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MINIMIFLORIN: A NEW 2′-HYDROXYFLAVANONE FROM *LONCHOCARPUS MINIMIFLORUS* SEEDS

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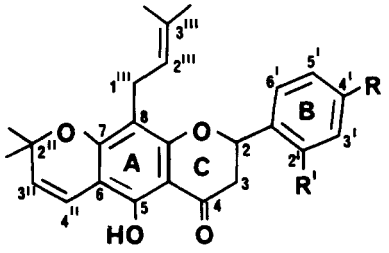
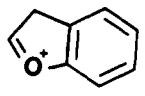
The genus *Lonchocarpus* (Leguminosae, Papilionaceae) is a well-known source of flavonoids and isoflavonoids (1). As part of an examination of the chemistry of *Lonchocarpus* species found in the Santa Rosa National Park, Costa Rica (2,3), we now report the results of an analysis of a small sample of seeds of the hitherto uninvestigated *Lonchocarpus minimiflorus* Donn. Smith.

By a combination of column chromatography and circular preparative tlc, three flavanones, one major and two minor, were isolated from a $CHCl_3$ extract of *L. minimiflorus* seeds. One of the minor compounds was identified as lupinifolin (**1**) by comparison of spectral data with that published. Lupinifolin has previously been reported from *Tephrosia lupinifolia* (4) and *Mundulea sericea* (5).

The major flavanone, which appears to be novel and has been assigned the trivial name minimiflorin, analyzed for $C_{25}H_{26}O_5$, identical to **1**. The ^{1}H-nmr spectrum confirmed the same H-bonded 5-hydroxy group, and 2,2-dimethylpyran and 3,3-dimethylallyl substituents in ring A. Acetylation yielded a diacetate in which a pronounced shielding for H-4″ required its placement *peri* to the 5-acetoxy group, thus confirming the same A-ring substitution pattern in minimiflorin as in **1**. Differences between the ^{1}H-nmr spectra of **1** and minimiflorin were noted for the resonance positions of the C-ring protons and for the coupling patterns among the four ring-B protons. In **1**, the latter form an AA′BB′ system typical of the *para*-substituted benzene ring, but in minimiflorin, they are resolved, at high-field, into an ABCD system due to four adjacent protons. Thus, minimiflorin must be **2**, in which the B-ring hydroxy group is at C-2′, where its proximity to the C-ring will lead to the observed shift in H-2 and H-3 compared to **1**. The proposed structure for **2** is supported by the ^{13}C-nmr spectrum and by the electron impact mass spectrum, which gives the ion **3**, typical of 2′-oxygenated flavonoids (6). The levorotatory nature of **2** indicated the normal flavanone stereochemistry, *S* at C-2.



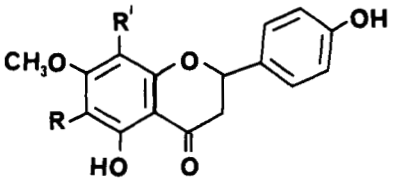
1 R=OH R′=H
2 R=H R′=OH



3

A third flavanone, isolated in trace amounts only, analyzed for $C_{21}H_{22}O_5$. The ^{1}H-nmr spectrum indicated a *para*-substituted B-ring, an H-bonded 5-hydroxy group, a 3,3-dimethylallyl unit, a methoxyl substituent, and a single A-ring proton. The mass spectrum gave a fragment *m/z* 120 for ring-B so requiring the placement of the second hydroxy group at C-4′ and the methoxyl at C-7. Making the assumption that this is a biogenetically normal flavonoid oxygenated at C-5 and C-7, two structures are

possible, **4** or **5**. A positive Gibb's test (7) indicated an unsubstituted position *para* to one of the hydroxy substituents, the only possibility for this being C-8. On this basis, the third flavanone is tentatively identified as **4**, which also appears to be novel.



4 R=$CH_2CH=C(CH_3)_2$ R′=H
5 R=H R′=$CH_2CH=C(CH_3)_2$

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were run in MeOH and ir spectra as KCl discs. ^{1}H-nmr spectra (250 MHz) and ^{13}C nmr (62.5 MHz) were run in $CDCl_3$ using TMS as internal standard. Electron impact mass spectra were obtained at 70 eV between 120 and 150°. Petroleum ether refers to the bp 60-80° fraction.

PLANT MATERIAL.—Seeds of *L. minimiflorus* were collected in the Santa Rosa National Park, Costa Rica, in 1983. A voucher specimen has been deposited at the Herbarium of the Royal Botanic Gardens, Kew, London, UK, as part of the Krukoff Carpalogical collection.

ISOLATION OF FLAVANONES.—Ground seeds (50 g) were extracted with petroleum ether (bp 60-80°), and then $CHCl_3$. Column chromatography of the $CHCl_3$ extract over silica gel, eluting with petroleum ether containing 10% EtOAc, gave crude **2**, which was further purified by preparative circular tlc (silica gel: solvent, toluene-EtOAc-HOAc, 96:4:1) to give **2** (127 mg). Elution with 20% EtOAc in petroleum ether gave a mixture of two minor components which were separated by preparative circular tlc (system as above) to give **1** (8 mg) followed by **4** (11 mg).

