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THREE NEW FLAVONOIDS IN *PRUNUS CERASUS*

Gobichettipalayam R. Nagarajan and Virinder S. Parmar
Department of Chemistry, University of Delhi, Delhi-110007, India

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Key Word Index—*Prunus cerasus*; Rosaceae; flavanone; cerasinone; chalcones; cerasidin and cerasin.

Prunus cerasus L. grows in India in the north-west Himalayan region. Earlier work on the flower stem led to the isolation of dihydrowogonin-7-glucoside [1]. In a previous communication [2] we reported the identification of eleven known flavonoids in the benzene and acetone extracts of the heartwood. Besides these, three more compounds were obtained in minor amounts; the structures of these compounds (A, B and C) have now been fully established.

Compound A

$C_{18}H_{18}O_6$, mp 200–201°, M^+ 330, was optically active. Its colour reactions and UV data indicated it to be a flavanone having a free —OH group at C-7 and lacking a chelated —OH group. Its NMR spectrum in C_5H_5N showed signals for three —OMe groups, *meta* coupled C-6 and C-8 protons besides the signals for C-2 and C-3 protons. This indicated A to have a phloroglucinol A ring system with —OMe group at C-5. On acetylation A yielded a monoacetate, whose NMR spectrum in $CDCl_3$ had signals attributable to a phenolic acetate, three —OMe groups, C-2 and C-3 protons and meta coupled C-6 and C-8 protons. Besides these, an ill resolved multiplet centred at δ6.57 and an *ortho* coupled doublet at δ7.45 integrating respectively for two and one proton showed the B ring to have 2′,4′-substitution pattern. From these data, A was assigned the structure, 7-hydroxy-5,2′,4′-trimethoxyflavanone. This structure was confirmed by alkali fission of A to yield 2,4-dimethoxybenzoic acid and mono-*O*-methylphloroglucinol. This is the first report of this compound in nature and it has been named cerasinone.

Compound B

$C_{19}H_{20}O_6$, mp 152–153°, M^+ 344, gave a dark brown ferric colour and a red colour with conc H_2SO_4. From its UV and IR spectral data, it was inferred to be a chalcone having a chelated —OH. Its NMR spectrum ($CDCl_3$, δ) showed peaks for the presence of four —OMe groups (3.81, *s*, 6H; 3.89, *s*, 6H), C-3′ and C-5′ protons (5.93, *d*, $J = 2$ Hz; 6.08, *d*, $J = 2$ Hz), C-3 and C-5 protons (ill-resolved *m*, 6.38–6.67), *ortho* coupled C-6 proton (7.53, *d*, $J = 9$ Hz), C-α proton (7.91, *d*, $J = 17$ Hz), C-β proton (8.24, *d*, $J = 17$ Hz) and C-2′ OH (14.4, *s*). The NMR spectrum of B in Me_2CO clearly showed peaks for C-5 proton as double-doublet ($J = 2$ Hz and 9 Hz) and for C-3 proton as *meta* coupled doublet ($J = 2$ Hz). From these data B was identified as 2′-hydroxy-2,4,4′,6′-tetramethoxychalcone. Its degradation by alkali to 2,4-dimethoxybenzoic acid and di-*O*-methylphloroglucinol and also the NMR spectrum of its acetate confirmed the above structure. This is the first report of this chalcone from a natural source and it has been named cerasidin.

Compound C

$C_{18}H_{18}O_6$, mp 157–159°, was obtained in poor yield. It gave a deep brown ferric colour, red colour with conc H_2SO_4 and did not develop any colour with Mg/HCl. These colour reactions and its UV and IR spectra indicated it to be a chalcone. Bathochromic shifts in its UV maxima were observed both on addition of NaOAc and $AlCl_3$–HCl. However due to the paucity of material, further data could not be obtained. On biogenetic grounds it was considered that it could be the corresponding chalcone of compound A i.e. 2′,4′-dihydroxy-2,4,6′-trimethoxychalcone. Accordingly, this chalcone was synthesized and it was found to be identical with C in all respects. This is the first reported isolation of this chalcone which has been named cerasin.

To our knowledge, this is the first report of natural chalcones and flavanones having 2,4-dimethoxylation pattern in the side ring.

EXPERIMENTAL

Mp's are uncorr.

