Phytochemistry, Vol. 24, No. 3, pp. 571–574, 1985.
Printed in Great Britain.

0031-9422/85 \$3.00 + 0.00
© 1985 Pergamon Press Ltd

FLAVONOIDS FROM THE SEEDS OF *LONCHOCARPUS COSTARICENSIS*

PETER G. WATERMAN and ELHADI N. MAHMOUD

Phytochemistry Research Laboratories, Department of Pharmacy (Pharmaceutical Chemistry), University of Strathclyde, Glasgow
GI 1XW, U.K.

(*Received* 3 *July* 1984)

Key Word Index—*Lonchocarpus costaricensis*; Leguminosae; β-hydroxychalcones; flavanones; flavones.

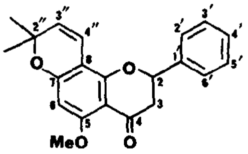
Abstract—Seven flavonoids have been isolated from the seeds of *Lonchocarpus costaricensis* of which four appear to be novel. The new compounds have been identified as the β-hydroxychalcone demethylpraecansone-B and the flavanones 7-(3,3-dimethylallyloxy)-8-(3-hydroxy-3-methyl-*trans*-but-1-enyl)flavanone, 7-(3,3-dimethylallyloxy)-8-(3,3-dimethylallyl)-5-methoxyflavanone and 8-(3,3-dimethylallyl)-5,7-dimethoxyflavanone.

INTRODUCTION

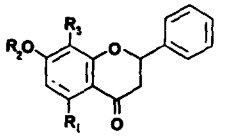
Lonchocarpus costaricensis Pittier is one of several trees of that genus found in the Santa Rosa National Park in Costa Rica [1]. As part of a wider investigation of plant chemistry in relation to patterns of herbivory in the Park [2], we have analysed the seeds of this species. This has yielded seven flavonoids typical of *Lonchocarpus* and related genera. Four of the isolated compounds are reported for the first time.

RESULTS AND DISCUSSION

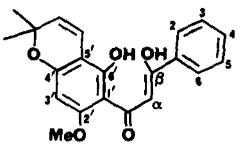
The powdered seeds were extracted with petrol (bp 60–80°). Column chromatography of the resulting concentrate followed, where necessary, by preparative circular TLC gave seven flavonoids, three of which were identified as ovalichalcone [3], obovatin methyl ether (**1**) [4] and isopongaflavone (**2**) [5]. The remaining four flavonoids appear to be novel and have been identified on the basis of spectral analysis as the β-hydroxychalcone (**3**)



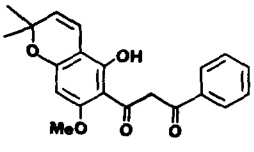
1
2 (Δ^{23})



	R_1	R_2	R_3
4	H	$CH_2CH=C(Me)_2$	$CH\overset{t}{=}CHC(OH)Me_2$
5	OMe	$CH_2CH=C(Me)_2$	$CH_2CH=C(Me)_2$
6	OMe	Me	$CH_2CH=C(Me)_2$



3



7

and the flavanones **4**–**6**. The ^{13}C NMR spectra of **1**–**6** have been recorded and are listed in Table 1.

The β-hydroxychalcone analysed for $C_{21}H_{20}O_5$. The ^{1}H NMR spectrum showed resonances typical of a 2,2-dimethylpyran ring, an H-bonded 6′-hydroxy substituent, a methoxy group, two multiplets for an unsubstituted aromatic ring and two singlets (1H each). The more shielded singlet (δ5.92) could be attributed to a single A-ring proton and the other (δ7.30) to the α-proton of the chalcone. These data suggested **3** or its isomer with a 4′-OMe substituent and the chromene between C-5′ and C-6′ and this was sustained by both the EI mass spectrum and the ^{13}C NMR spectrum. An interesting feature of the ^{1}H NMR spectrum run in $CDCl_3$ was the rapid appearance of a second series of signals, the most obvious of which were singlets at δ3.41 (α-methylene) and δ4.50 (2′-OMe), due to the conversion of **3** to the diketo tautomer **7**, which reached an approximately 50:50 equilibrium after 24 hr. The highly deshielded position of the methoxy resonance in **7** required its placement at C-2′ where it would be influenced by the diketo side chain. ^{1}H NMR analysis of **3** in CCl_4 failed to show formation of the tautomer.

