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ORIGINAL

Bark extractives of *Catalpa bungei*: isolation, purification and structural elucidation of triterpene, phytosterol and flavonoid derivatives

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Abstract

Extractives of tree barks have long been considered as a rich source of novel bioactive secondary metabolites, which are by far not well-explored. In the current work, bark extracts of *Catalpa bungei* were investigated for the first time and five extractives were isolated and purified, including a new triterpene saponin derivative, namely 3-*O*-*β*-D-glucuronopyranosyl-6′-methyl-21-*O*-*cis*-caffeoyl machaerinic acid (**4**), two known flavonoids [(+)-gallocatechin (**1**) and isoquercitrin-6″-gallate (**2**)], a known oleanane-type triterpene [machaerinic acid (**3**)] and a known phytosterol [stigmasterol (**5**)]. Chemical structural elucidation of extractives **1**–**5** was carried out mainly on the basis of their physicochemical and spectroscopic (IR, NMR, MS) evidences and analysis, as well as by detailed comparison of the analytical evidence with those in the literature. To the best of the authors' knowledge, this is the first time to find the occurrence of extractives **1**–**5** in the tree of *C. bungei*. It is noteworthy that the five constituents have never previously been reported in any species of *Catalpa* genus. Compound **4**, a previously undescribed triterpene saponin derivative, was isolated and elucidated in this work for the first time.

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Introduction

Plant extractives still present unrevealed novelties, which are relevant in terms of biosynthesis routes (Hu et al. 2017; Mangindaan et al. 2017; Si et al. 2001), markers for chemotaxonomical differentiation of wood species (Wang et al. 2016; Si et al. 2011), and various biological activities (Hu et al. 2016). Tree barks, long treated as wastes or residues in pulping and forestry industries, contain valuable bioactive substances, which could be commercialized as high value-added products, for example, in medicines and cosmetics.

Catalpa bungei C.A. Mey, a deciduous woody plant in Bignoniaceae family, is native to China. As an important ornamental arbor species, *C. bungei* is extensively used in urban forests in northern and central cities of China due to its straight stems, beautiful flowers and moderate efficiency in particulate matter removal (Xu et al. 2014; Lu et al. 2019). In addition to its value in landscaping, *C. bungei* wood exhibits superior mechanical properties and high durability that can resist the corrosion caused by insects and microorganisms (Lu et al. 2019). Plant materials of the tree have also been used in folk medicines to treat, alleviate or prevent various diseases, including nephritis, edema, cystitis, leprosy, eczema and gastric cancer. Previous biological and pharmaceutical studies showed that *C. bungei* extracts possess significant antioxidant and anti-cervical cancer effects (Xu et al. 2014, 2018), as well as inhibitions of soluble epoxide hydrolase, cholinesterase and nuclear factor kappa B activities (Tang et al. 2016).

Earlier phytochemical investigations of *C. bungei* leaves and seeds resulted in the isolation of several types of constituents such as lignans, triterpenoids, flavonoids, iridoids and phenylethanoid glycosides (Machida et al. 2004; Kanai et al. 1996; Xu et al. 2014, 2018; Tang et al. 2016). However, to the best of the authors` knowledge, no study has ever been performed to screen the extractives of *C. bungei* barks. In the present systematic search for chemical extractives, which may be responsible for the biological and pharmacological activities of this tree, the isolation, separation and structural characterization of one new and four known natural extractives from the stem barks of *C. bungei* were described in the current work.

Materials and methods

General experimental procedure

1D and 2D nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX 400 instrument (Rheinstetten, Germany) using deuterated solvent MeOH-d_4 with tetramethylsilane as an internal standard. Positive fast atom bombardment mass (FAB MS) experiments were done on a Micromass Autospec M363 spectrometer (Manchester, UK). IR spectra were acquired by KBr disk method on a FTIR-8400S spectrometer (Shimadzu, Kyoto, Japan). A

SGW-2 automatic polarimeter (Shanghai INESA Physico Optical Instrument Co., Ltd., Shanghai, China) was employed to determine the optical rotations. Melting points (M.P., uncorrected) were measured with the Electro Thermal 9100 apparatus (Electrothermal Engineering Ltd., Essex, UK).

