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# Phanerosides A-X, Phenylpropanoid Esters of Sucrose from the Rattans of Phanera championii Benth 

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#### Abstract

Twenty-four new phenylpropanoid esters of sucrose, phanerosides A-X (1-24), were isolated from an EtOH extract of the rattans of Phanera championii Benth. (Fabaceae). Their structures were elucidated on the basis of comprehensive spectroscopic data analysis. A wide range of structural analogues were presented due to the different numbers and positions of acetyl substituents and the structures of phenylpropanoid moieties. Phenylpropanoid esters of sucrose were isolated from the Fabaceae family for the first time. Biologically, the inhibitory effects of compounds $\mathbf{6}$ and 21 on NO production in LPS-induced BV-2 microglial cells were better than that of the positive control, with $\mathrm{IC}_{50}$ values of 6.7 and $5.2 \mu \mathrm{M}$, respectively. The antioxidant activity assay showed that compounds $\mathbf{5}$, 15,17 , and 24 displayed moderate DPPH radical scavenging activity, with $\mathrm{IC}_{50}$ values ranging from 34.9 to $43.9 \mu \mathrm{M}$.


Keywords: Phanera championii Benth.; Fabaceae; phenylpropanoid esters of sucrose; anti-inflammatory; antioxidant

## 1. Introduction

Phenylpropanoid esters of sucrose are characterized by the esterification of different hydroxy groups of sucrose with phenylpropanoid moieties [1,2]. These compounds have been isolated mainly from the families Arecaceae, Brassicaceae, Liliaceae, Polygonaceae, Rosaceae, Rutaceae, Smilacaceae, and Sparganiaceae [1,3]. The structural diversity of phenylpropanoid esters of sucrose generates extensive pharmacological antitumor [4-6], anti-inflammatory [7,8], antioxidant [9], an anti-HIV [10] activities, which are extremely thrilling to those engaged in medicinal chemistry $[11,12]$.

Fabaceae is the third largest plant family, comprising approximately 800 genera and 20,000 species worldwide $[13,14]$. As the largest of the several genera in the Fabaceae family, Phanera results from the reorganization of Bauhinia sensu lato. The genus Phanera encompasses about 90-100 species, mainly distributed in tropical Asia and Australasia [15]. As one of them, Phanera championii Benth. is widely distributed in Guangxi Province and was first recorded in 'Nanning Drug Chi' [16]. It is a well-known folk medicine with a rich history of being used as medication to treat rheumatoid arthritis and epigastric pain $[17,18]$. Phytochemical investigations of this plant have primarily resulted in the isolation of flavonoids, nitrile glucoside, dibenzofurans, and diterpenoid [16,19-21]. In our ongoing research in pursuit of novel and biologically active metabolites from ethnic medicines in Guangxi, 24 new phenylpropanoid esters of sucrose (1-24) were isolated from the rattans of $P$. championii. Herein, the isolation, structural elucidation, anti-inflammatory, and antioxidant activities in vitro of all the isolated compounds are described.

## 2. Results and Discussion

## Structural Elucidation

Compound 1 (Figure 1) was isolated as a white amorphous powder with a molecular formula of $\mathrm{C}_{30} \mathrm{H}_{34} \mathrm{O}_{15}$, as determined using HRESIMS $\left(\mathrm{m} / \mathrm{z} 657.1798[\mathrm{M}+\mathrm{Na}]^{+}\right.$, calcd for 657.1790) and ${ }^{13} \mathrm{C}$ NMR data. The ${ }^{1} \mathrm{H}$ NMR spectrum (Table 1) revealed two groups of $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}$ aromatic signals $\left[\delta_{\mathrm{H}} 7.49\left(2 \mathrm{H}, \mathrm{d}, J=8.8 \mathrm{~Hz}, \mathrm{H}-2^{\prime \prime} / 6^{\prime \prime}\right), 6.82(2 \mathrm{H}, \mathrm{d}, J=8.8 \mathrm{~Hz}\right.$, $\left.\mathrm{H}-3^{\prime \prime} / 5^{\prime \prime}\right)$ and $\left.7.51\left(2 \mathrm{H}, \mathrm{d}, J=8.8 \mathrm{~Hz}, \mathrm{H}-2^{\prime \prime \prime} / 6^{\prime \prime \prime}\right), 6.81\left(2 \mathrm{H}, \mathrm{d}, J=8.8 \mathrm{~Hz}, \mathrm{H}-3^{\prime \prime \prime} / 5^{\prime \prime \prime}\right)\right]$ and two sets of trans-olefinic protons $\left[\delta_{\mathrm{H}} 7.72\left(1 \mathrm{H}, \mathrm{d}, J=16.0 \mathrm{~Hz}, \mathrm{H}-7^{\prime \prime}\right), 6.39(1 \mathrm{H}, \mathrm{d}, J=16.0 \mathrm{~Hz}\right.$, $\left.\mathrm{H}-8^{\prime \prime}\right)$ and $7.67\left(1 \mathrm{H}, \mathrm{d}, J=16.0 \mathrm{~Hz}, \mathrm{H}-7^{\prime \prime \prime}\right), 6.43\left(1 \mathrm{H}, \mathrm{d}, J=16.0 \mathrm{~Hz}, \mathrm{H}-8^{\prime \prime \prime}\right]$. In addition, a characteristic doublet with a small coupling constant $(J=3.6 \mathrm{~Hz})$ at $\delta_{\mathrm{H}} 5.60$ was also shown in the ${ }^{1} \mathrm{H}$ NMR spectrum, which together with 12 oxygen-bearing carbon signals (including two anomers at $\delta_{\mathrm{C}} 105.7$ and 90.6 ) in the ${ }^{13} \mathrm{C}$ NMR data (Table 2 ) supposed the presence of a disaccharide moiety. Furthermore, detailed analysis of the 2D NMR correlations (Figure 2) and chiral HPLC analysis of monosaccharides after acid hydrolysis of 1 revealed that the two sugars were $\beta$-D-fructose and $\alpha$-D-glucose units connected via $\mathrm{C}-2 \rightarrow \mathrm{C}-1^{\prime}$ to construct a D-sucrose moiety. The ${ }^{13} \mathrm{C}$ NMR spectrum showed 30 carbon signals, apart from the 12 carbon signals occupied by the D-sucrose moiety; the other 18 ones were classified as 2 carbonyl carbons ( $\delta_{\mathrm{C}} 169.2,168.8$ ) and 16 olefinic or aromatic carbons with the assistance of the HSQC data. Two discrete spin systems, $\mathrm{H}-7^{\prime \prime} / \mathrm{H}-8^{\prime \prime}$ and $\mathrm{H}-7^{\prime \prime \prime} / \mathrm{H}-8^{\prime \prime \prime}$, in the ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum, and the correlations from $\mathrm{H}-7^{\prime \prime}$ to $\mathrm{C}-1^{\prime \prime} / \mathrm{C}-2^{\prime \prime} / \mathrm{C}-6^{\prime \prime} / \mathrm{C}-9^{\prime \prime}$ and $\mathrm{H}-7^{\prime \prime \prime}$ to $\mathrm{C}-1^{\prime \prime \prime} / \mathrm{C}-2^{\prime \prime \prime} / \mathrm{C}-6^{\prime \prime \prime} / \mathrm{C}-9^{\prime \prime \prime}$ in the HMBC spectrum (Figure 2), established two trans-p-coumaroyl moieties. Subsequently, the key HMBC correlations from $\mathrm{H}-2^{\prime}$ to $\mathrm{C}-9^{\prime \prime}$ as well as from $\mathrm{H}_{2}-6^{\prime}$ to $\mathrm{C}-9^{\prime \prime \prime}$ suggested that the two trans-p-coumaroyl moieties were located at C-2' and C-6'. Thus, the structure of $\mathbf{1}$ was identified and named phaneroside A.


| $\mathrm{R}_{1}$ | $\mathrm{R}_{2}$ | $\mathrm{R}_{3}$ | $\mathrm{R}_{4}$ | $\mathrm{R}_{5}$ | $\mathrm{R}_{6}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H | H | H | H | H | OH | $\Delta^{7 /, 8^{\prime \prime}} E \quad \Delta^{7 ", 8^{\prime \prime \prime}} E$ |
| H | H | H | H | H | H | $\Delta^{77,8^{\prime \prime}} E \quad \Delta^{77 \prime \prime 8^{\prime \prime \prime}} E$ |
| H | H | H | OMe | H | OH | $\Delta^{7 \prime, 8^{\prime \prime}} E \quad \Delta^{77 \prime \prime} 8^{\prime \prime \prime} E$ |
| H | H | H | H | OMe | OH | $\Delta^{7 \prime, 8^{\prime \prime}} E \quad \Delta^{7 \prime \prime \prime}, 8^{\prime \prime \prime} E$ |
| H | H | H | OMe | OMe | OH | $\Delta^{77 \prime 8^{\prime \prime}} E \quad \Delta^{77 \prime, 8^{\prime \prime \prime}} E$ |
| acetyl | H | H | H | H | OH | $\Delta^{77.8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | acetyl | H | H | H | OH | $\Delta^{7,8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | H | acetyl | H | H | OH | $\Delta^{77,8^{\prime \prime}} E \quad \Delta^{7 \% \prime \prime 8^{\prime \prime \prime}} E$ |
| acetyl | H | H | H | OMe | OH | $\Delta^{7 \prime, 8^{\prime \prime}} E \quad \Delta^{7 ", 8^{\prime \prime \prime}} E$ |
| H | acetyl | H | H | OMe | OH | $\Delta^{7 \prime \prime} 8^{\prime \prime} E \quad \Delta^{7 ", 8^{\prime \prime \prime}} E$ |
| H | H | acetyl | H | OMe | OH | $\Delta^{77,8^{\prime \prime}} E \quad \Delta^{77^{7 \prime \prime} 8^{\prime \prime \prime}} E$ |
| acetyl | H | H | OMe | H | OH | $\Delta^{7 \%, 8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | acetyl | H | OMe | H | OH | $\Delta^{7 \%, 8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | H | acetyl | OMe | H | OH | $\Delta^{77.8^{\prime \prime}} E \quad \Delta^{7+, 8^{\prime \prime \prime}} E$ |
| acetyl | H | H | OMe | OMe | OH |  |
| H | acetyl | H | OMe | OMe | OH | $\Delta^{77.8^{\prime \prime}} E \quad \Delta^{77.8^{7 \prime}} E$ |
| H | H | acetyl | OMe | OMe | OH | $\Delta^{77,8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | H | acetyl | OMe | OMe | OH | $\Delta^{7 \prime \prime} 8^{\prime \prime} Z \quad \Delta^{7 m, 8^{\prime \prime \prime}} E$ |
| H | H | acetyl | OMe | OMe | OH |  |
| acetyl | acetyl | H | H | H | OH | $\Delta^{7 / 88^{\prime \prime}} E \quad \Delta^{7 / 8^{\prime \prime} 8^{\prime \prime}} E$ |
| H | acetyl | acetyl | H | H | OH | $\Delta^{77,8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | acetyl | acetyl | OMe | H | OH | $\Delta^{7 /, 8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime}} E$ |
| acetyl | acetyl | H | H | OMe | OH | $\Delta^{7 / 8,8^{\prime \prime}} E \quad \Delta^{77,8^{\prime \prime \prime}} E$ |
| H | acetyl | acetyl | OMe | OMe | OH | $\Delta^{77.8^{\prime \prime}} E \quad \Delta^{7 m, 8^{\prime \prime \prime}} E$ |

Figure 1. Chemical structures of compounds 1-24.

Table 1. ${ }^{1} \mathrm{H}$ NMR data of compounds $\mathbf{1}-\mathbf{5}$ in $\delta$ ppm ( $J$ coupling in Hertz).

