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MYRICETIN 7,4′-DIMETHYL ETHER AND ITS 3-GALACTOSIDE FROM *RHUS LANCEA*

A G RAMACHANDRAN NAIR, J P KOTIYAL† and D K BHARDWAJ*

Department of Chemistry, Jawaharlal Institute, Pondicherry 605006, India, *Department of Chemistry, University of Delhi, Delhi, India

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Key Word Index—*Rhus lancea*, Anacardiaceae, leaves, flavonols, myricetin 7,4′-dimethyl ether, 3-galactoside

Abstract—Two new flavonoids have been isolated from the ethanolic extract of the leaves of *Rhus lancea* along with three common flavonols kaempferol, quercetin and myricetin One has been characterized as 3,5,3′,5′-tetrahydroxy-7,4′-dimethoxyflavone (7,4′-di-*O*-methylmyricetin) while the other is its 3-*O*-galactoside

INTRODUCTION

Continuing our search for new myricetin glycosides[1, 2] and prompted by the observation of the common occurrence of myricetin in the Anacardiaceae [3], we examined the leaves of *Rhus parviflora* earlier [4] and isolated myricetin 3-*O*-rhamnoside In the absence of any record of work on *Rhus lancea* [5], we studied the flavonoids of its leaves, and the isolation and characterization of two myricetin derivatives are presented here

RESULTS AND DISCUSSION

The aglycone from the ether layer of the aqueous alcoholic concentrate after chromatography separated as light yellow needles from Me_2CO, $C_{17}H_{14}O_8$, mp 241–242° It gave a yellow colour with ammonia, olive green with Fe^{3+} and pink with magnesium–hydrochloric acid It was yellow under UV and UV–ammonia It had UV $\lambda_{\max}$ nm (MeOH) 260, 362, (+NaOAc) 260, 362, (+NaOAc–H_3BO_3) 258, 362, (+NaOMe) 265, 405, (+$AlCl_3$) 269, 304 sh, 346, 418 and (+$AlCl_3$–HCl) 269, 304sh 347, 418 and IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} 3360, 1650, 1585 and 1025 indicating the presence of hydroxyl, carbonyl and methoxyl groups On acetylation it yielded a tetra-acetate, mp 198–199° and on methylation, a tetramethyl ether (hexamethoxyflavone), mp 155–156° On demethylation, it yielded myricetin showing the compound to be a dimethyl ether of myricetin The ^{1}H NMR spectrum of the acetate had a singlet for the B-ring protons and another singlet for two methoxyls besides other peaks

The compound did not develop any green colour with alkali indicating the absence of a vicinal trihydroxy system in the B-ring[1,2] The aluminium chloride–hydrochloric acid as well as sodium acetate–boric acid spectra ruled out an *o*-dihydroxyl in the B-ring [6] suggesting one methoxyl at the 4′ position Band II of the methanol spectrum was similar to that of myricetin, 7-*O*-methylmyricetin [7] and 7-*O*-glucosylmyricetin [1] suggesting one methoxyl at the 7 position which was supported by the sodium acetate spectrum [6] The ^{1}H NMR signal of the two B-ring protons, the UV fluorescence, the aluminum chloride spectrum, etc together revealed the absence of a methoxyl at C-3′ (5′), C-3 and C-5 [6], further supporting the presence of a methoxyl at C-7 and C-4′ Thus the compound is 3, 5, 3′, 5′-tetrahydroxy-7, 4′-dimethoxyflavone (7,4′-di-*O*-methylmyricetin)

The glycoside from the ethyl acetate extract separated from methanol as almost colourless needles, $C_{23}H_{24}O_{13}$, mp 227–228° It was purple under UV and yellow under UV–ammonia and had $\lambda_{\max}$ nm (MeOH) 262, 304 sh, 344, (+NaOAc) 262, 344, (+NaOAc–H_3BO_3) 262, 342, (+$AlCl_3$) 273, 304 sh, 348, 388 and (+$AlCl_3$–HCl) 272, 304, 352, 388 On hydrolysis with acid as well as with β-galactosidase, it yielded 7,4′-dimethyl myricetin and D-galactose in a equimolar ratio The ^{1}H NMR spectrum of the glycoside acetate showed the H-1 signal of galactose as a doublet ($J = 8$ Hz) while the result of periodate oxidation revealed a pyranoside moiety The UV spectra in methanol and with diagnostic reagents in addition to the UV fluorescence indicated [6] glycosylation at C-3 which was confirmed by permethylation and hydrolysis Thus, the compound was identified as 5,3′,5′-trihydroxy-7,4′-dimethoxy-3-*O*-β-D-galactopyranosylflavone (7,4′-di-*O*-methylmyricetin 3-galactoside) The other flavonols present in *R lancea* were identified as kaempferol, quercetin and myricetin

