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FLAVONOIDS FROM *PHYSALIS MINIMA*

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Key Word Index —*Physalis minima*, Solanaceae, 5,6,7-trimethoxyflavone, 5-methoxy-6,7-methylenedioxyflavone

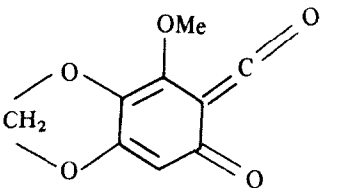
Abstract—5-Methoxy-6,7-methylenedioxyflavone was isolated from *Physalis minima* together with the known compound, 5,6,7-trimethoxyflavone

INTRODUCTION

Physalis minima is a common weed of vegetable farms in Singapore and Malaysia In studying the chemical constituents of the plant collected locally, two flavonoid substances, 5,6,7-trimethoxyflavone (**1**) and 5-methoxy-6,7-methylenedioxyflavone (**2**) were isolated from the plant extract 5,6,7-Trimethoxyflavone has been reported from a number of different plants [1-4] while 5-methoxy-6,7-methylenedioxyflavone has not been reported previously

RESULTS AND DISCUSSION

Compound **1** was identified as 5,6,7-trimethoxyflavone by comparison of spectral data with literature values [1–4] The molecular formula of compound **2** was established as $C_{17}H_{12}O_5$ (M^+ 296 0685, required 296.06847) by high resolution mass spectrometry The IR (1645 cm^{-1}, C=O), UV (215 6, 270 8, 307 0 nm) and ^1H NMR (δ6 73, *s*, 1H, C-3 hydrogen) spectra indicated that it was a flavone. The presence of a methylenedioxy group was suggested by the presence of a 2H signal at δ6.05 (*s*) in its ^1H NMR and a ^{13}C signal at δ102 12 (*t*) in its ^{13}C NMR spectra This was further supported by a positive Hansen [5] colour reaction for a methylenedioxy group given by **2** The ^1H NMR signals at δ7 7 -7 9 (2H, *m*) and 7.4–7 6 (3H, *m*) suggested that there was no B ring substituents so that the methylenedioxy group must be attached to the A ring of the flavonoid molecule. Examination of its mass spectrum indicated the usual fragmentation pattern for a flavone [6, 7] A retro-Diels–Alder reaction of **2** would produce a *m/z* 194 peak corresponding to the following radical ion



m/z 194

The base peak at *m/z* 166 was attributed to the loss of a CO unit from the above radical ion These were consistent with the suggestion that the methylenedioxy was attached to the A ring. Furthermore, by comparison with the ^1H NMR of 5,2′-dimethoxy-6,7-methylenedioxyisoflavone [8, 9], the singlet signal at δ6 64 (*s*, 1H, C-8 proton) indicated that the methylenedioxy group was at C-6 and C-7 Thus, **2** is identified as 5-methoxy-6,7-methylenedioxyflavone

EXPERIMENTAL

Mps were uncorr UV spectra were recorded in 95% EtOH, ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as int standard and mass spectra were recorded by direct inlet at 70 eV with VG Micromass 7035 Kieselgel 60 (Merck) was used for CC and Kieselgel G. $HF_{254+366}$ for TLC

Plant material Fruiting plants of *Physalis minima* (H N Ridley, *The Flora of Malay Peninsula*) were collected in Singapore, July 1985 and identified by Professor H Keng Voucher specimen was deposited at the herbarium of the National University of Singapore

Isolation The chopped aerial parts of freshly collected whole plants (800 g) were extracted with MeOH in two 2 l round bottom flasks for 2 days with occasional shaking The MeOH extract was filtered and the plant material re-extracted with fresh MeOH × 2 The combined MeOH extract was conc to *ca* 50 ml and the concd soln extracted with $CHCl_3$ Removal of the $CHCl_3$ gave 30 g of residue, which was washed with hexane to remove most of the dark green material It was then separated into fractions using CC with hexane, hexane–Et_2O and Et_2O as eluents The fraction containing the flavones was then run on TLC (C_6H_6–EtOAc 4 1) to give **1** and **2** which were recryst from CH_2Cl_2–MeOH Compound **1** was identified as 5,6,7-trimethoxyflavone by comparison of its mp, UV, IR, ^1H NMR and MS with literature values [1–4] Compound **2**, 5-methoxy-6,7-methylenedioxyflavone (60 mg) mp 278–280 , high resolution MS M^+ = 296 0685, $C_{17}H_{12}O_5$ requires 296 06847, UV λ_{max}^{EtOH} nm 215 6, 270 8, 307 0 (no changes were observed when NaOMe, $AlCl_3$, $AlCl_3$–HCl, NaOAc and NaOAc–H_3BO_3 were added), IR ν_{max}^{KBr} cm^{-1} 1645 (C=O), 920 (O–CH_2–O), ^1H NMR

