J. Indian Chem. Soc.,
Vol. 73, December 1996, pp. 666-668

New Coumarins from *Murraya paniculata*

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Manuscript received 15 December 1994, revised 18 April 1995, accepted 15 June 1995

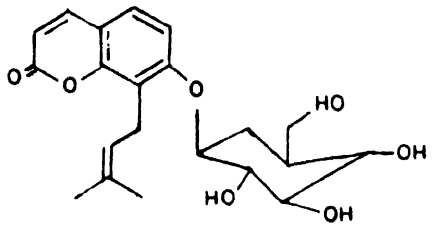
An extract of the stem bark of *Murraya paniculata* has yielded three new coumarins 8-(butenyl-3′-methyl)-7-*O*-β-D-galactopyranoside, 7-methoxy-8-(2′-isovaleryloxy-3-butenyl-3-methyl)coumarin and marmesin-4′-*O*-α-L-arabinopyranoside alongwith 3,5,6,7,8,3′,4′,5′-octamethoxyflavone, 7-methoxy-8-(3-butenyl-3-methyl-2-oxo)coumarin and 7-methoxy-8-(butenyl-3′-methyl)coumarin.

The plant, *Murraya paniculata* L. (Rutaceae) is known to yield coumarins, carbazoles and flavonoids[1]. The present communication deals with the isolation and characterisation of three new coumarins designated as 8-(butenyl-3′-methyl)-7-*O*-β-D-galactopyranoside (**1**), 7-methoxy-8-(2′-isovaleryloxy-3-butenyl-3-methyl)coumarin (**2**) and marmesin-4′-*O*-α-L-arabinopyranoside (**3**) alongwith known compounds 3,5,6,7,8,3′,4′,5′-octamethoxyflavone, 7-methoxy-8-(3-butenyl-3-methyl-2-oxo)coumarin and 7-methoxy-8-(butenyl-3′-methyl)coumarin from the stem bark of *M. paniculata*. The structures of the compounds were determined from the studies of spectra and chemical transformations.

Results and Discussion

The compounds **1-3** gave fluorescence under uv-light indicative for coumarins[2]. Compounds **1** and **3** also gave positive Molisch's test for glycoside. The compounds gave negative $FeCl_3$ reaction showing the absence of phenolic hydroxyl function. Compounds **1** and **2** showed the absorption maxima characteristic of a 7-oxygenated-8-substituted coumarin moiety[3].

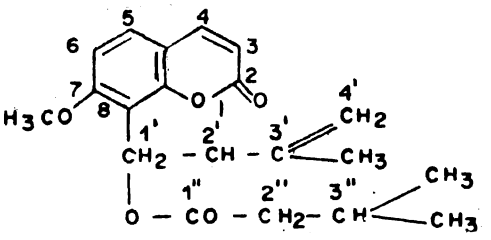
Compound **1**, $C_{20}H_{24}O_8$, m.p. 106–08°, on hydrolysis with acid, yielded an aglycone and D-galactose. The aglycone showed ir bands at 1 710 and 1 630 cm^{-1} and could be regenerated by acidification indicating the presence of a coumarinic system. The ^1H nmr spectrum of the aglycone showed signals for a phenolic proton (δ 6.50), two separate *ortho*-coupled doublets for two aromatic protons, two separate doublets (δ 6.20 and 7.60, *J* 9.50 Hz) for protons at 3- and 4-positions of coumarinic system, and a methylene doublet, a methine triplet and two quaternary methyl singlets characteristic of 3-methylbutenyl residue in the aglycone. These data were suggestive for 7-hydroxy-8-(butenyl-3′-methyl)coumarin. On methylation with methyl iodide, the aglycone yielded 7-methoxy-8-(butenyl-3′-methyl)coumarin which was identified by its m.p., spectral data, m.m.p. and co-tlc[4] on comparision with an authentic specimen. The HIO_4 oxidation[5] of **1** consumed 2 moles of periodate with the production of 1 mole of HCO_2H showing the presence of one unit of D-galactose in pyranose form. Since only one hydroxyl group was present in the aglycone at 7-position, D-galactose must be linked at position-7 of the aglycone part. Compound **1** on hydrolysis with almond enzyme solution afforded 7-hydroxy-8-(butenyl-3′-methyl)coumarin (m.p., m.m.p. and co-tlc) and D-galactose (co-pc) confirming the presence of β-linkage between an aglycone and D-galactose. Thus structure **1** was assigned to this new coumarin galactoside.



