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Isolation and Characterization of Stelladerol, a New Antioxidant Naphthalene Glycoside, and Other Antioxidant Glycosides from Edible Daylily (*Hemerocallis*) Flowers

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Daylily (*Hemerocallis* spp.) flowers are utilized as an important ingredient in traditional Asian cuisine and are also valued for their reputed medicinal effects. In studies of the bioactive methanol and aqueous methanol extracts of lyophilized *Hemerocallis* cv. Stella de Oro flowers, kaempferol, quercetin, and isorhamnetin 3-*O*-glycosides (**1**−**9**), phenethyl β-D-glucopyranoside (**10**), orcinol β-D-glucopyranoside (**11**), phloretin 2′-*O*-β-D-glucopyranoside (**12**), phloretin 2′-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside (**13**), a new naphthalene glycoside, stelladerol (**14**), and an amino acid (longitubanine A) (**15**) have been isolated. All of these compounds were tested for their antioxidant and cyclooxygenase inhibitory activities. Stelladerol was found to possess strong antioxidant properties, inhibiting lipid oxidation by 94.6% ± 1.4 at 10 μM in an in vitro assay. Several of the flavonol 3-*O*-glycoside isolates also demonstrated modest antioxidant activities at 10 μM. None of the isolates inhibited cyclooxygenase activity at 100 μM.

KEYWORDS: Daylily; edible flower; *Hemerocallis*; antioxidant activity; lipid oxidation; stelladerol; flavonol 3-*O*-glycoside; phenolic glycoside

INTRODUCTION

Daylilies (*Hemerocallis* spp., Hemerocallidaceae) have been harvested for thousands of years in eastern Asia, where they have been utilized as both a food item (*1*) and a medicinal agent (*2*, *3*) for the treatment of a host of diseases. Daylilies have been reported to possess antidepressant properties, reduce inflammation, and promote digestion. Both fresh and dried daylily flowers are widely consumed as an important component in traditional eastern Asian cuisine. Pharmacological studies have shown that daylilies can facilitate neurological changes in sleeping mice (*4*) and impact motor activity in rats as a result of alteration to the normal levels of several central nervous system neurotransmitters (*5*). Phytochemical investigations of *Hemerocallis* spp. have identified an assortment of chemical constituents including carotenoids (*1*), fulvanine lactams (*6*, *7*), anthocyanins (*8*, *9*), and anthraquinones (*10*). Unfortunately, very little is known regarding the chemical composition of edible daylily flowers.

We have undertaken this investigation to examine the bioactive chemical constituents of edible daylily flowers. Specifically, we have focused our research on the bioactive phenolic glycosides because these compounds are known to have a significant impact on the status of human health and disease prevention. In this paper we report the isolation and structure elucidation of 14 phenolic glycosides and one amino acid from lyophilized *Hemerocallis* cv. Stella de Oro flowers, as well as discuss their antioxidant and cyclooxygenase inhibitory activities.

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MATERIALS AND METHODS

General Experimental Procedures. ^{1}H NMR spectra were recorded at 300, 500, and 600 MHz on Varian (Palo Alto, CA) INOVA (for 300 and 600 MHz) or VRX (for 500 MHz) instruments. ^{13}C NMR spectra were obtained at 75 and 125 MHz on Varian INOVA and VRX instruments, respectively. All spectra were recorded in DMSO-d_6. Standard pulse sequences were employed for all NMR experiments. FAB mass spectra were acquired at the Michigan State University Mass Spectrometry Facility using a JEOL HX-110 double-focusing mass spectrometer (Peabody, MA) operating in the positive ion mode. The UV spectra were recorded in MeOH using a Shimadzu UV-260 recording spectrophotometer (Kyoto, Japan). Sephadex LH-20 was purchased from Sigma-Aldrich (St. Louis, MO). Silica gel PTLC plates (20 × 20 cm; 250, 500, and 1000 μm thick) were obtained from Analtech, Inc. (Newark, DE). Preparative HPLC was performed on a Japan Analytical Industry Co. model LC-20 recycling preparative HPLC with tandem JAIGEL-C_{18} columns (10 μm, 20 mm × 250 mm). All solvents and chemicals, including *tert*-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and vitamin E (α-tocopherol), were purchased from Sigma-Aldrich (St. Louis, MO) and were of ACS analytical grade.

