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Two Glucosides from *Pyracantha coccinea* Roots: a New Lignan and a new Chalcone*

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Abstract: Besides nine known terpenoids, two new compounds, a chalcone glucoside and a lignan glucoside have been isolated from the roots of *Pyracantha coccinea* (Rosaceae). The structures of these two products were identified as (*3R,4R*) 2-hydroxy-3,4-bis(3,5-dimetoxy-4-β-D-glucopyranosiloxybenzyl)tetrahydrofuran (1) and 4',6'-dihydroxy-2'-methoxy-chalcone-4-O-β-D-glucopyranoside (2) by detailed spectral studies including COSY, NOESY, HETCOR, and COLOC nmr techniques.

INTRODUCTION

Some plants of the *Pyracantha* genus (Rosaceae) are used in traditional medicine and the species *P. coccinea* is employed in Italy for the diuretic and cardiotonic properties of its fruits[1,2]. The genus includes only eight species and several varieties, largely growing in China, Laos, and Vietnam. *Pyracantha coccinea* is the only species distributed both in Southern Europe and West Asia[3].

The systematic position of these plants is not yet sufficiently clear; in fact the genus still awaits a critical chemotaxonomic study. Plants of this family, often used as hedges, are evergreen shrubs which bear small berries (red, orange, or yellow). Several studies have been done in order to isolate their constituents (sterols[4], triterpenes[5,6], flavonoids[7-10], carotenoids[11], and sorbitol[12]) and their biological activity is screened. For instance, *P. koidzumi* an has been reported to be endowed with an antitumor action against *Sarcoma*[13]; *P. crenato-serrata* has been used against tubercolosis[14]; *P. crenulata* has been claimed to have antiinflammatory properties[6]; a weak uterine stimulant effect has been reported for *P. angustifolia*[15], and ipotensive, antispasmodic, and cardiotonic actions have been reported for *P. crenulata*[16].

In our previous papers on *Pyracantha coccinea* we reported on the isolation of five new metabolites (coumarins and flavonoids) from its aerial parts[17] and three new flavonoids from the roots[18]. As a further work on this species, we wish to report now on eleven constituents which were isolated from the roots; two of these are new compounds.

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* DEDICATED TO PROF. GIANCARLO BERTI IN OCCASION OF HIS 70th BIRTHDAY

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RESULTS AND DISCUSSION

Ground *Pyracantha coccinea* roots were defattted with *n*-hexane and extracted in a Soxhlet apparatus with $CHCl_3$ and $CHCl_3$-MeOH (9:1). The residues yielded eleven substances; among these, **1** and **2** are new.

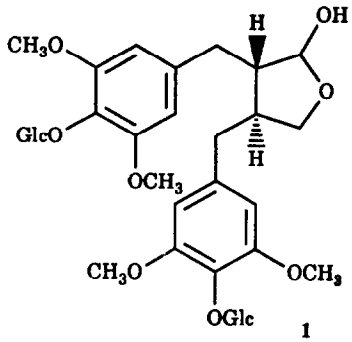
Compound **1** was obtained as an optically active ($[\alpha]_D$= -43°) colorless viscous oil. FAB MS spectrum (negative ion mode) showed a *quasi* molecular peak $[M-H]^-$ at *m/z* 743 corresponding to the formula $C_{34}H_{48}O_{18}$, also derived from the ^{13}C NMR and DEPT data. The following significant fragmentation peaks were also observed: $[M-H-Glc]^-$ at *m/z* 581 and $[M-H-2Glc]^-$ at *m/z* 419. The violet color reaction with $FeCl_3$ indicated the phenolic nature of the conpound.The IR spectrum showed a broad hydoxyl band centered at 3400 cm^{-1}, and a phenyl ring with isolated H (ν 1595, 1500, 1460, 805 cm^{-1}).