Compound **3** is closely allied to the β-oxygenated chalcones praecansone-A and -B reported from *Tephrosia praecans* [6]. On treatment with aluminium chloride praecansone-A was reported [6] to give the β-diketone **7** but both the structure shown and the ^{1}H NMR data reported for that product (run in CCl_4) agree with those recorded here for **3**.

The first of the new flavanones analysed for $C_{25}H_{28}O_4$. The IR spectrum showed the presence of an aliphatic hydroxyl and the ^{1}H NMR spectrum a flavanone skeleton with an unsubstituted B-ring. For the A-ring an AB quartet ($J = 10$ Hz) centred at δ6.64 and 7.78 indicated unsubstituted C-6 and C-5 and a series of signals typical of a 3,3-dimethylallyloxy unit which must be placed at C-7. The remaining C_5H_9O unit, to be placed at C-8, gave singlets at δ1.38 (6H) and 6.80 (2H) for equivalent methyl and olefinic protons. This suggested that the C-8 substituent was a 3-hydroxy-3-methyl-but-1-enyl unit in which H-1 and H-2 were equivalent. To confirm this, the

Table 1. ^{13}C NMR chemical shift values of flavonoids from *L. costaricensis**

Carbon No.	**3**	**7**	**4**	**5**	**6**	**1**	**2**
2 (β)	176.5	200.0	79.6	78.6	78.7	79.0	160.8
3 (α)	98.9	55.3	44.2	45.8	45.8	45.7	109.0
4 (C=O)	195.0	195.2	191.1	189.8	189.8	189.0	177.6
4a (1′)	103.4	103.8	115.4^{a}	106.1	106.2	105.8	109.0
5 (2′)	161.0^{a}	161.8^{a}	128.5^{b}	161.1	161.1	160.0	154.0
6 (3′)	92.3	93.0	106.4	90.1	88.9	93.8	96.7
7 (4′)	163.4	163.4	162.7	162.7	163.3	162.2	160.2
8 (5′)	104.9	106.1	114.2^{a}	110.7	110.4	102.9	102.8
8a (6′)	161.9^{a}	162.7^{a}	160.3	160.6	160.8	158.8	158.0
1′ (1)	135.0†	137.9†	139.0^{c}	139.4	139.4	139.0	131.9
2′ (2)	129.7†	129.6†	125.8	125.9	125.9	125.9	125.9
3′ (3)	127.5†	128.9†	128.7	128.6	128.6	128.7	129.0
4′ (4)	134.0†	132.9†	127.7^{b}	128.5	128.2	126.3^{a}	131.2
5′ (5)	127.5†	128.9†	128.7	128.6	128.6	128.7	129.0
6′ (6)	129.7†	129.6†	125.8	125.9	125.9	125.9	125.9
7,8-pyran							
2 (Me)$_2$	28.6	28.6				28.2/28.5	28.3
2	79.0	78.8				78.0	78.1
3	116.2	116.5				116.0	115.3
4	126.6	126.6				128.5^{a}	127.6
7-O-prenyl							
1			65.9	65.3			
2			119.2	122.7			
3			138.4^{c}	138.2			
3 (Me)$_2$			18.3/25.7	18.3/25.7			
8-prenyl							
1			115.0	22.2	21.9		
2			143.0	119.4	122.6		
3			71.5	131.1	131.3		
3 (Me)$_2$			29.2	17.7/25.8	17.7/25.8		
OMe	56.7	56.2		56.1	55.7/56.1	56.2	56.5

*Spectra run at 62.5 MHz in $CDCl_3$ with TMS as internal standard. Carbon numbers in parentheses refer to numbering for the chalcone nucleus. Identical superscripts within columns denote interchangeable signals.

