

SHORT COMMUNICATION

Coumarins of *Micromelum ceylanicum*

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The presence of a coumarin in *Micromelum ceylanicum* (Sinhalese Walkarapincha) was reported earlier.³ Previous work^{2,3} on *Micromelum* species (Rutaceae) have revealed the presence of coumarins, alkaloids and flavanoids in leaves and stems. In this study, the methanol extract of the fresh leaves yielded four coumarins.

The methanol extract of the fresh leaves was concentrated under reduced pressure. The residue on chromatography on silica gel yielded (a) Fractions 12-14 (Chloroform) containing coumarin I, (b) Fraction 15 (Chloroform) containing coumarin II, (c) Fractions 18-20 (Chloroform/ 2% methyl alcohol) containing coumarin III and (d) Fraction 17 (Chloroform) containing the previously isolated 7-[4'-(4''-methyl-5''-oxo-2'', 5''-dihydro-2''-furyl)-3' methyl-2'-butenyloxy] coumarin (IV).³ Coumarin I was obtained as a pale yellow crystalline solid m.p. 96-97°C. Its high resolution mass spectrum (MS) showed the molecular ion at m/z 312 corresponding to the molecular formula C₁₉H₂₀O₄. The structure was confirmed by comparison of ¹H NMR and mass spectra reported for I.¹ Coumarin II was obtained as white needles m. p. 66-67°C (softens at 63°C). Its high resolution MS showed the molecular ion m/z at 312 corresponding to the molecular formula of I viz. C₁₉H₂₀O₄. The structure was confirmed by comparison ¹H NMR and MS reported for II.¹ The two compounds differ in the position of double bonds at 2,3 and 3,4. Coumarins I and II were previously isolated from *Machaeranthera scabrella* (Greene) Shinnars (Compositae) by Bohlmann *et al.*^{1,7} and from *Ferula diversivittata* (Umbelliferae) by Kieseleva *et al.*^{6,7}

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Coumarin III was obtained as a white crystalline solid from water, m.p. 220-224°C. The structure was confirmed by comparison with an authentic sample of umbelliferone⁴ (m.m.p.; TLC). This is the first occasion that coumarins I and II are reported in the family Rutaceae.

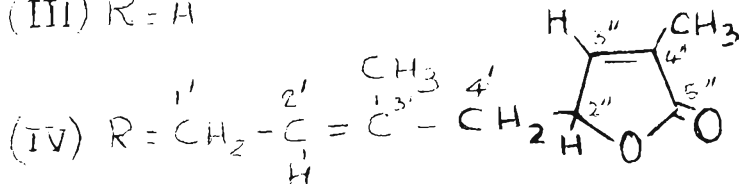
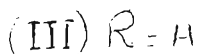
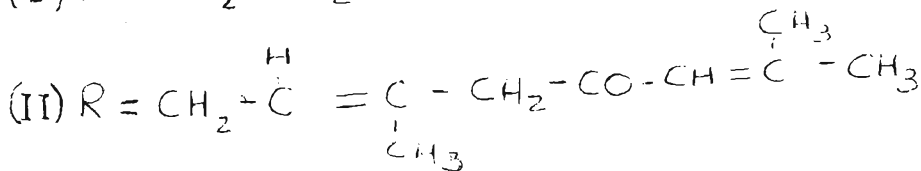
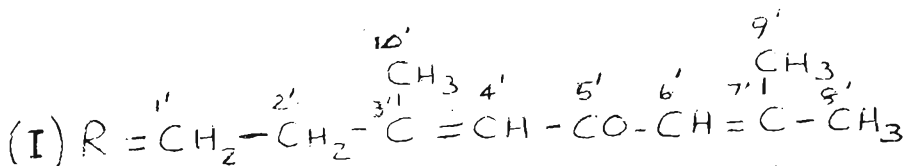
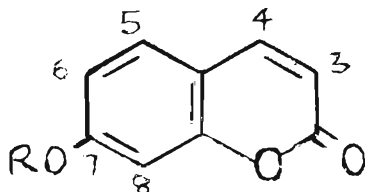
¹H NMR spectra were recorded on a HA - 100 MHz spectrometer. Chemical shifts are reported in δ scale relative to TMS as internal standard. MS were recorded on a Varian CH 5 instrument. Plant material was identified by Mr. D. T. Ekanayake, Superintendent, Royal Botanical Gardens, Peradeniya, Sri Lanka.