The ^1H NMR confirmed the above deductions. A strong signal corresponding to four MeO groups at δ 3.74 (12H, s) and a singlet in the aromatic region at δ 6.45 (4H) suggested the presence of two 3,5-dimethoxy-4-hydroxyphenylic moieties[19]. A broad singlet at δ 5.14 (1H) of a hemiacetalic proton was present, also supported by the ^{13}C NMR data, where the hemiacetalic carbon was observed at δ 103.5 as a doublet (CH). Signals for two benzylic protons and a hydroxy tetrahydrofuran ring (δ 2.18-2.86 and 3.53) were observed and confirmed by comparison with the ^{13}C NMR data reported for similar compounds[20,21]. The presence of a 3,5-dimethoxy aromatic substitution was evidenced by the presence in the ^{13}C NMR spectrum of a signal at δ 56.8. The stereochemistry of C-β and C-β' of the tetrahydrofuran ring was also derived from their resonances at 51.5 and 46.5 ppm and from the resonance of the hemiacetalic carbon at 103.5 ppm, and comparison with the data reported for (-) cubebin[22].

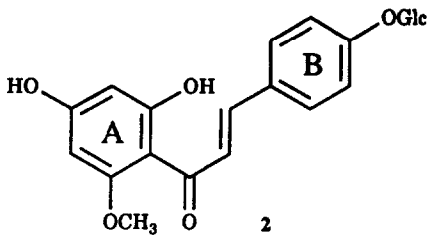
The sugar moiety was identified as β-D-glucopyranose from the protonic spectral data: two anomeric protons at δ 4.77 (2H, d) whose coupling constant (J=7.8 Hz), was in accordance with a β-pyranose form. This deduction was confirmed by ^{13}C NMR chemical shifts with those reported in the literature for methyl β-D-glucopyranoside[23,24]. The sugar linkage with a phenolic oxygen was deduced from the resonance of the anomeric carbon at δ 105.5.

The positions of glucose and of the MeO groups were also evidenced by ^1H, ^1H NOESY experiments. A cross peak from the methoxy protons to H-2 and H-6 of the aromatic moiety and from Glc-H_1 to MeO protons indicated for each aromatic ring the linkage of the sugar moieties at C-4, and a 3,5-dimethoxy substitution. The absolute stereochemistry of **1** was established as (*3R,4R*) from optical rotatory dispersion and circular dichroism evidence since it showed closely similar o.r.d. curves to cubebin[22] and to 2,3-*trans*-butyrolactone. Thus, the most logical structure for **1** appeared to be (*3R,4R*)2-hydroxy-3,4-bis(3,5-dimetoxy-4-β-D-glucopyranosyloxybenzyl) tetrahydrofuran.

Although two lignan glycosides were previously isolated from the genus *Prunus*[25] no lignan glucoside appears to have been isolated from the *Pyracantha* genus before now.



1



2

Compound 2 was obtained as a florescent yellow oil. The FAB MS spectrum (positive ion mode) showed a *quasi* molecular peak $[M+H]^+$ at *m/z* 349 corresponding to the formula $C_{22}H_{24}O_{10}$ [also derived from the ^{13}C and DEPT NMR data and from elemental analysis]. Two peaks at *m/z* 286 and 270 were also present: they appeared to be due to the loss of a hexosyl moiety, without or with the glycosidic oxygen. The purple coloration with Mg and HCl and the UV spectrum (see Experimental) indicated a chalcone skeleton. The IR spectrum showed hydroxyl aromatic and aliphatic groups (ν 3550, 3480 and 1000-1100, 1170 cm^{-1}), a carbonyl absorption (ν 1625 cm^{-1}), and aromatic rings (ν 1605, 1520 cm^{-1}).

The ^1H NMR confirmed the above suggestions: an AB spin system of α and β protons of a chalcone [δ 7.68 and 8.01 (1H each, J=15.5 Hz)] and two doublets at δ 6.14 and 6.33 (J=2.3 Hz) showed the presence of a 2', 4', 6'-trioxy- derivative. Furthermore, an A_2B_2 spin system at δ 6.81 and 7.61 (two protons each, J= 8.5 Hz) was also present, and it could be assigned to H-2, H-3, H-5 and H-6 of ring B. All the proton spin systems could be confirmed by the cross peaks in the $^1H,^1H$ COSY spectrum. The ^1H NMR showed also a singlet (3H) at δ 3.82, which was assigned to an aromatic methoxy group. The ^{13}C NMR spectrum confirmed the above deductions: a carbonyl resonance at δ 194.7, a methoxy resonance at 55.9 ppm, and two methine resonances at δ 144.7 and 125.7 were present in the spectrum, which were assigned to C-α and C-β of the chalcone moiety by means of a ^1H, ^{13}C HETCOR experiment. Furthermore, the presence of OH functions at C-4' and C-6' was deduced from the bathochromic shift of 84 nm of band I, without increasing of intensity in the presence of MeONa and from the shift of the same band of 58 nm with $AlCl_3$[26]. From these data it was deduced that the skeleton of the aglycone moiety would be either 4, 4', 6'-trihydroxy-2'-methoxychalcone or 2', 4', 6'-trihydroxy-4-methoxychalcone.

