Phytochemistry, Vol. 23, No. 2, pp. 443–447, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

FLAVONOIDS FROM *MILLETTIA PULCHRA*

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(*Received* 31 *May* 1983)

Key Word Index—*Millettia pulchra*; Leguminosae; Lototoidae; pterocarpans; 5-methoxypterocarpans; prenylated flavanones; prenylated dihydroflavonol; prenylated isoflavones.

Abstract—Chemical examination of *Millettia pulchra* yielded (−)-maackiain, (−)-pterocarpin, (−)-sophoranone and the new compounds (6*S*, 6a*S*, 11a*R*)-6α-methoxypterocarpin, (6*S*, 6a*S*,11a*R*)-6α-methoxyhomopterocarpin, (2*S*)-5,7,4′-trihydroxy-8,3′,5′-triprenylflavanone, (2*R*,3*R*)-7,4′-dihydroxy-8,3′,5′-triprenyldihydroflavanol, 5,7,2′,4′-tetrahydroxy-6,3′-diprenylisoflavone and 5,7,4′-trihydroxy-2′-methoxy-6,3′-diprenylisoflavone.

INTRODUCTION

In earlier articles we reported on the flavonoid constituents of the leaves and roots of *Milettia pachycarpa* from two different localities [1–3]. We now describe the isolation from *Millettia pulchra* Benth. of four pterocarpans, including two pterocarpans of a new type, two prenylated flavanones one of which is new, one new prenylated dihydroflavonol and two new prenylated isoflavones.

RESULTS AND DISCUSSION

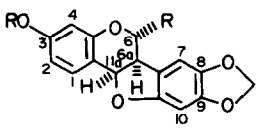
The pterocarpans were (−)-maackiain (**1a**) [4], (−)-pterocarpin (**1b**) [4] and the new 6-methoxypterocarpans **1c** (6α-methoxypterocarpin) and **2** (6α-methoxyhomopteocarpin). The nature and locations of the substituents on the aromatic rings of the two new compounds were obvious by comparing their ^{1}H NMR spectra (see Experimental) with those of other pterocarpans; the attachment of an aliphatic methoxyl (signal near δ 3.55) to C-6 of the pterocarpan nucleus was equally evident from the disappearance of one of the H-6 signals and the collapse of the H-6a signal to a double doublet. The magnitude of $J_{6,6a}$ (8.5 Hz) shows that the methoxyls of both new compounds are *cis* to H-6a and therefore α-orientated if the absolute configurations of **1c** and **2** were identical with those of (−)-maackiain and (−)-pterocarpin, a reasonable assumption in view of their co-occurrence.

That the absolute configurations of **1a** and **1b** are 6a*R*, 11a*R* as shown in the formulae [5] has been confirmed recently by X-ray analysis of (−)-4-bromo-3-*O*-methyledunal [6]. The effect of a C-6 methoxyl on the optical properties of pterocarpans is difficult to predict; although the CD curves of **1c** and **2** (see Experimental) exhibited a relatively strong positive Cotton effect near 290 nm opposite in sign to the relatively weak absorption shown in this vicinity by their unsubstituted 6a*R*, 11a*R*-analogs [6, 7], the strongly negative Cotton effect of **1c** and **2** centered near 235–240 nm tallied with that of ordinary 6a*R*,11a*R*-pterocarpans and we assume that it is this feature which indicates the absolute stereochemistry at C-6a. Consequently we ascribe the 6*S*, 6a*S*, 11a*R*-configuration shown in the formulae to **1c** and **2**.

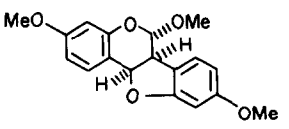
One of the two flavanones in *M. pulchra* was (−)-sophoranone (**3a**) [8]; the second was its new 5-hydroxy derivative **3b** as evidenced by the replacement, in the ^{1}H NMR spectrum, of the H-5 resonance of **3a** by a signal at δ 12.02. That the ring A prenyl group is attached to C-8 and not to C-6 was shown by the frequency of the remaining ring A proton signal at δ 6.01 [9]. The absolute stereochemistry of **3b** is that depicted in the formula because of its CD curve (see Experimental) which compares with those of other 2*S*-flavanones [10].

The new dihydroflavanol was the 3-hydroxy derivative **6a** of sophoranone. This deduction drawn from spectroscopic evidence was verified by zinc–acetic acid reduction of its triacetate **6b** to sophoranone diacetate (**3c**). The relative and absolute stereochemistry of **6a** shown in the formula is based on the magnitude of $J_{2,3}$ (12 Hz) and the CD curve (see Experimental), which compares with that of other 2*R*,3*R*-dihydroflavonols of established absolute configuration [10, 11].

