**FULL PAPER**

# Iridoid Glycosides and Phenolic Compounds from the Flowers of *Vitex agnus-castus*

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A new and rare type of iridoid glycoside, agnusoside (**1**), a new caffeoylquinic acid derivative, castusic acid (**2**), and a new sugar ester, 1,2-di-(4-hydroxybenzoyl)-*β*-glucopyranose (**3**), along with ten known compounds belonging to iridoid glycosides (agnuside, *trans*-eurostoside), caffeoylquinic acid derivatives (chlorogenic acid and isochlorogenic acid A), flavonoids (isoorientin, isovitexin, kaempferol 3-*O*-sophoroside, luteolin 6-*C*-(2″-*O*-*trans*-caffeoyl)glucopyranoside, and simple phenolic acids (4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid), chemical classes were isolated from the flowers of *Vitex agnus-castus*. The structures of the isolates were established by extensive 1D- and 2D-NMR spectroscopic analysis as well as HR-ESI-MS. Agnusoside (**1**) represents an unusual type of iridoid glycoside with its 6-keto C(4) nonsubstituted aglycone.

**Keywords:** *Vitex agnus-castus*, Secondary metabolites, Iridoid glycosides, Agnusoside, Caffeoylquinic acid derivative.

## Introduction

*Vitex agnus-castus* L. (chaste tree) is a shrub or small tree that belongs to Verbenaceae family. It is indigenous to temperate and subtropical zones including Mediterranean region and Central Asia [1]. It is one of the two representatives of the genus *Vitex* growing wild in the flora of Turkey and widely distributed in Anatolia, particularly in western and southern parts [2]. The fruits are used as diuretic, carminative, and sedative, while the flowering and leafy stems are intended for menstrual cycle disorders in Turkey [3][4]. The extracts prepared from the fruits of *V. agnus-castus* have been shown to possess analgesic [5], cytotoxic, apoptosis-inducing [6], antiepileptic [7], and opioidergic [8] activities. The fruits of chaste tree are highly reputed in phytotherapy for the treatment of premenstrual syndrome such as mastodynia as well as against menstrual cycle irregularities associated with hyperprolactinemia. Furthermore, the effectiveness of the extracts in the treatment of premenstrual syndrome and cycle irregularities were shown in some clinical studies [9][10]. A large number of secondary metabolites belonging to iridoids [11], flavonoids [12][13], diterpenes [14][15], and essential oils [16] were isolated from the fruits, leaves, and flowering stems of *Vitex agnus-castus*. Moreover, in very recent years, two analytical studies (UHPLC-DAD and LC-DAD/MS$^n$) have been performed on the fruits of this species aiming at identifying the chemical composition of the extracts and reported the presence of several iridoids, caffeoylquinic acid derivatives, diterpenes, and flavonoids [1][17]. However, no previous detailed phytochemical studies were conducted on the nonvolatile chemical constituents of the flowers of *V. agnus-castus*. In this study, we attempted to identify the secondary metabolites of the flowers of *V. agnus-castus* as a part of our ongoing studies on medicinal plants growing in Turkey. Herein, reported are the isolation and structural elucidation of three new compounds (**1** – **3**) together with ten known ones from the flowers of *V. agnus-castus*.

## Results and Discussion

The crude MeOH extract of the flowers of *Vitex agnus-castus* was partitioned between $H_2O$ and $CHCl_3$. The $H_2O$ subextract was then submitted to successive chromatographic methods including polyamide CC, $C_{18}$-MPLC, $SiO_2$ CC, and *Sephadex LH-20* CC to afford three new secondary metabolites, **1** – **3** (*Fig. 1*) along with ten known ones.

The known compounds were identified as agnuside [5], *trans*-eurostoside [18], chlorogenic acid [19], and isochlorogenic acid A [20], isoorientin, isovitexin [21], kaempferol 3-*O*-sophoroside [22], luteolin 6-*C*-(2″-*O*-*trans*-caffeoyl)glucopyranoside [12], 4-hydroxybenzoic acid, and 3,4-dihydroxybenzoic acid by comparison of their NMR data with those reported.