| Position | $1^{\text {a }}$ | $2^{\text {b }}$ | $3^{\text {a }}$ | $4^{\text {a }}$ | $5^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 3.51, d (12.0) | 3.51, d (12.0) | 3.52, d (12.0) | 3.51, d (12.0) | 3.51, d (11.6) |
|  | $3.31, \mathrm{~d}(12.0)$ | 3.31 , overlapped | $3.32, \mathrm{~d}(12.0)$ | 3.30, d (12.0) | 3.31 , overlapped |
| 3 | 4.22, d (8.8) | 4.22, d (9.0) | 4.22, d (8.8) | 4.22, d (8.4) | $4.22, \mathrm{~d}(8.8)$ |
| 4 | 4.04, t (8.8) | 4.04, t (9.0) | 4.04, t (8.8) | 4.07, dd (9.2, 8.4) | 4.07, t (8.8) |
| 5 | 3.79, m | 3.78, m | 3.79 , m | 3.79 , m | 3.79, m |
| 6 | 3.88, dd (12.0, 7.2) | $3.88, \text { dd (12.0, 7.2) }$ | 3.88, m | 3.88, m | 3.89 , overlapped |
|  | $3.77, \mathrm{~m}$ | $3.77 \text {, dd }(12.0,2.4)$ | 3.77, m | 3.77, m | $3.78, \mathrm{~m}$ |
| $1^{\prime}$ | 5.60, d (3.6) | 5.60, d (3.6) | 5.60, d (4.0) | 5.60, d (3.6) | 5.61, d (3.6) |
| $2^{\prime}$ | 4.73 , dd (10.0, 3.6) | 4.73 , dd ( $9.6,3.6)$ | 4.73, dd (10.0, 4.0) | 4.73 , dd (9.6, 3.6) | 4.73 , dd $(9.6,3.6)$ |
| $3^{\prime}$ | 4.01, dd (10.0, 9.2) | 4.01, t (9.6) | $4.01, \mathrm{t}(10.0)$ | 4.01, t (9.6) | 4.01, t (9.6) |
| $4^{\prime}$ | 3.45, t (9.2) | 3.46, t (9.6) | 3.46, t (10.0) | 3.45, t (9.6) | 3.45, t (9.6) |
| 5$6^{\prime}$ | 4.19, ddd (9.2, 6.0, 2.0) | 4.20, m | 4.18, dd (10.0, 6.0, 2.0) | 4.20, m | $4.20, \mathrm{~m}$ |
|  | $4.54 \text {, dd }(12.0,2.0)$ | $4.56, \text { br d (12.0) }$ | $4.54 \text {, dd }(12.0,2.0)$ | $4.54, \mathrm{~d}(12.0)$ | $4.54, \text { br d (12.0) }$ |
|  | $4.31, \mathrm{dd}(12.0,6.0)$ | $4.34, \mathrm{dd}(12.0,6.6)$ | $4.31, \mathrm{dd}(12.0,6.0)$ | $4.31, \mathrm{dd}(12.0,6.4)$ | $4.31, \text { dd }(12.0,6.4)$ |
| $2^{\prime \prime}$ | 7.49, d (8.8) | 7.49, d (8.4) | 7.21, d (2.0) | 7.48, d (8.4) | 7.21, br s |
| $3^{\prime \prime}$ | 6.82 , d (8.8) | 6.81, d (8.4) |  | 6.81, d (8.4) |  |
| $5^{\prime \prime}$ | 6.82 , d (8.8) | 6.81, d (8.4) | 6.82, d (8.0) | 6.81, d (8.4) | 6.82, d (8.4) |
| $6^{\prime \prime}$ | 7.49, d (8.8) | 7.49, d (8.4) | 7.11, dd (8.0, 2.0) | 7.48, d (8.4) | 7.11, br d (8.4) |
| $7^{\prime \prime}$ | 7.72, d (16.0) | 7.72, d (16.2) | 7.72 , d (16.0) | 7.72, d (16.0) | 7.72, d (16.0) |
| $8^{\prime \prime}$ | $6.39, \mathrm{~d}(16.0)$ | $6.39, \mathrm{~d}(16.2)$ | 6.42 , d (16.0) | 6.39 , d (16.0) | 6.42 , d (16.0) |
| $2^{\prime \prime \prime}$ | 7.51, d (8.8) | 7.65, m | 7.50, d (8.4) | 7.25, br s | 7.25, br s |
| $3^{\prime \prime \prime}$ | 6.81, d (8.8) | 7.41, overlapped | 6.81, d (8.4) |  |  |
| $4^{\prime \prime \prime}$ |  | 7.41, overlapped |  |  |  |
| $5^{\prime \prime \prime}$ | 6.81, d (8.8) | 7.41, overlapped | 6.81, d (8.4) | 6.81, d (8.4) | 6.81, d (8.4) |
| $6^{\prime \prime \prime}$ | 7.51, d (8.8) | 7.65, m | 7.50, d (8.4) | 7.10, br d (8.4) | 7.11 , br d (8.4) |
| $7^{\prime \prime \prime}$ | 7.67, d (16.0) | 7.75, d (16.2) | 7.67, d (16.0) | 7.65, d (16.0) | 7.66, d (16.0) |
| $8^{\prime \prime \prime}$ | $6.43, \mathrm{~d}(16.0)$ | 6.64 , d (16.2) | 6.43 , d (16.0) | $6.46, \mathrm{~d}(16.0)$ | 6.46, d (16.0) |
| $3^{\prime \prime}$-OMe |  |  | 3.90, s |  | 3.90, s |
| $3^{\prime \prime \prime}$-OMe |  |  |  | 3.89, s | 3.90, s |

${ }^{\mathrm{a}}$ In $\mathrm{MeOH}-d_{4},{ }^{1} \mathrm{H}$ NMR at $400 \mathrm{MHz} .{ }^{\mathrm{b}}$ In MeOH- $d_{4},{ }^{1} \mathrm{H}$ NMR at $600 \mathrm{MHz} . \mathrm{s}=$ singlet; $\mathrm{d}=$ doublet; $\mathrm{t}=$ triplet; $\mathrm{m}=$ multiplet; $\mathrm{br}=$ broad.

Table 2. ${ }^{13} \mathrm{C}$ NMR data of compounds $\mathbf{1 - 5}$ in $\delta \mathrm{ppm}$.

| Position | $\mathbf{1}^{\mathbf{a}}$ | $\mathbf{2}^{\mathbf{b}}$ | $\mathbf{3}^{\mathbf{a}}$ | $\mathbf{4}^{\mathbf{a}}$ | $\mathbf{5}^{\mathbf{a}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 62.9 | 62.9 | 62.9 | 62.9 | 63.0 |
| 2 | 105.7 | 105.7 | 105.7 | 105.6 | 105.7 |
| 3 | 77.0 | 77.0 | 77.0 | 77.0 | 77.0 |
| 4 | 75.6 | 75.6 | 75.6 | 75.7 | 75.7 |
| 5 | 84.0 | 84.0 | 84.0 | 84.0 | 84.0 |
| 6 | 64.2 | 64.2 | 64.2 | 64.2 | 64.2 |
| $1^{\prime}$ | 90.6 | 90.6 | 90.6 | 90.5 | 90.5 |
| $2^{\prime}$ | 74.4 | 74.4 | 74.4 | 74.4 | 74.4 |
| $3^{\prime}$ | 71.9 | 71.9 | 71.9 | 72.0 | 72.0 |
| $4^{\prime}$ | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 |
| $5^{\prime}$ | 71.9 | 71.9 | 71.9 | 71.9 | 71.9 |
| $6^{\prime}$ | 65.0 | 65.2 | 65.0 | 65.0 | 65.1 |
| $1^{\prime \prime}$ | 127.1 | 127.0 | 127.6 | 127.0 | 127.7 |
| $2^{\prime \prime}$ | 131.3 | 111.3 | 111.8 | 111.8 |  |
| $3^{\prime \prime}$ | 116.9 | 161.7 | 151.0 | 116.9 | 149.4 |
| $4^{\prime \prime}$ | 161.6 | 116.9 | 116.5 | 161.6 | 151.0 |
| $5^{\prime \prime}$ | 13.9 | 131.3 | 124.3 | 131.9 | 116.5 |
| $6^{\prime \prime}$ | 147.5 | 114.7 | 114.9 | 147.5 | 124.3 |
| $7^{\prime \prime}$ | 114.7 | 168.8 | 168.8 | 114.7 | 115.8 |
| $8^{\prime \prime}$ | 168.8 | 127.0 | 127.1 | 127.7 | 168.8 |
| $9^{\prime \prime}$ | $1^{\prime \prime \prime}$ |  |  |  | 127.6 |

Table 2. Cont.

| Position | $\mathbf{1}^{\mathbf{a}}$ | $\mathbf{2}^{\mathbf{b}}$ | $\mathbf{3}^{\mathbf{a}}$ | $\mathbf{4}^{\mathbf{a}}$ | $\mathbf{5}^{\mathbf{a}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $2^{\prime \prime \prime}$ | 131.3 | 129.4 | 131.3 | 111.6 | 111.6 |
| $3^{\prime \prime \prime}$ | 116.8 | 130.0 | 116.8 | 149.4 | 149.4 |
| $4^{\prime \prime \prime}$ | 161.4 | 131.6 | 161.4 | 150.7 | 150.8 |
| $5^{\prime \prime \prime}$ | 116.8 | 130.0 | 116.8 | 116.4 | 116.4 |
| $6^{\prime \prime \prime}$ | 131.3 | 129.4 | 131.3 | 124.3 | 124.3 |
| $7^{\prime \prime \prime}$ | 146.9 | 146.7 | 146.9 | 147.1 | 147.1 |
| $8^{\prime \prime \prime}$ | 114.9 | 118.7 | 115.0 | 115.2 | 115.2 |
| $9^{\prime \prime \prime}$ | 169.2 | 168.5 | 169.2 | 169.1 | 169.1 |
| $3^{\prime \prime}-\mathrm{OMe}$ |  |  | 56.4 | 56.5 |  |
| $3^{\prime \prime \prime}-\mathrm{OMe}$ |  |  | 56.5 | 56.5 |  |

${ }^{\text {a }}$ In MeOH- $d_{4},{ }^{13} \mathrm{C}$ NMR at $100 \mathrm{MHz} .{ }^{\mathrm{b}}$ In $\mathrm{MeOH}-d_{4},{ }^{13} \mathrm{C}$ NMR at 150 MHz .


1
$-{ }^{1} \mathrm{H}-1 \mathrm{H}$ COSY $\curvearrowleft \mathrm{HMBC}$
Figure 2. Key ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY and HMBC correlations of 1.
Compounds 2-24 were determined to be structurally related to $\mathbf{1}$ according to their extremely similar physicochemical properties and NMR data. The latter all showed the characteristics of a core D-sucrose unit, while the variation of substituents and their positions obtained different structures. The structural elucidation of 2-24 was as follows.

The molecular formula of compound 2 was assigned as $\mathrm{C}_{30} \mathrm{H}_{34} \mathrm{O}_{14}$ based on its HRESIMS ( $\mathrm{m} / \mathrm{z} 641.1847[\mathrm{M}+\mathrm{Na}]^{+}$, calcd for 641.1841 ) and ${ }^{13} \mathrm{C}$ NMR data, with 16 mass units less than 1. The analogous ${ }^{1} \mathrm{H}$ NMR data (Table 1) of $\mathbf{1}$ and 2 indicated that they were structural analogues, excepting of the presence of a monosubstituted aromatic moiety $\left[\delta_{\mathrm{H}} 7.65(1 \mathrm{H}, \mathrm{m}\right.$, $\left.\mathrm{H}-2^{\prime \prime \prime} / 6^{\prime \prime \prime}\right)$, $7.41\left(3 \mathrm{H}\right.$, overlapped, $\left.\mathrm{H}-3^{\prime \prime \prime} / 4^{\prime \prime \prime} / 5^{\prime \prime \prime}\right)$ ] and the absence of an $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}$ aromatic unit in 2. The long-range correlations from phenyl protons to olefinic carbons and correlations from olefinic protons to ester carbonyl carbons in the HMBC spectrum indicated that a trans-p-coumaroyl group and a trans-cinnamoyl group were presented (Figure 3). The HMBC correlations from $\mathrm{H}-2^{\prime}\left(\delta_{\mathrm{H}} 4.73\right)$ to $\mathrm{C}-9^{\prime \prime}$ and $\mathrm{H}_{2}-6^{\prime}\left(\delta_{\mathrm{H}} 4.56,4.34\right)$ to $\mathrm{C}-9^{\prime \prime \prime}$ confirmed the structure of $\mathbf{2}$ as shown, and this compound was named phaneroside B.
2


3


4


Figure 3. Key HMBC correlations of 2-5.

Compounds 3 and 4 had the same molecular formula, $\mathrm{C}_{31} \mathrm{H}_{36} \mathrm{O}_{16}$, as determined using the HRESIMS peaks at $m / z 687.1895$ and 687.1896 ( $[\mathrm{M}+\mathrm{Na}]^{+}$, calcd for 687.1896), respectively, indicating 30 mass units more than 1 , ascribed to a methoxy group. The ${ }^{1} \mathrm{H}$ NMR data (Table 1) of $\mathbf{3}$ and $\mathbf{4}$ were similar to those of $\mathbf{1}$, except for the presence of an $A B X$ aromatic moiety $\left[\delta_{\mathrm{H}} 7.21\left(1 \mathrm{H}, \mathrm{d}, J=2.0 \mathrm{~Hz}, \mathrm{H}-2^{\prime \prime}\right), 7.11\left(1 \mathrm{H}, \mathrm{dd}, J=8.0,2.0 \mathrm{~Hz}, \mathrm{H}-6^{\prime \prime}\right), 6.82\right.$ $\left(1 \mathrm{H}, \mathrm{d}, J=8.0 \mathrm{~Hz}, \mathrm{H}-5^{\prime \prime}\right)$ in 3 and $7.25\left(1 \mathrm{H}, \mathrm{br} \mathrm{s}, \mathrm{H}-2^{\prime \prime \prime}\right), 7.10\left(1 \mathrm{H}, \mathrm{br} \mathrm{d}, J=8.4 \mathrm{~Hz}, \mathrm{H}-6^{\prime \prime \prime}\right), 6.81$ $\left(1 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz}, \mathrm{H}-5^{\prime \prime \prime}\right)$ in 4] and a methoxy [ $\delta_{\mathrm{H}} 3.90(3 \mathrm{H}, \mathrm{s})$ in 3 and $3.89(3 \mathrm{H}, \mathrm{s})$ in 4$]$ and the absence of an $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}$ aromatic unit. The HMBC correlations from $\mathrm{H}-5^{\prime \prime} / 3^{\prime \prime}-\mathrm{OMe}$ to $\mathrm{C}-3^{\prime \prime}$ in 3 and from $\mathrm{H}-5^{\prime \prime \prime} / 3^{\prime \prime \prime}$-OMe to $\mathrm{C}-3^{\prime \prime \prime}$ in 4 , together with the ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY and HMBC correlations as mentioned previously, suggested that there were a trans-feruloyl group and a trans-p-coumaroyl group in both 3 and 4 (Figure 3). The complete structures of 3 and 4 were further established by the HMBC correlations from the protons of the sucrose unit to carbonyl carbons. Therefore, compounds 3 and 4 were determined to be phanerosides C and D, respectively.

Compound 5 gave the molecular formula of $\mathrm{C}_{32} \mathrm{H}_{38} \mathrm{O}_{17}$, as determined by an HRESIMS ion at $m / z 717.1990\left([\mathrm{M}+\mathrm{Na}]^{+}\right.$, calcd for 717.2001). The NMR data (Tables 1 and 2) indicated the presence of two trans-feruloyl moieties and a D-sucrose unit. The key HMBC crosspeaks from $\mathrm{H}-2^{\prime}\left(\delta_{\mathrm{H}} 4.73\right)$ to $\mathrm{C}-9^{\prime \prime}$ and $\mathrm{H}_{2}-6^{\prime}\left(\delta_{\mathrm{H}} 4.54,4.31\right)$ to $\mathrm{C}-9^{\prime \prime \prime}$ suggested that the two trans-feruloyl moieties were linked to C-2' and C-6' of glucopyranose unit (Figure 3). Thus, the structure of compound 5 was identified and named phaneroside E .