The two new isoflavones **4a** and **4b** were interrelated by demethylation of **4b** to **4a** and by methylation of both compounds with diazomethane to the same trimethoxyisoflavone **4e** which still retained a chelated 5-hydroxyl group. The distribution of functions in ring A was deduced from the chemical shift of the single ring A proton near δ 6.40 which located it at H-8, as a δ 6.00 shift is expected for an H-6 signal [9]. The location of the methoxyl group at C-2′ of **4b** was indicated by its chemical shift (δ 3.54), a failure to undergo a benzene-induced solvent shift and the mass spectral fragmentation sketched in Scheme 1. Treatment of **4b** with formic acid effected cyclization of both prenyl groups to give **7** with H-8 now at slightly higher field (δ 6.28). Cyclodehydrogenation of **4b** with DDQ gave **8**. That the prenyl group on ring A and not that on ring B had undergone cyclodehydrogenation was shown by the chemical shift of H-8 (identical with that



1a R, R^1 = H
1b R = H, R^1 = Me
1c R = OMe, R^1 = Me



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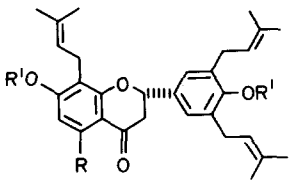
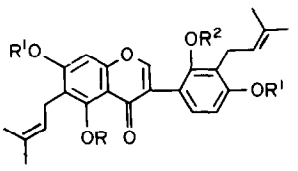
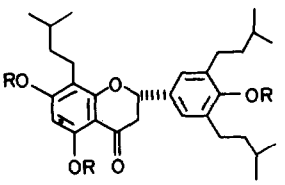


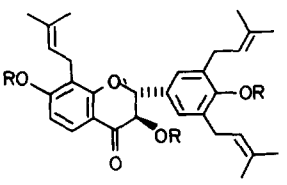
3a R, R^1 = H
3b R = OH, R^1 = H
3c R = H, R^1 = Ac
3d R = OAc, R^1 = Ac



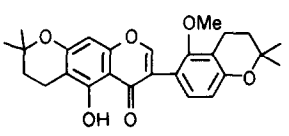
4a R, R^1, R^2 = H
4b R, R^1 = H; R^2 = Me
4c R, R^1, R^2 = Ac
4d R, R^1 = Ac; R^2 = Me
4e R = H; R^1, R^2 = Me



5a R = H
5b R = Ac



6a R = H
6b R = Ac



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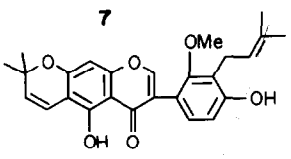

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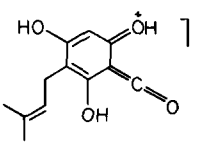
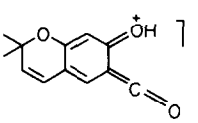


A(*m/z* 221)



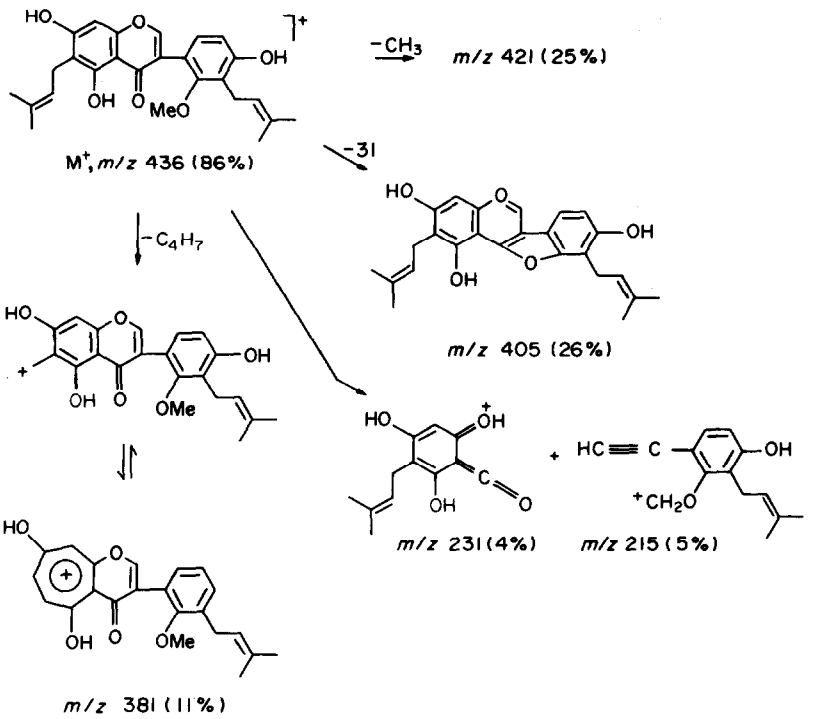
B(*m/z* 219)