Compound **1** was obtained as an amorphous powder. Its molecular formula was deduced as $C_{22}H_{24}O_{11}$ from the HR-ESI-MS (*m*/*z* 487.1212 ([*M* + Na]$^+$)) and $^{13}$C-NMR data. The $^1$H-NMR spectrum of **1** (*Table 1*) exhibited three olefinic signals at $\delta$(H) 6.43 (*dd*, *J* = 6.0, 2.0), 6.19 (br. *s*), and 5.20 (*dd*, *J* = 6.0, 3.8), signals for an O-bearing $CH_2$ group at $\delta$(H) 5.57 and 5.12 (each *d*, *J* = 17.8) as *AX* system, a hemiacetal signal at $\delta$(H) 4.92 (*d*, *J* = 7.1), and

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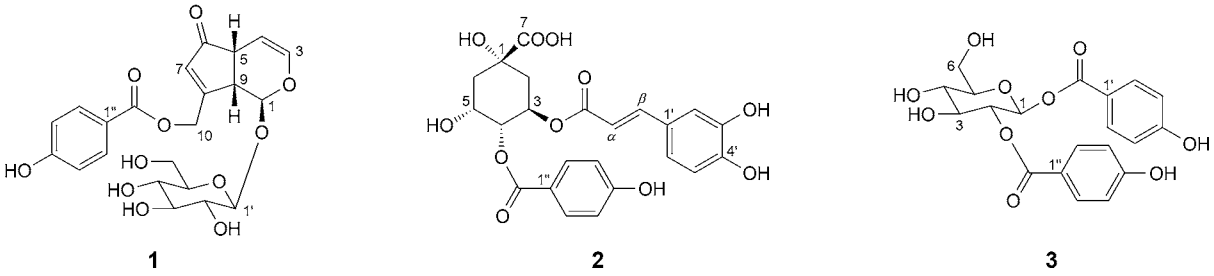

Fig. 1. Structures of compounds **1** – **3** isolated from *Vitex agnus-castus*.

Table 1. $^1$H- and $^{13}$C-NMR (400 and 100 MHz, resp.) data of **1** in $CD_3OD$. $\delta$ in ppm, $J$ in Hz

| Position | $\delta$(H)[a]) | $\delta$(C)[a]) |
|---|---|---|
| Aglycone | | |
| 1 | 4.92 (*d*, *J* = 7.1) | 98.4 |
| 3 | 6.43 (*dd*, *J* = 6.0, 2.0) | 142.6 |
| 4 | 5.20 (*dd*, *J* = 6.0, 3.8) | 102.3 |
| 5 | 3.28[b]) | 45.1 |
| 6 | – | 207.4 |
| 7 | 6.19 (br. *s*) | 129.4 |
| 8 | – | 174.5 |
| 9 | 3.33[b]) | 47.3 |
| 10 | 5.57 (*d*, *J* = 17.8) | 64.4 |
| | 5.12 (*d*, *J* = 17.8) | |
| $\beta$-Glucose | | |
| 1′ | 4.72 (*d*, *J* = 7.7) | 100.3 |
| 2′ | 3.28 (*dd J* = 7.7, 9.0) | 74.8 |
| 3′ | 3.38 (*t*, *J* = 9.0) | 77.8 |
| 4′ | 3.30[a]) | 71.4 |
| 5′ | 3.29[a]) | 78.4 |
| 6′ | 3.86 (*dd*, *J* = 11.9, 1.9) | 62.7 |
| | 3.64 (*dd*, *J* = 11.9, 5.4) | |
| 4-OH-benzoyl | | |
| 1″ | – | 121.4 |
| 2″,6″ | 7.94 (*d*, *J* = 8.8) | 133.1 |
| 3″,5″ | 6.85 (*d*, *J* = 8.8) | 116.4 |
| 4″ | – | 164.0 |
| C=O | – | 167.4 |

[a]) Assignments are based on COSY, HSQC, and HMBC experiments. [b]) Overlapped signals.

