# *Notes*

## Isolation and Characterization of Miscellaneous Secondary Metabolites of *Deprea subtriflora*
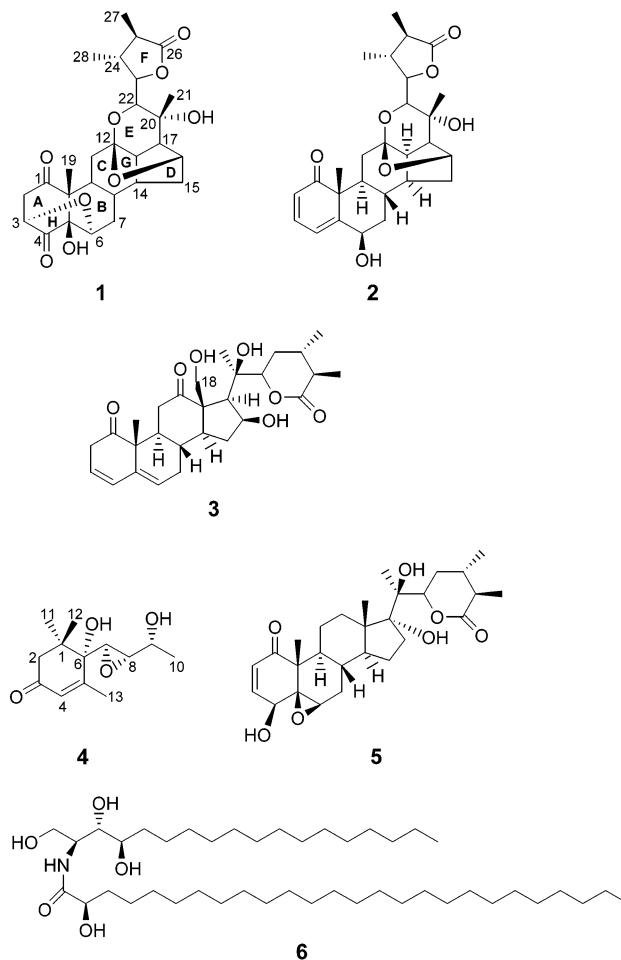
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Two new C-18 norwithanolides based on a $C_{27}$ skeleton, subtrifloralactones K (**1**) and L (**2**), a new C-18 oxygenated withanolide, 13$\beta$-hydroxymethylsubtrifloralactone E (**3**), and a new $\alpha$-ionone derivative, (+)-7$\alpha$,8$\alpha$-epoxyblumenol B (**4**), along with five known compounds, philadelphicalactone A (**5**), (2*S*,3*S*,4*R*)-2-[(2*R*)-2'-hydroxytetracosanoylamino]-1,3,4-octadecanetriol (**6**), *trans*-*N*-feruloyltyramine, *cis*-*N*-feruloyltyramine, and (*S*)-coriolic acid, were isolated from additional active fractions of the chloroform-soluble extract of *Deprea subtriflora*, using a quinone reductase (QR) induction assay as a monitor. The structures of compounds **1**−**4** were characterized by spectroscopic data interpretation. The potential cancer chemopreventive activities of all isolates in terms of their ability to induce QR activity with cultured Hepa 1c1c7 mouse hepatoma cells were evaluated.

Induction of Phase II drug-metabolizing enzymes such as quinone reductase is considered an effective and sufficient strategy for achieving protection against the toxic and neoplastic effects of many carcinogens.[1,2] During our collaborative research project to discover new cancer chemopreventive agents from plants, several withanolides isolated from *Physalis philadelphica* Lam. (tomatillo) (Solanaceae) have been found to be significant inducers of quinone reductase (QR).[3,4] Structural requirements for inducing activity and cytotoxicity in the cell-based QR assay have been investigated for several subclasses of withanolides isolated from a number of plants of the Solanaceae.[5] Moreover, 10 highly oxygenated novel C-18 norwithanolides based on a new type of $C_{27}$ skeleton, subtrifloralactones A−J, were isolated from the two most active fractions (F02 and F03) of a CHCl₃-soluble extract of the whole plants of *Deprea subtriflora* (Ruiz & Pavon) D'Arcy (Solanaceae).[6] Some of these new withanolides from *D. subtriflora* showed significant potential to induce QR.[6] In the present work, further purification of the two remaining active fractions (F04 and F05) of the CHCl₃-partitioned extract of *D. subtriflora*[6,7] has led to the isolation of four new compounds, namely, two C-18 norwithanolides, subtrifloralactones K (**1**) and L (**2**), a C-18 oxygenated withanolide, 13$\beta$-hydroxymethylsubtrifloralactone E (**3**), and a new $\alpha$-ionone derivative, (+)-7$\alpha$,8$\alpha$-epoxyblumenol B (**4**), as well as five known compounds, philadelphicalactone A (**5**),[4] (2*S*,3*S*,4*R*)-2-[(2*R*)-2'-hydroxytetracosanoylamino]-1,3,4-octadecanetriol (**6**),[4] *trans*-*N*-feruloyltyramine,[8,9] *cis*-*N*-feruloyltyramine,[8] and (*S*)-coriolic acid.[10,11] In this note, we wish to report the structure elucidation of compounds **1**−**4** and the bioassay evaluation results of all isolates in the QR induction assay.