†Tentative assignments.

flavanone was acetylated and the ^{1}H NMR spectrum rerun. In this case, the olefinic protons appeared as an AB quartet with $J = 18$ Hz, confirming the *trans* nature of the double bond. Both ^{13}C NMR (Table 1) and EI mass spectral data supported the identification of this compound as 7-(3,3-dimethylallyloxy)-8-(3-hydroxy-3-methyl-*trans*-but-1-enyl)flavanone (**4**).

The second flavanone analysed for $C_{26}H_{30}O_4$. The ^{1}H NMR spectrum again confirmed the presence of a flavanone, an unsubstituted B-ring and a 3,3-dimethylallyloxy unit. Further signals for a 3,3-dimethylallyl unit, a methoxy group and a single A-ring proton suggested structure **5**. This was substantiated by the ^{13}C NMR which showed shielded C-6 and 5-OMe resonances typical of 5-methoxy-7,8-disubstituted flavanones.

The final flavanone analysed for $C_{22}H_{24}O_4$ and gave a ^{1}H NMR spectrum identical to **5** except for the absence of signals for the 3,3-dimethylallyloxy unit and their replacement by the resonance of a second methoxy group. This compound must be assigned structure **6**, the ^{13}C signals for the two methoxy substituents at 55.7 and 56.1 ppm requiring that both have an adjacent carbon unsubstituted and thereby ruling out the alternative 6-prenyl compound. Surprisingly **6** appears to be novel.

The seven flavonoids isolated from *L. costaricensis* seeds are all simple 8-prenylated flavonoids. Both **3** and **4** have modifications typical of the Tephrosieae [7] but no isoflavonoids could be detected during this study.

EXPERIMENTAL

UV: MeOH. IR: KCl. ^{1}H NMR: in $CDCl_3$ at 90 MHz with TMS as internal standard. EIMS: 70 eV with direct probe insert at 120–140°. Petrol refers to bp 60–80° fraction. Mps are uncorr.

Plant material. Seeds of *L. costaricensis* were collected in the Santa Rosa National Park, Costa Rica in 1983.

Extraction and separation. Ground seeds (420 g) were extracted with petrol, then $CHCl_3$, and finally MeOH. Concn of the petrol extract gave a brown oil, part of which was subjected to CC over silica gel. Elution with petrol containing 5% EtOAc gave **3** (290 mg). Elution with 10% EtOAc gave a mixture which was separated by prep. TLC (silica gel, solvent: petrol–EtOAc, 4:1) to give more **3** (20 mg) and ovalichalcone (19 mg). Elution with 25% EtOAc gave a mixture from which **1** (413 mg) was obtained by repeated recrystallization. Prep. TLC of the supernatant (silica gel, solvent: toluene–EtOAc–HOAc, 94:5:1) gave **4** (54 mg). Elution with 40% EtOAc gave a mixture separated by prep. TLC (silica gel, solvent: toluene–EtOAc–HOAc, 90:10:1) to give **5** (43 mg) followed by **6** (430 mg). Finally, elution with 70% EtOAc gave **2** (67 mg).

Demethylpraecansone-B (**3**). Yellow needles from petrol–EtOAc, mp 128–130° (lit. [6] 105–107°). Found: $[M]^+$ 352.1317; $C_{21}H_{20}O_5$ requires: 352.1311. UV λ_{max} nm: 272, 295, 369. IR ν_{max} cm^{-1}: 1640, 1600, 1580, 1280. ^{1}H NMR: δ1.42 (6H, *s*, 2″-Me$_2$), 3 90 (3H, *s*, 2′-OMe), 5.45 (1H, *d*, $J = 10$ Hz, H-3″), 5.92 (1H, *s*, H-3′), 6.67 (1H, *d*, $J = 10$ Hz, H-4″), 7.30 (1H, *s*, H-α), 7.43 (3H, *m*, H-3, H-4, H-5), 7.85 (2H, *m*, H-2, H-6), 13.62 (1H, *s*, 6′-OH). ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 352 $[M]^+$ (66), 337 (64), 232 (4), 217 (100), 191 (27), 105 (27), 77 (20). On standing, a $CDCl_3$ solution of **3** formed an equilibrium mixture with **7** which showed the following NMR characteristics attributable to **7**. ^{1}H NMR: δ1.42 (6H, *s*, 2″-Me$_2$), 3.41 (2H, *s*, CH$_2$–), 4.50 (3H, *s*, 2′-OMe), 5.44 (1H, *d*, $J = 10$ Hz, H-3″), 5.79 (1H, *s*, H-3′), 6.66 (1H, *d*, $J = 10$ Hz, H-4″), 7.43 (3H, *m*, H-3, H-4, H-5), 7.85 (2H, *m*, H-2, H-6), 13.92 (1H, *s*, 6′-OH). ^{13}C NMR: see Table 1.