two signals for a CH group each at $\delta$(H) 3.28 and 3.33. Moreover, the spectrum also contained signals arising from a $\beta$-glucopyranose unit inferred from an anomeric signal at $\delta$(H) 4.72 (*d*, *J* = 7.7) and signals between $\delta$(H) 3.28 – 3.86) as well as signals for a set of an *AA′XX′* system at $\delta$(H) 7.94 and 6.85 (each *d*, *J* = 8.8) due to an 1,4-disubstituted aromatic ring. The $^{13}$C-NMR spectrum revealed 22 resonances, including one ester and one ketone CO functions at $\delta$(C) 167.4 and 207.4, respectively. Aside from the signals of a $\beta$-glucopyranose and a 4-hydroxybenzoyl unit, the remaining signals indicated the presence of a $C_9$-iridoid skeleton with a ketone function. The location of the ketone function was found to be C(6) by the help of HMBCs (*Fig. 2*) of C(6) ($\delta$(C) 207.4) with H–C(9) ($\delta$(H) 3.33) and H–C(7) ($\delta$(H) 6.19). Similarly, the $CH_2O$ group was unambiguously located at C(8) based on the cross-peak between C(7) ($\delta$(C) 129.4) and $CH_2$(10) ($\delta$(H) 5.57 and 5.12). The glycosidation site of the glucose as well the esterification point of 4-hydroxybenzoic acid were established with the help of the HMBC spectrum. The long-range coupling between C(1) ($\delta$(C) 98.4) of the aglycone and H–C(1′) of $\beta$-glucopyranose led to identification of the attachment point of glucose to be O–C(1). The long-range coupling of the C=O ($\delta$(C) 167.4) of 4-hydroxybenzoic acid with $CH_2$(10) confirmed the connection of the acyl unit to O–C(10). On the basis of the above data, compound **1** was elucidated as an ester iridoid glycoside which possesses a ketone group at C(6) in the aglycone. In fact, it was the oxidized derivative of agnuside [5], one of the characteristic compounds of *V. agnus-castus*. The downfield shift of the signals for H–C(5) and H–C(7) around 0.6 ppm and 0.4 ppm, respectively, compared to those of agnuside also supported this assumption. To the best of our knowledge, **1** is being reported for the first time and assigned the name agnusoside.

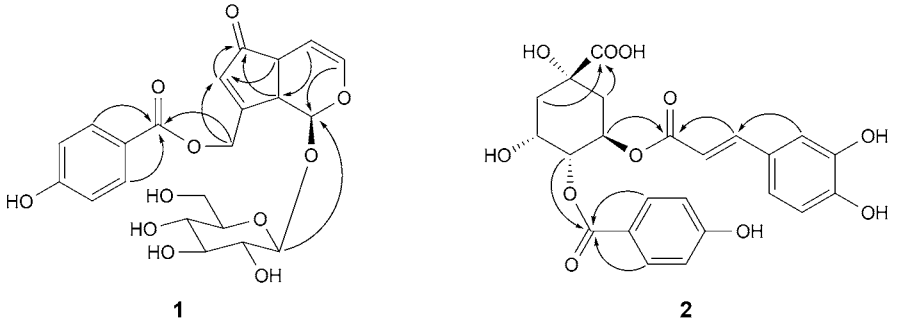

Fig. 2. Key HMBCs (H → C) of compounds **1** and **2**.

 

