

# ANTITUMOR PLANTS. PART IX.<sup>1</sup> STRUCTURAL REASSIGNMENTS FOR THREE FLAVONOIDS FROM *LYCHNOPHORA AFFINIS* GARDN.

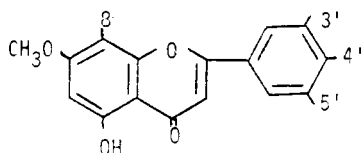
P. W. LE QUESNE, MARY D. MENACHERY and R. F. RAFFAUF

*Department of Chemistry, and Department of Medicinal Chemistry and Pharmacology, Northeastern University, Boston, Massachusetts 02115*

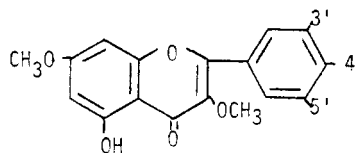
In previous work, structures 1-5 were assigned to five flavonoids obtained from *L. affinis* (1). Interest in these compounds was stimulated by observations that some of them showed activity *vs.* the KB cell culture; our investigations of the background of such activity have recently been published (2). At the time (1), the structural assignments were made primarily on the basis of ultraviolet and mass spectra. During the course of structural determination of some other flavonoids in our laboratory, we re-

to be *meta*-related doublets (H-6 and H-8).

Reinterpretation of all the spectral data leads us to revise the structures of compounds 1, 3, and 4, to 6, 7, and 8, respectively. Compound 6 is 5-hydroxy-3,3',4',7-tetramethylquercetin, compound 7 is 3,3',7-trimethylquercetin, and compound 8 is 3',5-dihydroxy-4',5',3,7-tetramethoxyflavone. These compounds are known to the literature. We do not wish to alter our assignments of structures 2 and 5.



	3'	4'	5'	8	KB
1	OCH <sub>3</sub>	OCH <sub>3</sub>	H	OCH <sub>3</sub>	-
2	OCH <sub>3</sub>	OCH <sub>3</sub>	H	H	-
3	OCH <sub>3</sub>	OH	H	OCH <sub>3</sub>	+
4	OH	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	+
5	OH	OCH <sub>3</sub>	H	H	+



	3'	4'	5'
6	OCH <sub>3</sub>	OCH <sub>3</sub>	H
7	OCH <sub>3</sub>	OH	H
8	OH	OCH <sub>3</sub>	OCH <sub>3</sub>

examined these spectral data, particularly in the context of a considerable body of nmr data which has accumulated.

In the nmr spectra first obtained, signals thought to be singlets were assigned to H-3 and H-6 (original structures). Better spectra obtained subsequently have shown these signals

## EXPERIMENTAL

*5-Hydroxy-3,3',4',7-tetramethylquercetin* 6.—Yellow crystals from chloroform-acetone mp 159-160°C (cf. lit (3) mp 158-159°); ir,  $\nu$  (KBr) 3350 weak (OH), 2900, 2800 (C-H), 1640 (C=O), 1570 and 1480 cm<sup>-1</sup> (aromatic); uv, (nm, log  $\epsilon$  in parentheses)  $\lambda$  max (MeOH) 253 (4.28), 269 (4.20), 303 sh (4.05), 352 (4.39) (cf. lit (4));  $\lambda$  max (MeOH-AlCl<sub>3</sub>) 275 (4.31) 298 (3.94), 365 (4.28), 298 (3.96), 360 (4.26), 402 (4.29);  $\lambda$  max (MeOH-AlCl<sub>3</sub>-HCl) virtually identical;  $\lambda$  max (MeOH-NaOCH<sub>3</sub>) 253 (4.32), 270 (4.27), 303 sh (4.18), 352 (4.40);  $\lambda$  max (MeOH-unfused NaOAc) 253 (4.30), 269 (4.21), 302 sh (4.06), 352 (4.39);  $\lambda$  max (MeOH-NaOAc-H<sub>3</sub>BO<sub>3</sub>) 252 (4.32), 268 (4.24), 305 sh (4.07), 352 (4.40); Nmr  $\delta$

<sup>1</sup>For Part VIII, see R. F. Raffaaf, M. P. Pastore, C. J. Kelley, P. W. Le Quesne, I. Miura, K. Nakanishi, J. Finer and J. Clardy, *J. Am. Chem. Soc.*, **100**, 7437 (1978).