Ovalichalcone. Yellow needles from petrol–EtOAc, mp 117° (lit. [3] 123–124°). Found: $[M]^+$ 352.1669; $C_{22}H_{24}O_4$ requires: 352.1674. UV, IR, ^{1}H NMR in agreement with published data [3].

7-(3,3-*Dimethylallyloxy*)-8-(3-*hydroxy*-3-*methyl*-trans-*but*-1-*enyl*)*flavanone* (**4**). Plates from petrol–EtOAc, mp 82°. Found: $[M]^+$ 392.1989; $C_{25}H_{28}O_4$ requires: 392.1987. UV λ_{max} nm: 259, 297, 345. IR ν_{max} cm^{-1}: 3350, 1680, 1600, 1440. ^{1}H NMR: δ1.38 (6H, *s*, 3‴-Me$_2$), 1.77 (6H, *s*, 3″-Me$_2$), 2.89 (1H, *dd*, $J = 18$, 5 Hz, H-3$_{eq}$), 3.15 (1H, *dd*, $J = 18$, 12 Hz, H-3$_{ax}$), 4.63 (2H, *d*, $J = 7$ Hz, H-1″), 5.45 (1H, *t*, $J = 7$ Hz, H-2″), 5.47 (1H, *dd*, $J = 12$, 5 Hz, H-2), 6.64 (1H, *d*, $J = 10$ Hz, H-6), 6.80 (2H, *s*, H-1‴, H-2‴), 7.43 (5H, *m*, H-2′–H-6′), 7.82 (1H, *d*, $J = 10$ Hz, H-5). ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 392 $[M]^+$ (6), 374 (37), 324 (17), 308 (17), 306 (78), 291 (72), 265 (33), 220 (23), 202 (40), 187 (61), 177 (25), 161 (37), 131 (28), 104 (46), 77 (31). Acetylation of **4** with acetic anhydride in C_5H_5N followed by normal work-up gave the acetate of **4**, mp 66–68°. IR ν_{max} cm^{-1}: 1740, 1680, 1600, 1460. ^{1}H NMR: δ1.24 (6H, *s*, 3‴-Me$_2$$^{),\ 1\ 75,\ 1\ 79\ (2}$ × 3H, 2 × *s*, 3″-Me$_2$), 1.92 (3H, *s*, Ac), 2.84 (1H, *dd*, $J = 16$, 5 Hz, H-3$_{eq}$), 3.08 (1H, *dd*, $J = 16$, 12 Hz, H-3$_{ax}$), 4.63 (2H, *d*, $J = 8$ Hz, H-1″), 5.49 (1H, *t*, $J = 8$ Hz, H-2″), 5.51 (1H, *dd*, $J = 12$, 5 Hz, H-2), 6.64 (1H, *d*, $J = 10$ Hz, H-6), 6.80, 7.31 (2H, AB*q*, $J = 18$ Hz, H-1‴, H-2‴), 7.41 (5H, *m*, H-2′–H-6′), 7.81 (1H, *d*, $J = 10$ Hz, H-5).

Obovatin methyl ether (**1**). Prisms from Et$_2$O, mp 155° (lit. [4] 163°). Found: $[M]^+$ 336.1364; $C_{21}H_{20}O_4$ requires: 336.1361. UV, IR, ^{1}H NMR in agreement with published data [4]. ^{13}C NMR: see Table 1.