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The HRTOFMS of subtrifloralactone K (**1**) provided a molecular formula of $C_{27}H_{34}O_9$ (*m/z* 503.2267 [M + H]⁺,

**Table 1.** NMR Spectral Data for Compounds **1**–**3** in CDCl$_3$ [a]

| position | 1 $\delta_H$ | 1 $\delta_C$ | 2 $\delta_H$ | 2 $\delta_C$ | 3 $\delta_H$ | 3 $\delta_C$ |
|---|---|---|---|---|---|---|
| 1 | | 208.5 s | | 205.3 s | | 208.9 s |
| 2 | 3.08, dd (20.0, 4.3) | 39.9 t | 6.01, d (9.7) | 126.5 d | 3.31, br d (20.2) | 39.5 t |
| | 2.49, dd (20.0, 1.3) | | | | 2.75–2.81, m | |
| 3 | 4.22–4.25, m | 74.8 d | 6.94, dd (9.7, 5.9) | 139.8 d | 5.68, dt (9.7, 3.8) | 122.4 d |
| 4 | | 208.1 s | 6.15, d (5.9) | 118.6 d | 6.09, br d (9.7) | 128.8 d |
| 5 | | 77.7 s | | 156.9 s | | 140.8 s |
| 6 | 3.99, br d (2.4) | 72.6 d | 4.52, br t (2.6) | 73.4 d | 5.64, br d (3.6) | 125.8 d |
| 7 | 2.06–2.17, m | 34.3 t | 2.05–2.17, m | 42.8 t | 2.14–2.31, m; 1.60–1.66, m | 30.8 t |
| | 1.72, br t (12.3) | | 1.37, m | | | |
| 8 | 1.83–1.91, m | 36.9 d | 1.90–1.95, m | 35.5 d | 2.07, m | 32.0 d |
| 9 | 2.06–2.17, m | 39.4 d | 1.71–1.77, m | 42.2 d | 2.14–2.31, m | 45.6 d |
| 10 | | 51.5 s | | 52.7 s | | 52.7 s |
| 11 | 2.31, t (13.8); 1.83–1.91, m | 30.5 t | 2.36, dd (15.0, 5.8); 2.05–2.17, m | 32.3 t | 2.85, t (12.4); 2.75–2.81, m | 38.6 t |
| 12 | | 104.8 s | | 104.8 s | | 211.9 s |
| 13 | 2.56, dd (5.0, 1.4) | 39.6 d | 2.43, dd (5.3, 1.3) | 39.2 d | | 64.7 s |
| 14 | 1.58, m | 37.0 d | 1.71–1.77, m | 37.3 d | 1.26, m[b] | 55.8 d |
| 15 | 1.83–1.91, m; 1.48, m | 41.6 t | 1.90–1.95, m | 41.7 t | 2.40, dt (13.4, 8.0) | 37.6 t |
| | | | 1.59, br d (12.5) | | 1.57, dd (13.4, 4.2) | |
| 16 | 4.30, br s | 79.1 d | 4.33, br s | 79.0 d | 4.71–4.74, m | 72.9 d |
| 17 | 2.04, br s | 58.8 d | 2.05, br s | 58.9 d | 2.14–2.31, m | 51.7 d |
| 18 | | | | | 4.34, m | 62.6 t |
| 19 | 0.96, s | 17.1 q | 1.43, s | 20.5 q | 1.50, s | 20.0 q |
| 20 | | 69.8 s | | 69.7 s | | 78.4 s |
| 21 | 1.40, s | 26.1 q | 1.40, s | 26.1 q | 1.43, s | 23.8 q |
| 22 | 3.74, d (8.4) | 78.5 d | 3.74, d (8.3) | 78.4 d | 4.71–4.74, m | 81.4 d |
| 23 | 4.22–4.25, m | 81.4 d | 4.23, t (8.3) | 81.5 d | 2.14–2.31, m; 1.60–1.66, m | 31.1 t |
| 24 | 2.06–2.17, m | 43.4 d | 2.05–2.17, m | 43.4 d | 1.60–1.66, m | 30.9 d |
| 25 | 2.06–2.17, m | 42.2 d | 2.05–2.17, m | 42.4 d | 2.14–2.31, m | 40.8 d |
| 26 | | 178.7 s | | 178.9 s | | 175.7 s |
| 27 | 1.23, d (6.8) | 13.4 q | 1.24, d (6.0) | 13.4 q | 1.27, d (6.7) | 14.3 q |
| 28 | 1.20, d (6.2) | 17.7 q | 1.25, d (6.7) | 17.9 q | 1.17, d (6.8) | 20.0 q |
| OH-5 | 3.64, s | | | | | |
| OH-16 | | | | | 4.20, d (5.1) | |
| OH-18 | | | | | 4.09, t (6.5) | |
| OH-20 | | | | | 4.84, s | |