in **7**) and the observation that in the mass spectrum of **8** ion **A** of **4a** and **4b** had been replaced by ion **B**.

EXPERIMENTAL

Extraction of Millettia pulchra. Above-ground material of *M. pulchra* Benth., wt 3 kg, collected in the Cherapunjee area of Meghalaya, India, was extracted with $CHCl_3$ in a Soxhlet until the extract was colorless. The crude extract obtained by evapn at red. pres. was dissolved in 500 ml MeOH containing 10% H_2O and left overnight. The ppt. was filtered and the filtrate washed with petrol (bp 60–80°, 6 × 200 ml). The MeOH layer was concd at red. pres. and the residue extracted with $CHCl_3$. Evapn of the washed and dried extract yielded 20 g of gum which was chromatographed over 350 g silica gel (60–120 mesh, BDH, India), 250 ml fractions being collected in the following order: fractions 1–35 (C_6H_6), 35–52 (C_6H_6–$CHCl_3$, 3:1), 53–61 (C_6H_6–$CHCl_3$, 2:1), 62–70 (C_6H_6–$CHCl_3$, 1:1), 71–86 ($CHCl_3$), 87–132 ($CHCl_3$–MeOH, 99:1), 133–168 ($CHCl_3$–MeOH, 49:1), 169–183 ($CHCl_3$–MeOH, 31:1), 184–198 ($CHCl_3$–MeOH, 19:1), 199–212 ($CHCl_3$–MeOH, 4:1), 213–219 ($CHCl_3$–MeOH, 9:1), 220–226 ($CHCl_3$–MeOH, 4:1), 227–229 ($CHCl_3$–MeOH, 1:1), 230–232 (MeOH).

Fractions 4–7 which showed a single spot on TLC (petrol–C_6H_6, 1:1) were combined (115 mg) and purified by TLC to give 90 mg (−)-pterocarpin (**1b**), mp 164–164.5° (MeOH–$CHCl_3$). lit. mp 165° [12], $[\alpha]_D$ −167° ($CHCl_3$, *c* 0.34 g/100 ml); ^{1}H NMR spectrum (270 MHz, $CDCl_3$): δ 7.40



Scheme 1. Selected mass spectral fragmentation of **4b**.

(*d*, 9, H-1), 6.71 (H-7), 6.63 (*dd*, 9, 2, H-2), 6.47 *d* (2, H-4), 6.43 (H-10), 5.90 (AB system, $-OCH_2O$), 5.49 (*d*, 7, H-11a), 4.23 (*dd*, 12, 5, H-6), 3.79 (OMe), 3.66 (*t*, 12, H-6'), 3.49 (*ddd*, H-6a); MS *m/z*: 298 $[M]^+$, 284, 267, 210, 175, 165 and 161.