Plant Material. Approximately 12000 *Hemerocallis* cv. Stella de Oro (Hemerocallidaceae) flowers (24.6 kg) were hand-harvested from Walters Gardens, Inc. (Zeeland, MI) on September 3 and 10, 1999, and frozen at −20 °C. The frozen flowers were lyophilized and ground

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in a Waring blender, yielding 2.8 kg of fine yellow powder that was stored at −20 °C until extracted.

Extraction and Isolation of Compounds 1, 3, 5—7, and 9. Powdered daylily flowers (1.8 kg) were successively extracted with hexanes (5 × 6 L) (27 g), EtOAc (6 × 6 L) (20 g), and MeOH (8 × 8 L) (584 g). Four 146 g portions of the bioactive MeOH extract were each applied to XAD-16 resin and eluted with H_2O (2 L) followed by MeOH (1.5 L). The total MeOH eluate (14.5 g) was divided into eight 1.8 g fractions and further fractionated by C_{18} MPLC under isocratic conditions with CH_3CN/H_2O (3:2). The bioactive constituents from each MPLC column were eluted as a single, dark UV-absorbing ($\lambda = 366$ nm) band and pooled (12 g). This material was dissolved in EtOH (3 × 300 mL), and the soluble portion (9 g) was again applied to a column of XAD-16 resin and sequentially eluted with H_2O (2 L) followed by 30 (2 L), 60 (2.5 L), and 100% (2 L) MeOH affording 2.9, 2.7, 1.8, and 1.2 g fractions, respectively.

The 60% MeOH eluate from XAD-16 (1.8 g) was subjected to C_{18} MPLC under a 50−100% MeOH/H_2O gradient. Eleven milliliter fractions were collected and pooled on the basis of their TLC ($CHCl_3$/EtOAc saturated with water/MeOH/HCOOH, 1:8:2:0.1) profiles. Fractions A−C, composed of subfractions 20−25, 29−37, and 50−64, respectively, were determined to be bioactive and subjected to further purification. PTLC of fraction A (44 mg) with CH_2Cl_2/MeOH/toluene (22:5:1) yielded one fraction (35 mg) that was further purified by C_{18} preparative HPLC under a 40−60% MeOH/H_2O (with 0.1% TFA) gradient to give compound **9** (beige amorphous solid; 8.3 mg). Using C_{18} preparative HPLC under a 40−60% MeOH/H_2O (with 0.1% TFA) gradient, fractions B (68 mg) and C (45 mg) provided compounds **6** (yellow powder; 43.1 mg) and **5** (yellow powder; 28.0 mg), respectively.

The 100% MeOH eluate (1.2 g) from XAD-16 was subjected to C_{18} MPLC under a 40−60% MeOH/H_2O gradient. Eleven milliliter fractions were collected and pooled on the basis of their TLC ($CHCl_3$/EtOAc saturated with water/MeOH/HCOOH, 1:8:2:0.1) profiles. Bioactive fractions D and E, composed of subfractions 41−70 and 71−100, respectively, were subjected to further purification. PTLC of fraction D (235 mg) with CH_2Cl_2/MeOH/toluene (130:15:2) provided fractions D1 (10 mg) and D2 (60 mg). Further purification of fractions D1 and D2 by C_{18} preparative HPLC under a 40−60% MeOH/H_2O (with 0.1% TFA) gradient afforded compounds **3** (yellow-brown amorphous solid; 3.0 mg) and **7** (yellow amorphous solid; 5.2 mg), respectively. Fraction E (36 mg) was also subjected to PTLC with CH_2Cl_2/MeOH/toluene (130:15:2), yielding fraction E1 (25 mg) that was subjected to C_{18} preparative HPLC under a 40−60% MeOH/H_2O (with 0.1% TFA) gradient yielding compound **1** (yellow amorphous solid; 2.0 mg).

Extraction and Isolation of Compounds 2, 4, 8, and 10—15. A 1.0 kg portion of the lyophilized flowers was exhaustively extracted with 1:1 MeOH/H_2O (6 × 5 L) and the extract reduced in vacuo, yielding 390 g of gummy amber extract. The extract was divided into three 130 g portions, and 500 mL of water was added to each. Each portion was partitioned with hexanes (3 × 200 mL) and then chloroform (3 × 250 mL). The resultant aqueous extracts were combined, concentrated in vacuo, and applied to an XAD-16 column. The column was eluted with water (2 L) followed by 20 (2 L) and 100% MeOH (2.5 L).