Silica gel (100–200 and 200–300 mesh, Qingdao Marine Chemical plant, Qingdao, China) and Sephadex LH-20 (Sigma) were used as packing materials for open column chromatography (OCC). Vacuum liquid chromatography (VLC) was performed using ODS (50 μm, YMC) and D-101. SBS-160 fraction collectors (Shanghai Huxi Analysis Instrument Factory Co., Ltd., Shanghai, P.R. China) were employed to collect the eluents. Thin layer chromatography (TLC) experiments were conducted with DC-Plastikfolien Cellulose F (Merck, Darmstadt, Germany) plates, with H_2O-HOAc (47:3, v/v, solvent A) and *t*-BuOH-H_2O-HOAc (3:1:1, v/v/v, solvent B) used as developing solvents. TLC spots visualizations were carried out by UV light exposure (365 and 254 nm) and by spraying with 1% $FeCl_3$ (in EtOH) solution, followed by heating. Analytical grade solvents were used for isolation and separation procedures.

Plant material

In the current work, tree stems of *C. bungei* (9 years old) were obtained in January of 2018 from a forest in Luoyang of Henan Province, P.R. China, which was constructed by Research Institute of Forestry, Chinese Academy of Forestry. Fresh barks were debarked from *C. bungei* stems and then shade-dried at room temperature. A voucher herbarium specimen with ID number Cb-20180305 was deposited in the herbarium of Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology.

Extraction, fractionation and purification

Stem barks of *C. bungei* (labeled as CbB, 4935 g) were dried in the shade at room temperature, and then finely ground with a Wiley mill (40-mesh sieve), followed by extraction at room temperature for more than 72 h with H_2O-EtOH (5:95, v/v, each 15 L) for four times. The extracts were combined together, filtered and concentrated to give a crude residue (496.46 g, yield 9.97%) and then suspended in distilled water. Petroleum ether (54.20 g, yield 1.10%), $CHCl_3$ (52.32 g, yield 1.06%) and EtOAc (70.38 g, yield 1.43%) soluble fractions, as well as EtOAc insoluble fraction (319.56 g, yield 6.48%) were obtained after successive solvent partitions, concentration and lyophilization.

As shown in Fig. 1, a portion of the above obtained $CHCl_3$ soluble fraction of extract from *C. bungei* barks (CbBC, 49.10 g) was chromatographed on a column packed with silica gel (200 ~ 300 mesh), eluted with a solvent gradient system of EtOAc–MeOH-$CHCl_3$ (1:4:95 → 2:19:79 → 2:49:49 → 5:90:5) to yield seven main fractions ($CbBC_1$–$CbBC_7$), which were monitored and grouped by TLC detection. The third main fraction ($CbBC_3$, 12.32 g) and the sixth one ($CbBC_6$, 18.05 g) were further subjected to silica gel (100–200 mesh) OCC elution with MeOH-$CHCl_3$-H_2O