1

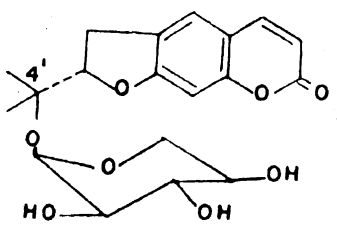
Compound **2**, $C_{20}H_{24}O_5$, m.p. 122–23° exhibited ir absorptions characteristic for coumarin skeleton, methyl, methoxyl, ester carbonyl and unsaturated groups. The ^1H nmr spectrum displayed signals for coumarinic protons in the form of a pair of doublets at C-3 and C-4 positions, and also a pair of doublets for *ortho*-coupled aromatic protons at C-5 and C-6 positions, indicating the absence of any oxygen function at C-5 position[6] and a carbon side-chain at C-8 position. A methoxyl group at position-7 appeared in the form of a singlet. The presence of $C_6H_5CH_2CH$- and -$COCH_2CH$- protons were observed in the form of multiplets. A *gem*-dimethyl group attached to CH was observed in the upfield region while another methyl group was present in downfield region. On comparision of the data with other related coumarins[2,7], it was found that the presence of a *gem*-dimethyl and the multiplets for C-2″ and C-3″ protons confirmed the attachment of an isovaleryl moiety through an oxygen at C-2′. Compound **2** on alkaline hydrolysis afforded 7-methoxy-8-(2′-hydroxy-3′-methylbutenyl)coumarin (m.p. and spectral data) and identified by its conversion into 7-methoxy-8-(2′-acetoxy-3′-methylbutenyl)cou-marin[7] supporting the attachment at C-2′ position. The mass spectrum of compound **2** was also in confirmity with the assigned structure **2**.

Compound **3**, $C_{18}H_{22}O_8$ m.p. 128–30° showed uv absorption maxima characteristic of a furanocoumarin[4,8], which was also substantiated by ir spectrum[4,8]. Acid hydrolysis of **3** yielded an aglycone and L-arabinose. Ir spectrum of the aglycone exhibited principal absorptions for hydroxyl, lactonic carbonyl and aromatic nucleus. The



2

^{1}H nmr spectrum of the aglycone displayed characteristic signals for two methyls, an alcoholic hydroxyl function (disappeared on D_2O shake), furanic protons at C-2′ and C-3′ positions, two aromatic *para* protons and coumarinic protons at C-3 and C-4 positions respectively. The mass spectrum of the aglycone exhibited *m/z* at 246 (M^+, 100%) corresponding to base peak. This together with the presence of peaks at *m/z* 187 (90%) and 160 (35%) suggest a furanocoumarin nucleus. These data closely resemble to that of marmesin[4]. Isolation of acetone and umbelliferone-6-carboxylic acid on CrO_3 oxidation and anhydromarmesin (m.m.p. and co-tlc)[4] by P_2O_5 from the aglycone confirms the structure as marmesin. HIO_4 oxidation on compound **3** confirmed arabinopyranose structure.



3

Experimental

M.ps. were determined on a Toshniwal apparatus and are uncorrected. Electronic spectra (EtOH) were obtained on a Perkin-Elmer 202 spectrophotometer, ir spectra (KBr) on an Acculab 10 spectrophotometer, ^{1}H nmr spectra ($CDCl_3$) on a CFT instrument with TMS as internal standard at 90 MHz and mass spectra on a JMS D-300 spectrometer. The analytical data of the compounds were found satisfactory.