This is the first record of 7,4′-dimethylmyricetin and its 3-*O*-galactoside The only other dimethylmyricetin known [8] is syringetin (the 3′,5′-dimethyl ether) It may be mentioned that both 7-methyl- (europetin) and 4′-methylmyricetin (mearnsetin) are known [8] and thus the formation of 7,4′-dimethyl ether is expected and comparable to the known 7,4′-dimethyl ethers [8,9] of apigenin, luteolin, scutellarein, kaempferol, quercetin and gossypetin

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†Present address Central Research Institute for Ayurveda, New Delhi, India

EXPERIMENTAL

Authentic leaves of *R lancea* L (supplied by the Forest Research Institute, Dehra Dun) were shade dried and extracted with hot 95% EtOH and the residue fractionated into C_6H_6, Et_2O and EtOAc soluble components The Et_2O concentrate was chromatographed over Si gel and eluted with C_6H_6–EtOAc followed by EtOAc to yield kaempferol, myricetin 7,4'-dimethyl ether, quercetin and myricetin The EtOAc concentrate on chromatography over Si yielded the new galactoside

Myricetin 7,4'-dimethyl ether tetra-acetate mp 198–199° (EtOAc–petrol) ^{1}H NMR (60 MHz, $CDCl_3$, TMS int standard) δ7 4 (2H, *s*), 6 8 (1H, *d*, *J* = 2 Hz), 6 6 (1H, *d*, *J* = 2 Hz) 3 85 (6H, *s*, 2 OMe), 2 4 (3H, *s*, OCOMe) and 2 3 (9H, *s*, 3 OCOMe)

The tetramethyl ether (myricetin hexamethyl ether) had mp 155–156° On demethylation with Ac_2O–HI, it gave myricetin R_fs (×100) of myricetin 7,4'-dimethyl ether 5 (30% HOAc), 52 (50% HOAc), 95 (BAW), 85 (PhOH), 78 (Forestal) and 90 (*t*-BAW)

The acetate of the 3-galactoside had mp 157–158° ^{1}H NMR 7 73 (2H, *s*), 6 8 (1H, *d*, *J* = 2 Hz), 6 6 (1H, *d*, *J* = 2 Hz), 5 55 (1H, *d*, *J* = 8 Hz,), 5 4–4 7 (6H, unresolved), 3 88 (6H, *s*, 2OMe), 2 4 (3H, *s*, OCOMe), 2 35 (6H, *s*, 2 OCOMe), 2 12 (6H, *s*, 2 OCOMe), 1 98 and 1 90 (3H each, *s* each, 2 OCOMe)

Periodate oxidation of 3-galactoside To 20 mg in 1 ml EtOH was added $NaIO_4$ (0 1 M, 25 ml) and allowed to stand in the dark for 48 hr Periodate consumed and HCOOH liberated were estimated to be 2 01 and 1 01 mol, respectively per mol of glycoside Methylation and hydrolysis of the 3-galactoside gave 3-hydroxy-5,7,3',4',5'-pentamethoxyflavone, mp 226–227°, UV λ_{max} nm 260, 310, 353 co-TLC with an authentic sample [10] R_f (×100) of the 3-galactoside 28 (15% HOAc), 50 (30% HOAc), 78 (50% HOAc), 80 (BAW), 86 (PhOH), 87 (Forestal) and 77 (t-BAW)

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OXYHYDRASTININE, AN ISOQUINOLONE ALKALOID FROM THE PAPAVERACEAE

S Fazal Hussain, Sally Nakkady*, Lajber Khan and Maurice Shamma†

P C S I R Laboratories, Peshawar, Pakistan, *National Research Centre, Dokki, Cairo, Egypt, †Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, U S A

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Key Word Index—*Argemone mexicana*, *Papaver dubium* var *glabrum*, Papaveraceae, isoquinolone alkaloid, oxyhydrastinine

Abstract—The new isoquinolone, oxyhydrastinine, has been obtained from *Argemone mexicana* and from *Papaver dubium* var *glabrum* (Papaveraceae)

INTRODUCTION

Although over a dozen isoquinolone alkaloids are known [1] the simple bicyclic structure oxyhydrastinine has not previously been reported as a natural product

RESULTS AND DISCUSSION

In continuation of our studies on the alkaloids of the Papaveraceae, we have obtained the new alkaloid oxyhydrastinine (1) from two different sources, namely from