TLC of fractions 8–10 showed two spots. Prep. TLC (petrol–C_6H_6, 1:1) yielded 10 mg of less polar **1c** as a gum, IR ($CHCl_3$) 1615, 1585, 1315, 1225, 1035, 925 and 875 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.39 (*d*, 8, H-1), 6.64 (*dd*, 8, 2, H-2), 6.49 (*d*, 2, H-4), 5.62 (*dbr*, 8.5, H-6), 3.46 (*ddbr*, 8.5, 7, H-6a), 6.80 (*br*, H-7), 6.39 (H-10), 4.72 (*d*, 7, H-11a), 5.90 ($-OCH_2O-$), 3.79, 3.56 (OMe); CD curve (MeOH) $[\theta]_{305}$ + 11 700 (max), $[\theta]_{295}$ + 10 400 (min), $[\theta]_{289}$ + 11 040 (max), $[\theta]_{266}$ 0, $[\theta]_{238}$ − 59 100 (neg. max); [Calc. for $C_{18}H_{16}O_6$: MW, 328.0947. Found: MW (MS), 329.0920]. Other significant ions were at *m/z* (rel. int.) 296 (39.3), 234 (14.9), 219 (10.8), 193 (7.2), 181 (43.6) and 169 (39.6). The more polar material (**2**, 14 mg) was also a gum, IR ($CHCl_3$) 1625, 1450, 1350, 1145, 950 and 875 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.40 (*d*, 8, H-1), 6.65 (*dd*, 8, 2, H-2), 6.50 (*d*, 2, H-4), 5.67 (*dbr*, 8.5, H-6), 3.56 (obsc., H-6a), 7.21 (*dbr*, 8, H-7), 6.47 (*dd*, 8, 2, H-8), 6.41 (*d*, 2, H-10), 4.76 (*d*, 6.5, H-11a), 3.79, 3.75, 3.56 (OMe); CD curve (MeOH) $[\theta]_{285}$ + 23 700 (max), $[\theta]_{260}$ 0; $[\theta]_{236}$ − 70 600 (neg. max); [Calc. for $C_{18}H_{18}O_5$: MW, 314.1154. Found: MW (MS), 314.1127]. Other significant ions were at *m/z* (rel. int.) 282 (23.1), 231 (12.9), 219 (5.5), 181 (44.1) and 169 (33.2).

Fractions 11–15 which showed two spots on TLC (275 mg) were combined. Prep. TLC (petrol–EtOAc, 7:1) gave 115 mg of less polar **3b**, mp 117–119° (MeOH), IR (KBr) 3200, 1630, 1605, 1250, 1190, 1150 and 1065 cm^{-1}; UV λ_{max}^{MeOH} 242, 288 nm; CD curve $[\theta]_{330}$ + 11 450 (max), $[\theta]_{313}$ + 6730 (sh), $[\theta]_{307}$ 0, $[\theta]_{290}$ − 53 900 (neg. max), $[\theta]_{262}$ 0, $[\theta]_{255}$ + 4040 (max); ^1H NMR (270 MHz, $CDCl_3$): δ 5.28 (H-2, part. obsc.), 3.04 (*dd*, 17, 13, H-3a), 2.77 (*dd*, 17, 3, H-3b), 6.01 (H-6), 7.05 (2H, H-2' and H-6'), 3.28 (*dbr*, 6, 2H, methylenes of ring A prenyl), 5.28 (*tbr*, 6, vinyl H of ring A prenyl), 3.36 (*dbr*, 6, 4H, methylenes of ring B prenyls), 5.32 (*tbr*, 6, 2H, vinyl Hs of ring B prenyls), 1.76 (*br*, 6Me), 12.02 (5-OH); [Calc. for $C_{30}H_{36}O_5$: MW, 476.2560. Found: MW(MS), 476.2568]. Other significant ions in the low resolution MS were at *m/z* (rel. int.) 459 (15.2), 421 (12.0), 282 (13.2), 256 (11.7), 243 (63.1), 233 (14.5), 221 (33.4), 220 (38.4), 219 (44.5), 2.05 (77.7), 203 (12.9), 201 (25.8), 192 (32.0), 187 (11.5), 185 (22.7), 177 (42.0) and 165 (81.9). Acetylation (Ac_2O–pyridine) of 50 mg **3b** followed by the usual work-up and prep. TLC (petrol–EtOAc, 10:1) gave 50 mg **3d** as a gum, IR ($CHCl_3$) 1755, 1680, 1600, 1365, 1262, 1175, 1120, 1035, 1000, 898 and 750 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 5.4 (*dd*, 13, 3, H-2), 2.96 (*dd*, 17, 13, H-3a), 2.76 (*dd*, 17, 3, H-3b), 6.52 (H-6), 7.14 (2H, H-2' and H-6'), 3.25 (*dbr*, 6, 2H, methylene of ring A prenyl), 5.09 (*tbr*, 6, vinyl H of ring A prenyl), 3.22 (*dbr*, 6, 4H, methylenes of ring B prenyls), 5.23 (*tbr*, 6, 2H, vinyl Hs of ring B prenyls), 2.36, 2.32, 2.30 (Ac), 1.76 (*br*, 2Me), 1.73 (*br*, Me), 1.69 (*br*, 2Me), 1.65 (*br*, Me); MS *m/z* (rel. int.): 560 $[M]^+$ (6.9), 559 (10.6), 543 (4.9), 533 (5.3), 518 (6.9), 517 (11.3), 515 (8.2), 501 (10.1), 321 (11.3), 305 (16.5), 279 (13.3), 263 (24.1), 261 (29.9), 255 (13.6), 247 (14.9), 243 (12.8), 239 (32.8), 237 (18.2), 227 (11.1), 221 (23.8), 220 (29.1), 219 (100).