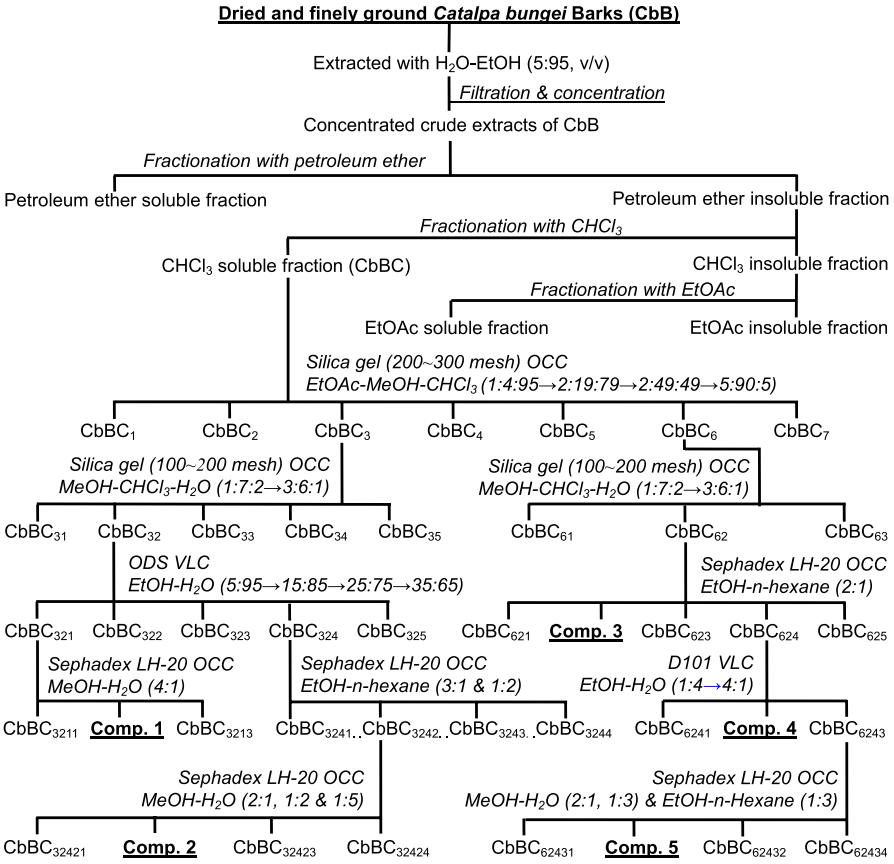


Fig. 1 Extraction, fractionation and purification procedures of extractives from barks of *C. bungei*

(1:7:2 → 3:6:1, v/v) to produce five ($CbBC_{31}$–$CbBC_{35}$) and three subfractions ($CbBC_{61}$–$CbBC_{63}$), respectively. Subfraction $CbBC_{32}$ (8.06 g) was then applied to VLC on ODS, eluted successively with 5%, 15%, 25% and 35% EtOH in H_2O, to yield five fractions $CbBC_{321}$–$CbBC_{325}$, respectively. Fraction $CbBC_{321}$ (952.24 mg) was further purified by Sephadex LH-20 OCC and eluted with MeOH-H_2O (4:1, v/v) to give compound **1** (123.15 mg) as white amorphous powder. Subfraction $CbBC_{324}$ (3.42 g) was further loaded over Sephadex LH-20 OCC eluted with EtOH-*n*-hexane (3:1 and 1:2, v/v) to yield four fractions $CbBC_{3241}$–$CbBC_{3244}$. In the same way, subfraction $CbBC_{3242}$ (1.26 g) was purified through Sephadex LH-20 OCC, with MeOH-H_2O (2:1, 1:2, 1:5, v/v) used as washing solvent system to get 88.38 mg of white amorphous compound **2**. Subfraction $CbBC_{62}$ (12.17 g) was also subjected to Sephadex LH-20 OCC eluted with EtOH-*n*-hexane (2:1, v/v) to give five fractions $CbBC_{621}$–$CbBC_{625}$. Compound **3** (46.73 mg) was obtained from $CbBC_{622}$ as an amorphous powder by recrystallization. $CbBC_{624}$ (5.73 g) was further separated by D101 VLC with EtOH-H_2O (1:4 → 4:1) used as eluting solvents to give 41.62 mg

of amorphous compound **4**, together with fractions $CbBC_{6241}$ and $CbBC_{6243}$. Compound **5** (72.27 mg) was purified from fraction $CbBC_{6243}$ (2.18 g) through OCC as Sephadex LH-20 used as packing material, while MeOH-H_2O (2:1 and 1:3, v/v) and EtOH-*n*-hexane (1:3, v/v) used as flowing phase successively.

