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FLAVONOIDS OF *CUPRESSUS SEMPERVIRENS* AND *CUPRESSUS CASHMERIANA*

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The genus *Cupressus* (Cupressaceae), comprising 12 species, is distributed in the Mediterranean region, tropical Asia, and North America (1). A survey of the literature shows that three biflavonoids—amentoflavone, cupressuflavone, and 4‴-mono-*O*-methyl amentoflavone (podocarpusflavone-A)—have been reported in *Cupressus sempervirens* var. *sempervirens* and var. *stricta* Ait. (2,3), but no flavonoid glycosides are known in any *Cupressus* species. The present paper describes the isolation and characterization of a flavonol glycoside, quercetin-3-*O*-α-L-rhamnopyranoside, along with quercetin, hinokiflavone, isocryptomerin, and reported biflavonoids from the leaf extracts of *Cupressus sempervirens* var. *horizontalis* (Mill.) Gordon. The chemical analysis of the leaf extracts of *Cupressus cashmeriana* Royle Carriere resulted in the isolation of a flavonol diglycoside, quercetin-3-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside together with amentoflavone, cupressuflavone, hinokiflavone, 7-*O*-methyl amentoflavone (sequoiaflavone), and isocryptomerin. No flavone aglycones were detected. Sequoiaflavone was found to be present only in this species while others contained podocarpusflavone-A. The presence of a flavonol diglycoside is, thus, reported in the Cupressaceae; this type of compound may serve as a useful taxonomic marker.

EXPERIMENTAL

PLANT MATERIALS.—*C. sempervirens* var. *horizontalis* was collected from Munger, Bihar, and *C. cashmeriana* from the Forest Research Institute, Dehra Dun, UP, India. These were identified by N. Bahadur, Officer-in-Charge, Systematic Botany Branch, F.R.I. Dehra Dun. Voucher specimens are deposited there in the Herbarium.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—MeOH extracts of air-dried and powdered leaves (4 kg in each case) were concentrated in vacuo and treated successively with *n*-hexane, C_6H_6, and $CHCl_3$. The residue was then poured into H_2O and filtered. The filtrate was extracted with *n*-BuOH, concentrated under reduced pressure, and purified by cc (Si gel, $CHCl_3$-MeOH, 4:1) followed by pc (Whatman No. 3, *n*-BuOH-HOAc-H_2O, 4:1:5) to yield quercetin-3-*O*-α-L-rhamnopyranoside (300 mg) from *C. sempervirens* and quercetin-3-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside (500 mg) from *C. cashmeriana*. These were characterized by chromatographic and hydrolytic studies, ^{1}H-nmr spectral studies of their acetates, and uv spectral shift data of the glycosides as well as the aglycones of permethylated glycosides (4). The latter glycoside was further clarified by ^{13}C-nmr data.

The dark brown precipitate on successive column chromatography (Si gel, C_6H_6/EtOAc) and tlc (Si gel, BDH, C_6H_6-pyridine-formic acid, 36:9:5) yielded quercetin (150 mg), amentoflavone (300 mg), cupressuflavone (200 mg), hinokiflavone (180 mg), podocarpusflavone-A (130 mg), and isocryptomerin (120 mg) from *C. sempervirens* var. *horizontalis* and amentoflavone, cupressuflavone, hinokiflavone, sequoiaflavone (140 mg), and isocryptomerin from *C. cashmeriana*. These were identified by comparison of ^{1}H-nmr spectral data of their acetates, the characteristic fluorescence in uv light of their permethyl ethers, Rf, mp, and mmp with authentic samples (5-7).

Full details of the isolation and identification of the compounds are available on request to the senior author.

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POLYPHENOLS ISOLATED FROM *PTEROCAULON PURPURASCENS*, I. 6-HYDROXYFLAVONOIDS

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The genus *Pterocaulon* is widely distributed in northeastern Argentina, southern Brazil, and Paraguay. Various species are used in folk medicine for various applications, as an insecticide and as an agent against snake bites (1-4). In previous papers we described the caffeoylquinic acid content from *Pterocaulon virgatum* DC. (5) and *Pterocaulon purpurascens* Malmé (6) and the isolation of coumarins (7) and flavonoids (8,9) from *P. virgatum*. Continuing our study of the Argentine Compositae with medicinal uses, we now report the isolation and identification of flavonoids from the CH_2Cl_2 extract of *P. purpurascens*. Six flavonoids were isolated and identified as quercetin, isorhamnetin, and the quercetagetin methyl ethers: quercetagetin-3,7,4′-trimethyl ether (10), quercetagetin-3,7-dimethyl ether (11), quercetagetin-3,3′-dimethyl ether (12), and quercetagetin-3,7-dimethyl ether (11). We give further information of the mass spectra which is not detailed in the current literature.

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *P. purpurascens* were collected from Chaco, Argentina, in 1983. The herbarium specimens are deposited at the Museo de Botánica "Juan A. Dominguez," Facultad de Farmacia y Bioquímica, U.B.A. (Schultz 1024).

EXTRACTION AND ISOLATION.—Dried and powdered plant material (800 g) was extracted by standard methods, first with petroleum ether (60-80°) and then with CH_2Cl_2. The extracts were concentrated in vacuo to dryness. The CH_2Cl_2 extract (7.52 g) was chromatographed over Polyclar, and the column was eluted with a CH_2Cl_2/C_6H_6 gradient up to 100% CH_2Cl_2 and then with a CH_2Cl_2/MeOH gradient to 100% MeOH. The column fractions gave a mixture of flavonoids that was separated on preparative paper chromatography with 40% HOAc. All the isolated flavonoids were purified on a Sephadex LH20 column eluted with CH_2Cl_2-MeOH (9:1) prior to spectral analysis.

IDENTIFICATION AND SPECTRAL DATA.—The spectra were recorded as follows: uv, Shimadzu model UV-240; ^1H nmr, Perkin-Elmer R12 80 MHz; eims, Varian Mat2 data system 166. The quercetagetin derivatives were identified by their uv and mass spectra. The uv spectra (MeOH) showed peaks and shoulders in Band II corresponding to a dioxygenated B-ring (13), but they also exhibited a shoulder at 238-245 nm which, in our experience, is present in all the flavonoids derived from the 6-hydroxyquercetin and 6-hydroxyluteolin structures. The presence of this substitution was confirmed by the bathochromic shift of Band I of about 30 nm in $AlCl_3$/HCl (14).