quinic acid)]⁻, 515.1454 [C₂₂H₂₇O₁₄, (M - H) - C₃H₂O₃ (propanedioic acid) - C₁₁H₁₁O₄ (sinapoyl group) + H]⁻, 367.1057 [C₁₇H₁₉O₉, (M - H) - C₃H₂O₃ (propanedioic acid) - C₇H₁₀O₆ (quinic acid) - C₉H₈O₃ (caffeoyl group)]⁻, 353.0905 [C₁₆H₁₇O₉, (M - H) - C₃H₂O₃ (propanedioic acid) - C₁₁H₁₁O₄ (sinapoyl group) - C₆H₉O₅ (glucosyl group)]⁻, 335.0749 [C₁₆H₁₅O₈, (M - H) - C₃H₂O₃ (propanedioic acid) - C₁₁H₁₁O₄ (sinapoyl group) - C₆H₉O₅ (glucosyl group) - H₂O]⁻, 233.0633 [C₉H₁₃O₇, C₃H₂O₃ (propanedioic acid) + C₇H₁₁O₆ (quinic acid) - CO₂ - H]⁻, 223.0586 [C₁₁H₁₁O₅, C₁₁H₁₂O₅ (sinapic acid) - H]⁻, 191.0517 [C₇H₁₁O₆, C₇H₁₂O₆ (quinic acid) - H]⁻ and 179.0313 [C₉H₇O₄, C₇H₁₂O₆ (caffeic acid) - H]⁻ (Table 2), which provided further proof of the attachment(s) of each subgroup in the structure. Thus, the structure of 1 was determined to be 1 β ,4 β -dihydroxy-3 β -carboxyacetoxo-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl]oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic acid (IUPAC numbering).

For compound 2 (Figure 1), the HR-ESI-MS molecular ion [M - H]⁻ gave the molecular formula C₃₆H₄₀O₂₁, which is isomeric to 1. The UV absorbance spectrum of 2 showed maxima at 321

and 221 nm very similar to those exhibited by **1**. On the basis of data from ^1H and ^{13}C NMR, H-HCOSY, HSQC, HMBC, and acid hydrolysis experiments, the structure of **2** was determined to be also composed of a caffeoyl, a sinapoyl, and a glucosyl group plus a quinic acid and a propanedioic acid (malonyl) moiety. The ^1H and ^{13}C NMR signals of **2** (Table 1) were nearly superimposable with those of **1**, except for chemical shifts of the H-3'' and H-4'' signals from quinic acid. The signals δ 4.24 (1H, dd, $J = 6.1, 3.3$ Hz, H-3'') and δ 4.99 (1H, dd, $J = 8.9, 3.1$ Hz, H-4'') in **2**, compared with δ 5.28 (1H, dd, $J = 5.8, 3.6$ Hz, H-3'') and δ 3.87 (1H, dd, $J = 7.9, 3.6$ Hz, H-4'') in **1**, indicated acylation at C-4'' rather than at C-3'' as in **1** (Table 1). The HMBC correlation between H-4'' and C-1''' showed that the propanedioic acid group is linked to C-4'' in **2**. When the aperture 1 voltage of the MS detector was set at 60 V, the fragmental cleavage profile from the HR-ESI-MS spectrum of **2** was closely similar to that of **1** (Table 2). This provided further evidence that these two compounds are isomers with the same skeleton. Thus, the structure of **2** was determined to be 1 β ,3 β -dihydroxy-4 β -carboxyacetoxo-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic acid.

For compound **3** (Figure 1), the HR-ESI-MS molecular ion $[\text{M} - \text{H}]^-$ indicated the molecular formula $\text{C}_{33}\text{H}_{37}\text{O}_{18}$. The UV absorbance spectrum of **3** showed maxima at 320 and 221 nm.

Similarity of the NMR and UV spectroscopic data for **3** with those for **1** and **2** (Table 1) indicated the same skeleton except for loss of the propanedioic acid group linked with quinic acid. Comparing TOF/MS data obtained under identical conditions, the fragment ions from **3** are similar to those from **1** and **2**, except that m/z 721.2002, 367.1042, and 353.0887 are much more abundant, and the ions m/z 233.0633, 763.2096, 807.1953 (from **1**) and 233.0658, 763.2093, 807.1957 (from **2**) are absent (Table 2). In the mass spectra of **1** and **2**, m/z 233.0633 and 233.0658 are ions representative of the *O*-linked quinic acid plus propanedioic acid moieties after characteristic loss of a COO group (17, 18). Thus, it can be concluded that the structural difference between **3** and the isomeric **1** and **2** is replacement of the propanedioic acid (malonyl) moiety *O*-linked at C3 or C4 of quinic acid with a free hydroxyl group (Figure 1). Accordingly, the structure of **3** was determined to be 1 β ,3 β ,4 β -trihydroxy-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylic acid by the corresponding NMR and HR-ESI-MS fragmental analysis experiments.