($CDCl_3$) δ 7 70–7 90 (*m*, 2H), 7 40–7 60 (*m*, 3H), 6 73 (*s*, 1H), 6 64 (*s*, 1H), 6 05 (*s*, 2H), 4 12 (*s*, 3H), ^{13}C NMR ($CDCl_3$): δ 177 5 (*s*, C=O, C-4), 160 8 (*s*, C-2 or C-9), 154 7 (*s*, C-2 or C-9), 152 9 (*s*, C-5), 141 4 (*s*, C-7), 134 9 (*s*, C-6), 131 4 (*s*, C-1'), 131.2 (*d*, C-4'), 128 9 (*d*, C-2' or C-6'), 125 9 (*d*, C-3' or C-5'), 112 9 (*s*, C-10), 108.3 (*d*, C-3), 102 1 (*t*, O–CH_2–O), 93 2 (*d*, C-8), 61 1 (*q*, OMe), EIMS *m/z* (rel Intensity) 296 (M^+ 34 1), 268 (55 5, M-CO), 250 (54 8), 222 (10 6), 237 (10 6), 194 (10 1), 166 (100), 164 (96 7), 136 (33 9), 105 (17 8), 102 (62 1)

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8-HYDROXYTRICETIN 7-GLUCURONIDE, A β-GLUCURONIDASE INHIBITOR FROM *SCOPARIA DULCIS*

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Key Word Index—*Scoparia dulcis*, Scrophulariaceae, flavonoids, 5,7,8,3',4',5'-hexahydroxyflavone 7-*O*-β-D-glucuronide, β-glucuronidase inhibitor

Abstract—A new flavone glycoside has been isolated from *Scoparia dulcis* together with 11 known compounds. The new glycoside was determined as 5,7,8,3',4',5'-hexahydroxyflavone glucuronide by spectral analysis. The new glycoside and isovitexin showed inhibitory activity against β-glucuronidase

INTRODUCTION

Scoparia dulcis L is a perennial herb which has been used for the treatment of stomach disease and hepatosis in Paraguay, as a cure for hypertension in Taiwan [1, 2] and for toothache, blennorrhagia and stomach problems in India [3]. From Indian *S. dulcis*, an antidiabetic compound named amellin was isolated by Nath [4] Earlier phytochemical studies on this medicinal plant resulted in isolation of hexacosanol, D-mannitol, sitosterol [3] and 6-methoxybenzoxazolinone [5] as well as triterpenoids [5, 6] and flavonoids [7] Previously, we reported the isolation and structural elucidation of five new diterpene acids from the 70% ethanolic extract of a plant collected in Paraguay [8–10] In a continuation of this work, we have examined the water-soluble fraction which showed mild inhibitory activity against β-glucuronidase. This paper deals with isolation of flavonoids from this fraction and their inhibitory activity against β-glucuronidase.

RESULTS AND DISCUSSION

Eleven flavonoids (**1**–**11**) and a phenylpropanoid (**12**) were isolated from the water-soluble fraction of a 70% ethanolic extract of *S. dulcis*. The compounds, **1**–**10**, **12**, were identified as apigenin (**1**), scutellarein (**2**), luteolin (**3**), vicenin-2 (**4**), linarin (**5**), vitexin (**6**), isovitexin (**7**), scutellarin (**8**), scutellarin methyl ester (**9**), luteolin 7-glucoside (**10**) and *p*-coumaric acid (**12**) by direct comparison of their physical and spectroscopic properties (mp, IR, UV, ^1H NMR and ^{13}C NMR) with those of authentic samples,