Compounds 6-8 shared the same molecular formula of $\mathrm{C}_{32} \mathrm{H}_{36} \mathrm{O}_{16}$, as obtained from their respective HRESIMS data. Their molecular masses were 42 mass units more than that of 1, which combined with the 1D NMR data of 6-8 (Tables 3 and 5) suggested that an acetyl group $\left[\delta_{\mathrm{H}} 2.01(3 \mathrm{H}, \mathrm{s}), \delta_{\mathrm{C}} 172.0,20.6\right.$ in $6 ; \delta_{\mathrm{H}} 2.18(3 \mathrm{H}, \mathrm{s}), \delta_{\mathrm{C}} 172.2,20.8$ in $7 ; \delta_{\mathrm{H}} 2.05(3 \mathrm{H}, \mathrm{s})$, $\delta_{\mathrm{C}} 172.4,20.8$ in 8 ] existed in each compound. The key HMBC correlations from $\mathrm{H}_{2}-1$ $\left(\delta_{\mathrm{H}} 4.11,4.06\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.0$ ) in 6 , from H-3 ( $\delta_{\mathrm{H}} 5.43$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.2$ ) in 7 , and from H-4 ( $\delta_{\mathrm{H}} 5.30$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.4$ ) in 8 indicated that the acetyl group was attached to C-1, C-3, and C-4 of the fructofuranose unit in compounds 6, 7, and 8, respectively (Figure 4). In addition, the chemical shifts of the protons linked to the acetyl group in 6-8 were obviously shifted downfield compared to those of 1, which also supported the above description. Thus, the structures of 6,7 , and 8 were established and named phanerosides F, $G$, and $H$, respectively.

Table 3. ${ }^{1} \mathrm{H}$ NMR data ( 400 MHz ) of compounds 6-11 in $\mathrm{MeOH}-d_{4}$.

| Position | 6 | 7 | 8 | 9 | 10 | 11 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.11, d (11.6) | $3.54, \mathrm{~d}$ (12.0) | 3.57, d (12.0) | 4.11, d (12.0) | $3.54, \mathrm{~d}(12.0)$ | 3.57 , br d (12.0) |
| 1 | 4.06 , d (11.6) | $3.35, \mathrm{~d}(12.0)$ | $3.40, \mathrm{~d}(12.0)$ | 4.06 , d (12.0) | $3.34, \mathrm{~d}(12.0)$ | 3.40, br d (12.0) |
| 3 | 4.08, d (8.8) | $5.43, \mathrm{~d}$ (8.4) | 4.47, d (8.4) | 4.08, d (6.8) | $5.44, \mathrm{~d}$ (8.4) | 4.47, d (8.4) |
| 4 | 4.04, t (8.8) | $4.35, \mathrm{t}$ (8.4) | $5.30, \mathrm{t}$ (8.4) | $4.07, \mathrm{t}$ (6.8) | $4.39, \mathrm{t}$ (8.4) | 5.28 , dd (8.4, 7.6) |
| 5 | $3.79, \mathrm{~m}$ | $3.90, \mathrm{~m}$ | 3.91 , m | 3.79 , m | 3.91 m | 3.91 , overlapped |
| 6 | 3.88 , dd (11.6, 7.2 ) | 3.84 , dd (12.0, 6.4) | 3.92 , m | 3.89 , overlapped | 3.85 , dd (11.6, 6.8) | $3.93, \mathrm{~m}$ |
| 6 | 3.75, m | 3.78 , dd (12.0, 3.2) | 3.77, dd (11.2, 2.4) | 3.76 , m | 3.78 , dd (11.6, 2.8) | $3.80, \mathrm{dd}(11.2,2.8)$ |
| $1-\mathrm{OAc}$ | 2.01, s |  |  | 2.01 , s |  |  |
| $3-\mathrm{OAc}$ |  | 2.18, s |  |  | 2.18, s |  |
| $4-\mathrm{OAc}$ |  |  | 2.05, s |  |  | 2.04, s |
| $1^{\prime}$ | 5.65, d (3.6) | $5.63, \mathrm{~d}(3.6)$ | $5.65, \mathrm{~d}$ (3.6) | 5.66, d (3.6) | 5.63, d (3.6) | 5.65, d (3.6) |
| $2{ }^{\prime}$ | 4.79 , dd ( $10.4,3.6$ ) | 4.72 , dd (10.0, 3.6) | 4.76 , dd (10.0, 3.6) | 4.80 , dd (10.0, 3.6) | 4.73 , dd (10.4, 3.6) | 4.76 , dd (10.0, 3.6) |
| $3^{\prime}$ | 4.00 , dd ( $10.4,9.2$ ) | 3.88, t (10.0) | 4.01 , dd (10.0, 9.6) | 4.00 , dd (10.0, 8.8) | 3.88 , overlapped | 4.01, t (10.0) |
| $4^{\prime}$ | 3.46 , dd (10.0, 9.2) | 3.47, t (10.0) | 3.43, t (9.6) | 3.45 , dd (10.0, 8.8) | 3.45 , dd (10.0, 8.8) | $3.44, \mathrm{t}$ (10.0) |
| $5^{\prime}$ | 4.20 , ddd (10.0, 6.0, 2.0) | 4.16 , ddd (10.0, 6.0, 2.0) | $4.23, \mathrm{~m}$ | 4.21 , ddd (10.0, 6.8, 2.0) | 4.19 , ddd (10.0, 6.8, 2.0) | 4.24 , ddd (10.0, 6.4, 1.6) |
| $6^{\prime}$ | 4.54, dd (12.0, 2.0) | 4.56 , dd (12.0, 2.0) | 4.57 , dd (12.0, 1.6) | 4.54, dd (12.0, 2.0) | 4.56 , dd (12.0, 2.0) |  |
| 6 | 4.31 , dd (12.0, 6.0) | 4.32 , dd (12.0, 6.0) | 4.31 , dd (12.0, 6.4) | 4.30 , dd (12.0, 6.8) | 4.31 , dd (12.0, 6.8) | $4.32 \text {, dd }(12.0,6.4)$ |
| $2^{\prime \prime}$ | 7.49, d (8.8) | 7.48, d (8.8) | 7.49, d (8.4) | 7.49, d (8.8) | $7.48, \mathrm{~d}(8.8)$ | 7.49, d (8.8) |
| $3^{\prime \prime}$ | $6.80, \mathrm{~d}(8.8)$ | $6.82, \mathrm{~d}(8.8)$ | $6.81, \mathrm{~d}(8.4)$ | $6.81, \mathrm{~d}$ (8.8) | $6.81, \mathrm{~d}(8.8)$ | $6.81, \mathrm{~d}$ (8.8) |
| $5^{\prime \prime}$ | $6.80, \mathrm{~d}(8.8)$ | $6.82, \mathrm{~d}(8.8)$ | 6.81, d (8.4) | $6.81, \mathrm{~d}$ (8.8) | $6.81, \mathrm{~d}$ (8.8) | $6.81, \mathrm{~d}$ (8.8) |
| $6^{\prime \prime}$ | 7.49, d (8.8) | $7.48, \mathrm{~d}(8.8)$ | 7.49, d (8.4) | $7.49, \mathrm{~d}$ (8.8) | $7.48, \mathrm{~d}$ (8.8) | $7.49, \mathrm{~d}$ (8.8) |
| $7^{\prime \prime}$ | $7.71, \mathrm{~d}(16.0)$ | $7.70, \mathrm{~d}(16.0)$ | 7.70, d (16.0) | 7.71, d (16.0) | 7.69, d (16.0) | 7.70, d (16.0) |
| $8^{\prime \prime}$ | $6.39, \mathrm{~d}(16.0)$ | 6.37 , d (16.0) | $6.40, \mathrm{~d}(16.0)$ | $6.41, \mathrm{~d}(16.0)$ | $6.37, \mathrm{~d}(16.0)$ | $6.41, \mathrm{~d}(16.0)$ |
| $2^{\prime \prime \prime}$ | 7.50, d (8.8) | $7.50, \mathrm{~d}(8.8)$ | 7.51, d (8.4) | 7.26, d (2.0) | $7.25, \mathrm{~d}$ (2.0) | $7.25, \mathrm{~d}$ (2.0) |
| $3^{\prime \prime \prime}$ | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.4)$ |  |  |  |
| $5^{\prime \prime \prime}$ | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.4)$ | $6.81, \mathrm{~d}$ (8.0) | 6.81, d (8.0) | $6.81, \mathrm{~d}$ (8.4) |
| $6^{\prime \prime \prime}$ | $7.50, \mathrm{~d}(8.8)$ | $7.50, \mathrm{~d}(8.8)$ | 7.51, d (8.4) | 7.11, dd (8.0, 2.0) | 7.09 , dd (8.0, 2.0) | 7.11 , dd (8.4, 2.0) |
| $7^{\prime \prime \prime}$ | 7.66, d (16.0) | 7.66, d (16.0) | 7.65, d (16.0) | 7.65, d (15.6) | 7.65, d (16.0) | $7.65, \mathrm{~d}(16.0)$ |
| $8^{\prime \prime \prime}$ | $6.43, \mathrm{~d}(16.0)$ | $6.43, \mathrm{~d}(16.0)$ | $6.49, \mathrm{~d}(16.0)$ | 6.47, d (15.6) | 6.47 , d (16.0) | $6.52, \mathrm{~d}(16.0)$ |
| $3^{\prime \prime}$-OMe |  |  |  |  |  | 3.90 , s |
| $3^{\prime \prime \prime}$-OMe |  |  |  | 3.90, s | $3.89, \mathrm{~s}$ |  |

$\mathrm{s}=$ singlet; $\mathrm{d}=$ doublet; $\mathrm{t}=$ triplet; $\mathrm{m}=$ multiplet; $\mathrm{br}=$ broad.


6


7


8
$\sim \mathrm{HMBC}$

Figure 4. Key HMBC correlations of 6, 7, and 8.
Compounds 9-11 were assigned the same molecular formula, $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17}$, according to their HRESIMS and ${ }^{13} \mathrm{C}$ NMR data. Compounds $9-11$ were determined to be acetylated derivatives of 4 , as their molecular masses were 42 mass units more than that of 4 . Their ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data (Tables 3 and 5) showed the characteristics of the acetyl group [ $\delta_{\mathrm{H}} 2.01$ $(3 \mathrm{H}, \mathrm{s}), \delta_{\mathrm{C}} 172.0,20.6$ in $9 ; \delta_{\mathrm{H}} 2.18(3 \mathrm{H}, \mathrm{s}), \delta_{\mathrm{C}} 172.2,20.8$ in $10 ; \delta_{\mathrm{H}} 2.04(3 \mathrm{H}, \mathrm{s}), \delta_{\mathrm{C}} 172.4$, 20.8 in 11]. Furthermore, the key HMBC correlations from $\mathrm{H}_{2}-1\left(\delta_{\mathrm{H}} 4.11,4.06\right)$ to carbonyl $\left(\delta_{\mathrm{C}} 172.0\right)$ in 9 , from H-3 ( $\delta_{\mathrm{H}} 5.44$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.2$ ) in 10, and from $\mathrm{H}-4\left(\delta_{\mathrm{H}} 5.28\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.4$ ) in 11 located the acetyl group at C-1, C-3, and C-4 for compounds 9 , 10, and 11, respectively. Thus, the structures of compounds $\mathbf{9 - 1 1}$ (phanerosides I-K) were defined as shown.

Compounds 12-14 possessed identical molecular formula, $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17}$, as determined by their respective HRESIMS ion peaks at $m / z 729.2018,729.2010$, and 729.1990 ( $[\mathrm{M}+\mathrm{Na}]^{+}$, calcd for 729.2001), which were 42 mass units more than that of 3 . Detailed analysis of their 1D NMR data (Tables 4 and 5) indicated that compounds 12-14 were acetylated derivatives of 3, with a difference in the position of the acetyl group. In their HMBC spectra, the correlations from $\mathrm{H}_{2}-1\left(\delta_{\mathrm{H}} 4.14,4.03\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.0$ ) in 12 , from $\mathrm{H}-3\left(\delta_{\mathrm{H}} 5.43\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.2$ ) in 13 , and from $\mathrm{H}-4\left(\delta_{\mathrm{H}} 5.31\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.3$ ) in 14 suggested that the acetyl group was linked to C-1, C-3, and C-4 in 12, 13, and 14, respectively. Therefore, the structures of compounds $\mathbf{1 2 - 1 4}$ (phanerosides $\mathrm{L}-\mathrm{N}$ ) were established as shown.

Compounds 15-17 were determined to have the same molecular formula, $\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18}$, on the basis of their HRESIMS and ${ }^{13} \mathrm{C}$ NMR data, displaying 42 mass units more than that of $\mathbf{5}$. Compounds $\mathbf{1 5 - 1 7}$ were suggested to be acetylated derivatives of $\mathbf{5}$ after an analysis of their 1D NMR data (Tables 4 and 5). The acetyl group was, respectively, located at C-1, C-3, and C-4 of the fructofuranose unit in 15,16 , and 17 , which was confirmed using the key HMBC correlations from the protons of the sugar unit to corresponding carbonyl carbons. Accordingly, the structure of compounds 15-17 (phanerosides $\mathrm{O}-\mathrm{Q}$ ) were determined as shown.