The more polar material from fractions 11–15 was (−)-maackiain (**1a**), 135 mg, mp 177–177.5° (MeOH–$CHCl_3$), lit. mp 178.5–179° [12], $[\alpha]_D$ − 223° (MeOH; *c* 0.07 g/100 ml); IR (KBr) 3350, 1610, 1500, 1145, 1025, 930 and 810 cm^{-1}; UV λ_{max}^{MeOH} 287 nm; ^1H NMR (270 MHz, $CDCl_3$): δ 7.36 (*d*, 8, H-1), 6.71 (H-7), 6.56 (*dd*, 8, 1.5, H-2), 6.43 (H-10), 6.42 (*d*, 1.5, H-4), 5.91 (*d*) and 5.86 *d* (AB, $-O-CH_2-O-$), 5.47 (*d*, 7, H-11a), 4.21 (*dd*, 11, 4, H-6), 3.36 (*t*, 11, H-6'), 3.47 (*m*, H-6a); MS: *m/z* 284 $[M]^+$, 267, 242, 235, 162 and 161. Methylation of **1a** with excess CH_2N_2 gave **1b**.

Fractions 18–25 (0.63 g) was a mixture which on separation by prep. TLC (petrol–EtOAc, 5:1) yielded as the less polar material 0.485 g **1a** and as the more polar material 109 mg (−)-sophoranone (**3a**), mp 107°; $[\alpha]_D^{20}$ − 15°; lit. mp 108°, $[\alpha]_D^{25}$ − 13°

[8]; IR (KBr) 3350, 1625, 1575, 1275, 1190 and 1030 cm^{-1}; UV λ_{max}^{MeOH} 369, 284 nm, λ_{max}^{NaOAc} 340, 284 nm. Acetylation (Ac_2O–pyridine) of 50 mg **1a** gave 45 mg **3c**, mp 123–124°, lit. mp 124° [8]; ^1H NMR (270 MHz, $CDCl_3$): δ 7.81 (*d*, 9, H-5), 7.14 (2H, H-2′, 6′), 6.75 (*d*, 9, H-6), 5.46 (*dd*, 13, 3, H-2), 5.21 (*tbr*, 7, two vinyl Hs of ring B prenyl), 5.10 (*tbr*, 7, vinyl H of ring A prenyl R) 3.28 (*dbr*, 7, 2H, benzylic Hs of ring A prenyl), 3.21 (*dbr*, 7, 4Hs, benzylic Hs of ring B prenyls), 2.93 (center of AB system of H-3a, b, $J_{3a,b}$ = 16 Hz, $J_{2,3a}$ = 13 Hz, $J_{2,3b}$ = 3 Hz), 2.31, 2.31 (Ac), 1.75 (2 vinyl Me), 1.69 (2 vinyl Me), 1.65, 1.61 (vinyl Me).

Fractions 26–32 (105 mg) were an inseparable mixture of several compounds. TLC of fractions 105–129 (0.23 g) indicated the presence of two compounds which were separated by prep. TLC (EtOAc–C_6H_6, 1 : 7). The less polar material was **4a** (105 mg), mp 145–146° ($CHCl_3$–C_6H_6); IR ($CHCl_3$) 3550, 1650, 1600, 1565, 1160, 1080, 1025, 925 and 885 cm^{-1}; UV λ_{max}^{MeOH} 320 nm, λ_{max}^{NaOAc} 350 nm; ^1H NMR (270 MHz, $CDCl_3$): δ 12.28 (5-OH), 8.01 (H-2), 6.39 (H-8), 6.90 (*d*, 8) and 6.50 (*d*, 8, H-5′ and H-6′), 3.55 (*dbr*, 6) and 3.50 (*dbr*, 6, 4H benzylic Hs), 5.32 (*tbr*, 6) and 5.24 (*tbr*, 6, 2H, vinyl Hs of prenyls), 1.84 (2Me) and 1.75 (2Me); [Calc. for $C_{25}H_{26}O_6$: MW, 422.1729. Found: MW(MS), 422.1699]. Other significant ions in the MS were at *m/z* (rel. int.) 379 (16.6), 367 (33.1), 351 (10.8), 323 (16.5), 311 (18.2), 253 (11.3), 221 (13.4), 219 (13.6), 205 (12.4), 203 (15.9) and 165 (42.0).

