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# Maple Syrup Phytochemicals Include Lignans, Coumarins, a Stilbene, and Other Previously Unreported Antioxidant Phenolic Compounds

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Twenty-three phenolic compounds were isolated from a butanol extract of Canadian maple syrup (MS-BuOH) using chromatographic methods. The compounds were identified from their nuclear magnetic resonance and mass spectral data as 7 lignans [lyoniresinol (**1**), secoisolariciresinol (**2**), dehydroconiferyl alcohol (**3**), 5′-methoxy-dehydroconiferyl alcohol (**4**), erythro-guaiacylglycerol-$\beta$-*O*-4′-coniferyl alcohol (**5**), erythro-guaiacylglycerol-$\beta$-*O*-4′-dihydroconiferyl alcohol (**6**), and [3-[4-[(6-deoxy-α-L-mannopyranosyl)oxy]-3-methoxyphenyl]methyl]-5-(3,4-dimethoxyphenyl)dihydro-3-hydroxy-4-(hydroxymethyl)-2(3*H*)-furanone (**7**)], 2 coumarins [scopoletin (**8**) and fraxetin (**9**)], a stilbene [(*E*)-3,3′-dimethoxy-4,4′-dihydroxystilbene (**10**)], and 13 phenolic derivatives [2-hydroxy-3′,4′-dihydroxyacetophenone (**11**), 1-(2,3,4-trihydroxy-5-methylphenyl)ethanone (**12**), 2,4,5-trihydroxyacetophenone (**13**), catechaldehyde (**14**), vanillin (**15**), syringaldehyde (**16**), gallic acid (**17**), trimethyl gallic acid methyl ester (**18**), syringic acid (**19**), syringenin (**20**), (*E*)-coniferol (**21**), *C*-veratroylglycol (**22**), and catechol (**23**)]. The antioxidant activities of MS-BuOH ($IC_{50}$ > 1000 $\mu$g/mL), pure compounds, vitamin C ($IC_{50}$ = 58 $\mu$M), and a synthetic commercial antioxidant, butylated hydroxytoluene ($IC_{50}$ = 2651 $\mu$M), were evaluated in the diphenylpicrylhydrazyl (DPPH) radical scavenging assay. Among the isolates, the phenolic derivatives and coumarins showed superior antioxidant activity ($IC_{50}$ < 100 $\mu$M) compared to the lignans and stilbene ($IC_{50}$ > 100 $\mu$M). Also, this is the first report of 16 of these 23 phenolics, that is, compounds **1**, **2**, **4**−**14**, **18**, **20**, and **22**, in maple syrup.

**KEYWORDS:** ***Acer saccharum*; sugar maple; maple syrup; butanol extract; phenolics; antioxidant**

## INTRODUCTION

Maple syrup is a natural sweetener obtained by concentrating the sap collected from certain maple species including the sugar maple (*Acer saccharum* Marsh.) tree, which is native to North America (*1*, *2*). Maple syrup is primarily produced in northeastern North America, and the vast majority of the world's supply comes from Canada (85%; primarily Quebec), followed by the United States (15%; primarily the New England/New York region) (*2*). Maple syrup is the largest commercially available food product consumed by humans that is derived totally from the sap of deciduous trees.

Maple syrup is produced by thermal evaporation of the colorless watery sap collected from maple trees in late winter to early spring. Because of its high water content, about 40 L of sap is required to produce 1 L of syrup (*1*). During the concentration process of transforming sap to syrup, the characteristic flavor, color, and odor of maple syrup develops. Typically, the color of the syrup becomes darker as the season progresses, and based on Canadian standards, maple syrup is graded as extra light (grade AA), light (grade A), medium/amber (grade B), and dark (grade C) (*2*).

Being a plant-derived natural product, it is not surprising that maple syrup contains phytochemicals (naturally present in the xylem sap), as well as process-derived compounds (formed during thermal evaporation of sap) (*1*−*4*). Apart from sucrose, which is its dominant sugar, maple syrup contains organic acids, amino acids, minerals, and lignin-derived flavor compounds (*1*−*4*). Among the phytochemicals that have been previously reported from maple syrup, the phenolic class predominates. For example, vanillin, syringaldehyde, coniferaldehyde, and cinnamic acid and benzoic acid derivatives, as well as flavonoids (flavanols and flavonols), have been identified in maple syrup extracts (*3*−*6*).

The presence of a diverse range of phenolic subclasses in maple syrup is interesting given that this large class of dietary phytochemicals has attracted significant research attention due to their diverse biological functions and potential positive effects on human health (*6*). Recently, phenolic-enriched extracts of maple syrup were shown to have antioxidant, antimutagenic, and human cancer cell antiproliferative properties (*7*, *8*). Thus, a comprehensive investigation of maple syrup phenolics is necessary to evaluate the biological properties and potential human health benefits of this natural sweetener. Previous phytochemical research has been conducted on maple syrup extracts, namely, ethyl acetate, chloroform, dichloromethane, and diethyl ether extracts (*3*−*6*). Whereas these organic solvents are commonly used for the extraction of phytochemicals from complex food matrices, it is possible that higher polarity solvents, such as *n*-butanol, may contain previously unreported phenolic compounds. However, there are no prior reported studies of compounds found in butanol extracts of maple syrup (MS-BuOH).

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Maple syrup is popularly consumed worldwide and is of significant cultural and economical importance to northeastern North America, particularly in Canada, where it is largely produced. Therefore, increased knowledge of the chemical constituents of Canadian maple syrup would aid in the authentication, characterization, and subsequent detection of intentional adulteration of this premium natural sweetener. Also, characterization of the different chemical subclasses of bioactive phenolics, and ascertaining their levels, would aid in evaluating the potential human health benefits resulting from consumption of Canadian maple syrup. Toward this end, our objectives were (1) to isolate and identify the phytochemicals present in a Canadian MS-BuOH and (2) to evaluate the Canadian MS-BuOH, and its purified constituents, for antioxidant potential in the diphenylpicrylhydrazyl (DPPH) radical scavenging assay.

Here we report the isolation and identification of 23 phenolic compounds, **1**−**23**, from MS-BuOH, among which 16 compounds, namely, **1**, **2**, **4**−**14**, **18**, **20**, and **22**, are being reported from maple syrup for the first time.

## MATERIALS AND METHODS

**General Experimental Procedures.** $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained either on a Bruker 400 MHz or on a Varian 500 MHz instrument using deuterated methanol ($CD_3OD$) as solvent. Electrospray ionization mass spectral (ESIMS) data were acquired on a Q-Star Elite (Applied Biosystems MDS) mass spectrometer equipped with a Turbo Ionspray source and were obtained by direct infusion of pure compounds. Analytical high-performance liquid chromatography (HPLC) was performed on a Hitachi Elite LaChrom system consisting of an L2130 pump, an L-2200 autosampler, and an L-2455 diode array detector, all operated by EZChrom Elite software. Semipreparative scale HPLC was performed on a Beckman-Coulter HPLC system consisting of a Beckman System Gold 126 solvent module pump, a 168 photodiode array (PDA) UV−vis detector, and a 508 autosampler, all operated by 32 Karat 8.0 software. All solvents were of either ACS or HPLC grade and were obtained from Wilkem Scientific (Pawcatuck, RI). Ascorbic acid (vitamin C), butylated hydroxytoluene (BHT), and DPPH reagent were purchased from Sigma-Aldrich (St. Louis, MO).

**Maple Syrup Butanol Extract (MS-BuOH).** Maple syrup (grade C, 20 L) was provided by the Federation of Maple Syrup Producers of Quebec (Canada). The syrup was kept frozen until extraction, when it was subjected to liquid−liquid partitioning with ethyl acetate (10 L × 3) followed by *n*-butanol (10 L × 3) solvents, to yield ethyl acetate (4.7 g) and *n*-butanol (108 g) extracts, respectively, after solvent removal in vacuo.

