

), 201 (7.5), 174 (10), 173 (3.3), 147 (3.2), 146 (2.1), 145 (4.2), (1), 118 (1), 117 (1), 97 (17), 89 (5.5), 69 (4.2), 63 (3.2), 41 (7.3), 2.6) and 18 (8.4). IR ν_{\max}^{KBr} cm^{-1} : 2920, 1755, 1710, 1615, 1590, 1400, 1325, 1290, 1210, 1180, 1150 and 1025. $^1\text{H NMR}$ (100 MHz, CDCl_3): Table 1. $^{13}\text{C NMR}$ [5] (50 MHz, CDCl_3 , solvent assignments, OFR): singlets 173.82 (C-10'), 160.37 (C-48.65 (C-8a), 148.26 (C-7), 137.02 (C-3'), 131.45 (C-8), 130.18 (C-6), 125.95 (C-6), 116.58 (C-4a); doublets 146.70 (C-2'), 144.32 (C-7'), 123.94 (C-2''), 114.76 (C-3), 113.54 (C-5), 106.83 (C-79.54 (C-6''); triplets 69.64 (C-1'), 43.37 (C-5''); quartets 17.24 (C-4').

Hydrolysis of wampetin. Wampetin (1) (30 mg) was dissolved in 1 ml HOAc to which 2 drops of conc H_2SO_4 were added. The reaction mixture was heated for 30 min, cooled, diluted with ice water and extracted with EtOAc. The EtOAc layer was washed with H_2O , dried (Na_2SO_4) and the solvent removed to afford the product (20 mg) which on purification by prep. TLC on silica gel yielded xanthoxol (6 mg) mp 240–243° (uncorr.), ν_{\max}^{KBr} cm^{-1} : 3400 (–OH), 1730, 1700 (coumarin carbonyl).

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VOLUBOLIN, A 4-PHENYL-2H-1-BENZOPYRAN-2-ONE FROM *DALBERGIA VOLUBILIS*

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Key Word Index—*Dalbergia volubilis*; Leguminosae; young branches; 7-hydroxy-4-methyl coumarin; dalbergin; biochanin-A; 7-hydroxy-4-(3-hydroxy-4-methoxyphenyl)-2H-1-benzopyran-2-one.

Abstract—From the ether soluble portion of a methanolic extract of young non-green branches of *Dalbergia volubilis*, sitosterol, 7-hydroxy-4-methyl-2H-1-benzopyran-2-one, dalbergin, *p*-hydroxy cinnamic acid, biochanin-A and a new 4-phenylcoumarin, volubolin, have been isolated. The structure of volubolin as 7-hydroxy-4-(3-hydroxy-4-methoxyphenyl)-2H-1-benzopyran-2-one has been established on the basis of spectral and chemical evidence. Cooccurrence of 7-hydroxy- and 4-phenyl-coumarins with isoflavones is of biogenetic interest.

Leaves and stem bark of *Dalbergia volubilis* have been reported earlier [1–5], but no work has been done on young non-green branches. We have now isolated five new compounds: dalbergin, biochanin-A, sitosterol, *p*-hydroxycinnamic acid, 7-hydroxy-4-methyl-2H-1-benzopyran-2-one and a new 4-phenyl-2H-1-benzopyran-2-one which we name volubolin.

The new compound, volubolin, analysing for $\text{C}_{17}\text{H}_{12}\text{O}_5$, showed a deep blue fluorescence under UV light and λ_{\max} at 224, 284 and 340 nm. It gave a red colour with alcoholic ferric chloride and showed strong absorption bands at 1715 and 3300 cm^{-1} indicating the presence of a lactone carbonyl and a hydroxylic function in it. The presence of strong absorption bands at 1624, 1607, 1580 and 1546 cm^{-1} in its IR spectrum indicated that the