Acetylation of 40 mg **4a** (Ac_2O–pyridine) followed by the usual work-up and purification by prep. TLC (C_6H_6–EtOAc, 9 : 1) gave 21 mg **4c** as a gum, IR ($CHCl_3$) 1750, 1650, 1605, 1365, 1260, 1155, 1075, 994 and 878 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.84 (H-2), 6.84 (H-8), 7.16 *d* (8) and 7.04 (*d*, H-5′ and H-6′), 3.47 (*dbr*, 6, 2H) and 3.36 (*dbr*, 6, 2H, methylenes of prenyls), 5.14 (*tbr*, 6) and 5.03 (*tbr*, vinyl Hs of prenyls), 2.37, 2.35, 2.29, 2.12 (Ac), 1.80 (Me), 1.72 (2Me), 1.68 (Me); ^1H NMR (C_6D_6): δ 7.24 (H-2), 6.78 (H-8) 7.04 and 6.83 (H-5′ and H-6′), 3.30 (methylenes), 5.24 and 5.16 (vinyl Hs of prenyls), 2.18, 1.85, 1.81, 1.75 (Ac), 1.64, 1.59, 1.55, 1.53 (Ac); MS *m/z* (rel. int.): 590 $[M]^+$ (37.4), 549 (27.1), 548 (46.7), 531 (13.7), 507 (24.6), 506 (88.2), 505 (81.7), 504 (20.2), 489 (22.7) 464 (48.6), 463 (100), 451 (20.6), 447 (28.7), 422 (27.1), 421 (60.1), 418 (24.4), 409 (30.5), 379 (24.0), 367 (29.6), 365 (45.2), 351 (20.9), 323 (41.1), 311 (32.1), 219 (45.5), 203 (27.4), 177 (20.6) and 165 (47.7).

The more polar material from fractions 105–129 (52 mg) was a mixture from which **6a** (23 mg) was separated by TLC (petrol–EtOAc, 1 : 2), mp 135–139° (C_6D_6–petrol); IR ($CHCl_3$) 3200, 1675, 1675, 1650, 1600, 1250 and 1130 cm^{-1}; UV λ_{max}^{MeOH} 348, 290 nm, λ_{max}^{NaOAc} 362 nm; CD (MeOH) $[\theta]_{320}$ + 15450 (max), $[\theta]_{310}$ 0, $[\theta]_{290}$ − 40630 (neg. max), $[\theta]_{265}$ 0, $[\theta]_{256}$ + 7310 (max), $[\theta]_{243}$ + 9750 (last reading); ^1H NMR (270 MHz, $CDCl_3$): δ 4.97 (*dbr*, 12, H-2), 4.53 (*d*, 12, H-3), 7.73 (*d*, 8, H-5), 6.56 (*d*, 8, H-6), 7.17 (*br*, 2H, H-2′ and H-6′), 3.39 (*dbr*, 6, 6H, methylenes of prenyls), 5.36 (*tbr*, 6, 2H, vinyl Hs of ring B prenyls), 5.26 (*tbr*, 6, vinyl of ring A prenyl), 1.78 *br* (3Me), 1.73 *br* (2Me), 1.72 *br* (Me); [Calc. for $C_{30}H_{36}O_5$: MW, 476.2560. Found: MW(MS), 476.2536]. Other significant ions were at *m/z* (rel. int.) 459 (51.6), 447 (16.2), 435 (12.4), 410 (83.7), 395 (10.7), 288 (11), 284 (23.2), 255 (96.6), 243 (16.9), 241 (13.6), 221 (40.8), 217 (32.3), 215 (11.3), 205 (90.5) and 149 (100).

Acetylation of 5 mg **6a** (Ac_2O–pyridine) followed by the usual work-up and purification by TLC (C_6H_6–EtOAc, 20 : 1) gave 4 mg **6b** which had ^1H NMR signals at δ 4.39 (*dbr*, 12, H-2), 5.73 (*d*, 12, H-3), 7.82 (*d*, 8, H-5), 6.83 (*d*, 8, H-6), 7.18 *br* (2H, H-2′, H-6′), 3.25 (*dbr*, 6, 2 Hs, methylene of ring A prenyl), 5.08 (*tbr*, 6, vinyl of ring A prenyl), 3.20 (*dbr*, 6, 4 Hs, methylenes of ring B prenyls), 5.22 (*tbr*, 6, 2H, vinyl Hs of ring B prenyls), 2.32, 2.04, (Ac), 1.75 (2Me), 1.69 (2Me), 1.65, 1.58 (Me); MS *m/z* (rel. int.) 602 $[M]^+$ (1.8), 452 (29.8) 410 (47.5), 362 (10.1), 328 (11.7), 310 (10.1), 277 (10.1), 272 (12.9), 270 (10.4), 263 (21.8), 257 (14.1), 254 (33.8), 247 (69. 0), 245 (76.4), 231 (11.4), 221 (27.0), 219 (16.9), 205 (53.0), 203 (100).