Compound **2** was isolated as a yellow solid. Its HR-ESI-MS *quasi*-molecular ion at *m*/*z* 497.1056 ([*M* + Na]$^+$) and $^{13}$C-NMR data were consistent with the molecular formula $C_{23}H_{22}O_{11}$ (calc. 392.1988). The $^1$H-NMR spectrum (*Table 2*) showed the presence of three *O*-bearing methine signals at $\delta$(H) 5.64 – 5.58 (*m*), 4.92 (*dd*, *J* = 10.2, 2.8), 4.18 (br. *d*, *J* = 2.8), two sets of nonequivalent $CH_2$ signals at $\delta$(H) 2.05, 1.88 (each br. *d*, *J* = 10.9) and 2.08 (*dd*, *J* = 14.0, 2.8), 1.70 (br. *d*, *J* = 14.0) which were observed in the same spin system in the $^1$H,$^1$H-COSY spectrum. Additionally, the spectrum contained three aromatic signals as an *ABX* type at $\delta$(H) 6.94 (*d*, *J* = 2.0), 6.88 (*dd*, *J* = 8.1, 2.0), 6.68 (*d*, *J* = 8.1), as well as a pair of *trans*-coupled olefinic signals at $\delta$(H) 7.36 and 6.10 (each *d*, *J* = 16.0) as an *AX* type. These findings indicated the presence of a quinic acid and (*E*)-caffeoyl moieties in the structure of **2** as in chlorogenic acid [19]. Besides these resonances, the $^1$H- and $^{13}$C-NMR spectra (*Table 2*) also contained signals characteristic for a 4-hydroxybenzoic acid at $\delta$(H) 7.74 and 6.78 (each 2 H, *d*, *J* = 8.8), $\delta$(C) 165.6, 162.5, 131.9 (2 C), 120.6, 115.6 (2 C). The downfield shift of the H–C(4) (4.92 ppm) of quinic acid approximately 1.3 ppm was the indicative of the esterification site of 4-hydroxybenzoic acid to be HO–C(4). This assumption was confirmed by the long-range correlation between C=O of the 4-hydroxybenzoic acid with H–C(4) (*Fig. 2*) in the HMBC spectrum. Similarly, the connection of the (*E*)-caffeoyl unit to the quinic acid moiety was established to be HO–C(3) based on the cross-peak between C=O ($\delta$(C) 166.5) of the (*E*)-caffeoyl unit and H–C(3). The relative configuration of the molecule was deduced by ROESY experiment. ROE cross-peaks of $H_\alpha$–C(3)/$H_\alpha$–C(2), $H_\alpha$–C(3)/$H_\alpha$–C(6) indicated that these protons were positioned on the same side ($\alpha$). Significant correlations between $H_\beta$–C(2)/$H_\beta$–C(4), $H_\beta$–C(2)/$H_\beta$–C(6), $H_\beta$–C(4)/$H_\beta$–C(6), $H_\beta$–C(4)/$H_\beta$–C(5), indicated them to be positioned on the other side ($\beta$) of the molecule. Furthermore, the absence of ROE correlation between H–C(3) and H–C(5) supported the proposed relative configuration. Hence, **2** was established as the *p*-(OH)-benzoic acid derivative of chlorogenic acid and given a trivial name of castusic acid.

Compound **3** was obtained as an almost colorless, amorphous, powder. The UV spectrum contained band (260 nm) indicating the presence of aromatic ring. The IR spectrum showed the presence of OH (3304 cm$^{-1}$), ester CO (1711 cm$^{-1}$), and aromatic functional groups (1608, 1593 and 1515 cm$^{-1}$). The molecular formula, $C_{20}H_{20}O_{10}$, was determined from HR-ESI-MS (443.0952 [*M* + Na]$^+$, calc. 443.0949) and NMR spectroscopic data (*Table 3*), indicated eleven degrees of unsaturation. The $^1$H-NMR spectrum (*Table 3*) of **3** showed two pairs of aromatic signals as *AA′XX′* type at $\delta$(H) 7.86 and 6.77 (each *d*, *J* = 8.6) and $\delta$(H) 7.81 and 6.76 (each *d*, *J* = 8.6) suggesting the presence of two 4-hydroxybenzoic acid units. The $^1$H-NMR spectrum also displayed one anomeric H-atom signal at $\delta$(H) 5.92 (*d*, *J* = 8.5) with a large coupling constant, implying the $\beta$-configuration. The $^{13}$C-NMR spectrum contained 20 C-atom resonances, 14 of which were assigned to two 4-hydroxybenzoic acid moieties. The remaining six

Table 2. $^1$H- and $^{13}$C-NMR (400 and 100 MHz, resp.) data for **2** in ($D_6$)DMSO. $\delta$ in ppm, *J* in Hz