Compounds 18 and 19 had the same molecular formula, $\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18}$, as $\mathbf{1 7}$ according to their HRESIMS and ${ }^{13} \mathrm{C}$ NMR data. The 1D NMR data (Tables 4 and 5) closely resembled those of 17, with the exception that one of the two trans-feruloyl groups was replaced by a cis-feruloyl group according to the smaller coupling constants of ${ }^{3} J_{7^{\prime \prime}, 8^{\prime \prime}}(12.6 \mathrm{~Hz})$ in 18 and ${ }^{3} J_{7^{\prime \prime \prime}, 8^{\prime \prime \prime}}(13.2 \mathrm{~Hz})$ in 19. The cis-feruloyl group was linked to $\mathrm{C}-2^{\prime}$ and $\mathrm{C}-6^{\prime}$ of the glucopyranose unit in 18 and 19, respectively, which was proved by the key HMBC cross-peaks from $\mathrm{H}-2^{\prime} / \mathrm{H}-7^{\prime \prime}$ to $\mathrm{C}-9^{\prime \prime}$ in 18 and from $\mathrm{H}-6^{\prime} / \mathrm{H}-7^{\prime \prime \prime}$ to $\mathrm{C}-9^{\prime \prime \prime}$ in 19 (Figure 5). Thus, the structures of compounds 18 and 19 were identified and named phanerosides R and $S$, respectively.

Table 4. ${ }^{1} \mathrm{H}$ NMR data of compounds 12 -19.

| Position | $12^{\text {a }}$ | $13^{\text {a }}$ | $14^{\text {a }}$ | $15^{\text {a }}$ | $16^{\text {b }}$ | $17^{\text {a }}$ | $18^{\text {b }}$ | $19^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.14, d (12.4) | $3.55, \mathrm{~d}$ (11.6) | $3.59, \mathrm{~d}$ (12.0) | 4.14, d (11.6) | $3.54, \mathrm{~d}$ (12.0) | $3.59, \mathrm{~d}$ (12.0) | $3.55, \mathrm{~d}$ (12.0) | $3.58, \mathrm{~d}$ (12.0) |
| 1 | 4.03, d (12.4) | 3.36, d (11.6) | $3.42, \mathrm{~d}$ (12.0) | 4.02, d (11.6) | $3.34, \mathrm{~d}$ (12.0) | 3.42 , d (12.0) | $3.39, \mathrm{~d}$ (12.0) | 3.42 , d (12.0) |
| 3 | 4.09, d (8.4) | 5.43, d (8.4) | 4.47, d (8.0) | $4.09, \mathrm{~d}$ (8.4) | 5.44, d (8.4) | 4.48 , d (8.8) | 4.47, d (8.4) | 4.46, d (8.4) |
| 4 | 4.04, t (8.4) | $4.35, \mathrm{t}$ (8.4) | 5.31, t (8.0) | 4.08, t (8.4) | $4.39, \mathrm{t}$ (8.4) | 5.29, dd (8.8, 7.6) | $5.26, \mathrm{t}$ (8.4) | $5.29, \mathrm{t}$ (8.4) |
| 5 | $3.79, \mathrm{~m}$ | 3.90 , overlapped | 3.91, overlapped | 3.80, m | 3.91, overlapped | 3.91 , overlapped | 3.90 , overlapped | 3.90 , overlapped |
|  | 3.88 , m | 3.84, dd (12.0, 6.4) | 3.92 , overlapped | 3.89, overlapped | 3.85 , dd (12.0, 6.6) | 3.92 , overlapped | 3.92 , overlapped | 3.90 , overlapped |
| 6 | 3.75 , dd (11.6, 2.8) | 3.78 , dd (12.0, 3.2) | $3.78, \mathrm{~m}$ | 3.76 , dd (11.6, 2.8) | 3.79 , dd (12.0, 2.4) | 3.81 , dd (11.2, 2.4) | 3.78 , dd (10.8, 2.4) | 3.78, m |
| $1-\mathrm{OAc}$ | 2.02, s |  |  | 2.02, s |  |  |  |  |
| $3-\mathrm{OAc}$ |  | 2.18, s |  |  | 2.18, s |  |  |  |
| 4 -OAc |  |  | 2.04, s |  |  | 2.03, s | 2.08, s | 2.05, s |
| $1^{\prime}$ | 5.64, d (3.6) | $5.63, \mathrm{~d}(4.0)$ | 5.67, d (3.6) | 5.65, d (4.0) | 5.64, d (3.6) | $5.66, \mathrm{~d}(4.0)$ | $5.62, \mathrm{~d}(3.6)$ | $5.66, \mathrm{~d}(3.6)$ |
| $2^{\prime}$ | 4.82 , dd (10.4, 3.6) | 4.72, dd (10.4, 4.0) | 4.76, dd (10.0, 3.6) | 4.82 , dd (10.0, 4.0) | 4.72, dd (10.2, 3.6) | 4.76 , dd (10.0, 4.0) | 4.75 , dd (10.2, 3.6) | 4.73 , dd (10.2, 3.6) |
| $3^{\prime}$ | 4.00 , dd (10.4, 9.2) | 3.88 , overlapped | 4.01, t (10.0) | 4.00 , dd (10.0, 8.8) | $3.87, \mathrm{t}(10.2)$ | 4.01 , dd (10.0, 8.8) | 3.98 , dd (10.2, 9.6) | 3.99 , dd (10.2, 9.0) |
| $4^{\prime}$ | 3.46 , dd (10.0, 9.2) | 3.47, t (10.0) | $3.43, \mathrm{t}$ (10.0) | 3.46 , dd (10.0, 8.8) | $3.45, \mathrm{t}$ (10.2) | 3.44 , dd (10.0, 8.8) | 3.43 , t (9.6) | 3.43 , dd (10.2, 9.0) |
| $5^{\prime}$ | 4.20, ddd (10.0, 6.4, 2.0) | 4.16, ddd (10.0, 6.0, 2.0) | 4.23, dd (10.0, 6.4) | 4.22, ddd (10.0, 6.4, 2.0) | 4.19, m | 4.23, ddd (10.0, 6.4, 1.6) | 4.23 , ddd ( $9.6,6.6,1.8)$ | 4.19, ddd (10.2, 5.4, 1.8) |
|  | 4.54 , dd (12.0, 2.0) | 4.56 , dd (12.0, 2.0) | 4.57 , br d (12.0) | 4.54 , dd (12.0, 2.0) | 4.56 , br d (12.0) | 4.57 , dd (12.0, 1.6) | 4.56 , dd (12.0, 1.8) | 4.53 , dd (12.0, 1.8) |
| 6 | 4.31 , dd (12.0, 6.4) | 4.32 , dd (12.0, 6.0) | 4.31, dd (12.0, 6.4) | 4.30 , dd (12.0, 6.4) | 4.31 , dd (12.0, 6.6) | 4.32 , dd (12.0, 6.4) | 4.31 , dd (12.0, 6.6) | 4.30 , dd (12.0, 5.4) |
| $2^{\prime \prime}$ | 7.26, d (2.0) | 7.21, d (2.0) | 7.23, d (2.0) | 7.26, d (2.4) | 7.21, br s | 7.23, d (2.0) | 7.93, d (2.4) | 7.23, d (1.8) |
| $5^{\prime \prime}$ | 6.81, d (8.4) | 6.82 , d (8.0) | 6.82 , d (8.0) | 6.81, d (8.0) | 6.82, d (7.8) | 6.81, d (8.0) | 6.77, d (8.4) | 6.81, d (8.4) |
| $6^{\prime \prime}$ | 7.09, dd (8.4, 2.0) | 7.10, dd (8.0, 2.0) | 7.09, dd (8.0, 2.0) | 7.09, dd (8.0, 2.4) | 7.10, overlapped | 7.09, dd (8.0, 2.0) | 7.19, dd (8.4, 2.4) | 7.09, dd (8.4, 1.8) |
| $7^{\prime \prime}$ | 7.70, d (15.6) | 7.69, d (15.6) | 7.69, d (16.0) | 7.70, d (16.0) | 7.69 , d (16.2) | 7.69, d (16.0) | $6.92, \mathrm{~d}(12.6)$ | 7.68, d (15.6) |
| $8^{\prime \prime}$ | $6.45, \mathrm{~d}$ (15.6) | $6.39, \mathrm{~d}$ (15.6) | $6.44, \mathrm{~d}$ (16.0) | $6.45, \mathrm{~d}$ (16.0) | $6.40, \mathrm{~d}$ (16.2) | $6.44, \mathrm{~d}$ (16.0) | $5.88, \mathrm{~d}(12.6)$ | $6.44, \mathrm{~d}$ (15.6) |
| $2^{\prime \prime \prime}$ | 7.51, d (8.4) | $7.50, \mathrm{~d}(8.8)$ | $7.51, \mathrm{~d}$ (8.0) | $7.26, \mathrm{~d}$ (2.4) | $7.26, \mathrm{br} \mathrm{s}$ | $7.24, \mathrm{~d}$ (2.0) | 7.25, d (2.4) | 7.87, d (1.8) |
| $3^{\prime \prime \prime}$ | 6.81, d (8.4) | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.0)$ |  |  |  |  |  |
| $5^{\prime \prime \prime}$ | 6.81, d (8.4) | $6.80, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.0)$ | 6.81, d (8.0) | 6.80, d (7.8) | 6.81, d (8.0) | 6.81, d (8.4) | 6.77, d (8.4) |
| $6^{\prime \prime \prime}$ | 7.51, d (8.4) | $7.50, \mathrm{~d}$ (8.8) | $7.51, \mathrm{~d}$ (8.0) | $7.11, \mathrm{dd}(8.0,2.4)$ | 7.10, overlapped | $7.11, \mathrm{dd}(8.0,2.0)$ | $7.11, \mathrm{dd}(8.4,2.4)$ | 7.15, dd (8.4, 1.8) |
| $7^{\prime \prime \prime}$ | 7.66, d (15.6) | 7.66, d (15.6) | 7.65, d (16.0) | 7.65, d (16.0) | 7.65, d (16.2) | $7.65, \mathrm{~d}(16.0)$ | 7.65, d (16.2) | $6.88, \mathrm{~d}(13.2)$ |
| $8^{\prime \prime \prime}$ | $6.43, \mathrm{~d}$ (15.6) | $6.43, \mathrm{~d}(15.6)$ | $6.49, \mathrm{~d}$ (16.0) | 6.47 , d (16.0) | 6.47 , d (16.2) | 6.52 , d (16.0) | $6.53, \mathrm{~d}(16.2)$ | $5.90, \mathrm{~d}(13.2)$ |
| $3^{\prime \prime}$-OMe | 3.92, s | 3.90 s | 3.92 s | 3.92, s | 3.90 s | 3.92 s | 3.88 , s | 3.92, s |
| $3^{\prime \prime \prime}$-OMe |  |  |  | 3.90, s | 3.89, s | 3.90, s | 3.90, s | 3.89 , s |

[^0]Table 5. ${ }^{13} \mathrm{C}$ NMR data of compounds 12 -19.