Fractions 142–165 (0.31 g) were repurified by prep. TLC (petrol–EtOAc, 3 : 2). The more polar material was a complex mixture, the less polar material (135 mg) was **4b**, mp 216–217° (EtOAc–petrol); IR (KBr) 3360, 3200, 1650, 1600, 1570, 1285, 1260, 1190, 1040, 960 and 825 cm^{-1}; UV λ_{max}^{MeOH} 348 and 310 nm, λ_{max}^{NaOMe} 330 and 292 nm, λ_{max}^{NaOAc} 349 nm; ^1H NMR (270 MHz, $CDCl_3$): δ 12.84 (5-OH), 7.95 (H-2), 6.42 (H-8), 7.01 (*d*, 8) and 6.73 (*d*, 8, H-5′ and H-6′), 5.27 (*tbr*, 6) and 5.24 (*tbr*, 6, vinyl Hs of prenyls), 3.54 (OMe), 3.42 (*dbr*, 6) and 3.40 (*dbr*, 6, each 2H, methylenes of prenyls), 1.81 (*br*) and 1.79 (*br*, Me) 1.70 (*br*, 2Me); [Calc. for $C_{26}H_{28}O_6$: MW, 436.1885. Found: MW(MS), 436.1881]. Other significant ions were at *m/z* (rel. int.) 421 (25), 405 (26), 389 (35.8), 381 (11), 365 (7), 349 (16.6), 337 (6.6), 221 (4) and 215 (5). Acetylation (Ac_2O–pyridine) of 26 mg **4b** followed by the usual work-up and prep. TLC (C_6H_6–EtOAc, 7 : 1) gave 24 mg **4d**, IR ($CHCl_3$) 1755, 1650, 1605 and 1155 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 8.00 (H-2), 6.85 (H-8), 7.21 (*d*, 8) and 6.89 (*d*, 8, H-5′ and H-6′), 5.14 (*tbr*, 6) and 5.11 (*tbr*, 6, vinyl Hs of prenyls), 3.53 (OMe), 3.48 (*dbr*) and 3.32 (*dbr*, 2H each, methylenes of prenyls), 2.37, 2.35, 2.28 (Ac), 1.80, 1.75, 1.71 and 1.69 (Me); ^1H NMR (C_6D_6): δ 7.33 (H-2), 6.81 (H-8), 7.29 and 6.94 (H-5′ and H-6′), 3.46 (2H) and 3.36 (2H, methylenes), 5.36 and 5.20 (vinyl Hs of prenyls), 3.26 (OMe), 2.23, 1.87, 1.78 (Ac), 1.66 (*br*, 2Me), 1.62 (*br*, Me); MS *m/z* (rel. int.) 562 $[M]^+$ (39.0), 531 (18.4), 521 (35.8), 520 (100), 505 (15.8), 490 (29.5), 278 (52.3), 465 (26.0), 461 (32.9), 447 (28.2), 435 (41.8), 431 (47.9), 423 (67.4), 405 (31.9), 393 (28.7), 389 (20.5), 381 (30.0), 365 (20.0), 351 (22.9), 349 (31.0) and 337 (20.3).

Hydrogenation of **3b**. Reduction of 54 mg **3b** in 25 ml EtOH with 0.1 g 10% Pd–C in an atmosphere of H_2 for 2 hr followed by the usual work-up and purification by prep. TLC (petrol–EtOAc, 5 : 1) yielded 53 mg **5a**, mp 125–126° (EtOH), IR (KBr) 3400, 1625, 1600, 1250, 1200, 1110 and 1065 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 12.02 (5-OH), 5.30 (*dd*, 13, 3, H-2), 3.02 (*dd*, 17, 13, H-3a), 2.81 (*dd*, 17, 3, H-3b), 5.98 (H-6), 7.05 (2H, H-2′ and H-6′), 2.55 (*c*, 6H, benzylic methylenes), 1.5 (*c*, 6H, non-benzylic methylenes), 0.97 (*d*, 7, 4Me), 0.91 (*d*, 7, 2Me). Acetylation of **5a** and purification by prep. TLC (petrol–EtOAc, 7 : 1) afforded **5b** as a gum, ^1H NMR (270 MHz, $CDCl_3$): δ 5.43 (*dd*, 13, 3), 2.98 (*dd*, 17, 3, H-3a), 2.79 (*dd*, 17, 3, H-3b), 6.52 (H-6), 7.16 (2H, H-2′ and H-6′), 2.5 (*c*, 6H), 2.36, 2.34, 2.31 (Ac), 1.45 (*c*, 6H), 0.94 (*d*, 7, 4 Me), 0.90 (*d*, 7, 2 Me).