[a] Spectra taken at 500 and 125 MHz for proton and carbon, respectively; chemical shift values were assigned on the basis of the observed 2D NMR correlations and are presented in ppm with TMS as the internal standard; $J$ values given in Hz in parentheses. [b] Partly overlapped with the signal of CH$_3$-27.
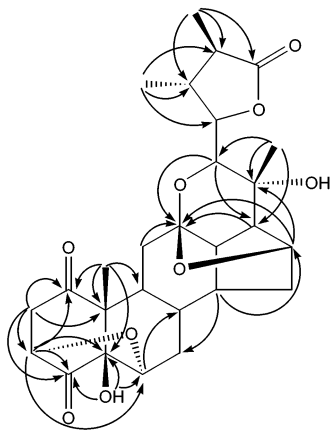


**Figure 1.** Selected HMBC correlations of subtrifloralactone K (**1**) (H → C).

calcd for C$_{27}$H$_{35}$O$_9$ $m/z$ 503.2281), indicating 11 degrees of unsaturation. Both the $^1$H and $^{13}$C NMR spectral data (Table 1) of compound **1** were closely comparable to those of subtrifloralactones A–G, which have been previously isolated from the title plant.[6] In the same manner as described earlier for subtrifloralactones A and B,[6] the $^{13}$C NMR spectrum of **1** displayed a diagnostic chemical shift for a doubly oxygenated quaternary carbon in a downfield region ($\delta_C$ 104.8, C-12). This 1D NMR observation, in combination with the 2D HMBC correlations (Figure 1) from H-16, H-22, H-9, H$_2$-11, H-13, H-14, and H-17 to C-12, suggested the presence of a ketal group in the molecule of

**1**, which could be located at C-12. The side chain lactone ring F and rings C, D, E, and G of compound **1** were assigned as being the same as those of subtrifloralactones A and B,[6] as a result of detailed comparison of their 1D and 2D NMR spectral data. The differences evident between compound **1** and subtrifloralactones A and B were apparent in their A and B rings. After assignment of the signals of rings C–G based on the 2D NMR correlations of **1**, the remaining oxygenated carbons were found to comprise two nonconjugated ketone signals at $\delta_C$ 208.5 (C-1) and 208.1 (C-4), two methine signals at $\delta_C$ 74.8 (C-3) and 72.6 (C-6), and a quaternary carbon signal at $\delta_C$ 77.7 (C-5). On the basis of the determined molecular formula and structural analysis described above, the presence of an oxygen ether bridge among the three oxygenated methine and quaternary carbons of rings A and B could be deduced for **1**. There was no correlation from the proton signal at $\delta_H$ 3.64 (OH-5) to any carbons in the HMQC spectrum of **1**, suggesting a hydroxyl proton resonance. In the HMBC spectrum, both the hydroxyl proton and CH$_3$-19 signals were correlated to quaternary carbons at $\delta_C$ 77.7 (C-5) and 51.5 (C-10). These correlations indicated that the hydroxyl group present in ring A and/or B was located at C-5. On further inspection of the HMBC spectrum of **1**, correlations from $\delta_H$ 3.64 (OH-5) to $\delta_C$ 208.1 (C-4) and 72.6 (C-6), from $\delta_H$ 0.96 (CH$_3$-19) to $\delta_C$ 208.5 (C-1) and 39.4 (C-9), and from $\delta_H$ 3.08 (H-2a) and 2.49 (H-2b) to $\delta_C$ 208.1 (C-4), 74.8 (C-3), 208.5 (C-1), and 51.5 (C-10) were observed. These correlations enabled the two oxygenated methines to be located at C-3 and C-6, and two nonconjugated ketone