The position of the methoxy group was evidenced by $^1H,^1H$ NOESY experiments. A cross peak from the methoxy protons to H-5' indicated that this substituent was at C-6'. Further evidence of the location of the OCH_3 was provided by COLOC experiments from the long range ^1H-^{13}C couplings: a cross peak from the methoxy proton at C-2' in the COLOC spectrum

H	δ (ppm)	COSY	NOESY	C	δ (ppm)	DEPT	HETCOR	COLOC
				C-1	128.3	C		H-β, H-3, H-5
H-2	7.61 (2H, d, *J*=8.5 Hz)	H-3,H-5	H-β	C-2	129.0	CH	7.61	
H-3	6.81 (2H, d, *J*=8.5 Hz)	H-2,H-6	H-1"	C-3	117.0	CH	6.81	
				C-4	161.4	C		H-1", H-2, H-6
H-5	6.81 (2H, d, *J*=8.5 Hz)	H-2,H-6	H-1"	C-5	117.0	CH	6.81	
H-6	7.61 (2H, d, *J*=8.5 Hz)	H-3,H-5	H-β	C-6	129.0	CH	7.61	
				C-1'	105.0	C		
				C-2'	167.2	C		OMe, H-3'
H-3'	6.14 (1H, d, *J*=2.3 Hz)	H-5'	OMe	C-3'	95.0	CH	6.14	
				C-4'	167.7	C		H-3',H-5'
H-5'	6.33 (1H, d, *J*=2.3 Hz)	H-3'		C-5'	96.5	CH	6.33	
				C-6'	161.8	C		H-5'
H-α	7.68 (1H, d, *J*=15.5 Hz)	H-β		C-α	125.7	CH	7.68	
H-β	8.01 (1H, d, *J*=15.5 Hz)	H-α	H-2, H-6	C-β	144.7	CH	8.01	
				C=O	194.7	C		H-α
H-1"	5.18 (1H, d, *J*=7.0 Hz)	H-2"	H-3,H-5,H-3",H-5"	C-1"	101.9	CH	5.18	
H-2"	3.21	H-1",H-3"		C-2"	75.0	CH		
H-3"	3.35	H-2",H-4"	H-1"	C-3"	78.5	CH		
H-4"	3.38	H-3",H-5"		C-4"	71.3	CH		
H-5"	3.42	H-4", CH_2-6"	H-1"	C-5"	78.6	CH		
H_2-6"	3.69 (1H, dd, *J*=11.0 and 5.8 Hz)	H-5"		C-6"	62.4	CH_2		
	3.82 (1H, dd, *J*=11.0 and 2.7 Hz)							
OMe	3.82 (3H, s)		H-3'	OMe	55.9	CH_3	3.82	

Table 1. ^{1}H and ^{13}C NMR spectral data of compound **2** (CD_3OD)

confirmed that the methoxy substituent was linked to this carbon. Thus, the skeleton of the aglycone was unambiguosly stated as 4, 4', 6'-trihydroxy-2'-methoxychalcone.

The sugar moiety was identified as glucose, in the β-pyranose form, by the chemical shift (δ 5.18) and the coupling constant (J=7.0 Hz) of the anomeric proton; the resonances of the other carbinolic protons were derived from the 2D COSY experiments, using the H-1" as starting point. Then, the $^{1}H,^{13}C$ HETCOR spectrum gave the carbon assignments and confirmed the presence of β-glucopyranose with a D configuration, as deduced by comparison of these resonances with those reported in the literature for methyl β-D-glucopyranoside[23,24]. The position of the glycosidic linkage at C-4 was derived from the values of the ^{13}C NMR resonances of ring B carbons, closely related to 4-O-glycosyl derivatives[27] and was supported by 2D NOESY experiments, where the cross peak from H-1" of the glucosyl moiety to H-3 and H-5 was observed. Thus, the structure of **2** was elucidated as 4',6'-dihydroxy-2'-methoxychalcone-4-O-β-D-glucopyranoside. This substance appears to be a new natural compound.