CDCl<sub>3</sub> (*cf. lit.* (5)) 3.85 (s, 6H, 2 OCH<sub>3</sub>); 3.95 (s, 6H, 2 OCH<sub>3</sub>); 6.32 d, (1H, *J*=2 Hz, H-6); 6.42 (d, 1H, *J*=2 Hz, H-8); 6.96 (d, 1H, *J*=9 Hz, H-5'); 7.66-7.72 (m, 2H, H-2', 6'); 12.62 (s, 1H, 5-OH); mass spectrum, *m/e* (relative intensity) 358 (100) M<sup>+</sup>, 357 (49) (M-H)<sup>+</sup>, 343 (45) (M-CH<sub>3</sub>)<sup>+</sup>, 327 (15)

(M-OCH<sub>3</sub>)<sup>+</sup>, 315 (50) (M-CH<sub>3</sub>C)<sup>+</sup>, 166 (12). Retro-Diels-Alder fragment at *m/e* 166 (*cf. lit.* (6)).

**3,3',7-Trimethylquercetin 7.**—Mp from MeOH 167.5-168°C (*cf. lit.* (7)) mp 167-168.5°; ir,  $\nu$  (KBr) 3400 (OH), 2925, 2850 (C-H), 1660 (C=O), 1580, 1500 and 1460 cm<sup>-1</sup> (aromatic); uv  $\lambda$  max (MeOH) 254 (4.01), 268 (4.00), 302 sh (3.79), 355 (4.27); (*cf. lit.* (4));  $\lambda$  max (MeOH-AlCl<sub>3</sub>) 272 (4.15), 300 (3.68), 370 (4.14), 405 (4.27);  $\lambda$  max (MeOH-AlCl<sub>3</sub>-HCl) 273 (4.14), 300 (3.77), 365 (4.14), 404 (4.24);  $\lambda$  max (MeOH-CH<sub>3</sub>ONa) 230 sh (4.16), 263 (4.21), 293 sh (3.88), 412 (4.50);  $\lambda$  max (MeOH-unfused NaOAc) 254 (4.11), 268 (4.00), 300 sh (3.74), 355 (4.23);  $\lambda$  max (MeOH-NaOAc-H<sub>3</sub>BO<sub>3</sub>) 253 (4.14), 268 (4.03), 300 sh (3.82), 355 (4.27); nmr  $\delta$  CDCl<sub>3</sub> 3.85 (s, 6H, 2-OCH<sub>3</sub>); 3.95 (s, 3H, -OCH<sub>3</sub>), 6.32 (d, 1H, *J*=2 Hz, H-6), 6.42 (d, 1H, *J*=2 Hz, H-8), 7.0 (d, 1H, *J*=9 Hz, H-5'), 7.64 (m, 2H, H-2' and H-6'), 12.62 (s, 1H, 5-OH); mass spectrum, *m/e* (rel. intensity) 344 (100) M<sup>+</sup>, 343 (55) (M-H)<sup>+</sup>, 329 (51) (M-CH<sub>3</sub>)<sup>+</sup>, 313 (17), (M-OCH<sub>3</sub>)<sup>+</sup>, 301 (56) (M-CH<sub>3</sub>CO)<sup>+</sup> (*cf. lit.* (6)).

**3',5-Dihydroxy-4',5',3,7-tetramethoxyflavone 8.**—Yellow crystals from MeOH, mp 141-146° (*cf. lit.* (7)) mp 145-150°; ir  $\nu$ -KBr 3390 (OH), 2900, 2825 (C-H), 1640 (C=O), 1580, 1500 and 1440 cm<sup>-1</sup> (aromatic), uv (*cf. lit.* (8))  $\lambda$  max (MeOH) 263 (3.95), 306 sh (3.69), 343 (3.79);  $\lambda$  max (MeOH-AlCl<sub>3</sub>) 276 (3.85), 300 sh (3.52), 354 (3.69), 398 (3.66);  $\lambda$  max

(MeOH-AlCl<sub>3</sub>-HCl) 276 (3.84), 300 sh (3.54) 348 (3.69), 398 (3.61);  $\lambda$  max (MeOH-CH<sub>3</sub>ONa) 263 (4.02), 350 (3.77);  $\lambda$  max (MeOH-unfused NaOAc) 263 (4.02), 340 (3.79);  $\lambda$  max (MeOH-NaOAc-H<sub>3</sub>BO<sub>3</sub>) 263

(4.02), 340 (3.80); nmr  $\delta$  CDCl<sub>3</sub>-C-CD<sub>3</sub> 3.88, 3.91, 3.92 and 3.93 (s, 12H, 4-OCH<sub>3</sub>), 6.34 (d, 1H, *J*=2 Hz, H-6), 6.67 (d, 1H, *J*=2 Hz, H-8), 7.35 (unresolved, 2H, H-2' and H-6'), 12.7 (s, 1H, 5-OH); mass spectrum, *m/e* (rel. intensity) 374 (100) M<sup>+</sup>, 373 (40) (M-H)<sup>+</sup>, 359 (75) (M-CH<sub>3</sub>)<sup>+</sup>, 331 (80)

(M-CH<sub>3</sub>C)<sup>+</sup>.

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