rate 2 ml/min; R_t (min), 5.3 (isovitexin), 6.2 (6-*C*-galactosylapigenin).

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PHENOLIC COMPOUNDS FROM *VEPRIS HETEROPHYLLA*

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Key Word Index—*Vepris heterophylla*; Rutaceae; *trans*-sinapic acid methyl ester; 2″-*O*-glucosylisovitexin; 2″-*O*-glucosylvitexin; isovitexin; vitexin; 7-*O*-acylscoparin; chrysoeriol 7-glucoside; chrysoeriol 7-rhamnosylgalactoside.

Abstract—From the leaves of *Vepris heterophylla*, *trans*-sinapic acid methyl ester, 2″-*O*-glucosylisovitexin, 2″-*O*-glucosylvitexin, isovitexin, vitexin, 7-*O*-acylscoparin and chrysoeriol 7-glucoside were identified. A novel compound, chrysoeriol 7-rhamnosylgalactoside, was also characterized.

Vepris heterophylla, an African member of the Rutaceae used in folk medicine as a diuretic and an antipyretic, has been examined previously for some chemical constituents [1–3]. We now report the identification of one phenolic acid ester (**1**) and seven glycosylflavones (**2**–**8**) from leaves of this plant.

The UV spectrum of **1** showed a strong base shift indicating the presence of a phenolic group. Bands at 3270, 1685, 1620 and 700–900 cm^{-1} in the IR spectrum suggested the presence of a hydroxyl group, an ester carbonyl function, an ethylene group and a substituted aromatic ring. The ^{1}H NMR spectrum exhibited a singlet at δ 3.80 (3H) attributable to a carbomethoxy function, a singlet at δ 3.91 (6 H) assignable to two methoxy groups and a singlet of two aromatic protons at δ 6.75 which was little affected (δ 6.76) by acetylation of **1**. Further evidence for the presence of one phenolic group was provided by the signal observed at δ 5.40 in the spectrum of **1**, which disappeared upon the addition of D_2O, and by the singlet at δ 2.35 (3H) in the spectrum of the acetate. These spectral data established **1** to be *trans*-sinapic acid methyl ester.

Five flavonoids were isolated and identified as 2″-*O*-glucosylisovitexin (**2**), 2″-*O*-glucosylvitexin (**3**), isovitexin (**4**), vitexin (**5**) and chrysoeriol 7-glucoside (**6**) by their chromatographic and spectral properties (UV [4], mass spectra of PM derivatives [5, 6]), their hydrolysis products and by direct comparison (TLC and HPLC of free compounds and TLC of PM derivatives) with authentic samples. Acid hydrolysis of **7** gave scoparin and isoscoparin which were identified from spectral data and direct comparison with authentic samples, but no sugar was formed. Alkaline hydrolysis gave scoparin in agreement with the presence of an acyl group which was assigned to the 7-position because of the absence of a bathochromic shift in band II with sodium acetate. Permethylation of **7** gave a mass spectrum similar to that of PM-orientin. Thus it was considered to be a 7-*O*-acylscoparin but the acyl group could not be identified because of an insufficient amount of the compound.

Compound **8** showed UV spectra and diagnostic shifts [4] characteristic of a 7,3′-substituted luteolin. Acid hydrolysis gave galactose, rhamnose and chrysoeriol, which was identified from its chromatographic properties and spectral data. Permethylated **8** gave the mass spectrum of a PM luteolin 7-*O*-deoxyhexosylhexoside: 720 $[M]^+$, 328 (69%), 189 (100%), 157 (70%), 125 (51%) [7, 8]. Therefore **8** was characterized as chrysoeriol 7-rhamnosylgalactoside, which is a new natural product.

EXPERIMENTAL

Plant material. *Vepris heterophylla* R. Letouzey (syn. *Toddaliopsis heterophylla* A. Engler, *Teclea sudanica* A. Chevalier) was collected from Mali. A voucher specimen has been deposited at the Herbarium of Faculté des Sciences Pharmaceutiques, Toulouse.

