solid which on repeated crystallization from MeOH gave 7-*O*-acetyl daphnoretin (**2**), yield 0.004%, mp 230–232°. IR ν_{max}^{KBr} cm^{-1}: 1760, 1725, 1620, 1500, 1210, 1190, 840; MS *m/z*: 394 $[M]^+$, 352, 324, 179 and 89.

Daphnoretin (**1**) was isolated from the C_6H_6–EtOAc (1:1) eluates and purified by crystallization from EtOH, yield 0.24%, mp 244–245°; MS *m/z*: 352 $[M]^+$, 324, 296, 191, 179 and 89.

Acetylation. Daphnoretin (50 mg) was refluxed with a mixture of Ac_2O (10 ml) and pyridine (2 ml) at 100° for 6 hr. The reaction mixture was kept at room temp. for 1 hr and then poured onto crushed ice with continuous stirring. The solid ppt was crystallized from $CHCl_3$–MeOH (1:1), yield 75%, mp 232°. The product was found to be identical to naturally occurring 7-*O*-acetyl daphnoretin (**2**) from mmp, co-TLC and superimposeable IR spectra.

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FLAVONE *C*-GLYCOSIDES OF *ALMEIDEA GUYANENSIS*

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Key Word Index—*Almeidea guyanensis*; Rutaceae; isoswertisin; 6,8-di-*C*-arabinosylapigenin; 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin; 6-*C*-glucosyl-8-*C*-arabinosylgenkwanin.

Abstract—From the stem and the root bark of *Almeidea guyanensis* were identified isoswertisin, 6,8-di-*C*-arabinosylapigenin and two new compounds 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin, and 6-*C*-glucosyl-8-*C*-arabinosylgenkwanin.

We have previously reported flavonoids and alkaloids from *Almeidea guyanensis* Pulle [1, 2]. The present paper describes the isolation and identification of other flavonoids of stem bark.

Two flavonoids were isolated and identified as isoswertisin (**1**) and 6,8-di-*C*-arabinosylapigenin (**2**) by their chromatographic and spectral properties (UV) [3], MS of PM derivatives [4, 5], their hydrolysis products and by direct comparison of TLC and HPLC of free compounds and TLC of PM derivatives with authentic samples. Compounds **3** and **4** showed UV spectra and diagnostic shifts [3] characteristic of 7-*O*-substituted apigenin derivatives. Their mobility in water on PC and the results of the acid hydrolysis (extraction was possible with *n*-butanol but not with ether) suggested their *C*-glycosidic nature [6]. Compound **3** gave on acid hydrolysis xylose what is in agreement with *O*-glycosyl-*C*-glycosylflavone. MS of PM **3** showed peaks at the following *m/z*: 646 $[M]^+$ (0, 23), 471 $[M-175]^+$ (22, 4), 455 $[M-191]^+$ (7), 341 $[M-305]^+$ (100). This fragmentation is characteristic of PM *O*-pentosyl-8-*C*-pentosylflavone [5, 7].

PM **3**, by acid hydrolysis, gave compound with fragmentation in MS identical with that of the hydrolysis product of PM 2″-*O*-glucosyl-8-*C*-arabinosylgenkwanin, what shows a free hydroxyl in the 2″-position. By acid hydrolysis then permethylation, PM **3** gave a compound identical with PM 8-*C*-arabinosylgenkwanin [8] (TLC and MS). Furthermore, after acid hydrolysis and purification by PC in BAW, **3** gave a compound that was identical with 8-*C*-arabinosylgenkwanin (UV, diagnostic shifts and cochromatography). Compound **3** was thus identified as 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin.

The MS of PM **4** showed peaks at the following *m/z*: 704 $[M]^+$, 689 $[M-15]^+$ (19), 673 $[M-31]^+$ (100) and a series of characteristic peaks of 6-*C*-hexosyl-8-*C*-pentosylapigenin with losses from the $[M]^+$ at $[M-119]^+$ (3), $[M-131]^+$ (9), $[M-145]^+$ (1), $[M-163]^+$ (29), $[M-175]^+$ (32), $[M-189]^+$ (18) [4]. Furthermore,

the intensity of $[M-175]^+$ was greater than that of $[M-131]^+$. Also, PM 4 was identical with PM schaftoside (MS, direct chromatographic comparison). Methylation of schaftoside with diazomethane yielded several compounds. After purification by TLC, 7-*O*-methylschaftoside was found to be identical with 4 (UV, diagnostic schifts and direct chromatographic comparison). Further, the ^{1}H NMR of 4 exhibited a singlet at δ3.80 (3H) assignable to one methoxy group which is in position 7 from the results of UV [6]. Thus, 4 was identified as 6-*C*-arabinosyl-8-*C*-glucosylgenkwanin. Compound 4 was isolated in such small quantity that it was impossible to confirm our identification by ^{13}C NMR.