**Analytical HPLC.** All analyses were conducted on a Luna C18 column (250 × 4.6 mm i.d., 5 $\mu$M; Phenomenex) with a flow rate at 0.75 mL/min and injection volume of 20 $\mu$L. A gradient solvent system consisting of solvent A (0.1% aqueous trifluoroacetic acid) and solvent B (methanol, MeOH) was used as follows: 0−10 min, from 10 to 15% B; 10−20 min, 15% B; 20−40 min, from 15 to 30% B; 40−55 min, from 30 to 35% B; 55−65 min, 35% B; 65−85 min, from 35 to 60% B; 85−90 min, from 60 to 100% B; 90−93 min, 100% B; 93−94 min, from 100 to 10% B; 94−104 min, 10% B. **Figure 1**, panels **A** and **B**, show the HPLC-UV profiles of the butanol extract and all of the isolated phenolics (combined into one solution/injection), respectively. Unfortunately, due to limited sample quantity, we were not able to include compound **13** in the HPLC-UV injection shown in **Figure 1B**.

**Isolation of Compounds from the MS-BuOH.** The butanol extract (108 g) of Canadian maple syrup was further extracted with methanol (100 mL × 3) to afford methanol-soluble (57 g; dark brown powder) and methanol-insoluble (51 g; off-white powder) fractions. Analytical HPLC-UV analyses of the methanol-soluble extract revealed a number of peaks characteristic of phenolic compounds at 220, 280, and 360 nm (see above for details of methodology; see **Figure 1A** for chromatogram). Therefore, this fraction was selected for further purification by repeated chromatography on a Sephadex LH-20 column (4.5 × 64 cm), eluting with a gradient system of MeOH/$H_2O$ (3:7 v/v to 7:3 v/v to 100:0 v/v), and then with acetone/$H_2O$ (7:3 v/v). On the basis of analytical HPLC-UV profiles, 12 combined fractions, fractions 1−12, were obtained. Fraction 4 (1.5 g) was subjected to column chromatography on a Sephadex LH-20 column (4.5 × 64 cm) using a gradient solvent system of MeOH/$H_2O$ (3:7 v/v to 7:3 v/v) to afford 12 subfractions, fractions 4.1−4.12. These were individually subjected to a series of semipreparative HPLC-UV separations using a Waters Sunfire Prep $C_{18}$ column (250 × 10 mm i.d., 5 $\mu$m; flow = 2 mL/min) and elution with a MeOH/$H_2O$ gradient system to yield compounds **1** (4.6 mg), **3** (3.8 mg), **5** (4.0 mg), **6** (41.6 mg), **7** (6.6 mg), **11** (3.5 mg), **15** (0.3 mg), **16** (0.8 mg), **18** (0.2 mg), **20** (1.3 mg), **22** (1.5 mg), and **23** (3.0 mg). Similarly, fraction 5 (0.47 g) was purified by semipreparative HPLC-UV using a Waters XBridge Prep $C_{18}$ column (250×19 mm i.d., 5 $\mu$m; flow = 3.5 mL/min) and a gradient solvent system of MeOH/$H_2O$ to afford four subfractions 5.1−5.4. These subfractions were separately subjected to a combination of semipreparative HPLC-UV and/or Sephadex LH-20 column chromatography with gradient solvents systems of MeOH/$H_2O$ to afford compounds **2** (1.9 mg), **4** (1.9 mg), **8** (2.0 mg), **9** (2.3 mg), **14** (2.5 mg), **17** (2.4 mg), **19** (1.8 mg), and **21** (1.3 mg). Similarly, fraction 6 (0.2 g) afforded compounds **12** (1.4 mg) and **13** (1.3 mg), and fraction 11 yielded compound **10** (4.8 mg).

**Identification of Compounds.** All of the isolated compounds (**Figure 2**) were identified by examination of their $^1$H and/or $^{13}$C NMR and mass spectral data and by comparison of these to published literature reports, when available (**Table 1**). The NMR data for compounds **12** and **13** have not been previously published and are provided here for the first time.

(+)-*Lyoniresinol* (***1***)*:* yellowish amorphous powder; (+) ESIMS, *m*/*z* 443.1719 $[M + Na]^+$, calcd for molecular formula $C_{22}H_{28}O_8$; $^1$H NMR ($CD_3OD$, 400 MHz) $\delta$ 1.64 (1H, m, H-8), 1.95 (1H, m, H-8′), 2.59 (1H, m, H-7a), 2.72 (1H, m, H-7b), 3.36 (3H, s, 3-$OCH_3$), 3.51 (2H, m, H-9a, 9a′), 3.61 (2H, m, H-9b, 9b′), 3.75 (6H, s, 3′, 5′-$OCH_3$), 3.87 (3H, s, 5-$OCH_3$), 4.31 (1H, d, $J$ = 5.6 Hz, H-7′), 6.39 (2H, s, H-2′, 6′), 6.60 (1H, s, H-6); $^{13}$C NMR ($CD_3OD$, 100 MHz) $\delta$ 149.09 (C-3′, 5′), 148.77 (C-5), 147.80 (C-3), 139.44 (C-4, 1′), 130.27 (C-1), 135.00 (C-4′), 126.36 (C-2), 107.84 (C-6), 106.91 (C-2′, 6′), 66.87 (C-9), 64.21 (C-9′), 60.26 (3-$OCH_3$), 56.85 (3′, 5′-$OCH_3$), 56.69 (5-$OCH_3$), 49.01 (C-8′), 42.43 (C-7′), 40.98 (C-8), 33.71 (C-7). $^1$H and $^{13}$C NMR data were consistent with the literature (*9*).

*Secoisolariciresinol* (***2***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 385.1447 $[M + Na]^+$, calcd for molecular formula $C_{20}H_{26}O_6$; $^1$H NMR ($CD_3OD$, 500 MHz) $\delta$ 1.89 (2H, m, H-8, 8′), 2.55 (2H, m, H-7a, 7a′), 2.66 (2H, m, H-7b, 7b′), 3.58 (4H, m, H-9, 9′), 3.74 (6H, s, 3, 3′-$OCH_3$), 6.55 (2H, d, $J$ = 8.0 Hz, H-6, 6′), 6.58 (2H, s, H-2, 2′), 6.66 (2H, s, H-5, 5′); $^{13}$C NMR ($CD_3OD$, 125 MHz) $\delta$ 147.38 (C-3, 3′), 144.05 (C-4, 4′), 132.45 (C-1, 1′), 121.28 (C-6, 6′), 114.34 (C-5, 5′), 111.93 (C-2, 2′), 60.69 (C-9, 9′), 54.74 (3, 3′-$OCH_3$), 42.69 (C-8, 8′), 34.61 (C-7, 7′). $^1$H and $^{13}$C NMR data were consistent with the literature (*10*).