Extraction and isolation. Dried leaves (2.5 kg) were extracted with petrol (60–80°), $CH_2Cl_2 + NH_4OH$ and MeOH. The conc. MeOH extract was taken up in H_2O and the aq. mixture extracted successively with Et_2O, EtOAc and *n*-BuOH. The Et_2O concentrate was chromatographed on cellulose (15% HOAc) and the neutralized acid phase extracted with $CHCl_3$. Compound **1** crystallized on concn of the $CHCl_3$ extract. The EtOAc concentrate was chromatographed on a polyamide column and eluted with EtOAc–MeOH (19:1 to 4:1). All flavonoids were isolated by PC on cellulose (BAW, 30% and 15% HOAc). The *n*-BuOH concentrate was chromatographed on Amberlite XAD_2 column with the following eluants: H_2O and aq. NH_4OH (5%). The basic fraction contained flavonoids which were chromatographed on a polyamide column with a gradient of H_2O–EtOH and isolated by PC on cellulose (BAW 4:1:5 and 30% up to 20% HOAc).

1 (Trans-*sinapic acid methyl ester*). Mp 90° (Me_2CO–MeOH, 9:1). UV λ_{max}^{MeOH} nm: 225 sh, 239, 327; + NaOH: 219, 255 sh, 394. IR ν_{max}^{KBr} cm^{-1}: 3270 (–OH), 1685 (–COOR), 1610–1620 (–CH =CH–), 1560, 1425, 1328, 1268, 1250, 1220, 1150, 1100, 1040, 980, 820, 728. EIMS *m/z* (rel. int.): 238 $[M]^+$ (100), 224 $[M-14]^+$ (30), 223 $[M-15]^+$ (37), 208 $[M-30]^+$ (27), 207 $[M-31]^+$ (47). ^1H NMR (60 MHz, $CDCl_3$) **1**: δ 3.80 (3H, *s*, OMe), 3.91 (6H, *s*, 2 OMe), 5.78 (1H, *s*, OH), 6.29 (1H, *d*, $J = 16$ Hz, H-α), 6.75 (2H, *s*, H-2,6), 7.63 (1H, *d*, $J = 16$ Hz, H-β); acetate: δ 2.35 (3H, *s*, OCOMe), 3.80 (3H, *s*, OMe), 3.85 (6H, *s*, 2 OMe), 6.37 (1H, *d*, $J = 16$ Hz, H-α), 6.76 (2H, *s*, H-2,6), 7.46 (1H, *d*, $J = 16$ Hz, H-β).

7 (7-O-*Acylscoparin*). UV λ_{max}^{MeOH} nm: 251, 272, 342; + $AlCl_3$ 262, 278, 360, 386; + $AlCl_3$ + HCl: 262, 278, 360, 386; + NaOAc: 252, 272, 350, 400; + NaOAc + H_3BO_3: 250, 271, 344; + NaOH: 280, 404. PM ether EIMS 70 eV, *m/z* (rel. int.) 560 $[M]^+$, (64), 546 $[M-14]^+$ (2), 531 $[M-29]^+$ (1), 457 $[M-103]^+$ (5), 399 $[M-161]^+$ (11), 397 $[M-163]^+$ (2), 385 $[M-175]^+$ (100), 371 $[M-189]^+$ (34), 355 $[M-205]^+$ (13), 341 $[M-219]^+$ (10).

8 (*Chrysoeriol 7-rhamnosylgalactoside*). UV λ_{max}^{MeOH} nm: 250, 269, 346; + $AlCl_3$: 262, 277, 356, 388; + $AlCl_3$ + HCl: 262, 277, 356, 388; + NaOAc: 252, 269, 392; + NaOAc + H_3BO_3: 252, 269, 346; + NaOH: 267, 408. PM ether EIMS 70 eV, *m/z* (rel. int.) 720 $[M]^+$ (8), 552 $[M-168]^+$ (11), 516 $[A+S'+2H]^+$ (19), 329 (40), 328 $[A+H]^+$ (69), 327 (16), 313 (27), 311 (16), 299 $[A-CO]^+$ (24), 189 $[T]^+$ (100), 157 (70), 125 (51).

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