The 20% MeOH eluate (11 g) was subjected to C_{18} MPLC under a 10−40% CH_3CN/H_2O gradient, and 200 mL fractions were collected affording fractions F and G. Fraction F (320 mg) was dissolved in 15 mL of warm MeOH and left on the benchtop for 14 days. Upon standing, fraction F yielded 176 mg of a powdery off-white precipitate. The precipitate was analyzed by HPLC (MeOH/H_2O, 3:7) and determined to be composed of an unresolved mixture of several compounds. The mother liquor (144 mg) was subjected to repeated isocratic preparative HPLC (MeOH/H_2O, 3:7) to give compound **15** (white powder; 34.0 mg).

Fraction G (400 mg) was applied to a Sephadex LH-20 column and eluted with MeOH, and 15 mL fractions were collected. Fractions 9−11 were pooled on the basis of their TLC (BuOH/HOAc/$CHCl_3$/H_2O, 5:1:1:4, upper phase) profiles, providing a 220 mg fraction that exhibited a strong UV absorption at $\lambda = 254$ nm. This fraction was further purified by PTLC with *n*-BuOH/HOAc/$CHCl_3$/H_2O (5:1:1:4, upper phase) and gradient preparative HPLC under 5−30% MeCN, affording compound **11** (clear, glasslike amorphous solid; 13.9 mg).

The 100% MeOH eluate from XAD-16 (20 g) was repeatedly purified by gradient C_{18} MPLC under a 20−100% MeOH/H_2O gradient, giving fractions H and I. Fraction H (600 mg) was applied to Sephadex LH-20 and eluted with 70% MeOH, giving 15 mL fractions that were pooled on the basis of their TLC (*n*-BuOH/HOAc/$CHCl_3$/H_2O, 5:1:1:4, upper phase) profiles, affording fractions H1−H3. Fraction H1 (230 mg) was subjected to PTLC with CH_2Cl_2/MeOH/toluene/HCOOH (15:6:0.2:0.2) to yield fractions H1A−H1C. Fractions H1A (20 mg) and H1C (17 mg) were further purified by PTLC with $CHCl_3$/EtOAc/MeOH/HCOOH (3:7:1.5:0.1) (yields 13 and 5 mg, respectively) and isocratic C_{18} preparative HPLC (10% MeCN) to give compounds **10** (clear glasslike amorphous solid; 9.0 mg) and **13** (clear glasslike amorphous solid; 4.0 mg), respectively. Fraction H1B (15.0 mg) was purified by isocratic C_{18} preparative HPLC (10% MeCN), yielding compound **14** (yellow amorphous solid; 12.0 mg).

PTLC of fraction H2 (130 mg) with CH_2Cl_2/MeOH/toluene/HCOOH (15:6:0.2:0.2) afforded a major dark, UV-absorbing band ($\lambda = 366$ nm) (120 mg) that was applied to Sephadex LH-20 (MeOH) to give fractions H2A (85 mg) and H2B (17 mg). Fractions H2A and H2B were both further purified by gradient preparative HPLC under 40−60% MeOH with 0.1% TFA (yields were 10 and 5 mg, respectively) followed by additional gradient preparative HPLC under 10−30% MeCN, affording compounds **4** (yellow-brown amorphous solid; 4.2 mg) and **2** (yellow amorphous solid; 2.5 mg), respectively.

Fraction H3 (100 mg) was subjected to further purification by gradient preparative HPLC under 40−60% MeOH with 0.1% TFA (yield was 15 mg) followed by gradient preparative HPLC under 10−30% MeCN that yielded compound **8** (yellow-brown amorphous solid; 2.3 mg).

Fraction I (1 g) was purified by repeated column chromatography on Sephadex LH-20 eluted with 70 and 100% MeOH, respectively. This provided a 120 mg fraction that was further purified by PTLC with $CHCl_3$/EtOAc/MeOH/HCOOH (3:7:1.5:0.1) (yield 20 mg) and gradient C_{18} preparative HPLC (5−35% MeCN) to give compound **12** (clear glasslike amorphous solid; 13.0 mg).