groups located at C-1 and C-4. Furthermore, the presence of an oxygen ether bridge from C-3 to C-6 could be inferred, and it was confirmed by the observed weak but diagnostic HMBC correlation from H-3 to C-6. The $\beta$-orientation of OH-5 was determined by the NOESY correlation between the signals of $CH_3$-19 and OH-5. The relative configuration of the C-3/C-6 oxygen ether functionality in the molecule of **1** was assigned on the basis of the comparison of the splitting patterns and coupling constants of $H_2$-2, H-3, and H-6 of **1** with those of previously reported analogues.[12,13] The ^{1}H and ^{13}C NMR data of **1** (subtrifloralactone K) were assigned on the basis of the interpretation of its $^1H-^1H$ COSY, HMQC, HMBC, and NOESY spectra.

A molecular formula of $C_{27}H_{34}O_7$ was determined for subtrifloralactone L (**2**) from its HRTOFMS (obtained at $m/z$ 471.2375 [M + H]$^+$, calcd for $C_{27}H_{35}O_7$, 471.2383). The ^{1}H and ^{13}C NMR spectral data (Table 1) of **2** were closely comparable to those of **1** and permitted the assignment of the rings C−G in subtrifloralactone L (**2**) in the same manner as **1**. The ^{13}C NMR spectrum of **2** displayed signals suggestive of an $\alpha,\beta$-unsaturated ketone at $\delta_C$ 205.3 (s, C-1) and two double bonds at $\delta_C$ 126.5 (d, C-2), 139.8 (d, C-3), 118.6 (d, C-4), and 156.9 (s, C-5). The proton signals of $\delta_H$ 6.01 (1H, d, $J = 9.7$ Hz, H-2), 6.94 (1H, dd, $J = 9.7, 5.9$ Hz, H-3), and 6.15 (1H, d, $J = 5.9$ Hz, H-4) were assigned to C-2, C-3, and C-4, respectively, on the basis of the observed HMQC correlations. The coupling constants of these three olefinic protons suggested the two double bonds in the molecule of **2** were conjugated. This was confirmed by the correlations from H-3 to both H-2 and H-4 obtained in the $^1H-^1H$ COSY spectrum. The positions of the double bonds were determined at C-2/C-3 and C-4/C-5 from the HMBC correlations from both H-2 and H-3 to C-1. In the ^{13}C and DEPT NMR spectra of **2**, another oxygenated methine was shown at $\delta_C$ 73.4 (d, C-6) in addition to C-16, C-22, and C-23, and the observed HMBC correlations from H-4 to C-6 and from H-6 to C-4, C-5, and C-10 suggested this carbon to be located at C-6. Generally, the H-6$\alpha$ ^{1}H NMR signal is observed as a broad singlet or a doublet of doublets with a very small coupling constant ($\leq 3.0$ Hz) when a withanolide possesses a 5$\beta$,6$\beta$-epoxy or a 6$\beta$-hydroxyl group.[4,14−20] However, H-6$\beta$ appears as a doublet with a larger coupling constant ($\geq 4$ Hz) for withanolides containing a 5$\alpha$,6$\alpha$-epoxy or a 6$\alpha$-hydroxyl group.[17−20] In compound **2**, the signal for H-6 was obtained as a broad triplet in both CDCl$_3$ (2.6 Hz) (Table 1) and pyridine-$d_5$ (2.4 Hz) (Table S1). On the other hand, in comparison with subtrifloralactones A−C,[4] a clear pyridine-induced chemical shift difference (−0.35 ppm) of $CH_3$-19 was evident (Table S1) for compound **2**. Accordingly, OH-6 should have a $\beta$-orientation in subtrifloralactone L (**2**). This was confirmed by comparison of the very close chemical shifts of H-6 and C-6 obtained for **2** to those of jaborosalactol N,[21] a withanolide possessing the same A and B rings as in **2**.