| Position | $6^{\text {a }}$ | $7{ }^{\text {a }}$ | $8^{\text {a }}$ | $9^{\text {a }}$ | $10^{\text {a }}$ | $11^{\text {a }}$ | $12^{\text {a }}$ | $13{ }^{\text {a }}$ | $14^{\text {a }}$ | $15^{\text {a }}$ | $16^{\text {b }}$ | $17^{\text {a }}$ | $18^{\text {b }}$ | $19^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 64.8 | 64.4 | 62.5 | 64.8 | 64.5 | 62.5 | 64.8 | 64.5 | 62.5 | 64.8 | 64.5 | 62.5 | 62.5 | 62.3 |
| 2 | 103.9 | 105.0 | 106.0 | 103.8 | 104.9 | 106.0 | 103.9 | 105.0 | 106.1 | 103.8 | 104.9 | 106.1 | 105.9 | 106.2 |
| 3 | 78.5 | 78.6 | 75.2 | 78.5 | 78.6 | 75.2 | 78.4 | 78.7 | 75.2 | 78.4 | 78.6 | 75.2 | 75.2 | 75.2 |
| 4 | 75.3 | 73.8 | 78.0 | 75.4 | 73.8 | 78.1 | 75.4 | 73.8 | 78.0 | 75.4 | 73.8 | 78.2 | 78.2 | 77.9 |
| 5 | 84.1 | 84.2 | 82.2 | 84.1 | 84.2 | 82.3 | 84.2 | 84.2 | 82.3 | 84.2 | 84.2 | 82.3 | 82.3 | 82.3 |
| 6 | 64.1 | 63.9 | 64.8 | 64.2 | 64.0 | 64.8 | 64.2 | 63.9 | 64.9 | 64.3 | 64.0 | 64.9 | 64.8 | 64.8 |
| 1-OAc | 172.0 |  |  | 172.0 |  |  | 172.0 |  |  | 172.0 |  |  |  |  |
| 1-OAc | 20.6 |  |  | 20.6 |  |  | 20.6 |  |  | 20.6 |  |  |  |  |
| $3-\mathrm{OAc}$ |  | 172.2 |  |  | 172.2 |  |  | 172.2 |  |  | 172.2 |  |  |  |
| $3-\mathrm{OAc}$ |  | 20.8 |  |  | 20.8 |  |  | 20.8 |  |  | 20.8 |  |  |  |
| 4-OAc |  |  | 172.4 |  |  | 172.4 |  |  | 172.3 |  |  | 172.4 | 172.4 | 172.3 |
| 4-OAc |  |  | 20.8 |  |  | 20.8 |  |  | 20.8 |  |  | 20.8 | 20.9 | 20.8 |
| $1^{\prime}$ | 90.9 | 90.5 | 91.1 | 90.9 | 90.4 | 91.1 | 91.0 | 90.6 | 91.2 | 90.9 | 90.4 | 91.2 | 91.0 | 91.3 |
| $2^{\prime}$ | 74.1 | 74.3 | 74.2 | 74.1 | 74.3 | 74.3 | 74.1 | 74.3 | 74.2 | 74.1 | 74.3 | 74.2 | 73.9 | 74.2 |
| $3^{\prime}$ | 72.1 | 72.3 | 72.0 | 72.2 | 72.3 | 72.0 | 72.2 | 72.3 | 72.0 | 72.2 | 72.3 | 72.1 | 71.9 | 72.0 |
| $4^{\prime}$ | 72.0 | 71.8 | 72.0 | 72.0 | 71.9 | 72.1 | 72.1 | 72.0 | 72.1 | 72.0 | 71.9 | 72.0 | 72.1 | 71.9 |
| $5^{\prime}$ | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 | 71.8 | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 | 71.8 |
| $6^{\prime}$ | 65.0 | 64.9 | 65.1 | 65.1 | 65.1 | 65.1 | 65.0 | 64.9 | 65.1 | 65.1 | 65.1 | 65.1 | 65.1 | 64.5 |
| $1^{\prime \prime}$ | 127.1 | 127.1 | 127.0 | 127.2 | 127.0 | 127.1 | 127.7 | 127.5 | 127.7 | 127.8 | 127.5 | 127.6 | 127.9 | 127.5 |
| $2^{\prime \prime}$ | 131.3 | 131.3 | 131.3 | 131.4 | 131.3 | 131.4 | 111.7 | 111.8 | 111.7 | 111.6 | 111.8 | 111.8 | 115.3 | 111.7 |
| $3^{\prime \prime}$ | 116.9 | 116.8 | 116.9 | 116.8 | 116.9 | 116.8 | 149.4 | 149.5 | 149.4 | 149.4 | 149.5 | 149.4 | 148.3 | 149.5 |
| $4^{\prime \prime}$ | 161.7 | 161.6 | 161.6 | 161.4 | 161.6 | 161.4 | 150.8 | 151.5 | 150.8 | 150.8 | 151.1 | 150.9 | 149.9 | 150.9 |
| $5^{\prime \prime}$ | 116.9 | 116.8 | 116.9 | 116.8 | 116.9 | 116.8 | 116.4 | 116.6 | 116.4 | 116.4 | 116.5 | 116.4 | 115.6 | 116.5 |
| $6^{\prime \prime}$ | 131.3 | 131.3 | 131.3 | 131.4 | 131.3 | 131.4 | 124.5 | 124.3 | 124.4 | 124.5 | 124.3 | 124.4 | 127.4 | 124.5 |
| $7^{\prime \prime}$ | 147.5 | 147.5 | 147.4 | 147.5 | 147.5 | 147.3 | 147.7 | 147.8 | 147.5 | 147.7 | 147.8 | 147.6 | 147.0 | 147.5 |
| $8^{\prime \prime}$ | 114.8 | 114.6 | 114.9 | 114.9 | 114.6 | 114.9 | 115.2 | 114.9 | 115.2 | 115.2 | 114.9 | 115.2 | 115.8 | 115.1 |
| $9^{\prime \prime}$ | 168.8 | 168.7 | 168.8 | 168.8 | 168.7 | 168.8 | 168.7 | 168.7 | 168.8 | 168.7 | 168.7 | 168.8 | 167.5 | 168.8 |
| $1^{\prime \prime \prime}$ | 127.1 | 127.0 | 127.2 | 127.7 | 127.6 | 127.8 | 127.2 | 127.1 | 127.3 | 127.7 | 127.6 | 127.8 | 127.7 | 128.0 |
| $2^{\prime \prime \prime}$ | 131.4 | 131.3 | 131.4 | 111.6 | 111.5 | 111.9 | 131.3 | 131.3 | 131.3 | 111.7 | 111.5 | 111.7 | 111.8 | 115.1 |
| $3^{\prime \prime \prime}$ | 116.9 | 116.9 | 116.8 | 149.4 | 149.4 | 149.4 | 116.8 | 116.9 | 116.8 | 149.4 | 149.5 | 149.4 | 149.4 | 148.4 |
| $4^{\prime \prime \prime}$ | 161.6 | 161.4 | 161.4 | 150.7 | 150.8 | 150.6 | 161.4 | 161.5 | 161.3 | 150.7 | 150.9 | 150.7 | 150.8 | 149.7 |
| $5^{\prime \prime \prime}$ | 116.9 | 116.9 | 116.8 | 116.4 | 116.4 | 116.4 | 116.8 | 116.9 | 116.8 | 116.4 | 116.4 | 116.5 | 116.4 | 115.7 |
| $6^{\prime \prime \prime}$ | 131.4 | 131.3 | 131.4 | 124.4 | 124.4 | 124.4 | 131.3 | 131.3 | 131.3 | 124.4 | 124.5 | 124.4 | 124.4 | 127.0 |
| $7^{\prime \prime \prime}$ | 146.9 | 146.9 | 146.8 | 147.1 | 147.1 | 147.1 | 146.9 | 146.9 | 146.8 | 147.1 | 147.2 | 147.1 | 147.1 | 146.0 |
| $8^{\prime \prime \prime}$ | 114.9 | 114.9 | 115.2 | 115.3 | 115.2 | 115.4 | 115.0 | 114.9 | 115.3 | 115.3 | 115.2 | 115.4 | 115.4 | 116.1 |
| $9^{\prime \prime \prime}$ | 169.2 | 169.2 | 169.3 | 169.1 | 169.1 | 169.3 | 169.2 | 169.2 | 169.3 | 169.1 | 169.1 | 169.3 | 169.3 | 168.1 |
| $3^{\prime \prime}$-OMe |  |  |  |  |  | 56.5 | 56.5 | 56.4 | 56.5 | 56.5 | 56.5 | 56.5 | 56.4 | 56.4 |
| $3^{\prime \prime \prime}$ - OMe |  |  |  | 56.5 | 56.5 |  |  |  |  | 56.5 | 56.4 | 56.5 | 56.5 | 56.4 |

${ }^{\text {a }}$ In $\mathrm{MeOH}-d_{4},{ }^{13} \mathrm{C}$ NMR at $100 \mathrm{MHz} .{ }^{\mathrm{b}}$ In $\mathrm{MeOH}-d_{4},{ }^{13} \mathrm{C}$ NMR at 150 MHz .


Figure 5. Key HMBC correlations of 18 and 19.
Compounds 20 and 21 were suggested to have the same molecular formula, $\mathrm{C}_{34} \mathrm{H}_{38} \mathrm{O}_{17}$, owing to their coincident positive HRESIMS ion at $m / z 741.2001[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for 741.2001), indicating 42 mass units more than that of 7. Comparison of their 1D NMR data (Tables 6 and 7) with those of 7 disclosed that one more acetyl group was presented in both 20 and 21. The key HMBC correlations from $\mathrm{H}_{2}-1\left(\delta_{\mathrm{H}} 4.17,4.00\right)$ to carbonyl ( $\delta_{\mathrm{C}} 172.0$ ) and H-3 ( $\delta_{\mathrm{H}} 5.29$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.1$ ) in 20, and from H-3 ( $\delta_{\mathrm{H}} 5.65$ ) to carbonyl ( $\delta_{\mathrm{C}} 171.8$ ) and H-4 ( $\delta_{\mathrm{H}} 5.48$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.0$ ) in 21, indicated that the two acetyl groups were located
at C-1 and C-3 in 20 and C-3 and C-4 in 21 (Figure 6). Thus, the structures of compounds 20 and 21 were characterized and named phanerosides $T$ and $U$, respectively.

Table 6. ${ }^{1} \mathrm{H}$ NMR data of compounds 20-24.

| Position | $20^{\text {a }}$ | $21^{\text {a }}$ | $22^{\text {b }}$ | $23{ }^{\text {a }}$ | $24^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 4.17, d (12.0) | $3.57, \mathrm{~d}$ (12.0) | $3.58, \mathrm{~d}$ (12.0) | 4.16, d (11.6) | $3.59, \mathrm{~d}$ (12.0) |
|  | $4.00, \mathrm{~d}$ (12.0) | $3.45, \mathrm{~d}$ (12.0) | $3.47, \mathrm{~d}$ (12.0) | $3.99, \mathrm{~d}$ (11.6) | $3.48, \mathrm{~d}$ (12.0) |
| 3 | $5.29, \mathrm{~d}$ (8.0) | 5.65, d (7.6) | $5.65, \mathrm{~d}(7.8)$ | 5.30, d (8.4) | 5.65, d (7.6) |
| 4 | 4.34, t (8.0) | $5.48, \mathrm{t}$ (7.6) | $5.50, \mathrm{t}(7.8)$ | 4.38 , t (8.4) | $5.49, \mathrm{t}$ (7.6) |
| 5 | 3.89 , m | 4.07, m | 4.08, m | 3.90, overlapped | $4.08, \operatorname{td}(7.6,4.4)$ |
| 6 | 3.84 , dd (11.6, 6.8) | 3.87, dd (12.0, 6.8) | 3.87 , dd (12.0, 7.2) | 3.85 , dd (12.0, 6.8) | 3.87 , overlapped |
|  | 3.77 , dd, (11.6, 2.8) | 3.77 , dd (12.0, 4.4) | 3.78 , dd (12.0, 4.2) | 3.77 , dd (12.0, 2.8) | $3.80, \mathrm{dd}(12.0,4.4)$ |
| 1-OAc | 2.02, s |  |  | 2.02, s |  |
| 3-OAc | 2.17, s | 2.11, s | 1.98, s | 2.18, s | 2.11, s |
| $4-\mathrm{OAc}$ |  | 1.99, s | 2.10, s |  | 1.97, s |
| $1{ }^{\prime}$ | 5.66, d (3.6) | $5.62, \mathrm{~d}(3.6)$ | 5.62 , d (3.6) | $5.66, \mathrm{~d}$ (3.6) | 5.62 , d (3.6) |
| $2^{\prime}$ | 4.78, dd (10.0, 3.6) | 4.76 , dd (10.0, 3.6) | 4.77 , dd (10.2, 3.6) | 4.78, dd (10.0, 3.6) | 4.77 , dd (10.0, 3.6) |
| $3^{\prime}$ | 3.88 , dd (10.0, 9.2) | 3.91 , dd (10.0, 9.2) | 3.91, m | 3.88 , m | 3.91, overlapped |
| $4^{\prime}$ | 3.47, t (9.2) | 3.47, t (9.2) | 3.46, t (10.2) | 3.46, dd (10.0, 9.2) | 3.47 , m |
| $5^{\prime}$ | 4.16, m | 4.19, ddd (10.0, 6.0, 2.0) | 4.18, ddd (10.2, 6.0, 1.8) | 4.18, m | 4.19, ddd (10.0, 6.4, 2.0) |
| $6^{\prime}$ | 4.57, dd (12.0, 2.0) | 4.60 , dd (12.0, 2.0) | 4.59 , dd (12.0, 1.8) | 4.57, dd (12.0, 2.0) | 4.60 , dd (12.0, 2.0) |
|  | 4.32 , dd (12.0, 6.0) | 4.33 , dd (12.0, 6.0) | 4.32 , dd (12.0, 6.0) | 4.30 , dd (12.0, 6.8) | 4.33 , dd (12.0, 6.4) |
| $2^{\prime \prime}$ | $7.49, \mathrm{~d}$ (8.8) | $7.49, \mathrm{~d}$ (8.8) | 7.25, br s | $7.49, \mathrm{~d}$ (8.8) | $7.24, \mathrm{~d}$ (2.0) |
| $3^{\prime \prime}$ | 6.81, d (8.8) | 6.81, d (8.8) |  | $6.81, \mathrm{~d}(8.8)$ |  |
| $5^{\prime \prime}$ | 6.81, d (8.8) | 6.81, d (8.8) | 6.81, d (8.4) | $6.81, \mathrm{~d}(8.8)$ | $6.82, \mathrm{~d}$ (8.0) |
| $6^{\prime \prime}$ | $7.49, \mathrm{~d}$ (8.8) | $7.49, \mathrm{~d}(8.8)$ | $7.10, \mathrm{dd}(8.4,1.8)$ | $7.49, \mathrm{~d}(8.8)$ | $7.10, \mathrm{dd}(8.0,2.0)$ |
| $7^{\prime \prime}$ | 7.68, d (15.6) | 7.69, d (16.0) | 7.69, d (16.2) | $7.68, \mathrm{~d}$ (16.0) | 7.69, d (16.0) |
| $8^{\prime \prime}$ | $6.38, \mathrm{~d}$ (15.6) | $6.41, \mathrm{~d}$ (16.0) | $6.45, \mathrm{~d}$ (16.2) | $6.38, \mathrm{~d}$ (16.0) | $6.45, \mathrm{~d}$ (16.0) |
| $2^{\prime \prime \prime}$ | $7.50, \mathrm{~d}(8.8)$ | $7.50, \mathrm{~d}(8.8)$ | $7.49, \mathrm{~d}$ (8.4) | 7.26, d (2.0) | $7.24, \mathrm{~d}$ (2.0) |
| $3^{\prime \prime \prime}$ | 6.81, d (8.8) | $6.81, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}(8.4)$ |  |  |
| $5^{\prime \prime \prime}$ | 6.81, d (8.8) | $6.81, \mathrm{~d}(8.8)$ | $6.80, \mathrm{~d}$ (8.4) | 6.81, d (8.0) | $6.82, \mathrm{~d}$ (8.0) |
| $6^{\prime \prime \prime}$ | $7.50, \mathrm{~d}$ (8.8) | $7.50, \mathrm{~d}(8.8)$ | $7.49, \mathrm{~d}$ (8.4) | 7.09, dd (8.0, 2.0) | 7.10 , dd (8.0, 2.0) |
| $7^{\prime \prime \prime}$ | $7.66, \mathrm{~d}$ (16.0) | 7.65, d (16.0) | 7.65, d (16.2) | 7.65, d (16.0) | 7.65, d (16.0) |
| $8^{\prime \prime \prime}$ | $6.43, \mathrm{~d}$ (16.0) | $6.45, \mathrm{~d}$ (16.0) | $6.44, \mathrm{~d}$ (16.2) | 6.47, d (16.0) | $6.49, \mathrm{~d}$ (16.0) |
| $3^{\prime \prime}$-OMe |  |  | 3.91, s |  | 3.90, s |
| $3^{\prime \prime \prime}$-OMe |  |  |  | 3.89, s | 3.91, s |

${ }^{\text {a }}$ In MeOH- $d_{4},{ }^{1} \mathrm{H}$ NMR at $400 \mathrm{MHz} .{ }^{\mathrm{b}}$ In MeOH- $d_{4},{ }^{1} \mathrm{H}$ NMR at $600 \mathrm{MHz} . \mathrm{s}=$ singlet; $\mathrm{d}=$ doublet; $\mathrm{t}=$ triplet; $\mathrm{m}=$ multiplet; $\mathrm{br}=$ broad.