Evaluation of Cyclooxygenase Inhibitory Activity of Compounds 1—15. Compounds **1**−**15** were tested for their ability to inhibit cyclooxygenase I and II enzymes in vitro. These experiments were performed and components obtained from sources as previously described (*11*). Briefly, cyclooxygenase enzyme preparations were incubated at 37 °C with arachidonic acid and test compound (100 μM) delivered in DMSO. The initial rates of oxygen consumption were recorded and compared to controls. All compounds were tested in triplicate.

Evaluation of Antioxidant Activity of Compounds 1—15. Compounds **1**−**15** were tested in vitro for their ability to inhibit the oxidation of large unilamellar vesicles (LUVs). In general, the vesicles were prepared by combing the phospholipid 1-stearoyl-2-linoleoyl-*sn*-glycero-3-phosphocholine (Avanti Polar Lipids, Inc., Alabaster, AL) with a fluorescent probe [3-[*p*-(6-phenyl)-1,3,5-hexantrienyl]phenylpropionic acid (Molecular Probe, Inc., Eugene, OR)] [in a molar ration of 350:1 (lipid/probe)]. A buffer maintained in Chelex resin and composed of 0.15 M NaCl, 0.01 M MOPS (pH 7.0), and 0.1 mM EDTA (all purchased from Sigma-Aldrich, St. Louis, MO) was used to suspend the lipid−probe mixture, and this was exposed to 10 freeze−thaw cycles in a dry ice−ethanol bath. The resultant material was passed through a 100 nm polycarbonate filter 29 times to give the LUVs.

Experiments were conducted by combining LUVs, 100 mM NaCl, 50 mM Tris-HEPES (pH 7.0), and test compound in DMSO (final concentration of 10 μM test compound in 2 mL). Oxidation of the lipid−probe substrate was initiated by the addition of 20 μL of a 0.5 mM $FeCl_2$ solution. Data represent the relative fluorescence intensity of the probe−lipid−test compound mixture as compared to a probe−lipid control. All compounds were tested in triplicate, and results are reported as the mean ± one standard deviation after 15 min of incubation. Full experimental details have been previously reported (*11*, *12*).

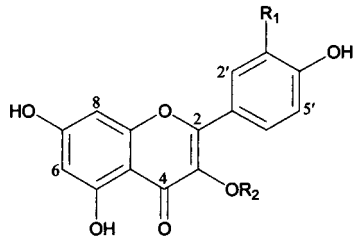
Table 1. Percent Yield of 15 Compounds Isolated from Methanol and Aqueous Methanol Extracts of Edible *Hemerocallis* cv. Stella de Oro Flowers and Literature Sources Containing Comparative Spectroscopic Data

	compd	yield (mg/kg of dry material)	ref
1	kaempferol 3-*O*-α-L-arabinopyranoside	1.1	13
2	quercetin 3-*O*-β-D-xylopyranoside	2.5	14
3	kaempferol 3-*O*-β-D-glucopyranoside	1.7	15
4	quercetin 3-*O*-β-D-glucopyranoside	4.2	15
5	kaempferol 3-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside	15.6	15
6	quercetin 3-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside	23.9	15
7	quercetin 3-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-galactopyranoside	2.9	16
8	quercetin 3-*O*-α-L-rhamnopyranosyl-(1→6)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside	2.3	17, 18
9	isorhamnetin 3-*O*-α-L-rhamnopyranosyl-(1→6)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside	4.6	19
10	phenethyl β-D-glucopyranoside	9.0	20
11	orcinol β-D-glucopyranoside	13.9	21, 22
12	phloretin 2′-*O*-β-D-glucopyranoside	13.0	23
13	phloretin 2′-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside	4.0	23
14	stelladerol (1-(1,5,8-trihydroxy-3-methylnaphthalen-2-yl)ethanone-8-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside)	12.0	novel compd
15	longitubanine A	15.0	24