In contrast to compounds **1** and **2**, the ^{13}C NMR spectrum of compound **3** displayed 28 carbon signals, and a molecular formula of $C_{28}H_{38}O_7$ was determined for **3** by HRTOFMS ($m/z$ 487.2715 [M + H]$^+$). In the ^{13}C NMR spectrum of **3**, an oxygenated methylene was observed at $\delta_C$ 62.6 (t, C-18), which was correlated with the proton signals at $\delta_H$ 4.34 (2H, m, $H_2$-18) in the HMQC spectrum. A clear $^1H-^1H$ COSY cross-peak was observed between the signals at $\delta_H$ 4.34 ($H_2$-18) and 4.09 (OH-18). This observation, combined with the fact that the proton signal at $\delta_H$ 4.09 (OH-18) was not correlated with any carbon in the HMQC spectrum, indicated that the signal of $\delta_H$ 4.09 (OH-18) belonged to the hydroxyl group of an oxygenated methylene. The other

^{1}H and ^{13}C NMR spectral data of **3** were very similar to those of subtrifloralactone E.[6] In the HMBC spectrum of **3**, the correlations from $\delta_H$ 4.34 ($H_2$-18) to $\delta_C$ 211.9 (s, C-12), 64.7 (s, C-13), 55.8 (d, C-14), and 51.7 (d, C-17) and from $\delta_H$ 4.09 (OH-18) to $\delta_C$ 62.6 (t, C-18) and 64.7 (s, C-13) were observed. These correlations verified the hydroxyl methylene in the molecule of **3** to be located at C-13. A $\beta$-orientation of this hydroxyl methylene was determined from the strong 2D NOESY correlation between $\delta_H$ 4.34 ($H_2$-18) and $\delta_H$ 2.07 (H-8). Accordingly, compound **3** was assigned as 13$\beta$-hydroxymethylsubtrifloralactone E. It is worthy of note that when they were observed, only a very weak signal appeared for C-17 in the previously structurally assigned C-12 keto $C_{27}$ withanolides, subtrifloralactones D−G.[6] In contrast, however, the C-17 signal was clearly observed at $\delta_C$ 51.7 (d, C-17) for 13$\beta$-hydroxymethylsubtrifloralactone E (**3**).

The HRTOFMS spectral data of compound **4** were used to establish a molecular formula of $C_{13}H_{20}O_4$, indicating four degrees of unsaturation. The ^{1}H, ^{13}C, and DEPT NMR spectral data of **4** suggested the presence of an $\alpha,\beta$-unsaturated ketone unit, an oxygenated quaternary carbon and methine, an epoxy group, an aliphatic methylene and quaternary carbon, and four methyl groups. The HMBC correlations from $CH_3$-11 to $CH_3$-12, from $CH_3$-12 to $CH_3$-11, and from both $CH_3$-11 and $CH_3$-12 to the aliphatic methylene (C-2) and quaternary carbon (C-1), as well as the oxygenated quaternary carbon (C-6), indicated not only that $CH_3$-11 and $CH_3$-12 were attached to the aliphatic quaternary carbon (C-1) but also the aliphatic methylene (C-2) and the oxygenated quaternary carbon must be connected with C-1. Further inspection of the HMBC spectrum of compound **4** revealed correlations from $CH_3$-13 to the double bond carbons (C-4 and C-5) and the oxygenated carbon and from $H_2$-2 to the unsaturated ketone (C-3) and olefinic methine (C-4). All of the above-mentioned HMBC correlations suggested the presence of a 6-hydroxy-1,1,5-trimethyl-4-cyclohexen-3-one structural unit in the molecule and that therefore compound **4** is an $\alpha$-ionone derivative.[22,23] The locations of the remaining four carbons (an epoxy, an oxygenated methine, and a methyl group) were assigned on the basis of the observed HMBC correlations from $\delta_H$ 3.76 (H-7) to $\delta_C$ 41.8 (C-1), 161.2 (C-5), 74.9 (C-6), 56.9 (C-8), and 64.1 (C-9) and were confirmed by the $^1H-^1H$ COSY correlations from H-7 to H-8, from H-8 to H-7 and H-9, and from H-9 to H-8 and $CH_3$-10. In a 2D NOESY spectrum of **4**, the correlations from H-7 to $CH_3$-12, H-8, H-2$\beta$, and $CH_3$-10, from $CH_3$-11 to H-2$\alpha$ and OH-6, and from H-8 to H-7, $CH_3$-13, and $CH_3$-10 were apparent. The relative configuration of compound **4** was determined as shown after a consideration of these NOESY correlations and the coupling constants of H-7 and H-8. The absolute stereochemistry of this compound was not established due to the limited amount of compound obtained. Compound **4** was therefore assigned as 7$\alpha$,8$\alpha$-epoxyblumenol B.