*Dehydroconiferyl alcohol* (***3***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 383.1208 $[M + Na]^+$, calcd for molecular formula $C_{20}H_{24}O_6$; $^1$H NMR ($CD_3OD$, 400 MHz) $\delta$ 1.81 (2H, m, H-8′), 2.64 (2H, m, H-7′), 3.48 (1H, m, H-8), 3.58 (2H, m, H-9′), 3.70 (1H, m, H-9a), 3.80 (1H, m, H-9b), 3.82 (3H, s, 3-$OCH_3$), 3.86 (3H, s, 3′-$OCH_3$), 5.50 (1H, d, $J$ = 6.0 Hz, H-7), 6.74 (2H, s, H-4′, 6′), 6.76 (1H, d, $J$ = 8.0 Hz, H-5), 6.82 (1H, d, $J$ = 8.0 Hz, H-6), 6.96 (1H, s, H-2); $^{13}$C NMR ($CD_3OD$, 100 MHz) $\delta$ 149.20 (C-3), 147.61 (C-4, 2′), 145.34 (C-3′), 137.03 (C-5′), 134.92 (C-1), 129.79 (C-1′), 119.81 (C-6), 118.01 (C-6′), 115.97 (C-5), 114.10 (C-4′), 110.56 (C-2), 89.11 (C-7), 65.09 (C-9), 62.35 (C-9′), 56.81 (3-$OCH_3$), 56.41 (3′-$OCH_3$), 55.61 (C-8), 35.99 (C-8′), 33.05 (C-7′). $^1$H and $^{13}$C NMR data were consistent with the literature (*11*).

*5-methoxydehydroconiferyl alcohol* (***4***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 413.1464 $[M + Na]^+$, calcd for molecular formula $C_{21}H_{26}O_7$; $^1$H NMR ($CD_3OD$, 500 MHz) $\delta$ 1.80 (2H, m, H-8′), 2.60 (2H, m, H-7′), 3.47 (1H, m, H-8), 3.58 (2H, m, H-9′), 3.76 (1H, m, H-9a), 3.80 (6H, s, 3,5-$OCH_3$), 3.84 (1H, m, H-9b), 3.86 (3H, s, 3′-$OCH_3$), 5.49 (1H, d, $J$ = 5.5 Hz, H-7), 6.64 (2H, s, H-2, 6), 6.72 (2H, s, H-4′, 6′); $^{13}$C NMR ($CD_3OD$, 125 MHz) $\delta$ 147.91 (C-3, 5), 146.10 (C-2′), 143.80 (C-3′), 135.56 (C-4, 5′), 132.64 (C-1), 128.40 (C-1′), 116.49 (C-6′), 112.71 (C-4′), 102.71 (C-2, 6), 87.68 (C-7), 63.75 (C-9), 60.80 (C-9′), 55.36 (3,5-$OCH_3$), 55.32 (3′-$OCH_3$), 54.17 (C-8), 34.39 (C-8′), 31.48 (C-7′). $^1$H and $^{13}$C NMR data were consistent with the literature (*12*).

*Erythro-guaiacylglycerol-β-O-4′-coniferyl alcohol* (***5***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 399.1156 $[M + Na]^+$, calcd for molecular formula $C_{20}H_{24}O_7$; $^1$H NMR ($CD_3OD$, 400 MHz) $\delta$ 3.81 (6H, s, 3,2′-$OCH_3$), 3.87 (2H, m, H-9), 4.20 (2H, d, $J$ = 5.6 Hz, H-9′), 4.37 (1H, m, H-8), 4.83 (1H, d, $J$ = 5.6 Hz, H-7), 6.24 (1H, dd, $J$ = 6.0, 16.0 Hz, H-8′), 6.52 (1H,

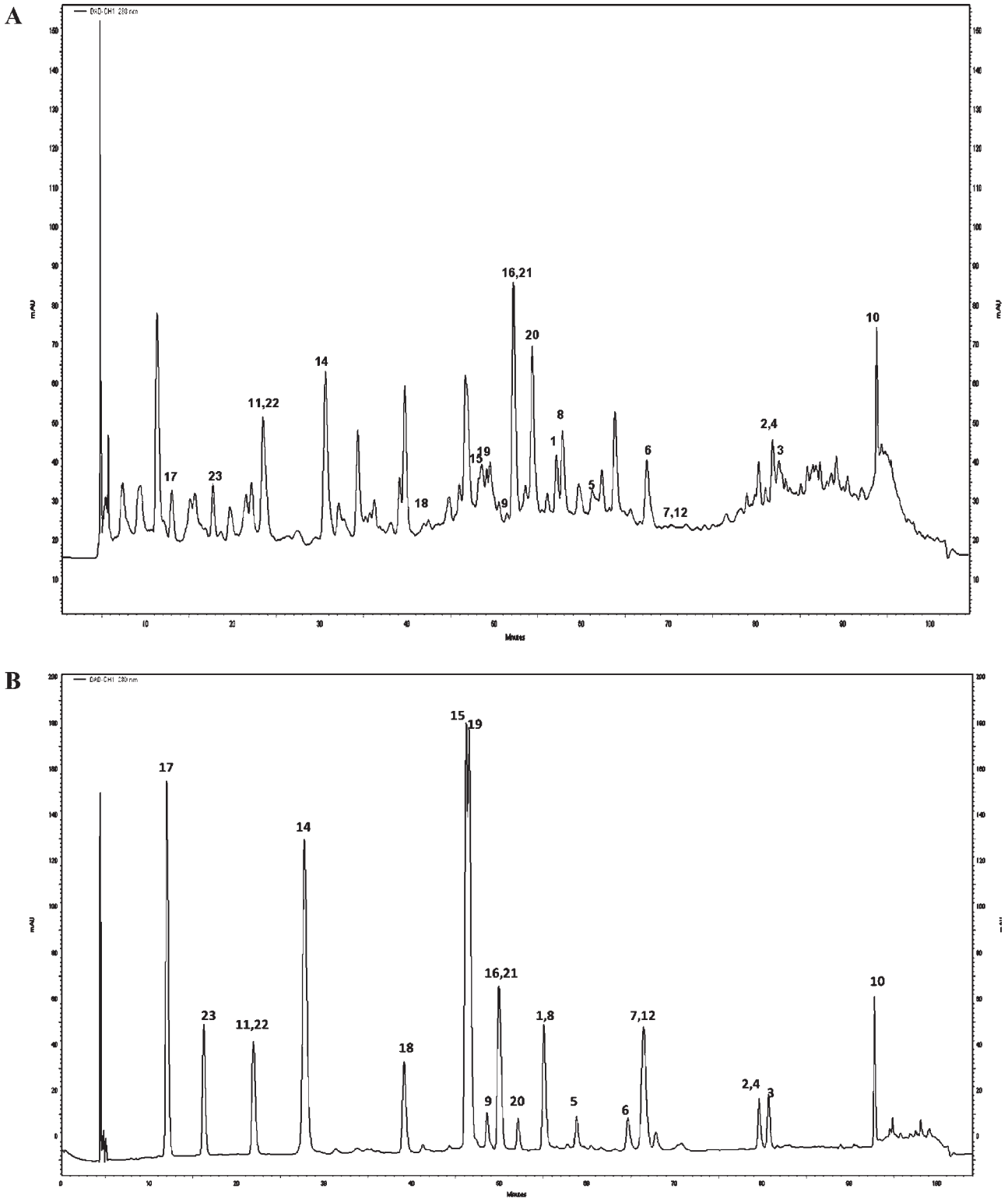


**Figure 1.** HPLC-UV chromatogram of (**A**) butanol extract of Canadian maple syrup (MS-BuOH) and (**B**) 23 phenolic compounds isolated and identified in MS-BuOH.

d, $J$ = 16.0 Hz, H-7′), 6.73 (1H, d, $J$ = 8.0 Hz, H-5), 6.84 (1H, d, $J$ = 8.0 Hz, H-6), 6.88 (2H, br s, H-5′, 6′), 7.01 (1H, s, H-3′), 7.03 (1H, s, H-2); $^{13}$C NMR ($CD_3OD$, 100 MHz) $\delta$ 151.80 (C-2′),149.00 (C-1′), 148.61 (C-3), 147.22 (C-4), 134.18 (C-1), 133.11 (C-4′), 130.81 (C-7′), 128.57 (C-8′), 121.13 (C-6), 120.77 (C-5′), 118.95 (C-6′), 115.74 (C-5), 111.92 (C-2), 110.79 (C-3′), 86.31 (C-8), 74.19 (C-7), 63.90 (C-9′), 62.32 (C-9), 56.58 (3,2′-$OCH_3$). $^1$H and $^{13}$C NMR data were consistent with the literature (*13*).

