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3′-*O*-β-XYLOSYLTRICETIN, A NOVEL FLAVONE GLYCOSIDE FROM *TREMA HUMBERTII*

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Key Word Index—*Trema humbertii*; Ulmaceae; glycosylflavone; 3′-*O*-β-xylosyltricetin.

Abstract—3′-*O*-β-xylosylflavone has been isolated for the first time from *Trema humbertii*; its structure was assigned on the basis of spectroscopic data.

INTRODUCTION

Trema humbertii Ler. is an endemic species of the Ulmaceae growing in Madagascar. The leaves and the bark of this tree are reported to be used in popular medicine for toothache. A survey of literature showed no work on its flavonoid constituents. We now report the isolation and identification of a new natural flavone glycoside, 3′-*O*-β-xylosyltricetin.

RESULTS AND DISCUSSION

The UV spectrum in methanol 240, 269, 300 sh and 346 nm indicated that this molecule was a flavonoid. The bathochromic shift observed upon addition of aluminium chloride (B I 422 nm) showed the presence of a *o*-dihydroxy group at C-3′ and C-4′, and the position of B Ia, after addition of hydrochloric acid at 384 nm, indicated that this compound was a flavone with a hydroxy group at C-5 [1]. The presence of B III (330 nm) after addition of sodium hydroxide revealed the existence of a hydroxy group at C-7 [2]. This flavone possessed thus free hydroxy groups at C-5,7 and 3′,4′.

As this compound was obtained from the ethyl acetate fraction during extraction and was relatively immobile in an aqueous chromatographic system, its glycosidic nature could be deduced. On acid hydrolysis, it gave xylose, identified by GC and tricetin, e.g. a flavonoid with the same UV spectral properties in methanol and in the presence of different reagents, except after addition of sodium hydroxide, the aglycone being unstable. From these spectral properties, the xylose could be only located at the C-3′. The glycoside was thus identified as 3′-*O*-xylosyltricetin.

The glycosidic nature was further supported by the ^{1}H NMR spectrum: the presence of a doublet at 4.87 ppm ($J = 7$ Hz) indicated the β-linkage of xylose on the aglycone. Moreover, the signals of aromatic protons confirmed the identification of aglycone. Finally, the mass spectrum with the base peak at m/z 433 (M–H; FAB−) 435 (MH +; FAB +) corresponded to the molecular ion of an *O*-pentosyltricetin. The structure of this new natural compound was thus established as 3′-*O*-β-xylosyltricetin.

Besides this compound, other known *C*- and *O*-glycosylflavones, mono- and di-glycosides have been identified; all are derivatives of apigenin, luteolin and tricetin [3]. These results are in accord with the data of Giannasi [4] who has reported the presence of *C*-glycosylflavones in other species of *Trema*. By contrast, we have not detected the mono- and di-acetates of 7-*O*-glycosyl-8-*C*-glucosyl-4′-*O*-methylapigenin, a compound described by Oelrichs *et al.* [5] in *Trema aspera*.

EXPERIMENTAL

Trema humbertii was collected in the central eastern parts of Madagascar. A voucher specimen is deposited at the Laboratory of Botany, C.N.R.T., Tsimbazaza, Antananarivo.

300 g of dried, ground leaves were extracted with MeOH–H_2O, 4:1 and 1:1. The extracts were concd under red. pres. to give a brown gummy solid which was dissolved with boiling H_2O. After cooling, the water was successively extracted with Et_2O, EtOAc and *n*-BuOH. The EtOAc fraction was chromatographed on Whatman 3 15% HOAc 16.5 hr. 5 principal bands were separated; the slowest band was eluted with EtOH; this fraction was chromatographed on Whatman 3 60% HOAc, 14 hr. Three compounds were separated; the new compound was in the middle band. Final purification was achieved by chromatography on LH20 Sephadex column. R_f values: TLC: Polyamide DC6 Merck. Toluene–MeOH–MeCOEt–*n*-BuOH (30:20:15:3): 0.17; Kieselgel GF 254 Merck: EtOAc–HCOOH–H_2O: (50:1:4) 0.66; Cellulose Merck, 60%: HOAc: 0.44. λ_{max} nm: MeOH 240sh, 269, 300sh, 346; + $AlCl_3$: 270, 305sh, 422; + $AlCl_3$ + HCl: 255sh, 277, 300sh, 355, 384, + NaOH: 262, 275sh, 330, 406sh; NaOAc: 266, 302sh, 400; + NaOAc + H_3BO_3: 256, 270sh, 302sh, 371. ^{1}H NMR: DMSO Cameca 350 MHz: δ (ppm/TMS) 7.20 (1H, *d*, $J = 2$ Hz, H-2′), 7.16 (1H, *d*, $J = 2$ Hz: H-6′), 6.69 (1H, *s*, H-3), 6.44 (1H, *d*, $J = 2$ Hz, H:8), 6.18 (1H, *d*, $J = 2$ Hz: H-6), 4.87 (1H, *d*, $J = 7$ Hz, H-

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1 xylose), 3.25–3.85 (*m*, H-sugar). MS: VG, ZABHF.Hydrolysis was performed with 2N HCl for 30 min. Xylose was identified by GC after trimethylsilylation with C5H5N and BSTFA + 1% TMCS. Tricetin extracted with Et_2O was identified by its chromatographic and spectrophotomeric properties.

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