The sample under investigation was procured from Baramulla (Kashmir, India). As reported in ref. [2], the heartwood (900 g) was extracted in hot petrol, C_6H_6 and Me_2CO in succession. The Et_2O and EtOAc solubles of the Me_2CO extract were mixed and chromatographed on a Si gel column. Fractions obtained from C_6H_6 and C_6H_6–EtOAc (9:1) eluents were mixed with the C_6H_6 extract of the wood and the mixture chromatographed on a Si gel column. Subsequent preparative TLC of the column fractions ($CHCl_3$–MeOH; 19:1) yielded compounds A, B and C (Si gel G, C_6H_6–petrol–Me_2CO: 4:2:1, R_f 0.15, 0.88 and 0.47 respectively).

Compound A. This crystallized as colourless needles (0.06 g) from MeOH, mp 200–201°, $[\alpha]_D^{22}$ +14.5° (*c*, 0.347, MeOH). It gave a light brown ferric colour, rose red colour with Mg/HCl and red colour with conc H_2SO_4. λ_{max}^{MeOH} nm (log ε): 229(4.481), 284(4.344): +$AlCl_3$ + HCl: 229, 284 nm; +NaOAc: 320 nm; +NaOAc + H_3BO_3: 230, 284 nm: ν_{max}^{KBr} cm^{-1}: 3130, 1645: NMR (C_5H_5N, δ): 2.95 (2H, *m*, C-3 protons), 3.64 (3H, *s*, —OMe), 3.69 (3H, *s*, —OMe), 3.78 (3H, *s*, —OMe), 5.85 (1H, *m*, C-2 proton), 6.46 (1H, *d*, $J = 2$ Hz, C-6 proton) and 6.53 (1H, *d*, $J = 2$ Hz, C-8 proton). MS (*m/e*): 330, 329, 299, 193, 167, 166, 164, 149, 138 and 121. (Found: C, 65.2; H, 5.8; $C_{18}H_{18}O_6$ requires C, 65.45: H, 5.45%). The acetate of A was prepared in cold by C_5H_5N/Ac_2O method and crystallized from $CHCl_3$–petrol (colourless needles), mp 146–147°; NMR ($CDCl_3$, δ): 2.31 (3H, *s*, —OCOMe), 2.88 (2H, *m*, C-3 protons), 3.88 (9H, *br. s*, 3 × —OMe), 5.75 (1H, *m*, C-2 proton), 6.33 (1H, *d*, $J = 2$ Hz, C-6 proton), 6.44 (1H, *d*, $J = 2$ Hz, C-8 proton), 6.57 (2H, ill resolved *m*, C-3′ and C-5′ protons) and 7.45 (1H, *d*, $J = 10$ Hz, C-6′

proton). (Found: C, 64.2: H, 5.8; $C_{20}H_{20}O_7$ requires C, 64.51: H, 5.38 %).

Alkali fission of A. (0.015 g) A was refluxed with 50 % ethanolic KOH (7 ml) for 15 hr. 10 ml H_2O was added and C_2H_5OH removed. After treatment with Et_2O, the aq. reaction mixture was acidified and extracted with EtOAc. Removal of EtOAc left a gummy residue from which by preparative TLC (Si gel G, C_6H_6–Me_2CO; 9:2), 2,4-dimethoxybenzoic acid, mp 109–110° (lit. mp 108° [3]), (R_f 0.12), and mono-*O*-methylphloroglucinol (R_f 0.42) were obtained. The identity of the above samples was confirmed by comparison with authentic samples (CO-IR).

Compound B. This separated as yellowish–orange needles (0.075 g) from $CHCl_3$–petrol, mp 152–153°. λ_{max}^{MeOH} nm (log ε): 250(3.953), 381(4.522); +$AlCl_3$ + HCl: 255, 410 nm: +NaOAc: 250, 380 nm; +NaOMe: 300, 345 nm; ν_{max}^{KBr} cm^{-1}: 2970, 1625 (Found: C, 66.5; H, 6.0; $C_{19}H_{20}O_6$ requires C, 66.28: H, 5.81 %). The acetate of B crystallized from $CHCl_3$–petrol as yellow plates, mp 116–117°; NMR ($CDCl_3$, δ): 2.24 (3H, *s*, —OCOMe), 3.92 (12H, *s*, 4 × —OMe), 6.53 (4H, *br. s*, C-3, C-5, C-3′ and C-5′ protons), 6.91 (1H, *d*, *J* = 17 Hz, C-α proton), 7.44 (1H, *d*, *J* = 8 Hz, C-6 proton) and 7.68 (1H, *d*, *J* = 17 Hz, C-β proton). (Found: C, 65.0; H, 6.0: $C_{21}H_{22}O_7$ requires C, 65.28: H, 5.7 %).

