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TROUPIN, A 4-METHYLCOUMARIN FROM *TAMARIX TROUPII*

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Key Word Index—*Tamarix troupii*; Tamaricaceae; leaves; troupin; 4-methyl-6-hydroxy-7,8-dimethoxycoumarin.

Abstract—Troupin has been isolated for the first time as a natural product from the leaves of *Tamarix troupii* along with some known compounds. Based on its spectral and analytical data and comparison with a synthesized sample, it has been assigned the structure 4-methyl-6-hydroxy-7,8-dimethoxycoumarin.

INTRODUCTION

The different species of *Tamarix* are therapeutically important; their fruit and leaves are good astringents and are used for the treatment of dysentery and chronic diarrhoea and are also considered to be effective in the treatment of leucoderma [1]. *Tamarix troupii* is an ornamental plant and is used in medicine and in tanning [2]. There are only two reports [3, 4] on phytochemical investigations of this plant and only one compound, tamarixin, has been reported from this plant. In the present paper we report the isolation and characterization of six additional compounds from the alcohol extract of the leaves of *T. troupii*.

RESULTS AND DISCUSSION

Air-dried fresh leaves of *T. troupii* were exhaustively extracted with hot ethanol. The concentrate of this extract was treated in succession with petrol and diethyl ether. By repeated column and thin-layer chromatographic separation of the petrol and ether solubles, six compounds (A–F) were isolated in amounts sufficient for characterization. From their spectral data and by preparation of their derivatives, five of these (A–E) were characterized as tamarixetin, sitosterol, lupeol, β-amyrin and ursolic acid; the identities of these compounds were confirmed by direct comparison with the corresponding known samples. These compounds have been isolated for the first time from this plant.

Compound F, mp 178–179°, analysed for $C_{12}H_{12}O_5$ and was indicated [5] to be a hydroxylated coumarin from its colour reactions, UV and IR spectral data. Its ^{1}H NMR spectrum (DMSO-d_6, δ) showed the presence of a C–Me group (broad singlet at 2.33), two methoxyl groups and a hydroxyl group; in addition, a broad singlet and a singlet, each integrating for 1H were present at 6.08 and 6.80. When ^{1}H NMR spectrum was taken in $CDCl_3$, the broad singlets at 2.33 and 6.08 were seen as an ill-resolved doublet and quartet at 2.30 and 5.95, integrating for 3H and 1H, respectively. It is well known that H-3 and H-4 appear in the ranges δ6.05–6.40 and 7.60–7.95, respectively, as *ortho*-coupled doublets if both the positions are free [6, 7]; if one of these positions is carrying a methyl group, the neighbouring proton appears as a quartet. It has been observed [7] that the C-3 methyl in coumarins appears around δ2.15 whereas the C-4 methyl appears in the range 2.36–2.55. The nature of the ^{1}H NMR spectrum of compound F indicated that it should contain a C-4 methyl group and that its C-3 position is free. Compound F did not show any bathochromic shift in its UV absorption maxima on addition of sodium acetate to its methanol solution, thus indicating that the hydroxyl group is present at either C-6 or C-8. The benzene-induced solvent shift values of the C-4 methyl signal in the ^{1}H NMR spectra of a number of synthetic coumarins have been studied and it has been concluded that in the absence of a C-5 methoxyl group, this shift is between 0.63 and 0.80 ppm while in the presence of such a group, it is reduced to 0.38–0.40 ppm [7]. As compound F showed a benzene-induced upfield shift for the C-4 methyl group of 0.68 ppm, it was inferred that no methoxyl group is located at C-5. Its structure could thus be either 4-methyl-6-hydroxy-7,8-dimethoxycoumarin or 4-methyl-6,7-dimethoxy-8-hydroxycoumarin. Cingolani [8] has reported that the C-6 hydroxyl group in coumarins shifts the λ_{max} from 275 and 310 nm to longer wavelengths whereas a C-8 hydroxyl group shifts the λ_{max} to lower values. The λ_{max} of compound F at 292 and 341 nm indicated that it should have the former structure, which was also supported by a negative Gibb's test [9, 10]. This structure is compatible with the fragmentation pattern observed in its mass spectrum (*m/z* 236 $[M]^+$, 221 $[M-Me]^+$, 208 $[M-CO]^+$, 193 $[M-CO-Me]^+$). The assigned constitution of compound F was conclusively proved by preparing [11] 4-methyl-6-hydroxy-7,8-dimethoxycoumarin and comparing the two samples. Two different mps have been reported for this compound in the literature (173–174° [11] and 179° [12]). Our synthetic sample melted at 174–175°, compound F melted at 178–179°, and the mp of a mixture of the two samples was 175–176°. The two compounds, however, recorded identical TLC mobility, IR, UV and ^{1}H NMR spectra.

This is the first report of this compound in any natural source and it has been named troupin. 4-Methylcoumarins are a recently discovered group of natural products; the first natural occurrence of a 4-methyl-

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coumarin was reported from *Dalbergia volubilis* [13]. These compounds are important because some synthetic 4-methylcoumarins have been found to possess strong choleretic property [14], analgesic activity [15] and anti-spermatogenic activity [16].

EXPERIMENTAL

The leaves of *Tamarix troupii* were collected in April 1981 from plants growing on the banks of Yamuna river in Delhi and were identified at the Department of Botany, University of Delhi. Air-dried leaves (2.5 kg) were exhaustively extracted with hot EtOH. By repeated column and TLC separation (over silica gel) of the petrol (60–80°) and Et_2O soluble portions of the concentrate of the EtOH extract, six compounds (A–F) were isolated.

Troupin (F) crystallized from MeOH as colourless needles (26 mg), mp 178–179°. (Found: C, 60.83; H, 5.48. $C_{12}H_{12}O_5$ requires: C, 61.02; H, 5.08%.) It furnished an intense blue fluorescence in UV light and gave a deep yellow colour in aq. NaOH, a yellow colour in hot conc. H_2SO_4 and a deep brown colour in ethanolic $FeCl_3$. IR ν_{max}^{KBr} cm^{-1}: 3350, 1700, 1610, 1555, 1490, 1430, 1392, 1345, 1292, 1160, 1103, 1050, 964, 848, 792. UV λ_{max}^{MeOH} nm (log ε): 292 (4.04), 341 (3.86). ^{1}H NMR (60 MHz, DMSO-d_6): δ6.80 (1H, *s*, C-5 H), 6.50 (1H, *br s*, C-6 OH, exchanged with D_2O), 6.08 (1H, *br s*, C-3 H), 3.92 (3H, *s*, C-7 OMe), 3.90 (3H, *s*, C-8 OMe), 2.33 (3H, *br s*, C-4 Me). ^{1}H NMR (60 MHz, $CDCl_3$): δ4.02 (3H, *s*, C-7 OMe), 4.00 (3H, *s*, C-8 OMe), 2.30 (3H, ill-resolved *d*, C-4 Me). ^{1}H NMR (60 MHz, $CDCl_3$–C_6H_6, 1:1): δ3.73 (3H, *s*, OMe), 3.70 (3H, *s*, OMe), 1.62 (3H, *d*, C-4 Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 236 (100), 221 (25), 208 (10), 193 (45).

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