LUPINIFOLIN.—Yellow needles from *n*-hexane-C_6H_6, mp 115-117° [lit. (4) 117-119°]; ms *m/z* 406.1753 (M^+) (calcd for $C_{25}H_{26}O_5$ 406.1780); uv, ir, ^{1}H nmr in agreement with published data (4,5). Acetylation gave a diacetate with physical and spectral properties in close agreement with those reported for lupinifolin diacetate (4).

MINIMIFLORIN (**2**).—Yellow needles from hexane-Me_2CO, mp 114°; $[\alpha]^{21}D$ −66° (*c*. 1.00, $CHCl_3$); ms *m/z* (rel. int.) 406.1775 (M^+, 83) (calcd. for $C_{25}H_{26}O_5$ 406.1780), 391 (100), 373 (35), 345 (23), 317 (39), 271 (21), 243 (8), 215 (52), 119 (4), 91 (12); uv 265, 273, 310 nm; ir 3250, 1650, 1600, 1460, 1380, 1360, 770 cm^{-1}; ^{1}H nmr δ 1.44, 1.46 (2×3H, 2×s, 2″-Me_2), 1.68, 1.69 (2×3H, 2×s, ‴3-Me_2), 2.95 (1H, dd, *J*=17.3, 12.1, H-3_{ax}), 3.06 (1H, dd, *J*=17.3, 3.7, H-3_{eq}), 3.24 (2H, d, *J*=6.6, ‴1-CH_2), 5.15 (1H, t, *J*=6.6, H-2‴), 5.52 (1H, d, *J*=10, H-3″), 5.67 (1H, dd, *J*=12.1, 3.7, H-2_{ax}), 6.64 (1H, d, *J*=10, H-4″), 6.88 (1H, dd, *J*=7.8, 1.2, H-3′), 6.96 (1H, ddd, *J*=7.5, 7.5, 1.2, H-5′), 7.05 (1H, s, 2′-OH), 7.24 (1H, ddd, *J*=7.8, 7.5, 1.7, H-4′), 7.37 (1H, dd, *J*=7.5, 1.7, H-6′), 12.19 (1H, s, 5-OH); ^{13}C nmr: quartets at 17.82 and 25.52 (3‴-Me_2), 28.37 and 28.45 (2″-Me_2), triplets at 25.52 (C-1‴), 41.91 (C-3), doublets at 76.80 (C-2), 115.66, 116.88 (C-3″, C-3′), 120.91 (C-5′), 122.38 (C-2‴), 126.20, 126.86 (C-6′, C-4″), 129.86 (C-4′), singlets at 78.31 (C-2″), 102.71, 103.35 (C-4a, C-8), 108.85 (C-6), 124.54 (C-1′), 131.65 (C-3‴), 153.74 (C-2′), 156.82 (C-5), 158.77 (C-7), 159.82 (C-8a), 196.43 (C-4).

MINIMIFLORIN DIACETATE.—Minimiflorin (54 mg) was dissolved in pyridine (5 ml) and treated with Ac_2O at room temperature. Normal work-up gave the diacetate (45 mg), mp 72°; ms *m/z* (rel. int.) 490.1981 (M^+, 19) (calcd. for $C_{29}H_{30}O_7$ 490.1991), 448 (69), 433 (100), 271 (8), 215 (18), 109 (7), 43 (14); uv: 258, 287, 340 nm; ir: 1770, 1680, 1600, 1460, 1380, 1200 cm^{-1}; ^{1}H nmr (90 MHz) 1.43 (6H, s, 2″-Me_2), 1.62 (6H, s, 3‴-Me_2), 2.25, 2.39 (2×3H, 2×s, 5 and 6′ OAc), 2.75 (1H, dd, *J*=18, 13, H-3_{ax}), 3.24 (2H, d, *J*=8, 1‴-CH_2), 3.47 (1H, dd, *J*=18, 6, H-3_{eq}), 5.13 (1H, t, H-2‴), 5.52 (1H, dd, *J*=13, 6, H-2_{ax}), 5.61 (1H, d, *J*=10, H-3″), 6.36 (1H, d, *J*=10, H-4″), 7.12 (4H, m, H-3′-H-6′).

4′,5-DIHYDROXY-6-(3,3-DIMETHYLALLYL)-7-METHOXYFLAVANONE (**4**).—Yellow needles from petroleum ether-EtOAc, mp 138°; ms *m/z* (rel. int.) 354.1460 (M^+, 60) (calcd. for $C_{21}H_{22}O_5$ 354.1467), 339 (16), 311 (16), 299 (67), 219 (24), 206 (14), 179 (100), 120 (14); uv 287, 338 nm; ir 3350, 1620, 1600, 1380, 1340 cm^{-1}; ^{1}H nmr (90 MHz) δ 1.69, 1.79 (2×3H, 2×s, 3″-Me_2), 2.73 (1H, dd, *J*=16, 5, H-3_{eq}), 3.09 (1H, dd, *J*=16, 12, H-3_{ax}), 3.23 (2H, d, *J*=8, 1″-CH_2), 3.82 (3H, s, 7-OMe), 5.21 (1H, t, *J*=8, H-2″), 5.35 (1H, dd, *J*=12, 5, H-2_{ax}), 6.08 (1H, s, H-8), 6.86 (2H, ABq, *J*=9, H-3′, H-5′), 7.36 (2H, ABq, *J*=9, H-2′, H-6′), 12.05 (1H, s, 5-OH).

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