The potential to induce quinone reductase of all isolates obtained in the present study was evaluated, and the data are shown in Table S2. Among the four new compounds (**1**−**4**), only subtrifloralactone K (**1**) was found to significantly induce quinone reductase (QR), with a CD value of 0.36 $\mu$M, an IC$_{50}$ value of 4.8 $\mu$M, and a chemopreventive index (IC$_{50}$/CD) of 13.3. Compounds **2**−**4** were inactive in this assay. We have previously published biological test data for philadelphicalactone A (**5**) and the ceramide (2$S$,3$S$,4$R$)-2-[(2$R$)-2′-hydroxytetracosanoylamino]-1,3,4-octadecanetriol (**6**) in the QR assay, as constituents of the

leaves and stems of *Physalis philadelphica*.[4] Compounds **5** and **6** were the only known substances found to be active in the QR assay, with *trans-N*-feruloyltyramine, *cis-N*-feruloyltyramine, and (*S*)-coriolic acid all being inactive (CD >10 $\mu$M) (Table S2). Unlike previously investigated withanolides with induction activity in the QR assay,[4,6] compound **1** is atypical in possessing a 1,4-diketo unit and a C-3/C-6 oxygen ether bridge.

## Experimental Section

**General Experimental Procedures and Plant Material.** As described previously.[6]

**Evaluation of Quinone Reductase (QR) Inducing Ability of Isolates.** As described previously.[5,6]

**Extraction and Isolation.** The procedures used for the extraction, solvent partitioning, and initial chromatography of the CHCl$_3$-soluble extract of *D. subtriflora* were the same as described previously.[6] The CD ($\mu$g/mL) values of eight combined fractions (F01−F08) obtained from the CHCl$_3$-soluble extract were >10, <2.5, <2.5, 3.7, 4.6, >10, 17.1, and >10, respectively. Subtrifloralactones A−J were previously isolated from fractions F02 and F03.[6] The two remaining active fractions, F04 and F05, were selected for further detailed purification in the present study.

Fraction F04 (1.38 g), eluted with CHCl$_3$−MeOH (25:1), was chromatographed over a Si gel column (3.2 × 60 cm), eluted with *n*-hexanes−EtOAc (3:1 to 1:1), to give four subfractions (F0401−F0404). Compound **5** (178 mg) was obtained as a white amorphous solid from subfraction F0401 (*n*-hexanes−EtOAc, ~3:1). Subfraction F0402 (eluted with *n*-hexanes−EtOAc, 3:1) was purified by preparative TLC (Merck 60 Å Si gel, 20 × 20 cm, 500 $\mu$m), developed with *n*-hexanes−EtOAc−MeOH (15:15:1), to afford compound **4** (0.8 mg, $R_f = 0.42$). Subfraction F0403 (eluted with *n*-hexanes−EtOAc, 2:1) was subjected to purification over a Si gel column (2.0 × 25 cm), eluted with *n*-hexanes−EtOAc−MeOH (10:10:1), to yield compound **3** (5.2 mg).

Fraction F05 (1.70 g), eluted with CHCl$_3$−MeOH (20:1), when fractionated over a further Si gel column (2.8 × 55 cm), with *n*-hexanes−EtOAc−MeOH (30:10:1) as solvents, led to four subfractions (F0501−F0504) being obtained. The major subfraction, F0503 (710 mg), was again subjected to passage over a Si gel column (2.8 × 55 cm) and, on elution with CHCl$_3$−MeOH (25:1), gave three further subfractions (F050301−F050303). Subfraction F050301 (210 mg) was then separated over a Si gel column (2.8 × 55 cm), eluted with the solvent system CHCl$_3$−acetone (8:1), and afforded compounds **1** (3.2 mg) and **2** (14.5 mg) and semipure coriolic acid (38 mg), in order of polarity. This last-mentioned compound (19 mg, $R_f = 0.45$) was finally purified by preparative TLC (Merck 60 Si gel, 20 × 20 cm, 500 $\mu$m), developed with *n*-hexanes−EtOAc−MeOH (10:10:1). Subfraction F050302 (307 mg) was chromatographed over a further Si gel column (2.0 × 25 cm), eluted with CHCl$_3$−acetone (5:1), to afford *trans-N*-feruloyltyramine (207 mg) and *cis-N*-feruloyltyramine (12.0 mg). Compound **6** (15.5 mg) was obtained as a white amorphous powder from a CHCl$_3$−MeOH (~2:1) solution of subfraction F050303.