Isolation of Coumarin I. Fresh leaves (700 g) collected in Dambulla, Sri Lanka, in February 1982 were macerated with methanol. After filtering, the residue was extracted with methanol in a soxhlet extractor for 18 hours. The combined extracts were concentrated under reduced pressure. The residue was chromatographed on silica gel 60 (70-230 mesh) ASTM Merck and eluted successively with light petroleum (60-80°C), benzene, chloroform and chloroform +2% methyl alcohol. Fractions (12-14) after standing for a few hours and trituration with a little methanol yielded a solid. The residue was taken up in acetone/methanol, decolourized with activated charcoal, concentrated and allowed to cool. The solid was collected and recrystallised from methanol/ether to give pale yellow needles (0.5g), m.p. 96-97°C (lit.^{1,7} m.p. 91°C); MS: m/z 312, 297, 256, 174.9, 161.9, 151, 135, 123, 109, 95, 83, 67, 54.9; high resolution MS: m/z 312.1364 (C₁₉H₂₀O₄ requires 312.1362); HNMR (CDCl₃); 6.24 (d, 3-H, J = 9.5 Hz), 7.58 (d, 4-H, J = 9.5 Hz), 7.37 (d, 5-H, J = 9 Hz), 6.85 (m, 8-H), 4.24 (t, 1'-H, J = 6.7), 3.10 (t(br)2' - H), 6.10 (s(br)6' - H), 6.17 (s(br)4' - H), 1.90 (d, 8' - H, J = 1 Hz), 2.20 (d, 9' - H, J = 1 Hz), 2.00 (d, 10 - H, J = 1 Hz), IR (KBr): 1k720, 1610 (coumarin) cm⁻¹.

Isolation of Coumarin II: Fraction 15 crystallized on standing for a long time and triturating with ether. The solid was collected dissolved in ether/methanol, clarified with charcoal and concentrated. The crystalline solid was further recrystallised from chloroform/light petroleum (60-80°C) and acetone/light petroleum (60-80°C) to give a pale yellow solid. The final clarification was effected by dissolving the solid in ether/light petroleum (60-80°C) 1:1 and passing down a column of alumina (1'') BDH. The eluate on concentration yielded white needles (0.6g) m.p. 66-67°C (lit. ^{1,7} m.p. 63.5°): MS: m/z 312, 297, 256, 244, 162, 150, 134, 121, 107, 95, 83, 67, 55; high resolution MS: m/z 312.1364 (C₁₉H₂₀O₄ requires 312.1362); ¹H NMR (CDCl₃); 6.22 (d, 3-H, J = 9.5 Hz), 7.62 (d, 4-H, J = 9.5 Hz), 7.35 (d, 5-H, J = 9 Hz), 6.85 (dd, 6-H), 6.80 (d, 8-H), 4.66 (d(br) 1'-H, J = 6.5 Hz), 5.60 (t(br)2' - H), 3.18 (s, 4' - H), 6.1 (m, 6' - H), 1.87 (d, 8' - H), 2.15 (d, 9' - H), 1.79 (d, 10' - H), IR (KBr): 1722, 1615 (coumarin) cm⁻¹.

Isolation of Coumarin III: Fraction 18-20 solidified on evaporation and standing for a week. This was triturated with ether to give a light brown crystalline solid. This was recrystallised from boiling water as needles (0.5g) m.p. 224°C (lit.⁷ m.p. 223-224°C).

Isolation of Coumarin IV: Fraction 17 yielded a solid which on recrystallisation from acetone/light petroleum (60-80°C) gave IV as a white crystalline solid (0.5g), m.p. 125°C.³



Acknowledgements

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