Compound 14 (stelladerol; 1-(1,5,8-trihydroxy-3-methylnaphthalen-2-yl)ethanone-8-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside) was obtained as a yellow amorphous solid; UV (MeOH) λ_{max} (log ϵ) 223 (4.97), 313 (4.15), 345 (4.18) nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 9.84 (1H, s, −OH, exchange with D_2O), 9.63 (1H, s, −OH, exchange with D_2O), 7.41 (1H, s, J = 1.5 Hz, H-4), 7.27 (1H, d, J = 8.3 Hz, H-7), 6.76 (1H, d, J = 8.3 Hz, H-6), 4.85 (1H, d, J = 7.5 Hz, H-1′), 4.23 (1H, d, J = 7.5 Hz, H-1″), 4.02 (1H, d, J = 10.5 Hz, H-6′), 3.69 (1H, dd, J = 5.3, 11.3 Hz, H-5″), 3.58 (1H, m, H-6′), 3.31 (2H, m, H-2′, H-5′), 3.29 (1H, m, H-4″), 3.18 (1H, t, J = 9.0 Hz, H-4′), 3.11 (2H, m, H-3′, H-3″), 3.02 (2H, m, H-2″, H-5″), 2.51 (3H, s, $-COCH_3$), 2.25 (3H, d, J = 1.5 Hz, $-CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 204.9 (s, C=O), 150.2 (s, C-1), 148.2 (s, C-5), 146.8 (s, C-8), 131.3 (s, C-3), 126.2 (s, C-10), 125.5 (s, C-2), 114.0 (s, C-9), 113.9 (d, C-4), 112.1 (d, C-7), 109.0 (d, C-6), 104.2 (d, C-1″), 103.4 (d, C-1′), 76.5 (d, C-3′, C-3″), 76.2 (d, C-5′), 73.4 (d, C-2′, C-2″), 70.0 (d, C-4′), 69.6 (d, C-4″), 68.6 (t, C-6′), 65.6 (t, C-5″), 32.0 (q, $-COCH_3$), 19.4 (q, $-CH_3$); FABMS, m/z 549 $[M + Na]^+$, 527 $[M + H]^+$, 395 $[M - Xyl + 2H]^+$, 233 $[M - Xyl - Glc + 2H]^+$; HRFABMS, m/z 527.1756 $[M + H]^+$ (calcd for $C_{24}H_{31}O_{13}$, 527.1765).

RESULTS AND DISCUSSION

Methanol and aqueous methanol extracts of edible *Hemerocallis* cv. Stella de Oro flowers were subjected to a series of chromatographic procedures, including C_{18} MPLC and preparative HPLC, silica gel PTLC, and Sephadex LH-20 column chromatography, affording 15 compounds (Table 1). The structures of these compounds, including nine flavonol-3-*O*-glycosides (**1**−**9**) (Figure 1), phenethyl β-D-glucopyranoside (**10**), orcinol β-D-glucopyranoside (**11**), two dihydrochalcone glycosides, and phloretin 2′-*O*-β-D-glucopyranoside and phloretin 2′-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside (**12** and **13**, respectively), one new naphthalene glycoside, stelladerol (**14**), and one amino acid, longitubanine A (**15**) (Figure 2), were



	R_1	R_2
1	H	α-L-arabinopyranoside
2	OH	β-D-xylopyranoside
3	H	β-D-glucopyranoside
4	OH	β-D-glucopyranoside
5	H	α-L-rhamnosyl-(1→6)-β-D-glucopyranoside
6	OH	α-L-rhamnosyl-(1→6)-β-D-glucopyranoside
7	OH	α-L-rhamnosyl-(1→6)-β-D-galactopyranoside
8	OH	α-L-rhamnopyranosyl-(1→6)-[α-L-rhamnosyl-(1→2)]-β-D-glucopyranoside
9	OMe	α-L-rhamnopyranosyl-(1→6)-[α-L-rhamnosyl-(1→2)]-β-D-glucopyranoside

Figure 1. Structures of kaempferol, quercetin, and isorhamnetin 3-*O*-glycosides (compounds **1**–**9**) isolated from *Hemerocallis* cv. Stella de Oro flowers.

established on the basis of UV and NMR (^{1}H, ^{13}C, DEPT, difference NOE, DQF-COSY, HMQC, and HMBC) and MS experiments and by comparisons with literature data (Table 1). All of these compounds are reported here for the first time as components of edible daylily flowers. The ^3J coupling constants of the anomeric protons were used to determine the absolute α-(L-arabinose and L-rhamnose) or β-(D-galactose, D-glucose, and D-xylose) configuration of the common, naturally occurring sugar residues found in each of the glycosides.