*Erythro-guaiacylglycerol-β-O-4′-dihydroconiferyl alcohol* (***6***)*:* yellowish amorphous powder; (+) ESIMS $m/z$ 401.1602 $[M + Na]^+$, calcd for molecular formula $C_{20}H_{26}O_7$; $^1$H NMR ($CD_3OD$, 400 MHz) $\delta$ 1.81 (2H, m, H-8′), 2.62 (2H, m, H-7′), 3.47 (1H, m, H-9a′), 3.58 (2H, m, H-9), 3.72 (1H, m, H-9b′), 3.82 (3H, s, 5-$OCH_3$), 3.85 (3H, s, 2′-$OCH_3$), 4.21 (1H, m, H-8), 4.90 (1H, m, H-7), 6.71 (1H, d, $J$ = 8.0 Hz, H-5′), 6.77 (1H, d, $J$ = 8.0 Hz, H-3), 6.86 (1H, s, H-3′), 6.88 (1H, d, $J$ = 8.0 Hz, H-2), 6.98 (1H, d, $J$ = 8.0 Hz, H-6′), 7.03 (1H, s, H-6); $^{13}$C NMR ($CD_3OD$, 100 MHz) $\delta$ 151.80 (C-2′), 148.95 (C-5), 147.69 (C-4), 147.29 (C-1′), 138.35 (C-4′), 133.88 (C-1), 122.18 (C-5′), 120.93 (C-2), 119.74 (C-6′), 116.01 (C-3), 114.02 (C-3′), 111.82 (C-6), 87.88 (C-8), 74.29 (C-7), 62.36 (C-9), 62.01 (C-9′), 56.65 (2′-$OCH_3$), 56.48

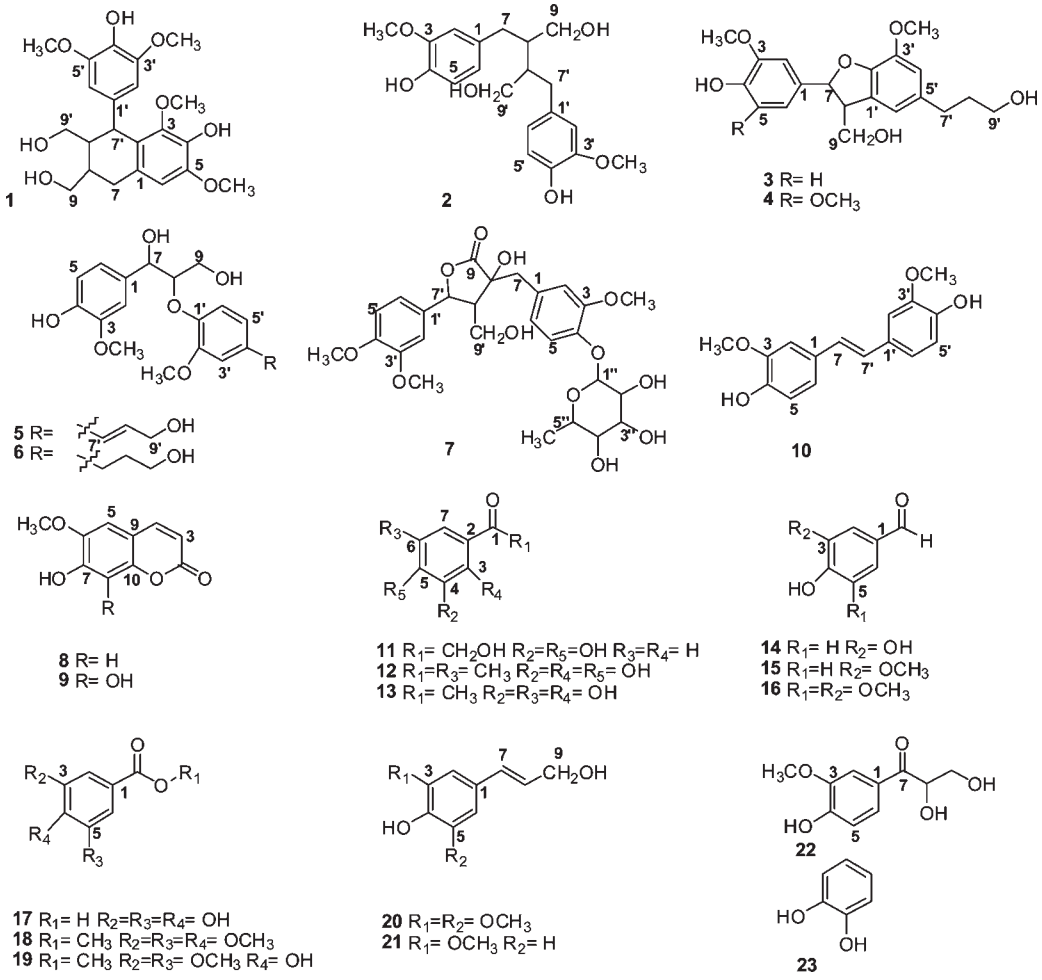


**Figure 2.** Structures of phenolic compounds (**1**−**23**) isolated and identified from a butanol extract of Canadian maple syrup (MS-BuOH).

(5-$OCH_3$), 35.71 (C-8′), 32.86 (C-7′). $^1$H and $^{13}$C NMR data were consistent with the literature (*14*).

[*3*-[*4*-[(*6-Deoxy*-α-*L-mannopyranosyl*)*oxy*]-*3-methoxyphenyl*]*methyl*]-*5*-(*3,4-dimethoxyphenyl*)*dihydro-3-hydroxy-4*-(*hydroxymethyl*)-*2*(*3H*)-*furanone* (*7*)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 573.1913 $[M + Na]^+$, calcd for molecular formula $C_{27}H_{34}O_{12}$; $^1$H NMR (400 MHz, $CD_3OD$) δ 1.25 (3H, d, *J* = 6.4 Hz, H-6″), 2.46 (1H, m, H-8′), 3.06 (1H, d, *J* = 13.2 Hz, H-7b), 3.35 (1H, d, *J*=13.2 Hz, H-7a), 3.5−3.90 (3H, m, H-3″, 4″, 5″), 3.55 (1H, m, 9′b), 3.63 (3H, s, 4′-$OCH_3$), 3.79 (3H, s, 3′-$OCH_3$), 3.80 (3H, s, 3-$OCH_3$), 3.95 (1H, m, 9′a), 4.07 (1H, s, H-2″), 5.10 (1H, d, *J* = 9.2 Hz, H-7′), 5.31 (1H, s, H-1″), 6.37 (1H, s, H-2′), 6.62 (1H, d, *J* = 8.0 Hz, H-6′), 6.85 (1H, d, *J* = 8.0 Hz, H-6), 6.87 (1H, d, *J* = 8.4 Hz, H-5′), 6.97 (1H, s, H-2), 7.05 (1H, d, *J* = 8.4 Hz, H-5); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 179.64 (C-9), 152.11 (C-3), 151.04 (C-3′), 150.74 (C-4′), 146.15 (C-4), 132.66 (C-1), 132.45 (C-1′), 124.54 (C-6), 120.92 (C-6′), 120.11 (C-5), 116.36 (C-2), 112.60 (C-5′), 110.39 (C-2′), 101.82 (C-1″), 82.89 (C-7′), 79.47 (C-8), 73.94 (C-4″), 72.33 (C-3″), 72.25 (C-2″), 71.02 (C-5″), 58.69 (C-9′), 56.75, 56.50 (C3,3′,4′-$OCH_3$), 51.79 (C-8′), 42.75 (C-7), 18.18 (C-6″). $^1$H and $^{13}$C NMR data were consistent with the literature (*15*).

