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 , Et₂O and EtOAc soluble components The Et₂O 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) ¹H NMR (60 MHz, CDCl₃, TMS int standard) δ 7 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_f s (×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 $157-158^{\circ}$ ¹H 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, 20 Me), 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 NaIO₄ (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†

PCSIR Laboratories, Peshawar, Pakistan, *National Research Centre, Dokki, Cairo, Egypt, †Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

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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

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Argemone mexicana, collected in Egypt near Helwan, south of Cairo, and from Papaver dubium var glabrum, gathered in the vicinity of Peshawar, Pakistan, UV $\lambda_{\max}^{\text{MeOH}}$ nm 207, 217, 222, 262 and 303 (log ϵ 4 39, 4 47, 4 46, 3 84 and 3 90), mass spectrum m/z 205 [M]⁺ (C₁₁H₁₁O₃N), 190, 162, 150, 134

The NMR spectrum of oxyhydrastinine offers conclusive evidence concerning the structure of the alkaloid. It shows H-5 and H-8 as singlets at $\delta 6.61$ and 7.54, respectively. The methylenedioxy singlet is at $\delta 5.99$ and the N-methyl singlet is appropriately downfield at $\delta 3.13$. The C-3 and C-4 protons appear as triplets at $\delta 3.51$. ($J_A = 6.5 \, Hz$) and 2.90. ($J_B = 7.0 \, Hz$), respectively

EXPERIMENTAL

The NMR spectrum was recorded at 200 MHz in CDCl₃ and the UV spectrum was determined in MeOH TLC was on Merck Si gel plates F-254

Papaver dubium The dried EtOH extract from 95 kg P dubium L var glabrum (whole plant) was taken up in 5% HCl and filtered Extraction of the aq acidic filtrate with CHCl₃ furnished extract A (96 g) The mother-liquor was made alkaline with

NH₄OH (pH 8) and extracted again with CHCl₃ to provide extract B (10 5 g)

Extract B was chromatographed on a column of S₁ gel in CHCl₃ The first few non-alkaloidal fractions were discarded The subsequent fraction which gave an alkaloidal spot at R_f 0.54 in C_6H_6 —CHCl₃—Et₂NH (5.4.1) was purified by prep TLC in the same solvent system to yield 1.4 mg oxyhydrastinine

Argemone mexicana 3 kg powdered A mexicana L was defatted with petrol and then extracted with EtOH The dried EtOH extract was shaken with 001 N HCl, filtered and the filtrate extracted with CHCl₃ Removal of the CHCl₃ furnished 7 g of material which was chromatographed on a column of Si gel in CHCl₃ Fractions eluted with 10% MeOH in CHCl₃ were combined and purified by prep TLC to yield 05 mg oxyhydrastinine

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NOTE ADDED IN PROOF

Following submission of this manuscript, an obscure literature reference was found relating to the presence of oxyhydrastinine in Fumaria schleicheri Soy-Will, see Markosyan, S S (1976) Tezisy Dokl Molodezhnaya konf Org Sint Bio-org Khim, 59, (1978) Chem Abstr 88, 133268g