Examination of the ^{1}H and ^{13}C NMR spectra of compound **14** indicated that it was composed of a highly substituted naphthalene moiety conjugated with a disaccharide. The aglycon spins in the ^{1}H NMR spectrum were represented by three doublets at δ_H 7.41 (1H, J = 1.5 Hz), 7.27 (1H, J = 8.3 Hz), and 6.76 (1H, J = 8.3 Hz). Analysis of the DQF-COSY spectrum confirmed the correlation between the ortho-coupled protons at δ_H 7.27 and 6.76, whereas the proton at δ_H 7.41 coupled weakly with the methyl doublet at δ_H 2.25. The multiplicities of the aglycon spins were determined by DEPT, demonstrating that the naphthalene nucleus was composed of three methine carbons (δ_C 113.9, 112.1, and 109.0) and seven quaternary spins (δ_C 150.2, 148.2, 146.8, 131.3, 126.2, 125.5, and 114.0). In addition, two methyls (δ_C 32.0 and 19.4) and one carbonyl (δ_C 204.9) were observed. On the basis of these data, HMQC and HMBC experiments were used to establish the structure of the aglycon as shown in Figure 3.

Additional methylene and methine spins were observed in compound **14** between δ_C 65.6 and 104.2, which were assigned to xylopyranose and glucopyranose residues. A 1→6 linkage was confirmed between the two sugar moieties on the basis of ^3J HMBC correlations between the H-6′ protons (δ_H 3.58 and 4.02) and C-1″ (δ_C 104.2) (Figure 3). Further confirmation of the structure for compound **14** was obtained as a result of 1D difference NOE experiments in which reciprocal NOE enhancements were observed between H-7 and H-6, between H-7 and H-1′, and between $-CH_3$ (δ_H 2.25) and H-4, as well as between $-CH_3$ (δ_H 2.25) and $-COCH_3$ (δ_H 2.51) (Figure 3). Therefore, the structure of the new naphthalene glycoside **14** was established as that illustrated in Figure 2. Compound **14** has been given the trivial name stelladerol in recognition of its biogenic source.

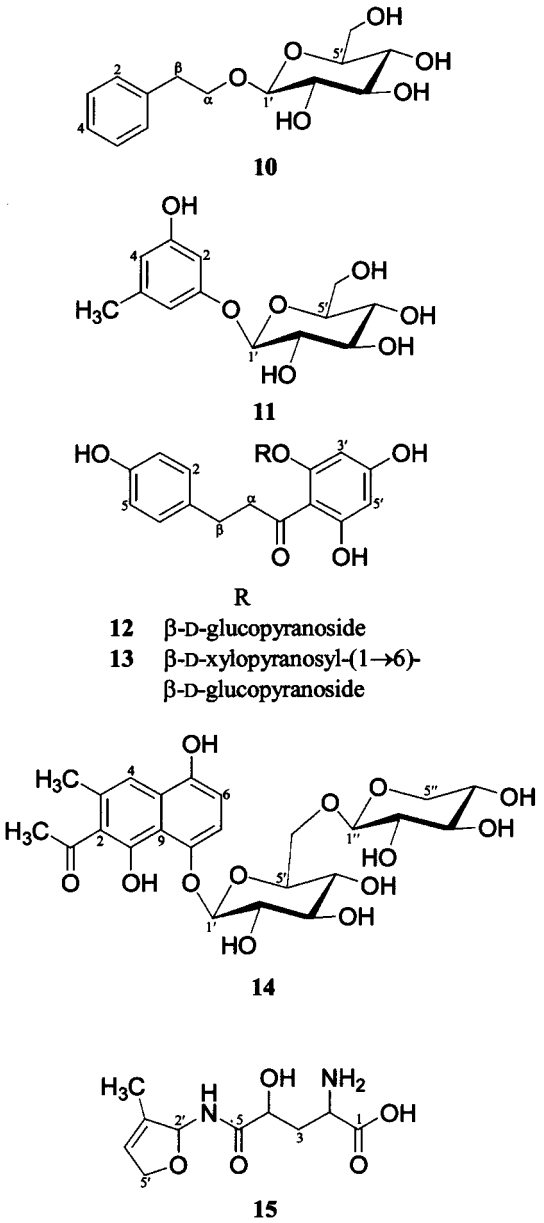


Figure 2. Structures for compounds **10**–**15** isolated from *Hemerocallis* cv. Stella de Oro flowers.