*Scopoletin* (***8***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 193.0787 $[M + H]^+$, calcd for molecular formula $C_{10}H_8O_4$; $^1$H NMR (500 MHz, $CD_3OD$) δ 3.81 (3H, s, 6-$OCH_3$), 6.10 (1H, d, *J* = 9.4 Hz, H-3), 6.67 (1H, s, H-8), 7.01 (1H, s, H-5), 7.75 (1H, d, *J* = 9.4 Hz, H-4). $^1$H NMR data were consistent with the literature (*15*).

*Fraxetin* (***9***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 209.0639 $[M + H]^+$, calcd for molecular formula $C_{10}H_8O_5$; $^1$H NMR (500 MHz, $CD_3OD$) δ 3.82 (3H, s, 6-$OCH_3$), 6.22 (1H, d, *J*=9.4 Hz, H-3), 6.73 (1H, s, H-5), 7.85 (1H, d, *J* = 9.4 Hz, H-4). $^1$H NMR data were consistent with the literature (*16*).

(*E*)-*3,3′-Dimethoxy-4,4′-dihydroxystilbene* (***10***)*:* yellowish amorphous powder; (+) ESIMS *m*/*z* 294.9650 $[M + Na]^+$, calcd for molecular formula $C_{16}H_{16}O_4$; $^1$H NMR (400 MHz, $CD_3OD$) δ 3.83 (6H, s, 3,3′-$OCH_3$), 6.76 (2H, d, *J* = 8.0 Hz, H-5, 5′), 6.92 (2H, s, H-7, 7′), 6.95 (2H, d, *J* = 8.0 Hz, H-6, 6′), 7.12 (2H, s, H-2, 2′); $^{13}$C NMR ($CD_3OD$, 100 MHz) δ 148.72 (C-3, 3′), 147.35 (C-4, 4′), 131.70 (C-1, 1′), 127.40 (C-7, 7′), 120.94 (C-6, 6′), 116.45 (C-5, 5′), 110.40 (C-2, 2′), 56.53 (3, 3′-$OCH_3$). $^1$H and $^{13}$C NMR data were consistent with the literature (*17*).

*2-Hydroxy-3′,4′-dihydroxyacetophenone* (***11***)*:* brown amorphous powder; (+) ESIMS *m*/*z* 191.0227 $[M + Na]^+$, calcd for molecular formula $C_8H_8O_4$; $^1$H NMR (500 MHz, $CD_3OD$) δ 4.68 (2H, s, H-8), 6.72 (1H, d, *J*=8.0 Hz, H-6), 7.27 (1H, d, *J*=8.0 Hz, H-7), 7.29 (1H, s, H-3). $^1$H NMR data were consistent with the literature (*18*).

*1-(2,3,4-Trihydroxy-5-methylphenyl)ethanone* (***12***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 181.0691 $[M - H]^-$, calcd for molecular formula $C_9H_{10}O_4$; $^1$H NMR (500 MHz, $CD_3OD$) δ 2.15 (3H, s, $CH_3$), 2.51 (3H, s, $CH_3CO$), 7.08 (1H, s, H-7).

*2,4,5-Trihydroxyacetophenone* (***13***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 167.0601 $[M - H]^-$; calcd for molecular formula $C_8H_8O_4$; $^1$H NMR (500 MHz, $CD_3OD$) δ 2.48 (3H, s, $CH_3$), 6.28 (1H, s, H-5), 7.16 (1H, s, H-7).

*Catechaldehyde* (***14***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 137.0341 $[M - H]^-$, calcd for molecular formula $C_7H_6O_3$; $^1$H NMR (400 MHz, $CD_3OD$) δ 6.92 (1H, d, *J* = 8.0 Hz, H-5), 7.31 (2H, br s, H-2, 6), 9.70 (1H, s, CHO). $^1$H NMR data were consistent with the literature (*19*).

*Vanillin* (***15***)*:* white amorphous powder; (−) ESIMS *m*/*z* 151.0667 $[M - H]^-$, calcd for molecular formula $C_8H_8O_2$; $^1$H NMR (500 MHz, $CD_3OD$) δ 6.94 (1H, d, *J*=8.0 Hz, H-5), 7.43 (1H, d, *J*=8.0 Hz, H-6), 7.44 (1H, s, H-2), 9.75 (1H, s, CHO). $^1$H NMR data were consistent with the literature (*20*).

*Syringaldehyde* (***16***)*:* white amorphous powder; (−) ESIMS *m*/*z* 181.0768 $[M - H]^-$, calcd for molecular formula $C_9H_{10}O_4$; $^1$H NMR

**Table 1.** Total Compounds Isolated from a Butanol Extract of Canadian Maple Syrup (MS-BuOH) Showing Those Reported for the First Time from Maple Syrup

| compd | identification | references of NMR data |
|---|---|---|
| **1** | lyoniresinol[a] | *9* |
| **2** | secoisolariciresinol[a] | *10* |
| **3** | dehydroconiferyl alcohol | *11* |
| **4** | 5′-methoxydehydroconiferyl alcohol[a] | *12* |
| **5** | guaiacylglycerol-*β*-*O*-4′-coniferyl alcohol[a] | *13* |
| **6** | guaiacylglycerol-*β*-*O*-4′-dihydroconiferyl alcohol[a] | *14* |
| **7** | [3-[4-[(6-deoxy-α-L-mannopyranosyl)oxy]-3-methoxyphenyl]methyl]-5-(3,4-dimethoxyphenyl)-dihydro-3-hydroxy-4-(hydroxymethyl)-2(3*H*)-furanone[a] | *15* |
| **8** | scopoletin[a] | *15* |
| **9** | fraxetin[a] | *16* |
| **10** | (*E*)-3,3′-dimethoxy-4,4′-dihydroxystilbene[a] | *17* |
| **11** | 2-hydroxy-3′,4′-dihydroxyacetophenone[a] | *18* |
| **12** | 1-(2,3,4-trihydroxy-5-methylphenyl)ethanone[a,b] | |
| **13** | 2,4,5-trihydroxyacetophenone[a,b] | |
| **14** | catechaldehyde[a] | *19* |
| **15** | vanillin | *20* |
| **16** | syringaldehyde | *20* |
| **17** | gallic acid | *21* |
| **18** | trimethyl gallic acid methyl ester[a] | *22* |
| **19** | syringic acid | *20* |
| **20** | syringenin[a] | *20* |
| **21** | (*E*)-coniferol | *23* |
| **22** | *C*-veratroylglycol[a] | *24* |
| **23** | catechol | *25* |

[a] First report from maple syrup. [b] NMR data provided for the first time herein.

(500 MHz, $CD_3OD$) $\delta$ 3.86 (6H, s, 3, 5-$OCH_3$), 7.24 (2H, s, H-2, 6), 9.76 (1H, s, CHO). $^1H$ NMR data were consistent with the literature (*20*).

*Gallic acid* (***17***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 169.1226 $[M - H]^-$, calcd for molecular formula $C_7H_6O_5$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 7.02 (2H, s, H-2, 6). $^1H$ NMR data were consistent with the literature (*21*).

*Trimethylgallic acid methyl ester* (***18***)*:* brown amorphous powder; (+) ESIMS *m*/*z* 249.0735 $[M + Na]^+$, calcd for molecular formula $C_{11}H_{14}O_5$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 3.35 (3H, s, $COOCH_3$), 3.92 (9H, s, 3, 4, 5-$OCH_3$), 7.34 (2H, s, H-2, 6). $^1H$ NMR data were consistent with the literature (*22*).

