

SHORT REPORTS

FERULOYLTYRAMINE FROM *HYPECOUM*

S. FAZAL HUSSAIN, BELKIS GÖZLER, MAURICE SHAMMA and TEKANT GÖZLER*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802; U.S.A.; *Ege Üniversitesi, Eczacılık Fakültesi, Farmakognozi Birimi, İzmir, Turkey

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Key Word Index—*Hypericum parviflorum*; *H. imberbe*; Papaveraceae; natural amides; feruloyltyramine.

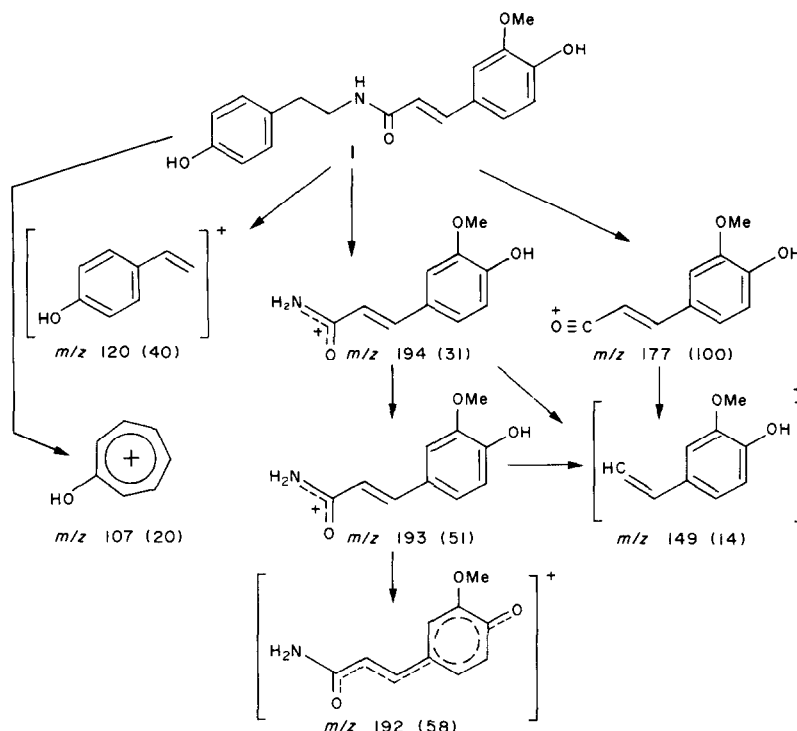
Abstract—Feruloyltyramine amide has been isolated from *Hypericum parviflorum* and from *H. imberbe*.

INTRODUCTION

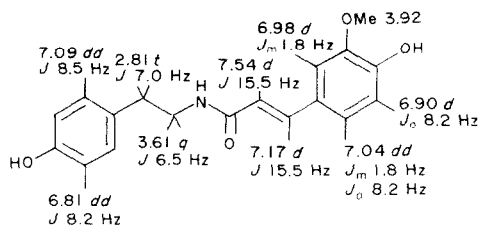
Various brief reports in the literature have indicated the presence of feruloyltyramine (1) in flowering plants [1–3]. We have now isolated this amide, for the first time in crystalline form, from two members of the Papaveraceae, namely *Hypericum parviflorum* Kar. and Kir. collected near Peshawar, Pakistan, and *H. imberbe* Lam., gathered in Bornova, near İzmir, Turkey. We also wish to describe the mass spectral fragmentation, as well as the proton and ^{13}C NMR spectra of this alkaloid.

RESULTS AND DISCUSSION

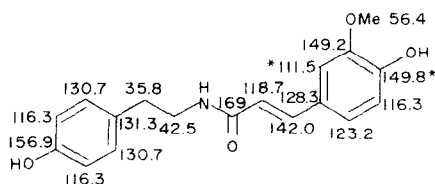
Feruloyltyramine, isolated by the procedure described in the Experimental, shows UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 220, 293, 319 ($\log \epsilon$ 4.39, 4.16, 4.26); $\lambda_{\text{max}}^{\text{MeOH}-\text{OH}^-}$ nm: 210, 242, 306, 362 ($\log \epsilon$ 4.80, 4.29, 3.88, 4.38). Significant fragments in the mass spectrum, besides the molecular ion m/z 313 ($\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$), include m/z 194 ($\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}$), 193 ($\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$), 192 ($\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}$), 177 (base, $\text{C}_{10}\text{H}_9\text{O}_3$), 149 ($\text{C}_9\text{H}_9\text{O}_2$), 120 ($\text{C}_8\text{H}_8\text{O}$), 107 ($\text{C}_7\text{H}_7\text{O}$) (Scheme 1). The proton and ^{13}C NMR spectra, summarized around expressions 1A and 1B, res-



Scheme 1.



I A



I B

pectively, provide conclusive evidence concerning the structure of this compound.

It has been tentatively suggested that analogs of feruloyltyramine could act in nature as precursors to 1-phenethylisoquinolines which could in turn be converted into colchicine, homoproaporphines or homoaporphines [4]. However, the acid-catalyzed cyclization of amides to form isoquinolines, commonly referred to as the Bischler-Napieralsky reaction, is not a natural process. Isoquinoline systems are instead formed *in vivo* through Pictet-Spengler-type cyclizations. It follows that feruloyltyramine and its close analogs in nature do not appear to act as precursors for any of the isoquinoline alkaloids.

EXPERIMENTAL

The ^1H NMR spectrum was recorded on a Bruker 360 MHz Supercon (FT) spectrometer in CDCl_3 , and the ^{13}C NMR spectrum was obtained in $\text{MeOH}-d_4$ at 50.32 MHz using a Bruker WP-200 Supercon (FT) instrument. The MS was obtained on a MS 9/50 instrument. TLC was on Merck Si gel F-254 plates.

The EtOH extracts of *H. parviflorum* (5 kg of entire dried plants—A) and *H. imberbe* (215 g of entire dried plants—B) were worked-up separately as follows. The dried extracts were taken up in 5% HCl, filtered and the filtrate made alkaline with NH_4OH . The crude alkaloids were then extracted into CHCl_3 . The concd extracts were passed through a column of Si gel. Elution with 2.5% MeOH in CHCl_3 supplied a fraction which was further purified by prep. TLC in $\text{MeCN}-\text{C}_6\text{H}_6-\text{EtOH}-18\text{ M NH}_4\text{OH}$ (8:4:6:1:1), (R_f 0.45), to provide feruloyltyramine (A, 79 mg; B, 4 mg), mp 92–93° CHCl_3 .

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