| Position | $\delta$(H)[a]) | $\delta$(C)[a]) |
|---|---|---|
| Quinic acid | | |
| 1 | – | 75.7 |
| 2$\alpha$ | 1.88 (br. *d*, *J* = 10.9) | 40.5 |
| 2$\beta$ | 2.05 (br. *d*, *J* = 10.9) | |
| 3 | 5.64 – 5.58 (*m*) | 68.3 |
| 4 | 4.92 (*dd*, *J* = 10.2, 2.8) | 77.1 |
| 5 | 4.18 (br. *d*, *J* = 2.8) | 69.2 |
| 6$\alpha$ | 2.08 (*dd*, *J* = 14.0, 2.8) | 38.8 |
| 6$\beta$ | 1.70 (br. *d*, *J* = 14.0) | |
| 7 | – | 176.4 |
| (*E*)-Caffeoyl | | |
| 1′ | – | 125.6 |
| 2′ | 6.94 (*d*, *J* = 2.0) | 115.3 |
| 3′ | – | 145.8 |
| 4′ | – | 149.2 |
| 5′ | 6.68 (*d*, *J* = 8.1) | 116.1 |
| 6′ | 6.88 (*dd*, *J* = 8.1, 2.0) | 121.7 |
| $\alpha$ | 6.10 (*d*, *J* = 16.0) | 114.0 |
| $\beta$ | 7.36 (*d*, *J* = 16.0) | 146.1 |
| C=O | – | 166.5 |
| *p*-OH-benzoyl | | |
| 1″ | – | 120.6 |
| 2″,6″ | 7.74 (*d*, *J* = 8.8) | 131.9 |
| 3″,5″ | 6.78 (*d*, *J* = 8.8) | 115.6 |
| 4″ | – | 162.5 |
| C=O | – | 165.6 |

[a]) Assignments are based on COSY, HSQC, HMBC, and ROESY experiments.

Table 3. $^1$H- and $^{13}$C-NMR (400 and 100 MHz, resp.) data for **3** in $CD_3OD$. $\delta$ in ppm, *J* in Hz

| Position | $\delta$(H)[a]) | $\delta$(C)[a]) |
|---|---|---|
| Glucose | | |
| 1 | 5.92 (*d*, *J* = 8.5) | 94.3 |
| 2 | 5.22 (*dd*, *J* = 9.5, 8.5) | 74.5 |
| 3 | 3.82 (*t*, *J* = 9.5) | 76.0 |
| 4 | 3.56[b]) | 71.4 |
| 5 | 3.56[b]) | 79.2 |
| 6 | 3.91 (*dd*, *J* = 12.0, 1.9) | 62.3 |
| | 3.76 (*dd*, *J* = 12.0, 4.5) | |
| 4-OH-benzoyl | | |
| 1′ | – | 121.3 |
| 2′/6′ | 7.81 (*d*, *J* = 8.6) | 133.3 |
| 3′/5′ | 6.76 (*d*, *J* = 8.6) | 116.3 |
| 4′ | – | 164.2 |
| C=O | – | 166.3 |
| *p*-OH-benzoyl | | |
| 1″ | – | 121.9 |
| 2″,6″ | 7.86 (*d*, *J* = 8.6) | 133.1 |
| 3″,5″ | 6.77 (*d*, *J* = 8.6) | 116.1 |
| 4″ | – | 163.7 |
| C=O | – | 167.4 |

[a]) Assignments are based on COSY, HSQC, and HMBC experiments. [b]) Overlapped signals.

 

resonances indicated the presence of a hexose unit in **3**. By the help of COSY, HSQC, and HMBC spectra, the hexose unit was identified as β-glucopyranose. However, the anomeric H-atom signal, as well as the signal at δ(H) 5.22 (*dd*, *J* = 9.5, 8.5) which coupled with an anomeric H-atom in the $^1$H,$^1$H-COSY spectrum, were found to be shifted downfield around 1 ppm. The chemical shift values of the deshielded H–C(1) and H–C(2) signals of glucose indicated the esterification points of aromatic acid units to be O–C(1) and O–C(2) of β-glucopyranose which was further confirmed by HMBCs of CO groups (δ(C) 166.3 and 167.4) with H–C(1) and H–C(2) of glucose. Accordingly, the structure of **3** was determined to be 1,2-di-(4-hydroxybenzoyl)-β-glucopyranose. In a recent study by *Högner et al.* [1] on the fruits of *Vitex agnus-castus*, 1,2-dibenzoic acid glucose was reported as one of the phytoconstituents of the fruit extract and was utilized as a marker compound in the analytic part of their study. When the depicted structure of this compound was checked in their work, it corresponded to 1,2-di-(4-hydroxybenzoyl)-α-glucopyranose, and not to 1,2-dibenzoic acid glucose. Probably, the aforementioned compound could be 1,2-di-(4-hydroxybenzoyl)-β-glucopyranose which was isolated in this study. The NMR data of compound **3** are being reported for the first time in this study.