Table 7. ${ }^{13} \mathrm{C}$ NMR data of compounds 20-24.

| Position | $\mathbf{2 0}^{\mathbf{a}}$ | $\mathbf{2 1}^{\mathbf{a}}$ | $\mathbf{2 2}^{\mathbf{b}}$ | $\mathbf{2 3}^{\mathbf{a}}$ | $\mathbf{2 4}^{\mathbf{a}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 66.1 | 63.6 | 63.4 | 66.2 | 63.5 |
| 2 | 103.3 | 106.1 | 106.2 | 103.2 | 106.2 |
| 3 | 79.5 | 76.6 | 76.6 | 79.5 | 76.7 |
| 4 | 73.5 | 76.5 | 76.5 | 73.5 | 76.6 |
| 5 | 84.2 | 82.7 | 82.7 | 84.3 | 82.7 |
| 6 | 63.8 | 64.1 | 64.2 | 63.9 | 64.3 |
| 1-OAc | 172.0 |  |  | 171.9 |  |
|  | 20.6 | 172.1 | 171.8 | 20.6 |  |
| $3-\mathrm{OAc}$ | 20.7 | 172.0 | 172.0 | 172.1 | 171.7 |
| $4-\mathrm{OAc}$ |  | 20.7 | 171.8 | 20.7 | 20.7 |
| $1^{\prime}$ | 91.0 | 74.3 | 90.7 |  | 172.0 |
| $2^{\prime}$ | 74.0 | 72.2 | 74.1 | 90.9 | 20.7 |
| $3^{\prime}$ | 72.3 | 71.8 | 72.2 | 74.0 | 74.4 |
| $4^{\prime}$ | 71.8 | 72.2 | 72.4 | 72.2 |  |
| $5^{\prime}$ |  |  |  | 72.2 | 71.9 |

Table 7. Cont.

| Position | $\mathbf{2 0}^{\mathbf{a}}$ | $\mathbf{2 1}^{\mathbf{a}}$ | $\mathbf{2 2}^{\mathbf{b}}$ | $\mathbf{2 3}^{\mathbf{a}}$ | $\mathbf{2 4}^{\mathbf{a}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $6^{\prime}$ | 64.9 | 64.9 | 64.9 | 65.1 | 64.9 |
| $1^{\prime \prime}$ | 127.1 | 127.2 | 127.4 | 127.1 | 127.6 |
| $2^{\prime \prime}$ | 131.3 | 131.3 | 111.7 | 131.4 | 111.7 |
| $3^{\prime \prime}$ | 116.8 | 116.8 | 149.5 | 116.8 | 149.4 |
| $4^{\prime \prime}$ | 161.5 | 161.6 | 151.2 | 161.5 | 150.7 |
| $5^{\prime \prime}$ | 116.8 | 116.8 | 116.5 | 116.8 | 116.4 |
| $6^{\prime \prime}$ | 131.3 | 131.3 | 124.6 | 131.4 | 124.3 |
| $7^{\prime \prime}$ | 147.5 | 147.5 | 147.8 | 147.5 | 147.8 |
| $8^{\prime \prime}$ | 114.7 | 114.8 | 115.0 | 114.8 | 115.1 |
| $9^{\prime \prime}$ | 168.7 | 168.7 | 168.7 | 168.7 | 168.7 |
| $1^{\prime \prime \prime}$ | 127.1 | 127.0 | 127.1 | 127.7 | 127.8 |
| $2^{\prime \prime \prime}$ | 131.4 | 131.4 | 131.3 | 111.5 | 111.8 |
| $3^{\prime \prime \prime}$ | 116.8 | 116.9 | 116.9 | 149.4 | 149.4 |
| $4^{\prime \prime \prime}$ | 161.4 | 161.4 | 161.6 | 150.7 | 150.8 |
| $5^{\prime \prime \prime}$ | 116.8 | 116.9 | 116.9 | 116.4 | 116.4 |
| $6^{\prime \prime \prime}$ | 131.4 | 131.4 | 131.3 | 124.5 | 124.5 |
| $7^{\prime \prime \prime}$ | 146.9 | 115.8 | 146.9 | 147.1 | 147.1 |
| $8^{\prime \prime \prime}$ | 114.9 | 169.2 | 115.0 | 115.3 | 115.4 |
| $9^{\prime \prime \prime}$ |  | 59.2 | 169.1 | 169.2 |  |
| $3^{\prime \prime}-\mathrm{OMe}$ |  |  |  | 56.5 | 56.5 |
| $3^{\prime \prime \prime}-\mathrm{OMe}$ |  |  |  | 5.5 |  |

${ }^{\mathrm{a}}$ In $\mathrm{MeOH}-d_{4},{ }^{13} \mathrm{C}$ NMR at $100 \mathrm{MHz} .{ }^{\mathrm{b}}$ In $\mathrm{MeOH}-d_{4},{ }^{13} \mathrm{C}$ NMR at 150 MHz .


Figure 6. Key HMBC correlations of 20, 21, and 24.
Compounds 22 and 23 showed the same molecular formula, $\mathrm{C}_{35} \mathrm{H}_{40} \mathrm{O}_{18}$, as determined by their ${ }^{13} \mathrm{C}$ NMR data and respective HRESIMS ion peaks at $m / z 771.2093$ and 771.2112 ([M + Na] ${ }^{+}$, calcd for 771.2107). Analysis of the NMR data (Figures S194-S199 and S203-S208) of 22 and 23 proclaimed that the sugar moieties in both compounds were acylated by a trans-ferulic acid, a trans-p-coumaric acid, and two acetic acids. The trans-feruloyl and trans- $p$-coumaroyl units were, respectively, located at C-2 ${ }^{\prime}$ and C-6' in 22 based on the key HMBC correlations from $\mathrm{H}-2^{\prime}$ to $\mathrm{C}-9^{\prime \prime}$ and $\mathrm{H}_{2}-6^{\prime}$ to $\mathrm{C}-9^{\prime \prime \prime}$, while the locations of these two substituents in 23 were the opposite. The key HMBC correlations from H-3 ( $\delta_{\mathrm{H}} 5.65$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.0$ ) and H-4 ( $\delta_{\mathrm{H}} 5.50$ ) to carbonyl ( $\delta_{\mathrm{C}} 171.8$ ) in 22, and from $\mathrm{H}_{2}-1\left(\delta_{\mathrm{H}} 4.16,3.99\right)$ to carbonyl ( $\delta_{\mathrm{C}} 171.9$ ) and H-3 ( $\delta_{\mathrm{H}} 5.30$ ) to carbonyl ( $\delta_{\mathrm{C}} 172.1$ ) in 23 , indicated that the two acetyl groups were placed at C-3 and C-4 in 22 and C-1 and C-3 in 23. Accordingly, the structures of compounds 22 and 23 (phanerosides V and W ) were defined as shown.

The molecular formula of compound 24 was assigned as $\mathrm{C}_{36} \mathrm{H}_{42} \mathrm{O}_{19}$ based on the HRESIMS ( $m / z 801.2226[\mathrm{M}+\mathrm{Na}]^{+}$, calcd for 801.2213) and ${ }^{13} \mathrm{C}$ NMR data. The NMR data (Figures S212-S217) indicated that it possessed two trans-feruloyl moieties, D-sucrose, and two acetyl groups. The two trans-feruloyl moieties were linked to C-2' and C-6' of the glucopyranose ring, and two acetyl groups were attached to C-3 and C-4 of the
fructofuranose ring, according to the key HMBC correlations as shown in Figure 6. Thus, the structure of compound 24 was identified and named phaneroside X .

## a. In Vitro Anti-inflammatory Effects of Compounds 1-24

Nitric oxide (NO) is one of the major inflammatory mediators, and phenylpropanoid esters of sucrose have been previously reported to possess potent anti-inflammatory activity $[3,7,22]$. Therefore, all the isolates were evaluated in vitro for their anti-inflammatory potential via the Griess reaction in LPS-induced BV-2 microglial cells (Figure 7) [23]. Especially, compounds 6 and 21 exhibited potent inhibitory activities on NO production, with $\mathrm{IC}_{50}$ values of $6.7 \pm 1.7$ and $5.2 \pm 3.5 \mu \mathrm{M}$, which were better than the positive control, L-NMMA ( $\mathrm{IC}_{50}=7.0 \pm 2.7 \mu \mathrm{M}$ ). Compounds 10, 14, and 19 showed moderate inhibitory effects on NO production, with $\mathrm{IC}_{50}$ values of $72.7,46.0$, and $57.7 \mu \mathrm{M}$, respectively. These results suggested that the anti-inflammatory activities of these compounds were not determined by a single variable, while the type, number, and position of the substituents may all affect their inhibitory activities.


Figure 7. Effects of compounds $\mathbf{6}, \mathbf{1 0}, \mathbf{1 4}, 19$, and 21 on NO inhibitory activity $(1-100 \mu \mathrm{M})$ in BV-2 microglial cells. * $p<0.001$, compared with the LPS-treated group; \# $p<0.001$, compared with the control group.

## b. Antioxidant Effects of Compounds 1-24

Many isolated phenylpropanoid esters of sucrose are thought to act as potential antioxidants [3]. Consequently, their antioxidant activities were also tested using the DPPH radical scavenging assay [24]. Compounds 5, 15, 17, and 24 exhibited moderate inhibitory effects with $\mathrm{EC}_{50}$ values of $43.9 \pm 0.2,43.8 \pm 0.1,34.9 \pm 0.1,39.4 \pm 0.3 \mu \mathrm{M}$, respectively. As it stands, the compounds whose $\mathrm{C}-2^{\prime}$ and $\mathrm{C}-6^{\prime}$ of the glucopyranose ring were both substituted by trans-feruloyl groups showed a more positive impact on their antioxidant effects.

## 3. Materials and Methods

General Experimental Procedures
Optical rotations were obtained on a JASCO P-2000 polarimeter. UV absorption spectra were determined on a PerkinElmer 650 spectrophotometer. NMR spectra were acquired on a 400 or 600 MHz Bruker AVANCE apparatus. Chemical shifts are expressed in $\delta$ (ppm) and referenced to the solvent residual peak. HRESIMS data were obtained on an Agilent 6545 Q-TOF LC-MS spectrometer. The other instruments and materials serving for the isolation and purification of compounds were coincident with previous papers [25,26].

## a. Plant Material

The rattans of P. championii Benth. were collected in November 2020 in Guilin, Guangxi Province, People's Republic of China (GPS: $24^{\circ} 47^{\prime} 32.7^{\prime \prime} \mathrm{N} 110^{\circ} 27^{\prime} 36.8^{\prime \prime}$ E). The specimen (No. PC-202011) was authenticated by Professor Shao-Qing Tang (College of Life Science, Guangxi Normal University) and deposited at the State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, Guangxi Normal University.
b. Extraction and Isolation

The dried rattans of $P$. championii ( 21.0 kg ) were soaked for 12 h in $95 \%$ aqueous $\mathrm{EtOH}(100 \mathrm{~L})$ at room temperature, and then extracted three times with $95 \%$ aqueous $\mathrm{EtOH}(3 \times 100 \mathrm{~L})$ via refluxing. The filtrate was concentrated under reduced pressure to afford 4.5 kg of crude extract, which was suspended in $\mathrm{H}_{2} \mathrm{O}$ and successively partitioned with EtOAc and $n$-BuOH. The EtOAc partition ( 1.8 kg ) was separated via silica gel (200-300 mesh) column chromatography (CC), eluting with a gradient of $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}$ (from 1:0 to 1:1) to give 11 fractions (Frs.1-11).

Fr. $6(20.7 \mathrm{~g})$ was separated via $\mathrm{C}_{18}$ reversed-phase (RP) CC, eluting with a gradient of $\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O}$ (30:70 to 70:30) to give 11 subfractions (Frs.6.1-6.11).

Fr. $6.2(656.8 \mathrm{mg})$ was subjected to Sephadex $\mathrm{LH}-20 \mathrm{CC}(\mathrm{MeOH})$ to yield six subfractions (Frs.6.2.1-6.2.6). Fr.6.2.5 ( 183.9 mg ) was applied to silica gel ( $200-300$ mesh) CC, eluting with $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}$ ( $50: 1$ to $5: 1$ ) to obtain nine subfractions (Frs.6.2.5.1-6.2.5.9). Fr.6.2.5.8 ( 14.3 mg ) was further purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}\right.$, $22: 78,8.0 \mathrm{~mL} / \mathrm{min})$ to afford compound $5\left(10.0 \mathrm{mg}, t_{\mathrm{R}} 37.1 \mathrm{~min}\right)$. Compounds 3 ( 12.0 mg , $\left.t_{\mathrm{R}} 38.5 \mathrm{~min}\right)$ and $4\left(35.0 \mathrm{mg}, t_{\mathrm{R}} 42.4 \mathrm{~min}\right)$ were obtained using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 22: 78,8.0 \mathrm{~mL} / \mathrm{min}\right)$ from Fr.6.2.5.9 $(91.5 \mathrm{mg})$.