**Subtrifloralactone K (1):** $[\alpha]^{20}_D$ +40.0° (*c* 0.10, MeOH); UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 222 (3.17), 279 (2.71) nm; IR (film) $\nu_{max}$ 3455, 1765, 1734, 1592, 1454, 1380, 1314, 1098 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; HRTOFMS *m/z* 503.2267 [M + H]$^+$ (calcd for C$_{27}$H$_{35}$O$_9$, 503.2281); MS-MS (30 eV) *m/z* 503.1995 (8), 485.2436 (100), 467.2257 (85), 439.2224 (40), 411.2025 (20), 393.1881 (42), 343.1596 (18), 315.1394 (8), 141.0618 (15), 113.0734 (35).

**Subtrifloralactone L (2):** $[\alpha]^{20}_D$ +46.3° (*c* 0.16, MeOH); UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 206 (3.74), 250 (3.68), 255 (3.70), 360 (3.64) nm; IR (film) $\nu_{max}$ 3458, 1761, 1657, 1621, 1568, 1453, 1377, 1319, 1242, 1180 cm$^{-1}$; $^1$H and $^{13}$C NMR data in both CDCl$_3$ and pyridine-$d_5$, see Table 2; HRTOFMS *m/z* 471.2375 [M + H]$^+$ (calcd for C$_{27}$H$_{35}$O$_7$, 471.2383); MS-MS (20 eV) *m/z* 471.2573 (35), 453.2429 (100), 435.2389 (100), 417.2247 (70),

391.2079 (40), 361.2035 (32), 301.1621 (50), 283.1516 (49), 265.1377 (16), 227.1178 (15), 135.0920 (10), 113.0734 (17).

**18$\beta$-Hydroxymethylsubtrifloralactone E (3):** $[\alpha]^{20}_D$ +54.3° (*c* 0.20, MeOH); UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 232 (3.42) nm; IR (film) $\nu_{max}$ 3411, 1712, 1523, 1439, 1376, 1201, 1096 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; HRTOFMS *m/z* 487.2715 [M + H]$^+$ (calcd for C$_{28}$H$_{39}$O$_7$, 487.2696); MS-MS (20 eV) *m/z* 487.2867 (3), 469.2570 (8), 457.2748 (10), 451.2812 (30), 439.2757 (100), 421.2526 (59), 395.2464 (25), 365.2248 (8), 347.2240 (8), 309.2118 (7), 297.2017 (7).