For compound **4** (Figure 1), the HR-ESI-MS molecular ion $[\text{M} - \text{H}]^-$ indicated the molecular formula $\text{C}_{34}\text{H}_{39}\text{O}_{18}$. The UV absorbance spectrum of **4** showed maxima at 320 and 219 nm. Comparing the ^1H NMR spectrum of **4** with that of **3**, the only clear difference is a 3H singlet at δ 3.62 (3H, s, H-8''), which suggested that **4** is a methylation product of **3** (Table 1). The HMBC correlation H-8''/C-7'' indicated that the carboxyl group of quinic acid in **4** is methyl-esterified (Figure 2). Further proof was evident in the HR-ESI-MS fragmental analysis data (Table 2). When the aperture 1 voltage of the TOF detector was set as 50 V, the most intense ion in the spectrum of **4** was m/z 367.1028, with no peak at m/z 353. By contrast, the ions m/z 353.0905, 353.0924, and 353.0887, representing a caffeoylquinic acid group, were predominant in **1**, **2**, and **3**, respectively. The mass spectra of **1**, **2**, and **3** also included major peaks at m/z 367.1057, 367.1076, and 367.1042, respectively, but these fragment ions represented sinapoylglucose minus a water molecule, whereas m/z 367.1028 in **4** is attributed to a methyl caffeoylquinic acid group. Another diagnostic fragment ion from **4** is m/z 529.1609, 14 Da higher than m/z 515.1454, 515.1429, and 515.1475 from **1**, **2**, and **3**, respectively. The m/z 515 ion fragments

in mass spectra of **1–3** represent a conjugate of glucosyl, caffeoyl, and quinic acid groups, and the unique presence of a peak at m/z 529.1609 in the spectrum of **4** indicates methylation of this conjugate. Thus, the structure of **4** was determined to be methyl 1 β ,3 β ,4 β -trihydroxy-5 α -[[3-[4-[1 β -(6-*O*-(*E*)-sinapoyl- β -D-glucopyranosyl)oxy]-3-hydroxyphenyl]-(*E*)-1-oxo-2-propenyl]oxy]cyclohexanecarboxylate.

Structural elements of the four new hydroxycinnamic acid conjugates isolated from fruit tissues of *S. viarum*, such as malonation and the specific linkages between caffeoyl, glucosyl, and sinapoyl moieties, are common in acylated and glycosylated phenylpropanoids, but have not previously been reported in complex derivatives of 5-*O*-(*E*)-caffeoylquinic acid. Malonyl-CoA acyltransferases catalyzing 6-*O*-malonation of the glucose moiety in flavonoid glucosides have been well characterized, and in some cases the genes have been cloned (19, 20). A 6-*O*-sinapoylglucose group has been reported in 4-*O*- β -D linkage with vanillic acid in fruit of *Gardenia jasminoides* (21), as well as in the structures of several complex phenolic glycosides from *Digitalis lantana* (22), while 4-*O*- β -D-glucopyranosylcaffeic acid has been identified in solanaceous species (23) and in *Chrysanthemum* (24). The 4-*O*-malonyl isomer of 5-*O*-(*E*)-caffeoylquinic acid was isolated from leaves of *Albizia julibrissin* (17), and various isomers of malonated as well as glucosylated mono-, di-, and/or tricaffeoylquinic acids were tentatively identified by ESI-MS in extracts of the medicinal herb *Erigeron breviscapus* (18). Finally, methyl dicafeoylquinic acid isomers have been reported in sweet potato leaves (25) and in propolis, a plant-derived substance gathered by bees (26). Additionally, isomers of methyl and ethyl 3-*O*- or 4-*O*-sinapoyl 5-*O*-(*E*)-caffeoylquinic acid were isolated from fruit of *Gardenia jasminoides* (21). Each of these sources of methyl or ethyl caffeoylquinic acids is used in traditional medicines, and has potent antioxidant and biological activities.

Solanum viarum, the tropical soda apple, is a member of the subgenus *Leptostemonum* or spiny solanums (27) native to South America and currently considered an invasive species in the southeastern United States (28). Since plants of this species were grown from seed supplied as USDA-GRIN accession PI 319855, designated as the African species *S. anguivi*, we can only speculate that fruit of invasive *S. viarum* were accidentally harvested at the USDA, ARS, Plant Genetic Resources Conservation Unit in Griffin, GA. This may explain our prior finding (7) that the complex hydroxycinnamic acid conjugates **1–4** identified in this investigation were present only in fruit of accession PI 319855, because *S. viarum* is taxonomically relatively distant from the other 114 accessions in the USDA eggplant core collection subset. Nevertheless, *S. viarum* can be hybridized with the cultivated species *S. melongena*, and one recent study explored the biochemical basis of increased shoot and fruit borer resistance (acquired from the *S. viarum* parent) in the progeny of such interspecific hybrids (29). It is noteworthy that increased total phenolics were better correlated with resistance to fruit borer than elevated levels of the steroidal glycoalkaloid solasodine. Fruit of *S. viarum* are a rich source of solasodine, a valued starting material for the synthesis of cortisone and other steroid drugs, and are cultivated for extraction of this compound (30). Perhaps because of this focus on fruit alkaloids, it appears that the content and composition of phenylpropanoids have not previously been investigated. Future studies of the antioxidant and biological activities of the newly discovered complex 5-*O*-(*E*)-caffeoylquinic acid derivatives **1–4** are planned.

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Supporting Information Available: Additional figures from HR-ESI-MS/MS, HR-ESI-MS, ^1H NMR, ^{13}C NMR, HSQC, and HMBC studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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