Among the isolated iridoid glycosides, compound **1** is a rare iridoid glycoside with its ketone function at C(6). Iridoids which possess a ketone function in the cyclopentane ring, particularly at C(6), are rarely encountered compounds in plant kingdom. Few examples are teuhircoside, teucardoside, and allobetonicoside, that were reported from the species of *Teucrium* and *Betonica* from the Lamiaceae family [18] while cornin, 10-hydroxycornin, hastatoside, and 10-hydroxyhastatoside were obtained from the genera *Cornus* (Cornaceae) [23] and *Penstemon* (Plantaginaceae) [24]. Another similar structure was reported from *Vitex negundo* as a tautomeric mixture [25]. However, all these compounds were either 5-OH-iridoid glycosides or C(4) substituted iridoid glycosides. Thus, the aglycone of compound **1**, a 6-keto, C(4)-nonsubstituted cyclopentanopyran skeleton, can be accepted as a novel iridoid aglycone. On the other hand, since iridoid glycosides are accepted as useful taxonomic markers particularly in dicotyledonous families and used for the chemotaxonomic evaluation of several genera and species [26], this new iridoid glycoside could be a chemotaxonomic marker for *V. agnus-castus*. Aside from the new compounds, isochlorogenic acid A and kaempferol 3-*O*-sophoroside are being reported for the first time from *V. agnus-castus*.

## Experimental Part

### *General*

Thin-layer chromatography (TLC): silica gel *60 $F_{254}$* plates ($SiO_2$; *Merck,* Darmstadt, Germany) on aluminum; eluents $CHCl_3$/MeOH/$H_2O$ 80:20:2, 70:30:3, and 61:32:7; visualization by spraying with 1% vanillin/$H_2SO_4$ soln., followed by heating at 105° for 2 – 3 min. Column chromatography (CC): $SiO_2$ *60* (0.063 – 0.200 mm; *Merck*, Darmstadt), *Polyamide* (*Sigma-Aldrich*, St. Louis, MO, USA), and *Sephadex LH-20* gel (*Sigma-Aldrich*, St. Louis, MO, USA). Medium-pressure liquid chromatography (MPLC): *Sepacore® Flash Systems X10/X50* (*Büchi Labortechnik AG*, Flawil, Switzerland), *Redi sep* columns (*LiChroprep $C_{18}$*, 130 and 100 g; *Teledyne Isco*, Lincoln, Nebraska, USA). UV Spectra: *HP Agilent 8453* spectrophotometer (*Agilent Techonologies*, Santa Clara, CA, USA); $\lambda_{max}$ (log ε) in nm. IR Spectra (KBr): *PerkinElmer 2000* FT-IR spectrometer (*PerkinElmer*, Waltham, Massachusetts, USA); $\tilde{\nu}$ in $cm^{-1}$. NMR Spectra: *Varian Mercury FT* spectrometer (Palo Alto, CA, USA; 400 ($^1$H) and 100 MHz ($^{13}$C)) in $CD_3OD$ or ($D_6$)DMSO; δ in ppm rel. $Me_4Si$ as internal standard, *J* in Hz. HR-ESI-MS: *Agilent G6530B* TOF/Q-TOF mass spectrometer (*Agilent Technologies*, Santa Clara, CA, USA) in MeOH; positive-ion mode; in *m/z*.

### *Plant Material*

The flowers of *Vitex agnus-castus* L. (Verbenaceae) were collected at full flowering stage from Akçay, Edremit, Balıkesir province of Turkey, in July 2013. The plant material was identified by one of us (Dr. *Hasan Kırmızıbekmez*). A voucher specimen (YEF 13002) has been deposited at the herbarium of the Faculty of Pharmacy, Yeditepe University, İstanbul, Turkey.