Compound 4

Obtained as a whitish amorphous powder in this work with M.P. 289–291 °C and $[\alpha]_D^{20}-15.6°$ (MeOH, *c* 0.5), compound **4** presented its IR (KBr) ν_{max} at 1510, 1605, 1700 and 3415 cm^{-1}, respectively. While its R_f values appeared at 0.19 and 0.80 in solvents A and B, respectively. In positive FAB MS spectrum, compound **4** gave $[M+K]^+$ at *m/z* 863, $[M+Na]^+$ at *m/z* 847, and $[M+H]^+$ at *m/z* 825, corresponding to molecular weight 824 and calculated for $C_{46}H_{64}O_{13}$. The ^1H (400 MHz, *δ,* MeOH-d_4), ^{13}C (100 MHz, *δ,* MeOH-d_4) and partial 2D NMR information are presented in Table 1.

Results and discussion

In the current study, the 95% ethanolic extract of *C. bungei* stem barks was fractionated with a serious of polar solvents to get several soluble parts. By means of a sequence of chromatographic techniques, purification and separation of the obtained chloroform soluble fraction led to the isolation of a new oleanane-type triterpene glycoside called 3-*O*-*β*-D-glucuronopyranosyl-6′-methyl-21-*O*-*cis*-caffeoyl machaerinic acid (**4**), together with four known extractives: a flavan-3-ol [(+)-gallocatechin, **1**] (Agrawal 1989), a flavonol glycoside (isoquercitrin-6″-gallate, **2**) (Collins et al. 1975), an oleanane-type triterpene (machaerinic acid, **3**) (Delgado et al. 1984) and a phytosterol compound (stigmasterol, **5**) (Forgo and Kövér 2004). The chemical structures of the five extractives are shown in Fig. 2. The known compounds (**1**–**3**, **5**) were identified by comparison of their spectroscopic evidences and physiochemical data with those in the literature.

Compound **4** was isolated as a whitish amorphous powder showing $[\alpha]_D^{20}-15.6°$ in MeOH at *c* 0.5 and M.P. 289–291 °C. Its molecular formula was calculated to be $C_{46}H_{64}O_{13}$ by Positive FAB MS spectrum, for its $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 863, 847, and 825, respectively, corresponding to its molecular weight 824. In compound **4**, the presence of phenolic hydroxyl groups was confirmed from gray-green color through TLC experiment when spraying 1% ethanolic $FeCl_3$ (R_f values 0.19 and 0.80 in developing solvents A and B, respectively) (Imakura et al. 1985; Si et al. 2011, 2018). For IR (KBr) spectrum, compound **4** exhibited absorptions for aromatic ring at 1510 and 1605 cm^{-1} (Si et al. 2008). While the bands of *α*,*β*-unsaturated carbonyl and hydroxyl groups were observed at 1700 and 3415 cm^{-1}, respectively (Peng et al. 2019).

For the aglycone part of compound **4**, its ^1H NMR spectrum revealed signals for seven methyl groups including five singlets [δ_H 1.06, 0.86, 0.97, 0.83 and 1.20] ascribable to the methyl protons H-23, H-24, H-25, H-26 and H-27 (each 3H), respectively, as well as two doublets with coupling constant of $J=6.1$ Hz due to the