positions 5 and 8 of the coumarin nucleus were free [6]. Since it gave a pink colour with Mg-HCl which changed from blue to brown, the compound was considered to be a 4-phenylcoumarin [7]. In its $^1\text{H NMR}$ spectrum it showed a one proton singlet at δ 5.93 which could be assigned to a proton at position 3 of the 4-phenylcoumarin. Two one proton singlets at δ 9.85 and 10.3, exchangeable with deuterium, could be assigned to two phenolic protons while a three proton singlet at δ 3.8 could be attributed to three methoxyl protons. It showed a prominent molecular ion at m/z 284 followed by a loss of CO to give a strong $[\text{M} - 28]^+$ peak at m/z 256 which further lost a molecule of CO to yield a peak at m/z 228 $[\text{M} - 56]^+$. Other prominent peaks at m/z 269 $[\text{M} - 15]^+$ and m/z 241 $[\text{M} - 43]^+$ could be accounted for

by the loss of a methyl radical and CO from the molecular ion. This spectral fragmentation is characteristic of a 7-hydroxycoumarin [6]. The strong peak at m/z 225 $[M - 59]^+$ could be due to the combined loss of a methoxyl radical and CO while that at m/z 210 $[M - 74]^+$ may be attributed to the loss of water from the $[M - 56]^+$ peak at m/z 228 or to the loss of a methoxyl radical from the $[M - 43]^+$ fragment. A peak at m/z 211 $[M - 73]^+$ may be considered to be due to the loss of two CHO radicals while the peak at m/z 213 $[M - 71]^+$ could be attributed to the loss of two CO molecules from the $[M - 15]^+$ (m/z 269) fragment. All the above evidence suggested this compound to be 7-hydroxy-4-(3-hydroxy-4-methoxyphenyl)-2H-1-benzopyran-2-one and this was supported by two multiplets each integrating for three protons at δ 6.7 and 7.2 in its ^1H NMR spectrum which could be assigned to three aromatic protons due to rings A and B respectively. The structure was confirmed by methylation followed by oxidation with neutral potassium permanganate when 3,4-dimethoxybenzoic acid, oxalic acid and 2-hydroxy-3,4,4'-trimethoxybenzophenone were identified by comparison with authentic samples. That the hydroxyl and methoxyl groups were in positions 3 and 4 respectively and not vice versa was proved by mild permanganate oxidation of volubolin when an acid, mp 250° , was isolated which corresponds to 3-hydroxy-4-methoxybenzoic acid (lit. [8] mp 255°).

EXPERIMENTAL

Air dried non-green young branches of *Dalbergia volubilis* were defatted with petrol (bp $60-80^\circ$) and extracted with MeOH which on concn yielded a dark yellow-black residue (4 g), which was extracted with Et_2O . The Et_2O extract on CC (silica gel) using C_6H_6 and petrol for elution yielded compounds A_1 , A_2 , A_3 , A_4 and A_5 .

Compound A_1 . Yield 50 mg. Crystallized from CHCl_3 -MeOH as colourless silky needles, mp $139-140^\circ$, $[\alpha]_D^{25} = -30.5^\circ$ (c 0.60, CHCl_3). It was identified as sitosterol by comparison with an authentic sample (mp, mmp, Co-IR, Co-TLC).

Compound A_2 . Yield 30 mg. Crystallized from EtOAc-petrol as light yellow shining needles, mp $181-182^\circ$. It gave a bright blue fluorescence (UV light). $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 325. The acetate crystallized from EtOAc, with mp $150-151^\circ$. ^1H NMR (δ , CDCl_3) 2.32 (3H, s, OCOMe), 2.4 (3H, d, $J = 1.5$ Hz, Me), 6.18 (1H, q, H-3), 6.79 (2H, m, H-6, H-8), 7.54 (1H, d, $J = 10$ Hz, H-5). It was identified as 7-hydroxy-4-methyl coumarin by comparison with an authentic synthetic sample (mp, mmp, Co-TLC and Co-IR).