Extraction and isolation : The stem bark (2 kg) of *M. paniculata* (procured from United Chemical and Allied Products, Calcutta) was successively extracted with hexane, C_6H_6 and $CHCl_3$. The hexane extract was subjected on Si-gel column and eluted with hexane-C_6H_6 (5 : 5) and petroleum ether-C_6H_6 (2 : 8) mixture. The hexane-C_6H_6 eluate was concentrated to give a light yellow crystalline compound, m.p. 124–26°, $C_{23}H_{26}O_{10}$ (M^+ 462); λ_{max} 330, 270 (infl.), 260 and 210; ν_{max} 2 870, 1 650, 1 610, 1 480 and 1 175 cm^{-1}; δ 7.60 (2H, s, H-2′ and H-6′), 4.10 (s, 8 × OCH_3), which was found to be identical with exoticin (m.m.p. and co-tlc, isolated from the leaves of *M. paniculata*[9]). The petroleum ether-C_6H_6 eluate was concentrated to afford a crystalline compound, m.p. 128–30°, $C_{15}H_{14}O_4$ (M^+ 258); λ_{max} 325, 258, 250 and 218 nm; ν_{max} 1 730 (δ-lactone), 1 680 (C=O), 1 615 (unsat.) 1 580 (aromatic), 1 350 (C-methyl) and 950 cm^{-1} (–C=CH_2); δ 7.65 (d, *J* 9.50 Hz, H-4), 7.40 (d, *J* 8.50 Hz, H-5), 6.90 (d, *J* 8.50 Hz, H-6), 6.30 (d, *J* 9.50 Hz, H-3), 6.20 and 5.90 (m, exomethylene), 4.30 (s, CH_2), 4.00 (s, OCH_3) and 190 (s, CH_3); *m/z* 258, 230, 213, 199, 189, 175 and 69, which was found to be identical with 7-methoxy-8-(3-butenyl-2-oxo)-coumarin (m.m.p. and co-tlc, isolated from the leaves of *M. paniculata*[10]). The benzene extract was passed over Si-gel column and eluted with C_6H_6-$CHCl_3$ (8 : 2), C_6H_6-$CHCl_3$ (5 : 5) and $CHCl_3$ respectively. The C_6H_6-$CHCl_3$ eluate was concentrated to give a crystalline compound, m.p. 82–83°, $C_{15}H_{16}O_3$ (M^+ 244); λ_{max} 320, 260, 250 and 217 nm; ν_{max} 3 000, 2 970, 2 860, 1 720, 1 670, 1 600, 1 560, 1 510, 1 460, 1 275, 1 240, 1 170, 1 130 and 1 080 cm^{-1}; δ 7.60 (d, *J* 9.50 Hz, H-4), 7.30 (d, *J* 8.00 Hz, H-5), 6.80 (d, *J* 8.00 Hz, H-6), 6.20 (d, *J* 9.50 Hz, H-3), 5.20 (t, *J* 7.00 Hz, C*H*CMe_2), 3.90 (s, OCH_3), 3.50 (d, *J* 7.00 Hz, CH_2CH=), 1.80 and 1.70 (each s, 2 × CH_3); *m/z* 244, 213, 176, 148, 133, 105, 77 and 43, which was shown to be osthol (m.m.p. and co-tlc)[4]. The C_6H_6-$CHCl_3$ and $CHCl_3$ eluates were concentrated to afford crystalline compounds **1** and **2** respectively. The $CHCl_3$ extract was chromatographed over Si-gel column and eluted with $CHCl_3$-EtOAc (9 : 1) to give crystalline compound **3**.

Compound **1** : λ_{max} 320, 260, 250 and 210 nm; ν_{max} 3 450 (OH), 2 965 (CH_3), 1 715 and 1 615 (coumarinic lactone), 1 590 (aromatic), 1 550, 1 510, 1 470, 1 270, 1 250, 1 120, 1 090 and 825 cm^{-1} (glycoside); tetra acetate, δ 7.60 (d, *J* 9.50 Hz, H-4), 7.25 (d, *J* 8.50 Hz, H-5), 6.60 (d, *J* 8.50 Hz, H-6), 6.40 (d, *J* 9.50 Hz, H-3), 5.80-5.60 (m, sugar-H), 5.20 (t, *J* 7.00 Hz, H-2′), 4.90 (d, *J* 7.00 Hz, gal H-1), 3.50 (d, *J* 7.00 Hz, H-1′), 2.00 2.10, 2.15 and 2.20 (each s, 4 × OAc), 1.90 and 1.70 (each s, 2 × CH_3).

Acid hydrolysis of **1** : Compound **1** (500 mg) was hydrolysed with 7% H_2SO_4 (30 ml) by refluxing for 5 h. The resulting solid was washed with H_2O to afford 7-hydroxy-8-(butenyl-3′-methyl)coumarin (aglycone) and D-galactose (co-pc and osazone); aglycone, λ_{max} 321, 260, 248 and 220 nm; ν_{max} 3430 (OH), 3000, 2960, 1710, 1630 and 1 600 cm^{-1}; ^{1}H nmr δ 7.60 (H-4), 7.20 (H-5), 6.70 (H-6), 6.50 (s, OH), 6.30 (H-3) 5.30 (H-2′), 3.60 (H-1′), 1.90 and 1.70 (each s, 2 × CH_3); *m/z* 230, 212, 162, 134, 106, 105 and 43.

Methylation of the aglycone : The aglycone (50 mg) in Me_2CO (20 ml) was refluxed with CH_3I in the presence of anhydrous K_2CO_3 for 4 h. The acetone solution was filtered and the residue washed thrice with hot acetone. On working up, needle shaped crystals of 7-methoxy-8-(butenyl-3′-methyl)coumarin was obtained from benzene which was identified from its m.m.p., co-tlc and spectral data[4].

Compound **2** : λ_{max} 322, 258, 249 and 217 nm; ν_{max} 2 990 (Me), 2 970 and 1 170 (OMe), 1 725–1 710 (ester carbonyl and coumarin lactone), 1 620 (unsat.), 1 660,

1 560 and 1 500 cm^{-1} (aromatic); ^1H nmr δ 7.65 (d, *J* 9.50 Hz, H-4), 7.30 (d, *J* 8.50 Hz, H-5), 6.80 (d, *J* 8.50 Hz, H-6), 6.60 (d, *J* 9.50 Hz, H-3), 4.90 and 3.10 (each m, C_6H_5-CH_2CH), 4.70 and 1.20 (each m, $COCH_2CH$), 3.85 (s, OCH_3), 1.80 (s, CH_3), 0.70 and 0.65 (each d, *J* 6.00 Hz, a *gem*-dimethyl); *m/z* 344 (M^+, 20), 243 (100), 229 (60), 193 (20), 170 (20) and 164 (15%).