Alkali fission of B. 0.01 g B was subjected to alkali fission by the procedure described earlier. By preparative TLC of the reaction mixture in the same solvent system, 2,4-dimethoxybenzoic acid and di-*O*-methylphloroglucinol (R_f 0.66, identified by comparison with an authentic sample) were obtained.

Compound C. This was obtained as orange plates (0.015 g) from EtOAc–C_6H_6, mp 157–159°: λ_{max}^{MeOH} nm (log ε): 250(3.902), 378(4.338): + $AlCl_3$ + HCl: 260, 400 nm: +NaOAc: 255, 395 nm: +NaOMe: 400 nm: ν_{max}^{KBr} cm^{-1}: 3300, 2965, 1615 (Found: C, 65.1: H, 5.7: $C_{18}H_{18}O_6$ requires C, 65.45; H, 5.45 %).

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FLAVONOID AGLYCONES FROM *FLOURENSIA*

M. O. Dillon and T. J. Mabry

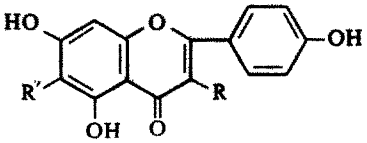
The Cell Research Institute and the Department of Botany, The University of Texas at Austin, Austin, TX 78712, U.S.A.

Key Word Index—*Flourensia*; Asteraceae; flavonoids; 5,7-dihydroxyflavanone; methyl ethers of galetin; kaempferol; quercetagetin.

INTRODUCTION

In the continuing biosystematic investigation of the genus *Flourensia* [1, 2] we report here seven flavonoid aglycones from three *Flourensia* taxa. *Flourensia ilicifolia* Blake elaborates a complex mixture of aglycones including: 5,7-dihydroxyflavanone (pinocembrin) (1) [3], kaempferol 3-methyl ether (2) [4], galetin (6-hydroxykaempferol) 6-methyl ether (3) [5], galetin 3,6-dimethyl ether (4) [4], quercetagetin 3,6-dimethyl ether (axillarin) (5) [6], and quercetagetin 3,6,3′-trimethyl ether (jaceidin) (6) [3]. *Flourensia retinophylla* Blake yielded 1 in addition to kaempferol 3,7-dimethyl ether (kumatakenin) (7) [7], a flavonol previously reported from *F. cernua* DC [2]. *Flourensia campestris* Griseb. also contains 4 (see Table 1). This is the first report of compounds 1, 3 and 5 in the Asteraceae [8].

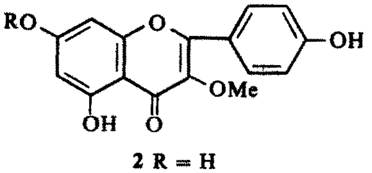
All compounds were isolated and identified by UV, NMR and co-chromatography (TLC) with authentic samples. Spectral values and color reactions for these compounds were identical with previously reported values.



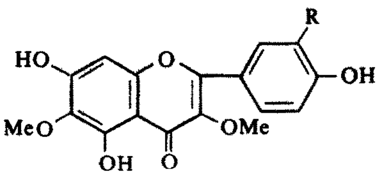
3 R = OH, R′ = OMe
4 R = R′ = OMe

EXPERIMENTAL

Two-dimensional chromatograms employed Whatman 3MM paper and were developed first in TBA (*t*-BuOH–HOAc–H_2O, 3:1:1) and then in 15 % HOAc. The NMR spectra were recorded using TMS as an internal standard. Preparation of the TMS ethers and TLC co-chromatography were carried out by standard procedures [3, 8]. Air-dried and powdered leaves (69 g) of *Flourensia ilicifolia* were extracted exhaustively with $CHCl_3$. The combined extracts were taken to dryness *in vacuo*, yielding a dark green syrup (5.8 g). This syrup was chromatographed over polyamide (150 g packed in the first elution solvent); the column was initially developed with $CHCl_3$–



2 R = H
5 R = Me



6 R = OH
7 R = OMe