Compound A_3 . Yield 40 mg. Crystallized from a C_6H_6 -MeOH mixture as light yellow needles, mp $211-212^\circ$. It exhibited $\lambda_{\text{max}}^{\text{MeOH}}$ at 235, 260 and 380 nm and yielded a methyl ether which crystallized from MeOH to yield prisms, mp $146-147^\circ$, (lit. [10] mp of methyl dalbergin $145-146^\circ$). Compound A_3 was therefore identified as dalbergin by comparison with an authentic sample (mp, Co-IR).

Compound A_4 . Yield 40 mg. Crystallized from EtOAc as colourless needles, mp $214-216^\circ$. It analysed for $\text{C}_{16}\text{H}_{12}\text{O}_5$. (Found: C, 67.7, H, 4.25; $\text{C}_{16}\text{H}_{12}\text{O}_5$ requires C, 67.6; H, 4.23%) It was identified as 5,7-dihydroxy-4'-methoxy isoflavone (biochanin-A) by spectral measurements and by comparison with an authentic sample [10] (Co-TLC, Co-IR).

Compound A_5 . Yield 25 mg. Crystallized from MeOH as colourless needles, mp $210-212^\circ$ and was identified as *p*-hydroxycinnamic acid (mp, mmp, Co-TLC).

Compound A_6 . Yield 90 mg. Obtained from the petrol- C_6H_6 (7:3) eluate and was further purified by prep. TLC (silica gel, petrol- C_6H_6 , 1:1), when a yellow semisolid was obtained. It analysed for $\text{C}_{16}\text{H}_{12}\text{O}_5$. (Found: C, 67.4; H, 4.4; $\text{C}_{16}\text{H}_{12}\text{O}_5$ requires C, 67.6; H, 4.3%) $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 224 (e 4.19), 284 (e 4.40), 340 (e 3.98). $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 1715, 1480, 1345. MS (m/z % abundance) 284 (21.9), 272 (40.00), 270 (2.12), 263 (26.8), 268 (89.40), 267 (13.6), 256 (25.6), 255 (14.4), 141 (14.1), 240 (14.6), 239 (12.1), 230 (17.8), 229 (17.3), 228 (45.6), 227 (18.1), 226 (18.4), 225 (54.0), 213 (33.3), 212 (41.0), 211 (38.4), 210 (90.2), 209 (24.7), 208 (16.0), 207 (30.5), 205 (13.6), 201 (26.0).

KMnO₄ oxidation of volubolin. A soln of volubolin in Me_2CO (10 mg, 5 ml) and a soln of KMnO_4 in Me_2CO (50 mg, 10 ml) were warmed on a water bath till the colour of reaction mixture persisted. The solvent was distilled off, decolourized by adding NaHSO_3 (0.5 g) and acidified with HCl. It was extracted with EtOAc and the residue obtained after evaporation of solvent subjected to prep. TLC when an acid, mp 250° was obtained (lit. [8] mp of 3-hydroxy-4-methoxybenzoic acid, 255°).

Oxidation of volubolin methyl ether. A soln of volubolin in Me_2CO (50 mg, 60 ml) was refluxed with Me_2SO_4 (2 ml) and Na_2CO_3 (2 g) for 20 hr. The reaction mixture was filtered and the filtrate concd under red. pres. to 20 ml. KMnO_4 (1 g) was added to it and the mixture warmed till the colour persisted. MnO_2 was decomposed with NaHSO_3 soln (5 ml, 10%) and the soln was extracted with EtOAc. The EtOAc extract, after concn, was again extracted with 10% KHCO_3 which on acidification with HCl yielded oxalic acid and 3,4-dimethoxybenzoic acid (confirmed by their TLC comparison with authentic synthetic samples). The non-aqueous organic extract on evaporation of solvent yielded a pale yellow compound (10 mg), mp $135-137^\circ$. The compound was identified to be 2-hydroxy-3',4,4'-trimethoxybenzophenone (lit. [11] mp 140°) by comparison with an authentic synthetic sample (mp, mmp, Co-IR).

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