Fr. $6.3(475.2 \mathrm{mg})$ was separated via a Sephadex LH-20 column, eluting with MeOH to yield six subfractions (Frs.6.3.1-6.3.6). Fr.6.3.5 ( 223.1 mg ) was fractionated using silica gel (200-300 mesh) with gradient elution $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 50: 1\right.$ to $\left.5: 1\right)$ to provide seven subfractions (Frs.6.3.5.1-6.3.5.7). Purification of Fr.6.3.5.3 ( 25.4 mg ) using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 24: 76,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to yield compounds $18\left(4.0 \mathrm{mg}, t_{\mathrm{R}} 54.9 \mathrm{~min}\right)$, $17\left(12.0 \mathrm{mg}, t_{\mathrm{R}} 64.4 \mathrm{~min}\right)$, and $19\left(3.0 \mathrm{mg}, t_{\mathrm{R}} 77.7 \mathrm{~min}\right)$. Fr.6.3.5.4 $(93.5 \mathrm{mg})$ was purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 24: 76,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to obtain compounds $14\left(15.0 \mathrm{mg}, t_{\mathrm{R}} 48.1 \mathrm{~min}\right), 16\left(3.0 \mathrm{mg}, t_{\mathrm{R}} 49.2 \mathrm{~min}\right)$, and $11\left(25.0 \mathrm{mg}, t_{\mathrm{R}} 52.0 \mathrm{~min}\right)$. Fr.6.3.5.5 $(32.6 \mathrm{mg})$ was further purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 24: 76\right.$, $8.0 \mathrm{~mL} / \mathrm{min}$ ) to afford compounds $13\left(8.0 \mathrm{mg}, t_{\mathrm{R}} 40.2 \mathrm{~min}\right)$ and $10\left(18.5 \mathrm{mg}, t_{\mathrm{R}} 44.4 \mathrm{~min}\right)$.

Fr. $6.5(532.6 \mathrm{mg})$ was separated via Sephadex LH-20 CC $(\mathrm{MeOH})$ and then silica gel (200-300 mesh) CC $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 50: 1\right.$ to 8:1) to provide nine subfractions (Frs.6.5.1-6.5.9). Fr.6.5.3 ( 15.0 mg ) was further purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}\right.$, $25: 75,8.0 \mathrm{~mL} / \mathrm{min}$ ) to produce compound $24\left(6.0 \mathrm{mg}, t_{\mathrm{R}} 77.7 \mathrm{~min}\right)$. Fr.6.5.4 ( 59.0 mg ) was chromatographed on a Sephadex $\mathrm{LH}-20$ column using MeOH as a solvent and then purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 27: 73,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to give compound 22 ( $3.5 \mathrm{mg}, t_{\mathrm{R}} 89.4 \mathrm{~min}$ ). Fr.6.5.5 $(35.4 \mathrm{mg})$ and Fr.6.5.9 $(11.9 \mathrm{mg})$ were further purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 27: 73,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to produce compounds 23 $\left(11.0 \mathrm{mg}, t_{\mathrm{R}} 50.0 \mathrm{~min}\right)$ and $2\left(3.0 \mathrm{mg}, t_{\mathrm{R}} 58.1 \mathrm{~min}\right)$, respectively. Further purification of Fr.6.5.6 $(26.5 \mathrm{mg})$ using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 26: 74,8.0 \mathrm{~mL} / \mathrm{min}\right)$ yielded compound 15 ( $7.0 \mathrm{mg}, t_{\mathrm{R}} 42.9 \mathrm{~min}$ ). Purification of $\mathrm{Fr} \cdot 6.5 .7(26.5 \mathrm{mg})$ using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 25: 75,8.0 \mathrm{~mL} / \mathrm{min}\right)$ gave compounds $12\left(6.0 \mathrm{mg}, t_{\mathrm{R}} 42.3 \mathrm{~min}\right)$ and 9 ( $11.0 \mathrm{mg}, t_{\mathrm{R}} 45.0 \mathrm{~min}$ ).

Fr. $7\left(14.0 \mathrm{~g}\right.$ ) was chromatographed over an MCI-gel column, eluting with $\mathrm{MeOH} / \mathrm{H}_{2} \mathrm{O}$ (20:80 to $85: 15$ ) to give 12 subfractions (Frs.7.1-7.12).

Fr.7.4 $(527.6 \mathrm{mg})$ was fractionated using a silica gel (200-300 mesh) column $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}\right.$, 50:1 to $5: 1$ ) to obtain seven subfractions (Frs.7.4.1-7.4.7). Fr.7.4.6 ( 252.4 mg ) was purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 20: 80,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to give compound 1 ( $80.0 \mathrm{mg}, t_{\mathrm{R}} 49.1 \mathrm{~min}$ ).

Fr.7.6 ( 740.5 mg ) was partitioned into six subfractions (Frs.7.6.1-7.6.6) using a Sephadex LH-20 column (MeOH). Fr.7.6.4 ( 449.3 mg ) was separated via silica gel (200-300 mesh) CC to provide eight subfractions (Frs.7.6.4.1-7.6.4.8). Fr.7.6.4.4 $(77.3 \mathrm{mg}$ ) was further purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 24: 76,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to yield compound 8 ( 25.0 mg , $t_{\mathrm{R}} 39.8 \mathrm{~min}$ ). Fr.7.6.4.6 ( 80.6 mg ) was purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 24: 76,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to obtain compounds $7\left(30.0 \mathrm{mg}, t_{\mathrm{R}} 44.1 \mathrm{~min}\right)$ and 6 $\left(8.0 \mathrm{mg}, t_{\mathrm{R}} 56.2 \mathrm{~min}\right)$.

Fr. $7.7(833.7 \mathrm{mg})$ was separated using Sephadex LH-20 $(\mathrm{MeOH})$ to obtain eight subfractions (Frs.7.7.1-7.7.8). Fr.7.7.2 ( 258.5 mg ) was then fractionated via silica gel (200-300 mesh) CC to give six subfractions (Frs.7.7.2.1-7.7.2.6). Fr.7.7.2.2 (74.3 mg) and Fr.7.7.2.3 ( 69.8 mg ) were purified using semipreparative RP-HPLC $\left(\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}, 27: 73,8.0 \mathrm{~mL} / \mathrm{min}\right)$ to yield compounds 21 ( $25.0 \mathrm{mg}, t_{\mathrm{R}} 54.4 \mathrm{~min}$ ) and $20\left(35.0 \mathrm{mg}, t_{\mathrm{R}} 50.2 \mathrm{~min}\right)$, respectively.
c. Physicochemical Properties and Spectroscopic Data of Compounds 1-24

Phaneroside A (1): white amorphous powder; $[\alpha]_{D}^{20}+33(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 211$ (3.87), 228 (3.92), 314 (4.27) nm; IR (KBr) $v_{\max } 3348,1696,1605,1516,1171$, $1054 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $\mathrm{m} / \mathrm{z} 657.1798$ [M + Na] ${ }^{+}$(calcd for $\mathrm{C}_{30} \mathrm{H}_{34} \mathrm{O}_{15} \mathrm{Na}, 657.1790$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 1 and 2. All significant data are presented in Supplementary Materials (Figures S1-S9).

Phaneroside B (2): white amorphous powder; $[\alpha]_{D}^{20}+36$ (c 0.08, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217$ (3.95), 320 (4.25) nm; IR (KBr) $v_{\max } 3432,1696,1605,1516,1271,1169$, $1050 \mathrm{~cm}^{-1} ;(+)$ HRESIMS m/z $641.1847[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{30} \mathrm{H}_{34} \mathrm{O}_{14} \mathrm{Na}, 641.1841$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 1 and 2. All significant data are presented in Supplementary Materials (Figures S11-S19).

Phaneroside C (3): white amorphous powder; $[\alpha]_{D}^{20}+22(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 219$ (3.82), 320 (4.10) nm; IR (KBr) $v_{\max } 3417,1691,1631,1605,1516,1170$, $1052 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $687.1895[\mathrm{M}+\mathrm{Na}]^{+}$, (calcd for $\mathrm{C}_{31} \mathrm{H}_{36} \mathrm{O}_{16} \mathrm{Na}, 687.1896$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 1 and 2. All significant data are presented in Supplementary Materials (Figures S20-S28).

Phaneroside D (4): white amorphous powder; $[\alpha]_{D}^{20}+19$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 231$ (3.94), 320 (4.25) nm; IR (KBr) $\nu_{\max } 3348,1694,1632,1604,1516,1270$, $1170 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $687.1896[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{31} \mathrm{H}_{36} \mathrm{O}_{16} \mathrm{Na}, 687.1896$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 1 and 2. All significant data are presented in Supplementary Materials (Figures S29-S37).

Phaneroside E (5): white amorphous powder; $[\alpha]_{D}^{20}+36$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217(4.07), 237(4.01), 328(4.28) \mathrm{nm}$; IR (KBr) $v_{\max } 3418,1694,1606,1517$, 1246, 1170, $1053 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $717.1990[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{32} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}$, 717.2001); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 1 and 2. All significant data are presented in Supplementary Materials (Figures S38-S46).

Phaneroside F (6): white amorphous powder; $[\alpha]_{D}^{20}+31$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 211$ (3.86), 228 (3.91), 314 (4.26) nm; IR (KBr) $v_{\max } 3431,1693,1605,1516,1171$, $1051 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z 699.1915 [M + Na] ${ }^{+}$(calcd for $\mathrm{C}_{32} \mathrm{H}_{36} \mathrm{O}_{16} \mathrm{Na}, 699.1896$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5. All significant data are presented in Supplementary Materials (Figures S47-S55).

Phaneroside G (7): white amorphous powder; $[\alpha]_{D}^{20}+36(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 211$ (3.88), 228 (3.93), 315 (4.28) nm; IR (KBr) $\nu_{\max } 3421,1694,1606,1516$, 1259, 1171, $1059 \mathrm{~cm}^{-1}$; (+) HRESIMS $m / z 699.1898[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{32} \mathrm{H}_{36} \mathrm{O}_{16} \mathrm{Na}$, 699.1896); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5 . All significant data are presented in Supplementary Materials (Figures S56-S64).

Phaneroside H (8): white amorphous powder; $[\alpha]_{D}^{20}+33(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 211$ (3.93), 228 (3.98), 314 (4.32) nm; IR (KBr) $v_{\max } 3326,1696,1605,1516,1171$, $1063 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $\mathrm{m} / \mathrm{z} 699.1899[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{32} \mathrm{H}_{36} \mathrm{O}_{16} \mathrm{Na}, 699.1896$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5 . All significant data are presented in Supplementary Materials (Figures S65-S73).

Phaneroside I (9): white amorphous powder; $[\alpha]_{D}^{20}+23(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 217$ (4.00), 319 (4.29) nm; IR (KBr) $\nu_{\max } 3427,1695,1632,1605,1516,1270$, 1170, $1051 \mathrm{~cm}^{-1}$; (+) HRESIMS $m / z 729.2015[\mathrm{M}+\mathrm{Na}]^{+}\left(\right.$calcd for $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5. All significant data are presented in Supplementary Materials (Figures S74-S82).

Phaneroside J (10): white amorphous powder; $[\alpha]_{D}^{20}+23(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 216$ (3.98), 320 (4.28) nm; IR (KBr) $v_{\max } 3436,1691,1632,1605,1516,1268$, $1170 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $729.2012[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001$ );
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5. All significant data are presented in Supplementary Materials (Figures S83-S91).

Phaneroside K (11): white amorphous powder; $[\alpha]_{D}^{20}+19$ (c 0.05, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 216(4.01), 319$ (4.29) nm; IR (KBr) $\nu_{\max } 3429,1695,1632,1605,1516,1268$, $1170,1053 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z 729.1989 [M + Na] ${ }^{+}\left(\right.$calcd for $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 3 and 5. All significant data are presented in Supplementary Materials (Figures S92-S100).

Phaneroside L (12): white amorphous powder; $[\alpha]_{D}^{20}+19$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 218$ (4.03), 319 (4.30) nm; IR (KBr) $v_{\max } 3436,1695,1632,1605,1516,1274$, $1171 \mathrm{~cm}^{-1} ;(+)$ HRESIMS m/z $729.2018[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5. All significant data are presented in Supplementary Materials (Figures S101-S109).

Phaneroside M (13): white amorphous powder; $[\alpha]_{D}^{20}+22(c 0.05, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 217$ (4.04), 319 (4.32) nm; IR (KBr) $v_{\max } 3436,1695,1632,1605,1516,1268$, $1170,1053 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $729.2010[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5. All significant data are presented in Supplementary Materials (Figures S110-S118).

Phaneroside N (14): white amorphous powder; $[\alpha]_{D}^{20}+28(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 232(4.03), 319(4.32) \mathrm{nm} ;$ IR (KBr) $\nu_{\max } 3432,1692,1606,1518,1172,1051 \mathrm{~cm}^{-1}$; $(+)$ HRESIMS $m / z 729.1990[\mathrm{M}+\mathrm{Na}]^{+}\left(\right.$calcd for $\left.\mathrm{C}_{33} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 729.2001\right) ;{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5. All significant data are presented in Supplementary Materials (Figures S119-S127).

Phaneroside O (15): white amorphous powder; $[\alpha]_{D}^{20}+22(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 217$ (4.13), 237 (4.06), 327 (4.34) nm; IR (KBr) $v_{\text {max }} 3429,1695,1632,1602,1516$, 1273, 1163, $1051 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $759.2124[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}$, 759.2107); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5 . All significant data are presented in Supplementary Materials (Figures S128-S136).

Phaneroside P (16): white amorphous powder; $[\alpha]_{D}^{20}+27$ (c 0.05, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217$ (4.22), 236 (4.15), 325 (4.37) nm; IR (KBr) $v_{\max } 3432,1690,1605,1517,1169$, $1056 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $m / z 759.2095[\mathrm{M}+\mathrm{Na}]^{+}\left(\right.$calcd for $\left.\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}, 759.2107\right)$; ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5 . All significant data are presented in Supplementary Materials (Figures S137-S145).