Reactions of **4b**. (a) Methylation of 11 mg **4b** with excess CH_2N_2 in Et_2O followed by the usual work-up and purification by TLC (C_6H_6–EtOAc, 10 : 1) gave 9 mg **4e** as a gum, IR ($CHCl_3$) 1650, 1610, 1255, 1160, 1075, 994 and 898 cm^{-1}. The substance was identical with material prepared by methylation of **4a**.

(b) A soln of 23 mg **4b** in 3 ml 85% HCO_2H was heated at 100° for 15 min, cooled, diluted with H_2O and extracted with $CHCl_3$. The washed and dried extract was evapd and purified by TLC (EtOAc–C_6H_6, 1 : 20) to give 8 mg **7** as a gum; ^1H NMR (270 MHz, $CDCl_3$): δ 12.60 (5-OH), 7.94 (H-2), 6.28 (H-8), 7.08 (*d*, 8) and 6.66 (*d*, 8, H-5′ and H-6′), 3.60 (OMe), 2.79 (*t*, 6, 2H) and 2.78 (*t*, 6, 2H, benzylic methylenes), 1.86 (*t*, 6, 2H) and 1.81 (*t*, 6, 2H, non-benzylic methylenes), 1.38 and 1.35 (each 2 Me); [Calc. for $C_{28}H_{28}O_6$: MW, 436.1885. Found: MW(MS), 436.1902]. Other significant ions were at *m/z* (rel. int.) 421 (8), 405 (40.7), 381 (16.4), 380 (13.5), 349 (22.5), 297 (13.8), 293 (13.6), 279 (10.1), 221 (14.1), 215 (5.6), 205 (7.9), 203 (9.3), 190 (8.6) and 167 (21.0).

(c) Cyclodehydrogenation of 15 mg **4b** with 10 mg DDQ in 5 ml dry C_6H_6 for 10 min at 100°, filtration and CC of the crude product over silica gel gave in the $CHCl_3$–MeOH (99 : 1) eluate 9 mg **8**, ^1H NMR (270 MHz, $CDCl_3$): δ 12.90 (5-OH), 7.94 (H-2), 6.30 (H-8), 7.11 (*d*, 8) and 6.69 (*d*, 8, H-5′ and H-6′), 6.69 (*d*, 10) and

5.59 (*d*, 10, H-1″ and H-2″ of chromene), 5.46 (*dbr*, vinyl H of prenyl), 3.55 (OMe), 3.46 (*dbr*, 6, 2H, methylene of prenyl), 1.84 *br* and 1.76 *br* (vinyl Me's of prenyl), 1.48 (2 Me); MS *m/z* (rel. int.): 434 $[M]^+$ (38.2), 419 (100), 403 (19.2), 361 (8.8), 349 (8.7), 254 (53.7), 219 (5.3), 203 (36.0), 167 (13.8).

(d) A soln of 15 mg **4b** in 1 ml piperidine and 3 drops H_2SO_4 was refluxed at 120° for 4 hr, cooled, diluted with H_2O and extracted with CH_2Cl_2. Evapn of the washed and dried extract and purification of the residue by prep. TLC (EtOAc–C_6H_6, 1:7) gave 3 mg **4a**.

Conversion of **6b** *to* **3c**. To soln of 11 mg **6b** in 1 ml HOAc and 0.8 ml H_2O was added at 100° 50 mg Zn dust in small portions over 1 hr at which time TLC (petrol–EtOAc, 5:1) indicated complete disappearance of starting material. The mixture was poured into H_2O, neutralized with $NaHCO_3$ and extracted with CH_2Cl_2. Evapn of the washed and dried extract and TLC of the residue furnished 9 mg **3c**.

Acknowledgement—Work at the Florida State University was supported in part by a grant from the United States Public Health Service (CA-13121) through the National Cancer Institute.

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