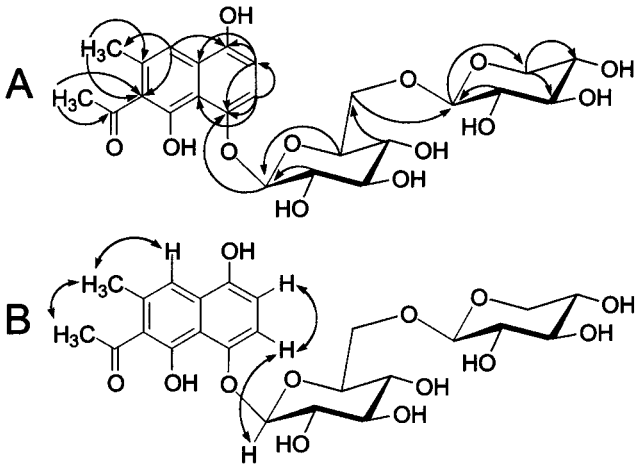


Figure 3. Selected HMBC (A) and difference NOE (B) correlations used to determine the structure of stelladerol (**14**).

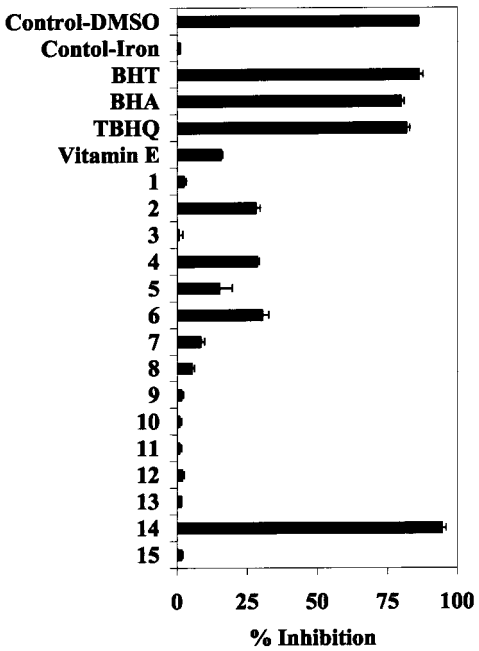


Figure 4. Inhibition of LUV phospholipid oxidation by synthetic antioxidants and compounds **1**–**15**. "Control-DMSO" represents LUVs with the DMSO carrier added. "Control-Iron" represents LUVs with oxidation initiated with the addition of $FeCl_2$ solution. All compounds were tested in triplicate at 10 μM. Results are expressed as the mean percent inhibition ± one standard deviation.

Compounds **1**−**15** were evaluated for their potential antioxidant activity at 10 μM (Figure 4). Under these experimental conditions, stelladerol (**14**) exhibited strong antioxidant activity (94.6 ± 1.4% inhibition) that was more pronounced than those of the commercial synthetic antioxidants TBHQ, BHA, and BHT (81.8 ± 1.2, 80.0 ± 1.0, and 86.4 ± 1.3%, respectively) and vitamin E (15.7 ± 0.6%). Several of the flavonol 3-*O*-glycosides in which quercetin represented the aglycon moiety, such as compounds **2**, **4**, and **6**, exhibited more modest antioxidant effects with 28.2 ± 1.5, 28.6 ± 0.8, and 31 ± 2.3% inhibition, respectively. In comparison, the flavonol 3-*O*-glycosides that possessed a kaempferol or isorhamnetin aglycon moiety generally exhibited lower antioxidant inhibitory effects at the same concentration. Our results are in agreement with previously published studies which have demonstrated that substitutions to the B-ring of flavonoids, such as the hydroxyl substituents at C-3′ and C-4′ in quercetin, make this flavonol a more effective antioxidant than kaempferol (C-4′ hydroxyl) or isorhamnetin (C-3′ methoxy and C-4′ hydroxyl) due to their comparatively hindered ability to chelate metal ions (*25*, *26*). None of the compounds tested inhibited cyclooxygenase I or II mediated prostaglandin synthesis at 100 μM.

Phenolic compounds are highly regarded for their important dietary roles as chemopreventive agents (*27*). The noted beneficial effects of these bioactive compounds are mitigated in part by means of their antioxidant effects as free radical scavengers or metal ion chelators (*25*, *28*, *29*). Today, in vivo oxidative events are widely recognized as factors in the onset and progression of various diseases such as cancer, arteriosclerosis, and neural degenerative disorders (*30*). In light of the complex array of phenolic compounds observed in daylily flowers, in addition to the host of antioxidant carotenoids present in these tissues, it can be conjectured that the dietary consumption of *Hemerocallis* flowers may convey a variety of beneficial chemopreventive effects to humans.

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