Phaneroside Q (17): white amorphous powder; $[\alpha]_{D}^{20}+28(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 217$ (4.07), 237 (4.01), 327 (4.29) nm; IR (KBr) $v_{\max } 3426,1697,1632,1598$, 1516, 1272, $1161 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z 759.2097 [M + Na] (calcd for $\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}$, 759.2107); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5 . All significant data are presented in Supplementary Materials (Figures S146-S154).

Phaneroside R (18): white amorphous powder; $[\alpha]_{D}^{20}+27$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217$ (4.13), 234 (4.04), 324 (4.20) nm; IR (KBr) $v_{\max } 3428,1696,1605,1517$, 1261, 1170, $1054 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $m / z 759.2096[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}$, 759.2107); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5 . All significant data are presented in Supplementary Materials (Figures S155-S163).

Phaneroside S (19): white amorphous powder; $[\alpha]_{D}^{20}+23$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217$ (4.17), 235 (4.07), 325 (4.26) nm; IR (KBr) $v_{\max } 3397,2921,2850,1646,1516$, $1272 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $m / z 759.2097[\mathrm{M}+\mathrm{Na}]^{+}\left(\right.$calcd for $\left.\mathrm{C}_{34} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}, 759.2107\right)$; ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 4 and 5 . All significant data are presented in Supplementary Materials (Figures S164-S172).

Phaneroside T (20): white amorphous powder; $[\alpha]_{D}^{20}+25$ (c 0.06, MeOH); UV (MeOH) $\lambda_{\max }(\log \varepsilon) 211$ (3.92), 229 (3.97), 314 (4.32) nm; IR (KBr) $v_{\max }$ 3420, 1697, 1606, 1516, 1262, 1171, $1056 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z $741.2001[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{34} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}$ 741.2001); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 6 and 7 . All significant data are presented in Supplementary Materials (Figures S173-S181).

Phaneroside $\mathrm{U}(\mathbf{2 1})$ : white amorphous powder; $[\alpha]_{D}^{20}+26(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 211$ (3.89), 228 (3.94), 314 (4.28) nm; IR (KBr) $v_{\max } 3432,1695,1606,1516,1170$,
$1061 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $\mathrm{m} / \mathrm{z} 741.2001[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{34} \mathrm{H}_{38} \mathrm{O}_{17} \mathrm{Na}, 741.2001$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 6 and 7 . All significant data are presented in Supplementary Materials (Figures S182-S190).

Phaneroside V (22): white amorphous powder; $[\alpha]_{D}^{20}+26(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 230$ (4.02), 316 (4.28) nm; IR (KBr) $v_{\max } 3429,1697,1606,1516,1269,1170$, $1054 \mathrm{~cm}^{-1}$; (+) HRESIMS m/z 771.2093 [M + Na] ${ }^{+}$(calcd for $\mathrm{C}_{35} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}, 771.2107$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 6 and 7. All significant data are presented in Supplementary Materials (Figures S191-S199).

Phaneroside W (23): white amorphous powder; $[\alpha]_{D}^{20}+23(c 0.06, \mathrm{MeOH})$; UV (MeOH) $\lambda_{\max }(\log \varepsilon) 217$ (4.04), 319 (4.33) nm; IR (KBr) $v_{\max } 3436,1696,1633,1605,1516,1268$, $1170,1053 \mathrm{~cm}^{-1} ;(+)$ HRESIMS $\mathrm{m} / \mathrm{z} 771.2112[\mathrm{M}+\mathrm{Na}]^{+}\left(\right.$calcd for $\mathrm{C}_{35} \mathrm{H}_{40} \mathrm{O}_{18} \mathrm{Na}, 771.2107$ ); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 6 and 7. All significant data are presented in Supplementary Materials (Figures S200-S209).

Phaneroside X (24): white amorphous powder; $[\alpha]_{D}^{20}+25(c 0.06, \mathrm{MeOH}) ; \mathrm{UV}(\mathrm{MeOH})$ $\lambda_{\max }(\log \varepsilon) 217$ (4.16), 238 (4.10), 328 (4.37) nm; IR (KBr) $\nu_{\max } 3436,1712,1633,1601$, 1515, 1273, $1177 \mathrm{~cm}^{-1}$; (+) HRESIMS $m / z 801.2226[\mathrm{M}+\mathrm{Na}]^{+}$(calcd for $\mathrm{C}_{36} \mathrm{H}_{42} \mathrm{O}_{19} \mathrm{Na}$, 801.2213); ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR data, see Tables 6 and 7 . All significant data are presented in Supplementary Materials (Figures S210-S217).

## d. Acid Hydrolysis of Compound 1

Compound $1(4.0 \mathrm{mg})$ was added to 5.0 mL of $9 \%$ aqueous HCl in a sealed flask, which was refluxed at $80^{\circ} \mathrm{C}$ for 5 h . The acidic aqueous mixture was dried, $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$ was added, and the mixture was extracted with EtOAc $(3 \times 2 \mathrm{~mL})$. The aqueous layer was concentrated to obtain the sugar fraction, which was dissolved with MeOH and analyzed using chiral-phase HPLC equipped with a Daicel Chiralpak AD-H column ( $250 \times 4.6 \mathrm{~mm}$, $5 \mu \mathrm{~m}$ ) and an evaporative light-scattering detector (ELSD) using $n$-hexane:EtOH (82:18) as the mobile phase ( $0.7 \mathrm{~mL} / \mathrm{min}$ ) [27]. The sugars were confirmed to be D-glucose and D-fructose by comparing their retention times with those of D-glucose ( 17.4 min ), L-glucose ( 18.2 min ), D-fructose ( 25.6 min ), and L-fructose ( 26.4 min ) (Figure S10).

## e. NO Production Measurements and Cell Viability Assays

The inhibitory effects of the isolated compounds on LPS-stimulated NO production were evaluated using the Griess reaction, and the cytotoxicities of compounds on BV-2 microglial cells were evaluated using MTT assays, as described in our previous report [23]. The result is shown in Figure 7.

## f. Antioxidant Activity Assay

The antioxidant activity of the isolated compounds was tested using a DPPH radical scavenging assay as previously described, and vitamin $C$ was used as the positive control [24].

## 4. Conclusions

In conclusion, 24 new phenylpropanoid esters of sucrose were isolated from the rattans of $P$. championii. Their structures were determined via extensive spectroscopic methods. The configuration of sugar moiety was determined via chiral-phase HPLC equipped with an evaporative light-scattering detector (ELSD) after acid hydrolysis of compound $\mathbf{1}$. This is the first report of phenylpropanoid esters of sucrose isolated from the family Fabaceae. Structurally, these compounds revealed a huge structural diversity in terms of the number and position of phenylpropanoid and acetyl substituents. Biologically, all the isolated compounds were evaluated for their anti-inflammatory and antioxidant activities, and several compounds showed potent or moderate effects. Additionally, the structure-activity relationship was briefly discussed. These compounds may serve as potential leads for the development of anti-inflammatory agents.

Supplementary Materials: The following supporting information can be downloaded at: https: / /www.mdpi.com/article/10.3390/molecules28124767/s1, Figure S1: UV Spectrum of compound 1. Figure S2: IR (KBr disc) spectrum of compound 1. Figure S3: (+) HRESIMS spectrum of compound 1. Figures S4-S9: 1D and 2D NMR spectra of compound 1. Figure S10: Chiral-HPLC profile from acid hydrolysis of $\mathbf{1}$ compared to authentic standard. Figure S11: UV spectrum of compound 2. Figure S12: IR ( KBr disc) spectrum of compound 2. Figure S13: (+) HRESIMS spectrum of compound 2. Figures S14-S19: 1D and 2D NMR spectra of compound 2. Figure S20: UV spectrum of compound 3. Figure S21: IR ( KBr disc) spectrum of compound 3. Figure S22: (+) HRESIMS spectrum of compound 3. Figures S23-S28: 1D and 2D NMR spectra of compound 3. Figure S29: UV spectrum of compound 4. Figure S30: IR (KBr disc) spectrum of compound 4. Figure S31: (+) HRESIMS spectrum of compound 4. Figures S32-S37: 1D and 2D NMR spectra of compound 4. Figure S38: UV spectrum of compound 5. Figure S39: IR ( KBr disc) spectrum of compound 5. Figure S40: (+) HRESIMS spectrum of compound 5. Figures S41-S46: 1D and 2D NMR spectra of compound 5. Figure S47: UV spectrum of compound 6. Figure S48: IR ( $\mathrm{KBr} \mathrm{disc} \mathrm{)} \mathrm{spectrum} \mathrm{of} \mathrm{compound} \mathrm{6} .\mathrm{Figure} \mathrm{S49:}$ (+) HRESIMS spectrum of compound 6. Figures S50-S55: 1D and 2D NMR spectra of compound 6. Figure S56: UV spectrum of compound 7. Figure S57: IR ( KBr disc) spectrum of compound 7. Figure S58: (+) HRESIMS spectrum of compound 7. Figures S59-S64: 1D and 2D NMR spectra of compound 7. Figure S65: UV spectrum of compound 8. Figure S66: IR ( KBr disc) spectrum of compound 8. Figure S67: (+) HRESIMS spectrum of compound 8. Figures S68-S73: 1D and 2D NMR spectra of compound 8. Figure S74: UV spectrum of compound 9. Figure S75: IR ( KBr disc) spectrum of compound 9. Figure S76: (+) HRESIMS spectrum of compound 9. Figures S77-S82: 1D and 2D NMR spectra of compound 9. Figure S83: UV spectrum of compound 10. Figure S84: IR (KBr disc) spectrum of compound 10. Figure S85: (+) HRESIMS spectrum of compound 10. Figures S86-S91: 1D and 2D NMR spectra of compound 10. Figure S92: UV spectrum of compound 11. Figure S93: IR ( KBr disc) spectrum of compound 11. Figure S94: (+) HRESIMS spectrum of compound 11. Figures S95-S100: 1D and 2D NMR spectra of compound 11. Figure S101: UV spectrum of compound 12. Figure S102: IR ( KBr disc) spectrum of compound 12. Figure S103: (+) HRESIMS spectrum of compound 12. Figures S104-S109: 1D and 2D NMR spectra of compound 12. Figure S110: UV spectrum of compound 13. Figure S111: IR (KBr disc) spectrum of compound 13. Figure S112: (+) HRESIMS spectrum of compound 13. Figures S113-S118: 1D and 2D NMR spectra of compound 13. Figure S119: UV spectrum of compound 14. Figure S120: IR ( KBr disc) spectrum of compound 14. Figure S121: (+) HRESIMS spectrum of compound 14. Figures S122-S127: 1D and 2D NMR spectra of compound 14. Figure S128: UV spectrum of compound 15. Figure S129: IR ( KBr disc) spectrum of compound 15. Figure S130: (+) HRESIMS spectrum of compound 15. Figures S131-S136: 1D and 2D NMR spectra of compound 15. Figure S137: UV spectrum of compound 16. Figure S138: IR ( KBr disc) spectrum of compound 16. Figure S139: (+) HRESIMS spectrum of compound 16. Figures S140-S145: 1D and 2D NMR spectra of compound 16. Figure S146: UV spectrum of compound 17. Figure S147: IR ( KBr disc) spectrum of compound 17. Figure S148: (+) HRESIMS spectrum of compound 17. Figures S149-S154: 1D and 2D NMR spectra of compound 17. Figure S155: UV spectrum of compound 18. Figure S156: IR (KBr disc) spectrum of compound 18. Figure S157: (+) HRESIMS spectrum of compound 18. Figures S158-S163: 1D and 2D NMR spectra of compound 18. Figure S164: UV spectrum of compound 19. Figure S165: IR ( $\mathrm{KBr} \mathrm{disc} \mathrm{)} \mathrm{spectrum} \mathrm{of} \mathrm{compound} \mathrm{19} .\mathrm{Figure} \mathrm{S166:} \mathrm{(+)}$ HRESIMS spectrum of compound 19. Figures S167-S172: 1D and 2D NMR spectra of compound 19. Figure S173: UV spectrum of compound 20. Figure S174: IR ( KBr disc) spectrum of compound 20. Figure S175: (+) HRESIMS spectrum of compound 20. Figures S176-S181: 1D and 2D NMR spectra of compound 20. Figure S182: UV spectrum of compound 21. Figure S183: IR ( KBr disc) spectrum of compound 21. Figure S184: (+) HRESIMS spectrum of compound 21. Figures S185-S190: 1D and 2D NMR spectra of compound 21. Figure S191: UV spectrum of compound 22. Figure S192: IR (KBr disc) spectrum of compound 22. Figure S193: (+) HRESIMS spectrum of compound 22. Figures S194-S199: 1D and 2D NMR spectra of compound 22. Figure S200: UV spectrum of compound 23. Figure S201: IR ( KBr disc) spectrum of compound 23. Figure S202: (+) HRESIMS spectrum of compound 23. Figures S203-S208: 1D and 2D NMR spectra of compound 23. Figure S209: UV spectrum of compound 24. Figure S210: IR ( KBr disc) spectrum of compound 24. Figure S211: (+) HRESIMS spectrum of compound 24. Figures S212-S217: 1D and 2D NMR spectra of compound 24.


#### Abstract

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[^0]:    ${ }^{\mathrm{a}}$ In MeOH- $d_{4},{ }^{1} \mathrm{H}$ NMR at $400 \mathrm{MHz} .{ }^{\mathrm{b}}$ In MeOH- $d_{4},{ }^{1} \mathrm{H}$ NMR at $600 \mathrm{MHz} . \mathrm{s}=$ singlet; $\mathrm{d}=$ doublet; $\mathrm{t}=$ triplet; $\mathrm{m}=$ multiplet; br $=$ broad