Furthermore, 1, 2, 3 and 4 have been identified from root bark of *Almeidea guyanensis*; only 2, 3 and 4 have been found in the leaves. Compounds 3 and 4 do not appear to have been isolated previously, but three genkwanin glycosides have been identified already from *Almeidea guyanensis*.

EXPERIMENTAL

UV: MeOH; ^{1}H NMR (90 MHz: $CDCl_3$, TMS as int. standard); EIMS (70 eV).

Plant material. Almeidea guyanensis was collected from French Guyana. Voucher specimen is deposited in Herbarium of ORSTOM n° CM 771 (Cayenne, Guyane Française).

Extraction and isolation. Air-dried stem barks (300 g) were extracted with MeOH. The concd MeOH extract was purified as it was initially reported [1]. The purified extract was chromatographed on a silica gel column and eluted with $CHCl_3$–MeOH–H_2O (65:25:4). Four flavonoids were isolated by chromatography on cellulose column with 30% HOAc or polyamide column with a gradient of H_2O–MeOH and purified by PC on cellulose (30% HOAc). After hydrolysis (2 N HCl, 2 hr, 100°) 3 gave xylose identified by TLC and CPG [9]. PM 3 and its hydrolysis products (2 N HCl, 2 hr, 100°) were purified by TLC (SiO_2, $CHCl_3$–EtOAc–Me_2CO, 5:4:1).

2″-O-*Xylosyl*-8-C-*arabinosylgenkwanin* (3). UV λ_{max}^{MeOH} nm 269, 298 sh, 335; + NaOMe: 254, 268, 299 sh, 396; + $AlCl_3$: 276, 305, 346, 390; + $AlCl_3$ + HCl: 277, 304, 344, 388; + NaOAc: 269, 298 sh, 347, 400 sh. $R_f \times 100$, PC 15% AcOH = 50; PC BAW = 35. PM ether EIMS 70 eV, *m/z* (rel. int.) 646 $[M]^+$ (0, 2), 501 $[M-145]^+$ (14), 471 $[M-175]^+$ (22, 4), 455 $[M-191]^+$ (7), 341 $[M-305]^+$ (100). MS of PM 3 hydrolysed, *m/z* (rel. int.) 472 $[M]^+$ (90), 341 $[M-131]^+$ (100), 327 $[M-145]^+$ (74), 311 $[M-161]^+$ (65), 297 $[M-175]^+$ (27). By acid hydrolysis then purification 3 gave a compound with UV spectrum: λ_{max}^{MeOH} nm: 268, 298 sh, 335; + NaOMe: 250, 266, 300 sh, 390; + $AlCl_3$: 274, 304, 346, 390; $AlCl_3$ + HCl: 278, 304, 343, 388; + NaOAc: 268, 298 sh, 349, 401 sh. $R_f \times 100$, PC 15% AcOH = 25; PC BAW = 63. By acid hydrolysis then permethylation, PM 3 gave a compound with MS: 486 $[M]^+$ (94), 355 $[M-131]^+$ (100), 341 $[M-145]^+$ (65), 325 $[M-161]^+$ (10), 311 $[M-175]^+$ (10).

6-C-*Glucosyl*-8-C-*arabinosylgenkwanin* (4). Needles from MeOH, mp 253° decomp.; λ_{max}^{MeOH} nm: 272, 333; + NaOMe: 252, 269, 394; + $AlCl_3$: 265 sh, 280, 301, 348, 384; $AlCl_3$ + HCl: 265 sh, 278, 303, 349, 384; + NaOAc: 269, 310 sh, 398. $R_f \times 100$. PC 15% HOAc = 60; PC BAW = 32. PM ether EIMS 70 eV *m/z* (rel. int.) 704 $[M]^+$ (17), 689 $[M-15]^+$ (19), 673 $[M-31]^+$ (100), 601 $[M-103]^+$ (14), 585 $[M-119]^+$ (3), 573 $[M-131]^+$ (9), 559 $[M-145]^+$ (1), 541 $[M-163]^+$ (29), 529 $[M-175]^+$ (32), 515 $[M-189]^+$ (18), 499 $[M-205]^+$ (6), 483 $[M-221]^+$ (3). PM 4, $R_f \times 100$ = 28 SiO_2, $CHCl_3$–EtOAc–Me_2CO (5:4:1). ^{1}H NMR (60 MHz, DMSO): 8.15 (2H, *d*, *J* = 9 Hz, H-2′, 6′), 6.85 (2H, *d*, *J* = 9 Hz, H-3′, 5′), 6.81 (1H, *s*, H-3), 5.0–3.0 (*m*, sugar protons), 3.80 (3H, *s*, OMe-7).

7-O-*Methylschaftoside*. Purification by TLC (BAW); λ_{max}^{MeOH} nm: 272, 333; + NaOMe: 270, 297 sh, 392; + $AlCl_3$: 261, 280, 301, 346, 384; $AlCl_3$ + HCl: 261 sh, 280, 302, 348. $R_f \times 100$, PC 15% AcOH = 25; PC BAW = 63.

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