Chalcones represent a minor class of flavonoids, and exhibit several biological activities. For example, they find application as sweetners and show insecticidal, anti-microbial, anti-fungal, and hypotensive actions[28,29].

Compound **2** appears to constitute the second example of a chalcone isolated from the family of Rosaceae; other compounds of this class have been previously isolated only from the genus *Prunus*[30-32]. Finally, the isolation from the same plant of flavonoids (mainly flavanones), coumarins, and terpenoids is interesting from the chemotaxonomic point of view, in agreement with a strong relationship between *Pyracantha* and *Prunus* genera.

EXPERIMENTAL

General procedures: Silica gel (type 60, Merck) was used both for gravity column (60-230 mesh) and for *flash* cc (230-400 mesh) chromatography. Aluminium-backed plates coated with silica gel 60 F_{254} 0.2 mm thick (Merck) were used for TLC. Sephadex LH-20 (25-100 μm, *Pharmacia*, Fine Chemicals) was used for cc gel filtration (100x5 cm).Lobar was carried out using a LiChroprep RP18 cc (310x25 mm, 40-63 mm, Merck). The following instruments were used: nmr, Bruker AC-200 Spectrospin spectrometer; fabms spectra in positive or negative ion mode in a glycerol matrix, VG ZAB instrument; optical rotation, Perkin Elmer 241 polarimeter; lpc, Duramat pump. Ir and uv spectra were determined with Perkin-Elmer spectrophotometer models 684 and 330. One- and two-dimensional nmr spectra were measured in CD_3OD as described previously[17,18].

Plant material: roots of *P. coccinea* were collected in Pisa on May 1990. A dried voucher specimen is deposited in the Department of Bioorganic Chemistry , Pisa, Italy.

Extraction and isolation: dried ground roots (700 g) were defatted with petroleum ether and extracted in Soxhlet with $CHCl_3$ and $CHCl_3$-MeOH (9:1). The $CHCl_3$ extract (3.5 g)

was evaporated to dryness and was subjected to gel filtration (Sephadex LH-20) using a mixture of $CHCl_3$-MeOH (1:9), to obtain four main fractions. Fraction III (340 mg) was further purified by gravity Si gel CC (eluents: $CHCl_3$-*n*-hexane 9:1 and $CHCl_3$-MeOH from 100% to 95%) followed by *flash* Si gel CC (eluent: *n*-hexane-EtOAc 7:3) to obtain pure β-sitosterol (8 mg), ursolic (21 mg) and maslinic (17 mg) acids. Fraction IV (260 mg) was further purified by gravity Si gel CC (eluent: $CHCl_3$-MeOH from 100% to 80%) to give four main fractions (IVa-IVd). Fraction IVb (70 mg) was subjected to *flash* Si gel CC (eluent: $CHCl_3$-MeOH 9:1) to yield pure 2α-hydroxyursolic (11 mg) and 2α,3α-dihydroxyurs-12-ene-28-oic (15 mg) acids. Fraction IVd (90 mg) was subjected to a *flash* Si gel CC (eluent: $CHCl_3$-MeOH 93:7) to give pure tormentic (38 mg) and 23-hydroxytormentic (9 mg) acids.

The $CHCl_3$-MeOH extract (8.5 g) was evaporated to dryness and subjected to gel filtration (Sephadex LH-20) using MeOH, to obtain five main fractions (I-V). Fraction II (1580 mg) was further purified by centrifugal partition chromatography (eluents: $CHCl_3$-MeOH-H_2O 5:6:4) to give five main fractions (IIa-IIe). Fraction IIc (80 mg) was subjected to *flash* Si gel CC (eluent: $CHCl_3$-MeOH 4:1) to give pure roseoside (18 mg). Fraction IId (400 mg) was subjected to *flash* Si gel CC (eluent: $CHCl_3$-MeOH 4:1) to give pure **1**. Fraction IIe (380 mg) was subjected to *flash* Si gel CC (eluent: $CHCl_3$-MeOH 87:13) to give pure 3β,16β-dihydroxyurs-12-ene (11 mg), 3β,28-dihydroxyurs-12-ene (8 mg), 2α,3β,28-trihydroxyurs-12-ene (19 mg). Fraction III (430 mg) was partitioned with EtOAc, *n*-BuOH and H_2O; the butanolic layers were subjected to *flash* Si gel CC (eluent: $CHCl_3$-MeOH 4:1) to give pure benzoic acid β-D-glucopyranosyl ester (34 mg). Fraction V (211 mg) was further purified by Si gel gravity CC (eluent: $CHCl_3$-MeOH 4:1) to give three main fractions (Va-Vc). Fraction Vb was subjected to Lobar RP18 CC (eluent: MeOH-H_2O 4:1) to give pure **2**.