Table 1 NMR spectroscopic data (δ, ppm) for compounds **3** and **4**

Position	Compound **3**			Compound **4**		
	δ_H (M, *J* in Hz)	δ_C	DEPT	δ_H (M, *J* in Hz)	δ_C	DEPT
Aglycone						
1	0.97 and 1.62 (2H, m)	39.02	CH_2	0.98 and 1.63 (2H, m)	39.05	CH_2
2	1.69 and 1.71 (2H, m)	27.26	CH_2	1.79 and 1.70 (2H, m)	26.47	CH_2
3	3.14 (1H, dd, 11.0 & 4.3)	78.96	CH	3.13 (1H, dd, 11.3 and 4.4)	89.72	CH
4	–	37.88	C	–	39.55	C
5	0.75 (1H, m)	56.39	CH	0.78 (1H, m)	56.80	CH
6	1.43 and 1.54 (2H, m)	18.45	CH_2	1.42 and 1.55 (2H, m)	18.28	CH_2
7	1.35 and 1.49 (2H, m)	32.61	CH_2	1.34 and 1.48 (2H, m)	33.12	CH_2
8	–	39.65	C	–	39.36	C
9	1.58(1H, m)	48.31	CH	1.60 (1H, m)	48.39	CH
10	–	37.68	C	–	37.51	C
11	1.84 and 2.07 (2H, m)	24.43	CH_2	1.80 and 2.10 (2H, m)	24.78	CH_2
12	5.28 (1H, t, 3.5)	123.10	CH	5.32 (1H, t, 3.7)	123.08	CH
13	–	143.99	C	–	143.81	C
14	–	42.15	C	–	42.20	C
15	1.10 and 1.76 (2H, m)	27.98	CH_2	1.14 and 1.77 (2H, m)	28.04	CH_2
16	1.83 and 2.02 (2H, m)	23.26	CH_2	1.85 and 2.10 (2H, m)	23.42	CH_2
17	–	48.47	C	–	48.73	C
18	2.90 (1H, dd, 4.3, 11.2)	41.77	CH	2.98 (1H, dd, 4.0, 11.5)	41.59	CH
19	1.29 and 1.76 (2H, m)	47.33	CH_2	1.32 and 1.96 (2H, m)	47.56	CH_2
20	–	36.96	C	–	35.64	C
21	4.84 (1H, dd, 4.8, 11.3)	72.02	CH	4.94 (1H, dd, 5.0, 11.6)	76.16	CH
22	1.55 1.68 (2H, m)	40.41	CH_2	1.82 and 1.77 (2H, m)	37.01	CH_2
23	1.12 (3H, s)	27.46	CH_3	1.06 (3H, s)	27.18	CH_3
24	0.89 (3H, s)	16.29	CH_3	0.86 (3H, s)	15.75	CH_3
25	1.02 (3H, s)	15.98	CH_3	0.97 (3H, s)	15.10	CH_3
26	0.82 (3H, s)	16.54	CH_3	0.83 (3H, s)	16.68	CH_3
27	1.19 (3H, s)	25.57	CH_3	1.20 (3H, s)	25.59	CH_3
28	–	178.61	C	–	179.33	C
29	0.98 (3H, d, 6.1)	28.63	CH_3	0.96 (3H, d, 6.1)	28.52	CH_3
30	0.94 (3H, d, 6.1)	17.57	CH_3	1.10 (3H, d, 6.1)	18.01	CH_3
Glucuronosyl acid moiety						
1’	–	–	–	4.65 (1H, d, 7.1)	105.77	CH
2’	–	–	–	3.86 (1H,m)	75.27	CH
3’	–	–	–	3.70 (1H, m)	77.18	CH
4’	–	–	–	3.96 (1H, m)	72.88	CH
5’	–	–	–	4.09 (1H,d, 9.3)	76.94	CH
6’	–	–	–	–	170.52	C
6′-Me	–	–	–	3.70 (3H, s)	51.91	CH_3
Cis-caffeoyl						
1″	–	–	–	–	127.52	C

Table 1 (continued)

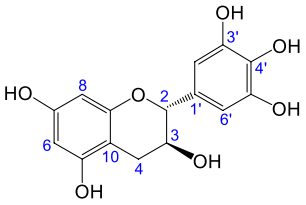
Position	Compound **3**			Compound **4**		
	δ_H (M, *J* in Hz)	δ_C	DEPT	δ_H (M, *J* in Hz)	δ_C	DEPT
2″	–	–	–	7.35 (1H, d, 2.1)	115.90	CH
3″	–	–	–	–	147.76	C
4″	–	–	–	–	145.27	C
5″	–	–	–	6.66 (1H, d, 7.9)	118.24	CH
6″	–	–	–	7.04 (1H, dd, 7.9, 2.1)	124.73	CH
α″	–	–	–	6.73 (1H, d, 12.2)	145.38	CH
β″	–	–	–	5.74 (1H, d, 12.2)	115.27	CH
γ″	–	–	–	–	167.96	C