Alkaline hydrolysis of compound **2** : A mixture of compound **2** (100 mg) in MeOH (5 ml) and MeOH-KOH (10 ml; 3.3%) was refluxed for 1 h. After the usual work-up, 7-methoxy-8-(2′-hydroxy-3′-methylbutenyl)coumarin was crystallised from petroleum ether-Me_2CO (5 : 5) mixture, m.p. 105–06°; ν_{max} 3 460 (OH), 3 000, 2 970, 1 700, 1 625 and 1 600 cm^{-1}; ^1H nmr δ 7.55 (d, *J* 9.50 Hz, H-4), 7.30 (d, *J* 8.50 Hz, H-5), 6.80 (d, *J* 8.50 Hz, H-6), 6.20 (d, *J* 9.50 Hz, H-3), 4.80 (m, *exo*-methylene), 4.30 (m, C*H*OH), 3.90 (s, OMe), 3.00 (m, CH_2), 2.10 (br s, OH) and 1.80 (s, CH_3); *m/z* 276 (M^+), 260, 190, 189, 175, 161, 160, 131 and 103; *7-methoxy-8-(2′-acetoxy-3′-methylbutenyl)coumarin* (prepared by Ac_2O-Py as usual way), m.p. 87–89°, ν_{max} 1 730 and 1 250 (acetate carbonyl), 1 700 and 1 605 cm^{-1}; ^1H nmr δ 7.60, 7.40, 7.30, 6.90, 6.80, 6.20, 5.50, 4.85, 3.80, 3.20, 2.00 (s, OAc) and 1.85; m.m.p. and co-tlc.

Compound **3** : λ_{max} 315, 260, 240, 230 and 217 nm; ν_{max} 3 450 (OH), 2 990 (CH_3), 1 705 and 1 630 (coumarin lactone), 1 590 (aromatic), 1 130 (ethereal oxygen) and 820 cm^{-1} (glycoside); tetraacetate, ^1H nmr δ 7.55 (d, *J* 9.50 Hz, H-4), 7.30 (s, H-8), 6.70 (s, H-5), 6.30 (d, *J* 9.50 Hz, H-3), 4.60 (t, *J* 8.50 Hz, H-2′). 4.90–5.10 (m, sugar-H), 4.80 (d, *J* 7.00 Hz, arab. H-1), 3.20 (d, *J*, 9.50 Hz, H-3′), 2.00, 2.10, 2.15 and 2.20 (each s, 4 × OAc), 1.35 and 1.25 (each s, 2 × CH_3).

Acid hydrolysis of **3** : Compound **3** (500 mg) was hydrolysed with 7% H_2SO_4 (30 ml) and worked up as usual to yield marmesin (aglycone) and L-arabinose (co-pc); aglycone, λ_{max} 320, 258, 238, 230 and 215 nm; ν_{max} 3 455, 2 990, 1 710, 1 625, 1 580 and 1 125 cm^{-1}; ^1H nmr δ 7.60 (H-4), 7.30 (H-8), 6.60 (H-5), 6.20 (H-3), 4.60 (H-2′), 3.20 (H-3′), 1.80 (s, C-4′, OH), 1.30 and 1.20 (each s, 2 × CH_3); *m/z* 246, 228, 213, 188, 187, 160, 159, 132, 131 and 59. The aglycone (50 mg) was kept with CrO_3 (25 mg in 10 ml gl. AcOH) followed by treatment with C_6H_5CHO to give dibenzalacetone, m.p. 110–12° (m.m.p. and co-tlc). The aglycone (50 mg) was refluxed with H_2SO_4 (3%: 5 ml) and $K_2Cr_2O_7$ in H_2O (5 ml) to yield umbelliferone-6-carboxylic acid, m.p. 258–60°d (m.m.p. and co-tlc). The aglycone (50 mg) in $CHCl_3$ (10 ml) was refluxed with P_2O_5 (50 mg) for 5 h to afford dihydromarmesin, m.p. 138–39° (m.m.p. and co-tlc).

Acknowledgement

The authors express their thank to R.S.I.C., C.D.R.I., Lucknow, and I.I.T., Bombay, for recording the spectra and microanalysis of the compounds. Some work is a part of Research Project sponsored by U.G.C., New Delhi for which one of the authors (S.D.S.) is grateful.

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