7-(3,3-*Dimethylallyloxy*)-8-(3,3-*dimethylallyl*)-5-*methoxyflavanone* (**5**). Plates from petrol–EtOAc, mp 115–116°. Found: $[M]^+$ 406.2134; $C_{26}H_{30}O_4$ requires: 406.2144. UV λ_{max} nm: 287, 319. IR ν_{max} cm^{-1}: 1680, 1600, 1580. ^{1}H NMR: δ1.60 (6H, *s*, 3‴-Me$_2$), 1.80 (6H, *s*, 3″-Me$_2$), 2.79 (1H, *dd*, $J = 16$, 5 Hz, H-3$_{eq}$), 3.02 (1H, *dd*, $J = 16$, 12 Hz, H-3$_{ax}$), 3.30 (2H, *d*, $J = 8$ Hz, H-1‴), 3.90 (3H, *s*, 5-OMe), 4.60 (2H, *d*, $J = 8$ Hz, H-1″), 5.19 (1H, *t*, $J = 8$ Hz, H-2‴), 5.46 (1H, *dd*, $J = 12$, 5 Hz, H-2), 5.49 (1H, *t*, $J = 8$ Hz, H-2″), 6.11 (1H, *s*, H-6), 7.40 (5H, *m*, H-2′–H-6′). ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 406 $[M]^+$ (99), 338 (70), 323 (13), 295 (22), 283 (17), 270 (10), 234 (97), 233 (34), 219 (26), 179 (56), 104 (13), 69 (100).

8-(3,3-*Dimethylallyl*)-5,7-*dimethoxyflavanone* (**6**). Needles from petrol–EtOAc, mp 98°. Found: $[M]^+$ 352.1663; $C_{22}H_{24}O_4$ requires: 352.1674. UV λ_{max} nm: 289, 319. IR ν_{max} cm^{-1}: 1680, 1600, 1580. ^{1}H NMR: δ1.62 (6H, *s*, 3″-Me$_2$), 2.79 (1H, *dd*, $J = 16$, 5 Hz, H-3$_{eq}$), 3.01 (1H, *dd*; $J = 16$, 12 Hz, H-3$_{ax}$), 3.27 (2H, *d*, $J = 8$ Hz, H-1″), 3.89, 3.90 (2 × 3H, 2 × *s*, 5-OMe, 7-OMe), 5.14 (1H, *t*, $J = 8$ Hz, H-2″); 5.40 (1H, *dd*, $J = 12$, 5 Hz, H-2), 6.11 (1H, *s*, H-6), 7.41 (5H, *m*, H-2′–H-6′). ^{13}C NMR: see Table 1 EIMS *m/z* (rel. int.): 352 $[M]^+$ (95), 284 (10), 248 (36), 233 (46), 219 (17), 205 (24), 193 (42), 191 (50), 104 (5), 77 (8).

Isopongaflavone (**2**). Plates from $CHCl_3$–MeOH, mp 203° (lit. [5] 201–205°). UV, IR, ^{1}H NMR in agreement with published data [5]. ^{13}C NMR: see Table 1.

Acknowledgements—One of us (E.N.M.) wishes to acknowledge the National Council for Research, Sudan, for the award of a scholarship Professor D. H. Janzen is thanked for the supply of plant material used in this study.

REFERENCES

1. Janzen, D. H. and Liesner, R. (1980) *Brenesia* **18**, 15.
2. Janzen, D. H. and Waterman, P. G. (1984) *Biol. J. Linn. Soc.* **21**, 439.
3. Gupta, R. K. and Krishnamurti, M. (1977) *Phytochemistry* **16**, 293.
4. Chen, Y. L., Wang, Y. S., Lin, Y. L., Munakata, K. and Ohta, K.

(1978) *Agric. Biol. Chem.* **42**, 2431.

5. Khalid, S. A. and Waterman, P. G. (1981) *Phytochemistry* **20**, 1719.
6. Camele, G., Delle Monache, F., Delle Monache, G. and Marini Bettolo, G. B. (1980) *Phytochemistry* **19**, 707.
7. Gomes, C. M. R., Gottlieb, O. R., Marini Bettolo, G. B., Delle Monache, F. and Polhill, R. M. (1981) *Biochem. Syst. Ecol.* **9**, 129.