*Syringic acid* (***19***)*:* white amorphous powder; (−) ESIMS *m*/*z* 197.0256 $[M - H]^-$, calcd for molecular formula $C_9H_{10}O_5$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 3.90 (6H, s, 3,5-$OCH_3$), 7.34 (2H, s, H-2, 6). $^1H$ NMR data were consistent with the literature (*20*).

*Syringenin* (***20***)*:* brown amorphous powder; (+) ESIMS *m*/*z* 233.0630 $[M + Na]^+$, calcd for molecular formula $C_{11}H_{14}O_4$; $^1H$ NMR (500 MHz, $CD_3OD$) $\delta$ 3.75 (6H, s, 3,5-$OCH_3$), 4.10 (2H, d, $J$ = 5.5 Hz, H-9), 6.12 (1H, d, $J$ = 16.0 Hz, H-8), 6.39 (1H, d, $J$ = 16.0 Hz, H-7), 6.60 (2H, s, H-2, 6). $^1H$ NMR data were consistent with the literature (*20*).

(*E*)-*Coniferol* (***21***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 179.0833 $[M - H]^-$, calcd for molecular formula $C_{10}H_{12}O_3$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 3.88 (3H, s, 3-$OCH_3$), 4.20 (2H, d, $J$ = 5.0 Hz, H-9), 6.20 (1H, d, $J$ = 16.0 Hz, H-8), 6.51 (1H, d, $J$ = 16.0 Hz, H-7), 6.74 (1H, d, $J$ = 8.0 Hz, H-5), 6.86 (1H, d, $J$ = 8.0 hz, H-6), 7.01 (1H, s, H-2). $^1H$ NMR data were consistent with the literature (*23*).

*C-Veratroylglycol* (***22***)*:* brown amorphous powder; (+) ESIMS *m*/*z* 235.0582 $[M + Na]^+$, calcd for molecular formula $C_{10}H_{12}O_5$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 3.78 (1H, m, H-9a), 3.90 (1H, m, H-9b), 3.93 (3H, s, $OCH_3$), 5.13 (1H, dd, $J$ = 3.5, 5.5 Hz, H-8), 6.89 (1H, d, $J$ = 8.0 Hz, H-5), 7.60 (1H, d, $J$ = 8.0 Hz, H-6), 7.61 (1H, s, H-2); $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$ 199.52 (C-7), 153.11 (C-4), 150.04 (C-3), 128.14 (C-1), 125.19 (C-6), 116.03 (C-5), 112.51 (C-2), 75.59 (C-8), 66.39 (C-9). $^1H$ and $^{13}C$ NMR data were consistent with the literature (*24*).

*Catechol* (***23***)*:* brown amorphous powder; (−) ESIMS *m*/*z* 109.0448 $[M - H]^-$, calcd for molecular formula $C_6H_6O_2$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 6.66 (2H, m, H-2, 5), 6.76 (2H, m, H-3, 4); $^{13}C$ NMR (100 Hz, $CD_3OD$) $\delta$ 144.67 (C-1,6), 121.04 (C-2,6), 116.52 (C-3,4). $^1H$ and $^{13}C$ NMR data were consistent with the literature (*25*).

**Table 2.** Antioxidant Activities of Pure Compounds Isolated from a Butanol Extract of Canadian Maple Syrup (MS-BuOH) Showing 50% Inhibitory Concentrations ($IC_{50}$) in the Diphenylpicrylhydrazyl (DPPH) Radical Scavenging Assay[a]

| compd | $IC_{50}$ ($\mu$M) | compd | $IC_{50}$ ($\mu$M) |
|---|---|---|---|
| **1** | 101.5 ± 5.9 | **12** | 31.3 ± 0.6 |
| **2** | 147.9 ± 3.6 | **14** | 35.5 ± 3.7 |
| **3** | 1040.9 ± 103 | **15**[b] | >2600 |
| **4** | 136.7 ± 3.9 | **16**[c] | 357.1 |
| **5** | 943.5 ± 21.9 | **17** | 20.3 ± 0.3 |
| **6** | 1335.9 ± 47.6 | **19** | 191.85 ± 20.99 |
| **7** | 679.3 ± 45.6 | **21**[c] | 115 |
| **8** | 68.2 ± 31.2 | **22** | 641 ± 1 0.6 |
| **9** | 46.5 ± 3.6 | **23** | 89.5 ± 2.7 |
| **10**[b] | >2600 | vitamin C | 58.6 ± 10.7 |
| **11** | 51.8 ± 8.1 | BHT | 2651.5 ± 285.9 |

[a] Values are mean ± SD. BHT, a synthetic commercial antioxidant, butylated hydroxytoluene. All compounds were evaluated except **13**, **18**, and **20** (because of limited sample quantity). [b] Stated as >2600 $\mu$M when $IC_{50}$ values of sample exceed that of BHT; MS-BuOH and sugar fraction of maple syrup had $IC_{50}$ values >1000 $\mu$g/mL. [c] Only tested once because of the quantity.

**Antioxidant Assay.** The antioxidant potentials of MS-BuOH, the sugar fraction of maple syrup, and the pure compounds were determined on the basis of the ability to scavenge the DPPH radical as previously reported (*26*). The DPPH radical scavenging activity of ascorbic acid (vitamin C) and the synthetic commercial antioxidant, BHT, were also assayed as positive controls (see **Table 2**). The assay was conducted in a 96-well format using serial dilutions of 100 $\mu$L aliquots of test compounds (ranging from 2500 to 26 $\mu$g/mL), ascorbic acid (1000−10.4 $\mu$g/mL), and BHT (250,000−250 $\mu$g/mL). Then DPPH (150 $\mu$L) was added to each well to give a final DPPH concentration of 137 $\mu$M. Absorbance was determined after 30 min at 515 nm, and the scavenging capacity (SC) was calculated as $SC\% = [(A_0 - A_1/A_0)] \times 100$, where $A_0$ is the absorbance of the reagent blank and $A_1$ is the absorbance with test samples. The control contained all reagents except the compounds, and all tests were performed in triplicate. $IC_{50}$ values denote the concentration of sample required to scavenge 50% DPPH free radicals.

## RESULTS AND DISCUSSION

**Isolation and Identification of Compounds in Canadian Maple Syrup Butanol Extract (MS-BuOH).** The primary objective of this study was to isolate and identify the phytochemicals present in Canadian maple syrup butanol extract. Because the constituents of ethyl acetate, chloroform, dichloromethane, and diethyl ether extracts of maple syrup have already been reported (*3*−*6*), we focused our isolation and structural elucidation efforts on the butanol extract. We speculated that the butanol extract may contain phenolic compounds not previously identified from the aforementioned organic extracts of maple syrup.

**Figure 1A** shows the HPLC-UV profile of MS-BuOH, which revealed several peaks at 280 and 360 nm characteristic of phenolic compounds. The extract was subjected to a series of chromatographic isolation procedures to yield 23 (**1**−**23**) phenolics. **Figure 1B** shows the HPLC-UV profile of the purified isolates all combined into a single injection. All of the compounds were identified on the basis of their $^1H$ and/or $^{13}C$ NMR and mass spectral data and by correspondence to published literature data when available (**Table 1**). **Figure 2** shows the structures of the compounds grouped into their individual phenolic subclasses for ease of discussion as follows.