two methyl protons at δ_H 0.96 (3H, H-29) and 1.10 (3H, H-30) (Wang et al. 2018). The aglycone also presented a double doublet centering at δ_H 2.98 (1H, dd, $J=4.0$ and 11.5 Hz, H-18) assignable to a methine proton, together with olefinic proton signal resonating at δ_H 5.32 (1H, *t*-like, $J=3.7$, H-12), which typically indicated that the aglycone moiety is a 3*β*,21*β*-dihydroxy oleanolic-type triterpene (Lehbili et al. 2018). The ^{13}C NMR spectrum of compound **4** additionally supported the above conclusion, for its carbons of C-12, 13, 18, 19, 20 and 21 on the aglycone unit gave characteristic peaks at δ_C 123.08, 143.81, 41.59, 47.56, 35.64 and 76.16, respectively (Bitchi et al. 2019). By a more detailed inspection, the 1D and 2D NMR spectrum data of the aglycone part of triterpene skeleton in compound **4** (in Table 1) were very similar to those in compound **3**, an oleanolic acid named machaerinic acid (Mair et al. 2018), which are also summarized in Table 1. Thus, the identification led to the confirmation of the aglycone part of compound **4** to be machaerinic acid.

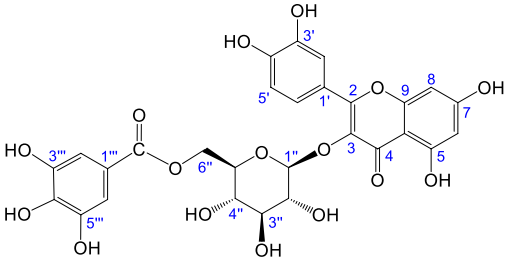
Besides the aglycone part signals, in ^{1}H NMR spectrum of compound **4**, a pair of ABX style proton signals [δ_H 7.35 (1H, d, $J=2.1$ Hz, H-2″), δ_H 6.66 (1H, d, $J=7.9$ Hz, H-5″) and δ_H 7.04 (1H, d, $J=2.1$ & 7.9 Hz, H-6″)] corresponding to a catechol ring (Hu et al. 2017), and a set of AB type signals for *cis* olefinic protons exhibiting distinctive doublets at δ_H 6.73 (1H, H-*α*″) and δ_H 5.74 (1H, H-*β*″) with coupling constant of $J=12.2$ Hz were ascribable to a *cis*-caffeoyl group (Si et al. 2016; Yahagi et al. 2012).

Furthermore, in ^{1}H NMR spectrum of compound **4**, the proton signals including an anomeric proton irritating at δ_H 4.65 (1H, d, $J=7.1$ Hz, H-1′) and others ranging from δ_H 3.70 to δ_H 4.09 (4H, m, H-2′, 3′, 4′, 5′), were assignable to a *β*-D-glucuronic acid residue (Si et al. 2009). In ^{13}C NMR spectrum, the carboxyl carbon C-6′ of the *β*-D-glucuronic acid moiety characteristically resonated at δ_C 170.52 (Fig. 3). The proton signals at δ_H 3.70 (3H) as a singlet in ^{1}H NMR and a carbon signal at δ_C 51.91 in ^{13}C NMR spectra indicated the existence of a methoxy in compound **4** (Li et al. 2020).