Known Compounds: β-Sitosterol, ursolic, maslinic, 2α-hydroxyursolic, 2α,3α-dihydroxyurs-12-ene-28-oic, tormentic and 23-hydroxytormentic acids were identified by comparison ^{1}H-nmr and ir data with those in the literature[33-37] and by comparison (co-Tlc) with authentic samples; roseoside, 3β,16β-dihydroxyurs-12-ene, 3β,28-dihydroxyurs-12-ene, 2α,3β,28-trihydroxyurs-12-ene, and benzoic acid β-D-glucopyranosyl ester were identified by comparison ^{1}H- and ^{13}C-nmr data with those of the literature[38-42].

Compound 1: 32 mg ; tlc: R_f 0.34 ($CHCl_3$-MeOH 4:1); $[\alpha]^{25}_D$ -43.0 (*c*=0.8, MeOH); ir ν max (NaCl) 3400, 2910, 1720, 1595, 1500, 1460, 1440, 1320, 1250, 1157, 1055, 1030, 890, 805 cm^{-1}; UV λ_{max} (MeOH): 240, 268, 320 nm; CD: $\Delta\epsilon$240 -1.100 and $\Delta\epsilon$268 -0.190 (MeOH; *c* 0.05); FAB-MS (negative ion mode), *m/z*: $[M-H]^-$ 743, $[(M-H)-162]^-$ 581, $[(M-H)-2x162]^-$ 419; ^{1}H NMR (CD_3OD) : δ 2.18-2.86 (6H, m, 2xAr-$\underline{CH_2}$ and H-β, H-β'), 3.53 (2H, OCH_2-g'), 3.74 (12H, s, OMe x 4), 4.77 (2H, d, *J*=7.8 Hz, anomeric protons), 5.14 (1H, br s, γ hemiacetalic proton) 6.45 (4H, s, aromatic protons); ^{13}C NMR (CD_3OD) : ppm 40.3 (C-α'), 41.4 (C-α), 46.5 (C-β'), 51.5 (C-β), 56.8 (OCH_3), 74.2 (C-γ'), 62.5 (Glc-6), 71.8 (Glc-4), 76.0 (Glc-2),

78.5 (Glc-3), 78.9 (Glc-5), 103.5 (C-γ), 105.5 (Glc-1), 107.3 (C-2', C-6', C-2", C-6"), 137.9 (C-4' e C-4"), 154.0 (C-3', C-3", C-5', C-5").

Compound 2: 24 mg; tlc: Rf 0.42 ($CHCl_3$-MeOH 17:3); $[\alpha]^{25}_D$ -86.5 (*c*=0.9,MeOH); ir ν max (NaCl): 3550, 3480, 3240, 1625, 1605, 1570, 1520, 1265, 1170, 1100, 1060 cm^{-1}; uv λ max (MeOH) 368 nm ; MeOH/$AlCl_3$ 426 nm ; MeOH/MeONa 452 nm ; Found C 58.63, H 5.37; $C_{22}H_{24}O_{10}$ requires C 58.92, H 5.40 %; FAB-MS (positive ion mode), *m/z*: $[M+Na]^+$ 371, $[M+H]^+$ 349, [(M+H)-162] 286, $[(M+H)-178]^+$ 270; ^{1}H-NMR and ^{13}C-NMR data: Table 1.

Acid hydrolysis of 1-2 : 5 mg of glucosides **1-2** were refluxed with 0.5 ml 0.5 M H_2SO_4 for 1 hr. After neutralization, glucose was identified in the aqueous phase as described previously[43].

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