*Lignans*. Seven lignans were isolated from MS-BuOH and identified as lyoniresinol (**1**), secoisolariciresinol (**2**), dehydroconiferyl alcohol (also known as dihydrodehydrodiconiferyl alcohol) (**3**), 5′-methoxydehydroconiferyl alcohol (**4**), erythro-guaiacylglycerol-*β*-*O*-4′-coniferyl alcohol (**5**), erythro-guaiacylglycerol-*β*-*O*-4′-dihydroconiferyl

alcohol (**6**), and [3-[4-[(6-deoxy-α-L-mannopyranosyl)oxy]-3-methoxyphenyl]methyl]-5-(3,4-dimethoxyphenyl)dihydro-3-hydroxy-4-(hydroxymethyl)-2(3*H*)-furanone (**7**).

With the exception of dehydroconiferyl alcohol (**3**), which has been previously reported as a lignin-derived flavor compound in maple syrup (*1*, *2*), this is the first reported occurrence of all of the other lignans in maple syrup. Notably, compound **7** was recently described as a constituent of the hardwood collected from the sugar maple tree, *A. saccharum* (*15*), and thus its occurrence in maple syrup is not surprising. Also, apart from dehydroconiferyl alcohol (**3**), previously found in maple syrup (*1*, *2*), and lyoniresinol (**1**), previously reported from leaves of *Acer truncatum* (*27*), this may be regarded as the first reported occurrence of these lignans in the *Acer* genus.

Lignan-rich foods such as flaxseed, which contains secoisolariciresinol (**2**), have attracted significant research attention for their biological effects (*28*, *29*). Thus, the presence of these compounds in maple syrup is interesting from a human health perspective. However, determination of the levels of these lignans (as well as the other bioactive phenolic subclasses described below) in different grades of maple syrup consumed by humans and whether these compounds achieve physiologically relevant levels after maple syrup consumption would be required to evaluate their impact on human health.

*Coumarins*. Two coumarins, not previously reported from maple syrup, were isolated from MS-BuOH and identified as scopoletin (**8**) and fraxetin (**9**). Notably, scopoletin (**8**) has recently been identified from the wood of *A. saccharum* (*15*) and has also been reported from the bark of *Acer nikoense* (*30*). From a biosynthetic perspective, it is interesting that coumarinolignans have been previously reported from the heartwood of *A. nikoense* (*31*), which would account for the occurrence of these two individual phenolic subclasses, namely, coumarins and lignans, in maple syrup.

*Stilbene*. A stilbene was isolated from MS-BuOH and identified as (*E*)-3,3′-dimethoxy-4,4′-dihydroxystilbene (**10**). Whereas stilbene glycosides have been previously reported from the leaves of *Acer mono* (*32*), this is the first reported occurrence of a stilbenoid in maple syrup. Foods containing stilbenes have attracted immense public attention for their potential human health benefits due in large part to emerging research on resveratrol, a stilbene present in red wine, grapes, and berries (*33*).

*Phenolic Derivatives*. Thirteen phenolic derivatives were found in MS-BuOH including 2-hydroxy-3′,4′-dihydroxyacetophenone (**11**), 1-(2,3,4-trihydroxy-5-methylphenyl)ethanone (**12**), 2,4,5-trihydroxyacetophenone (**13**), catechaldehyde (**14**), vanillin (**15**), syringaldehyde (**16**), gallic acid (**17**), trimethyl gallic acid methyl ester (**18**), syringic acid (**19**), syringenin (**20**), (*E*)-coniferol (**21**), *C*-veratroylglycol (**22**), and catechol (**23**). Whereas several of these compounds have been previously found in maple syrup (*3*, *4*), this is the first report of catechaldehyde (**14**), trimethyl gallic acid methyl ester (**18**), syringenin (**20**), and *C*-veratroylglycol (**22**) in maple syrup.

*Other Unidentified Compounds*. It is noteworthy that similar to the observations of Abou Zaid et al. (*4*), a number of peaks/compounds in maple syrup remain unidentified (see **Figure 1A**). Despite starting our initial extraction protocol with 20 L of maple syrup, several compounds were unobtainable due to either rapid degradation/decomposition on our columns or low yields.

In addition, we cannot rule out the presence of compounds previously reported in the other organic extracts of maple syrup (*3*−*6*), such as ethyl acetate (MS-EtOAc), being present in the MS-BuOH. Toward this end, we conducted HPLC-UV comparisons of the retention times of authentic phenolic standards of several of these previously reported compounds with the unidentified peaks in **Figure 1A**, along with comparisons of HPLC-UV chromatograms of MS-BuOH and MS-EtOAc (data not shown). However, due to considerable overlapping and coelution of compounds in these HPLC-UV profiles, our results were inconclusive. Our future work will include the isolation and identification of compounds in MS-EtOAc in order to have a comprehensive phytochemical/phenolic characterization of maple syrup.

Finally, we speculate that apart from the "natural products" identified here, there are "un-natural, artifacts or process-derived" compounds present in maple syrup, possibly formed under the conditions of intensive heating involved in transforming sap to syrup. These compounds could potentially be formed in situ as (1) decomposition/degradation products from the natural compounds and (2) due to chemical reactions between native and process-derived compounds. Further research to identify these compounds is warranted because their contribution to the potential health benefits and biological activity of maple syrup may be significant.

**Antioxidant Activity.** Phenolic compounds identified from maple syrup and maple syrup extracts have been reported to show antioxidant activity (*4*, *7*, *8*). Therefore, MS-BuOH, the sugar fraction of maple syrup, and the pure isolates along with positive controls, vitamin C and the synthetic commercial antioxidant BHT, were evaluated for antioxidant potential in the DPPH assay (**Table 2**). Vitamin C (ascorbic acid) and BHT showed $IC_{50}$ values of 58 μM (ca. 10 μg/mL) and 2651 μM (ca. 583 μg/mL), respectively. Whereas the antioxidant activity of the MS-BuOH ($IC_{50}$ > 1000 μg/mL), the sugar fraction ($IC_{50}$ > 1000 μg/mL), the stilbene (**10**), and vanillin (**15**) all exceeded that of BHT, compounds **11**, **12** and **14** all showed superior antioxidant activity compared to vitamin C. Among the diverse phenolic subclasses of compounds identified in MS-BuOH, the general trend in antioxidant activity was phenolic derivatives, coumarins > stilbene, lignans.

In summary, 23 phenolics (**1**−**23**) with various antioxidant activities were isolated and identified from MS-BuOH. Among the isolates, 16 compounds (**1**, **2**, **4**−**14**, **18**, **20**, and **22**) are being reported from maple syrup for the first time. However, to get a comprehensive phenolic profile and characterization of maple syrup, further isolation work on other extracts (e.g., MS-EtOAc) would be necessary. The results of the current study suggest that the "cocktail" of bioactive phenolics present in Canadian maple syrup may impart potential health benefits to this natural sweetener. However, further research would be required to confirm this.

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## LITERATURE CITED

(1) Ball, D. W. The chemical composition of maple syrup. *J. Chem. Educ.* **2007**, *84*, 1647−1650.

(2) Perkins, T. D.; van den Berg, A. K. Maple syrup − production, composition, chemistry, and sensory characteristics. *Adv. Food Nutr. Res.* **2009**, *56*, 101−143.

(3) Kermasha, S.; Goetghebeur, M.; Dumont, J. Determination of phenolic compound profiles in maple products by high performance liquid chromatography. *J. Agric. Food Chem.* **1995**, *43*, 708−716.

(4) Abou-Zaid, M. M.; Nozzolillo, C.; Tonon, A.; Coppens, M.; Lombardo, A. D. A. High performance liquid chromatography characterization and identification of antioxidant polyphenols in maple syrup. *Pharm. Biol.* **2008**, *46*, 117−125.