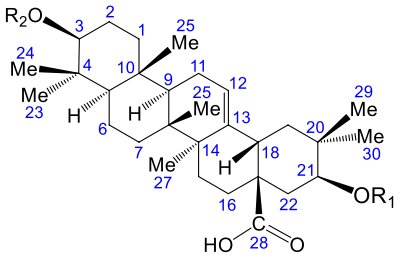
As for the HMBC spectrum of compound **4**, long-range correlations were observed between the anomeric proton at δ_H 4.65 (1H, d, $J=7.1$ Hz, H-1′) and the carbon at δ_C 89.72 (C-3), between proton peak at δ_H 4.94 (1H, dd, $J=5.0$ and



(+)-Gallocatechin (**1**)



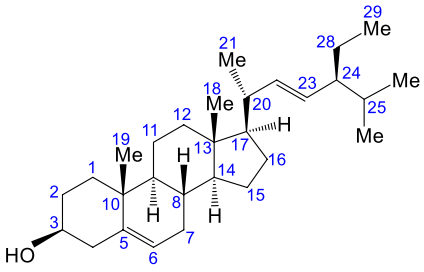
Isoquercitrin-6''-*O*-gallate (**2**)



R_1=R_2=H: Machaerinic acid (**3**)

R_1=3-*O*-*β*-D-Glucuronopyranosyl-6'-methyl; R_2=*Cis*-caffeoyl:

3-*O*-*β*-D-glucuronopyranosyl-6'-methyl-21-*O*-*cis*-caffeoyl machaerinic acid (**4**)



Stigmasterol (**5**)

Fig. 2 Chemical structures of the identified extractives from the barks of *C. bungei*

11.6 Hz, H-21) and carbon signal at δ_C 167.96 (C-γ''), between proton signals at δ_H 3.70 (3H, s, H-6′-Me) and carbon at δ_C 170.52 (C-6′), which confirmed that the glucuronic acid and *cis*-caffeoyl residues were combined to sites C-3 and C-21 of the

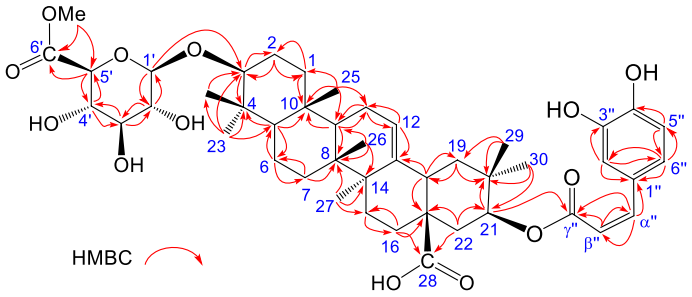


Fig. 3 Selected HMBC correlations (H → C) observed in compound 4

triterpene aglycone, respectively (Yoshikawa et al. 2001; Bitchi et al. 2019; Si et al. 2017), while the methoxy group attached to position C-6′ of glucuronic acid moiety (Li et al. 2020).

In compound **4**, the ^{13}C NMR spectrum gave resonances for 46 carbons, which were assigned to the presence of 8 methyl, 9 methene, 16 methine and 13 tertiary carbons, as shown in Table 1, by analysis of DEPT spectrum. More detailed analysis of the 1D and 2D spectroscopic data combined with careful comparison to other known literature data, led to the structural elucidation of extractive **4** as 3-*O*-*β*-D-glucuronopyranosyl-6′-methyl-21-*O*-*cis*-caffeoyl machaerinic acid, which is a new triterpene saponin derivative and has not previously been isolated from any other plant species.

Conclusion

To date, this is the first chemical investigation of extractives in the stem barks *C. bungei*. Successive silica gel OCC, VLC and Sephadex LH-20 separation and purification of $CHCl_3$ fraction of H_2O-EtOH (5:95, v/v) extracts from *C. bungei* stem barks resulted in the isolation of five low-molecular-weight extractives. Structures of the isolated extractives were identified and elucidated extensively on the basis of their spectroscopic evidences, chemical data and a careful comparison with those in the literature. Among them, 3-*O*-*β*-D-glucuronopyranosyl-6′-methyl-21-*O*-*cis*-caffeoyl machaerinic acid (**4**) is a new triterpene saponin derivative isolated and established for the first time here. The two flavonoids, (+)-gallocatechin (**1**) and isoquercitrin-6″-gallate (**2**), together with machaerinic acid (**3**), an oleanane-type triterpene, as well as stigmasterol (**5**), a phytosterol, have never been reported from *Catalpa* genus previously.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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