**(+)-7$\alpha$,8$\alpha$-Epoxyblumenol B (4):** $[\alpha]^{20}_D$ +78° (*c* 0.03, MeOH); UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 235 (3.56) nm; IR (film) $\nu_{max}$ 3458, 1659, 1583, 1129 cm$^{-1}$; $^1$H NMR (CDCl$_3$, TMS, 500 MHz) $\delta$ 1.07 (3H, s, CH$_3$-11), 1.12 (3H, s, CH$_3$-12), 1.25 (3H, d, *J* = 6.6 Hz, CH$_3$-10), 1.98 (3H, d, *J* = 1.3 Hz, CH$_3$-13), 2.27 (1H, br s, OH-6), 2.35 (1H, dd, *J* = 17.8, 0.9 Hz, H-2$\alpha$), 2.62 (1H, br d, *J* = 17.8 Hz, H-2$\beta$), 3.17 (1H, dd, *J* = 2.7, 2.3 Hz, H-8), 3.34 (1H, d, *J* = 2.3 Hz, H-7), 4.08 (1H, m, H-9), 5.97 (1H, s, H-4); $^1$H NMR (pyridine-$d_5$, TMS, 500 MHz) $\delta$ 1.26 (3H, s, CH$_3$-11), 1.36 (3H, s, CH$_3$-12), 1.45 (3H, d, *J* = 6.4 Hz, CH$_3$-10), 2.21 (3H, d, *J* = 1.1 Hz, CH$_3$-13), 2.47 (1H, dd, *J* = 17.2, 0.9 Hz, H-2$\alpha$), 2.95 (1H, br d, *J* = 17.2 Hz, H-2$\beta$), 3.45 (1H, dd, *J* = 4.8, 2.0 Hz, H-8), 3.76 (1H, d, *J* = 1.8 Hz, H-7), 4.10 (1H, m, H-9), 6.11 (1H, s, H-4), 6.61 (1H, s, OH-6); $^{13}$C NMR (CDCl$_3$, TMS, 125 MHz) $\delta$ 18.8 (C-10, q), 19.5 (C-13, q), 23.3 (C-11, q), 24.0 (C-12, q), 41.8 (C-1, s), 49.2 (C-2, t), 54.2 (C-7, d), 56.9 (C-8, d), 64.1 (C-9, d), 74.9 (C-6, s), 128.5 (C-4, d), 161.2 (C-5, s), 197.0 (C-3, s); HRTOFMS *m/z* 263.1250 [M + Na]$^+$ (calcd for C$_{13}$H$_{20}$O$_4$Na, 263.1259); no fragmentations were observed for this compound by MS-MS, even at a collision energy of 50 eV.

**Philadelphicalactone A (5) and (2S,3S,4R)-2-[(2R)-2′-Hydroxytetracosanoylamino]-1,3,4-octadecanetriol (6).** These two compounds were obtained as a white amorphous solid (*n*-hexanes−EtOAc, ~3:1) and a powder (CHCl$_3$−MeOH, ~2:1), respectively; the physical and spectroscopic data (mp, $[\alpha]_D$, $^1$H NMR, $^{13}$C NMR, DEPT, 2D NMR, and MS) of **5** and **6** were identical to those of the same compounds previously isolated from *Physalis philadelphica*,[4] and their structures were confirmed by direct comparison with authentic samples.

***trans-N*-Feruloyltyramine:** colorless crystal (CHCl$_3$−MeOH, ~4:1), mp 138−140 °C; UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 219 (4.10), 293 (3.58), 320 (3.82) nm; $^1$H and $^{13}$C NMR spectral data, consistent with literature values.[9,10]

***cis-N*-Feruloyltyramine:** white amorphous powder (CHCl$_3$−MeOH, ~4:1), mp 128−132 °C; UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 220 (4.05), 294 (3.61), 319 (3.85) nm; $^1$H and $^{13}$C NMR spectral data, consistent with literature values.[9]

**(*S*)-Coriolic acid:** colorless oil, $[\alpha]^{20}_D$ +2.8° (*c* 0.20, CHCl$_3$) [lit.[11] +9.3°; lit.[12] +8.7°]; $^1$H and $^{13}$C NMR spectral data, consistent with published values.[12] TOFMS *m/z* 295 [M − H]$^-$; MS-MS (25 eV) *m/z* 295.1197 (100), 277.1168 (80), 195.0715 (80), 183.0708 (65), 179.0820 (15), 112.9951 (20).

**Supporting Information Available:** Tables of $^1$H and $^{13}$C NMR spectral data for **2** in both pyridine-$d_5$ and CDCl$_3$ and of the quinone reductase induction activity data of compounds **1**, **5**, and **6**. $^1$H, $^{13}$C, and DEPT135 NMR spectra for compounds **1−4** in CDCl$_3$; $^1$H, $^{13}$C, and DEPT135 NMR spectra for compound **2**; and $^1$H NMR spectrum for compound **4** in pyridine-$d_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(7) Part of the present study was presented at the 43rd Annual Meeting of the American Society of Pharmacognosy and Third Monroe Wall Symposium, New Brunswick, NJ, July 27−31, 2002, Abstract O-6. After our initial taxonomic identification, the species name for the plant material investigated was changed from *Solanum altissimum* to *Deprea subtriflora*. To prevent unnecessary confusion in the literature and consistent with ref 6, we are accordingly changing herein the trivial names of altissimumlactones K (**1**) and L (**2**) and 13$\beta$-hydroxymethylaltissimumlactone E (**3**) accorded earlier to subtrifloralactones K and L and 13$\beta$-hydroxymethylsubtrifloralactone E, respectively.

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