### *Extraction and Isolation*

The air-dried and powdered flowers of *V. agnus-castus* (220 g) were macerated overnight with MeOH (2 l) at r.t. and then extracted twice at 45 °C for 4 h. The combined MeOH extracts were concentrated under reduced pressure to yield a crude extract (68.42 g, yield: 31.1%). The crude MeOH extract was dispersed in $H_2O$ (120 ml) and extracted with $CHCl_3$ (3 × 120 ml). Each extract was evaporated to dryness under reduced pressure and the $H_2O$ subextract (40.1 g) was fractionated by CC (*Polyamide*, 0 – 100% MeOH in $H_2O$, in steps of 20%) to yield seven main fractions, *Frs. A – G*. *Fr. D* (2.58 g) was subjected to MPLC (*LiChroprep $C_{18}$*; 0 → 100% MeOH/$H_2O$) to obtain agnuside (66 mg) and *Frs. $D_2$ – $D_4$*. *Fr. $D_3$* (78 mg) was applied to CC ($SiO_2$; $CH_2Cl_2$/MeOH 90:10 → 70:30) and yielded compound **1** (5 mg) and kaempferol 3-*O*-sophoroside (5 mg). Compound **1** (2 mg) was also purified from the latter fraction *Fr. $D_4$* (110.2 mg) by CC, ($SiO_2$; $CH_2Cl_2$/MeOH/$H_2O$ 90:10:0 → 70:30:3) in addition to *trans*-eurostoside (53 mg). *Fr. F* (2.92 g) was subjected to MPLC (*LiChroprep $C_{18}$*, 20 → 100% MeOH/$H_2O$) to obtain chlorogenic acid (44 mg), 3,4-dihydroxybenzoic acid (9 mg), and 4-hydroxybenzoic acid (81 mg), along with *Frs. $F_4$* and *$F_5$*. Purification of *Fr. $F_4$* (212 mg) by CC ($SiO_2$; $CH_2Cl_2$/MeOH/$H_2O$ 90:10:0 → 80:20:1) yielded **3** (6 mg), 4-hydroxybenzoic acid (4 mg),

 

agnuside (54 mg), and isoorientin (18 mg). *Fr. F*$_5$ (230 mg) was applied to CC ($SiO_2$; $CH_2Cl_2$/MeOH/$H_2O$ 90:10:0 → 70:30:3) to yield isovitexin (20 mg) and **2** (17 mg). *Fr. G* (1.77 g) was similarly applied to MPLC (*LiChroprep C*$_{18}$; 10 → 90% MeOH/$H_2O$) to give isochlorogenic acid A (81 mg), agnuside (17 mg), and impure luteolin 6-*C*-(2″-*O*-*trans*-caffeoyl)glucopyranoside which was further purified (15 mg) by CC (*Sephadex LH-20*; MeOH).

**Agnusoside** (= **[(1*S*,4a*R*,7a*S*)-1-(*β*-D-Glucopyranosyloxy)-1,4a,5,7a-tetrahydro-5-oxocyclopenta[*c*]pyran-7-yl]methyl 4-Hydroxybenzoate**; **1**). Amorphous powder. UV (MeOH): 202 (4.29), 259 (3.99). IR (KBr): 3396, 2925, 1704, 1646, 1608, 1515, 1445, 1384, 1312, 1276, 1167. $^1$H- and $^{13}$C-NMR: see *Table 1*. HR-ESI-MS (pos.): 487.1212 ([*M* + Na]$^+$, $C_{22}H_{24}NaO_{11}^+$; calc. 487.1211.

**Castusic Acid** (= **(1*S*,3*R*,4*R*,5*R*)-3-{[(2*E*)-3-(3,4-Dihydroxyphenyl)prop-2-enoyl]oxy}-1,5-dihydroxy-4-[(4-hydroxybenzoyl)oxy]cyclohexanecarboxylic Acid**; **2**). Amorphous powder. UV (MeOH): 214*sh* (3.89), 253 (3.81), 330 (3.76). IR (KBr): 3349, 2925, 1697, 1630, 1607, 1515, 1451, 1383, 1280, 1167, 1119, 1046. $^1$H- and $^{13}$C-NMR: see *Table 2*. HR-ESI-MS (pos.): 497.1056 ([*M* + Na]$^+$, $C_{23}H_{22}NaO_{11}^+$; calc. 497.1054.

**1,2-Bis-*O*-(4-hydroxybenzoyl)-*β*-D-glucopyranose** (**3**). Amorphous powder. UV (MeOH): 210*sh* (4.50), 260 (4.55). IR (KBr): 3304, 2966, 1711, 1608, 1593, 1515, 1447, 1383, 1313, 1282, 1169, 1066. $^1$H- and $^{13}$C-NMR: see *Table 3*. HR-ESI-MS (pos.): 443.0952 ([*M* + Na]$^+$, $C_{20}H_{20}NaO_{10}^+$; calc. 443.0949.

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