(5) Filipic, V. J.; Underwood, J. C. Some aromatic compound in sap. Composition of maple sap and syrup. *J. Food Sci.* **1964**, *29*, 464.
(6) Potter, T. L.; Fagerson, I. S. Phenolic compounds in maple sap. In *Phenolic Compounds and Their Effects on Health*; Ho, C. T., Lee, C. Y., Huang, M. T., Eds.; ACS Symposium Series 506; American Chemical Society: Washington, DC, 1992; Part I.
(7) Theirault, M.; Caillet, S.; Kermasha, S.; Lacroix, M. Antioxidant, antiradical and antimutagenic activities of phenolic compounds present in maple products. *Food Chem.* **2006**, *98*, 490−501.
(8) Legault, J.; Girard-Lalancette, K.; Grenon, C.; Dussault, C.; Pichette, A. Antioxidant activity, inhibition of nitric oxide overproduction, and in vitro antiproliferative effect of maple sap and syrup from *Acer saccharum*. *J. Med. Food* **2010**, *13*, 460−468.
(9) Takemoto, M.; Fukuyo, A.; Aoshima, Y.; Tanaka, K. Synthesis of lyoniresinol with combined utilization of synthetic chemistry and biotechnological methods. *Chem. Pharm. Bull.* **2006**, *54*, 226−229.
(10) Baderschneider, B.; Winterhalter, P. Isolation and characterization of novel benzoates, cinnamates, flavonoids, and lignans from Riesling wine and screening for antioxidant activity. *J. Agric. Food Chem.* **2001**, *49*, 2788−2798.
(11) Junxiu, M.; Tao, J.; Huma, A. B.; Bina, S.; Siddiqui, S. D.; Jeremy, D. K. Synthesis of dihydrodehydrodiconiferyl alcohol: the revised structure of lawsonicin. *Org. Biomol. Chem.* **2010**, *8*, 107−113.
(12) Chin, Y.-W.; Chai, H.-B.; Keller, W. J.; Kinghorn, A. D. Lignans and other constituents of the fruits of *Euterpe oleracea* (acai) with antioxidant and cytoprotective activities. *J. Agric. Food Chem.* **2008**, *56*, 7759−7764.
(13) Han, H.-Y.; Wang, X.-H.; Wang, N-Li.; Ling, M.-T.; Wong, Y.-C.; Yao, X.-S. Lignans isolated from *Campylotropis hirtella* (Franch.) Schindl. decreased prostate specific antigen and androgen receptor expression in LNCaP cells. *J. Agric. Food Chem.* **2008**, *56*, 6928−6935.
(14) De Marino, S.; Gala, F.; Zollo, F.; Vitalini, S.; Fico, G.; Visioli, F.; Iorizzi, M. Identification of minor secondary metabolites from the latex of *Croton lechleri* (Muell-Arg) and evaluation of their antioxidant activity. *Molecules* **2008**, *13*, 1219−1229.
(15) Yoshikawa, K.; Kawahara, Y.; Arihara, S.; Hashimoto, T. Aromatic compounds and their antioxidant activity from *Acer saccaharum*. *J. Nat. Med.* **2010**, in press (published online Aug 5, 2010, DOI 10.1007/s11418-010-0450-5).
(16) Liu, R.; Sun, Q.; Sun, A.; Cui, J. Isolation and purification of coumarin compounds from *Cortex fraxinus* by high-speed counter-current chromatography. *J. Chromatogr., A* **2005**, *1072*, 195−199.
(17) Hajdu, Z.; Varga, E.; Hohmann, J.; Kalman, A.; Argay, G.; Guenther, G. A stilbene from the roots of *Leuzea carthamoides*. *J. Nat. Prod.* **1998**, *61*, 1298−1299.
(18) Tsuda, T.; Watanabe, M.; Ohshima, K.; Yamamoto, A.; Kawakishi, S.; Osawa, T. Antioxidative components isolated from the seed of tamarind (*Tamarindus indica* L.). *J. Agric. Food Chem.* **1994**, *42*, 2671−2674.
(19) Prachayasittikul, S.; Buraparuangsang, P.; Worachartcheewan, A.; Isarankura-Na-Ayudhya, C.; Ruchirawat, S.; Prachayasittikul, V. Antimicrobial and antioxidative activities of bioactive constituents from *Hydnophytum formicarum* Jack. *Molecules* **2008**, *13*, 904−921.
(20) Bonini, C.; D'Auria, M.; Ferri, R. Singlet oxygen mediated degradation of lignin − isolation of oxidation products from steam-exploded lignin from pine. *Photochem. Photobiol. Sci.* **2002**, *1*, 570−573.
(21) Le Gall, G.; Colquhoun, I. J.; Defernez, M. Metabolite profiling using $^{1}$H NMR spectroscopy for quality assessment of green tea, *Camellia sinensis* (L.). *J. Agric. Food Chem.* **2004**, *52*, 692−700.
(22) Avila-Zarraga, J. G.; Martinez, R. Efficient methylation of carboxylic acids with potassium hydroxide/methyl sulfoxide and iodomethane. *Syn. Commun.* **2001**, *31*, 2177−2183.
(23) Yao, C.-S.; Lin, M.; Wang, L. Isolation and biomimetic synthesis of anti-inflammatory stilbenolignans from *Gnetum cleistostachyum*. *Chem. Pharm. Bull.* **2006**, *54*, 1053−1057.
(24) Baderschneider, B.; Winterhalter, P. Isolation and characterization of novel benzoates, cinnamates, flavonoids, and lignans from Riesling wine and screening for antioxidant activity. *J. Agric. Food Chem.* **2001**, *49*, 2788−2798.
(25) Loo, A. Y.; Jain, K.; Darah, I. Antioxidant activity of compounds isolated from the pyroligneous acid, *Rhizophora apiculata*. *Food Chem.* **2007**, *107*, 1151−1160.
(26) Nanjo, F.; Goto, K.; Seto, R.; Suzuki, M.; Sakai, M.; Hara, Y. Scavenging effects of tea catechins and their derivatives on 1, 1-diphenyl-2-picrylhydrazyl radical. *Free Radical Biol. Med.* **1996**, *21*, 895−902.
(27) Dong, L. P.; Ni, W.; Dong, J. Y.; Li, J. Z.; Chen, C. X.; Liu, H. Y. A new neolignan glycoside from the leaves of *Acer truncatum*. *Molecules* **2006**, *11*, 1009−1014.
(28) Adlercreutz, H. Lignans and human health. *Crit. Rev. Clin. Lab. Sci.* **2007**, *44*, 483−525.
(29) Adolphe, J. L.; Whiting, S. J.; Juurlink, B. H.; Thorpe, L. U.; Alcorn, J. Health effects with consumption of the flax lignan secoisolariciresinol diglucoside. *Br. J. Nutr.* **2010**, *103*, 929−938.
(30) Inoue, T.; Ishidate, Y.; Fujita, M.; Kubo, M.; Fukushima, M.; Nagai, M. Studies on the constituents of Aceraceae plants. I. Constituents in the leaves and the stem bark of *Acer nikoense* Maxim. *Yakugaku Zasshi* **1978**, *98*, 41−46.
(31) Iizuka, T.; Nagumo, S.; Yotsumoto, H.; Moriyama, H.; Nagai, M. Vasorelaxant effects of *Acer nikoense* extract and isolated coumarinolignans on rat aortic rings. *Biol. Pharm. Bull.* **2007**, *30*, 1164−1166.
(32) Yang, H.; Sung, S. H.; Kim, Y. C. Two new hepatoprotective stilbene glycosides from *Acer mono* leaves. *J. Nat. Prod.* **2005**, *68*, 101−103.
(33) Sadruddin, S.; Arora, R. Resveratrol: biologic and therapeutic implications. *J. Cardiometab. Syndr.* **2009**, *4*, 102−106.

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