présence du groupement propénol sur un C situé entre deux CH) la formule **1** a été retenue sur des considérations biogénétiques. En effet la position de ces substituants sur le squelette benzofuranne permet de considérer ce néolignane comme le produit de condensation de deux unités phényl-propanoïdes (ici l'alcool coniférylique).

PARTIE EXPERIMENTALE

Les graines de *Herpetospermum caudigerum* proviennent du Népal (Mission Népal, RCP 253); après broyage et dégraissage à l'éther de pétrole, le matériel végétal a été épuisé au $CHCl_3$ puis au MeOH—L'extrait alcoolique précipité par l'eau a été ensuite chromatographié à travers une colonne de polyamide MN SC 6—L'herpétal élué par 5% de MeOH dans le benzène, cristallisant dans ce solvant, est recristallisé dans MeOH.

Les spectres UV ont été enregistrés dans le MeOH et le spectre IR vans le KBr. Les spectres de RMN ont été réalisés sur XL-100 (Varian) et les spectres de masse sur MS 902 (AEI) au Centre de SM de l'Université Lyon I.

Les spectres UV ont été enregistrés dans le MeOH et le spectre IR dans le KBr. Les spectres de RMN ont été réalisés sur XL-100 (Varian) et les spectres de masse sur MS 902 (AEI) au Centre de SM de l'Université Lyon I.

Herpétal: F = 160–161°. UV λ_{max} nm: 220; 250: (290); 340. λ_{max} (NaOH) nm: 210; 267; 395. IR cm^{-1}: 3435, 1678, 1670; 1610; 1607; 1520; 1475; 1440; 1410; 1375; 1320; 1285; 1265; 1220; 1145; 1115; 1035; 970; 900; 820; 710 et 670. SM (70 eV, 180°C) *m/e*: 354 (M^+; 100%; 354.1088; $C_{20}H_{18}O_6$ = 354.1103); 336, (M − H_2O: 40%: 336.1000: $C_{20}H_{16}O_5$ = 336.0997); 325 (M − CHO; 35%; 325.1068; $C_{19}H_{17}O_5$ = 325.10759); 311 (7%); 307 (7%); 296 (6%); 281 (5%); 165 (6%); 163 (6%); 151 (13%) − RMN: cf. tableau ci-dessus.

Dérivé silylé (obtenu par action de BSTFA sur le produit naturel en solution pyridinique). SM *m/e*: 498 (M^+; 100%); 483 (M − 15; 28%); 426 (M − 72; 22%); 408 (M − 90; 47%); 397 (11%); 378 (42%); 336 (33%).

Dérivé réduit: (obtenu par hydrogénation à pression et température ambiantes en présence de charbon palladié à 10% et purifié par CCM préparative de silice). UV λ_{max} nm: 216; 308; SM *m/e*: 358 (100%); 328 (10%); 314 (89%); 299 (7%); 298 (7%); 297 (7%); 296 (12%); 284 (17%); 283 (13%); 269 (7%); 268 (8%); 265 (11%); 264 (9%); 165 (6%); 151 (22%).

Remerciements—Nous remercions Mr Petiaud, I.R.C Lyon pour l'enrigistrement des spectres RMN, Mr Arpin pour la lecture critique du manuscrit, et les Laboratoires Roussel UCLAF pour leur aide financière.

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Phytochemistry, 1978, Vol 17, pp 2135–2136 © Pergamon Press Ltd Printed in England. 0031-9422/78/1201-2135 $02.00/0

APIUMETIN—A NEW FURANOCOUMARIN FROM THE SEEDS OF *APIUM GRAVEOLENS*

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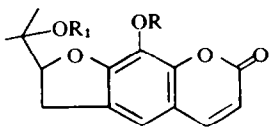
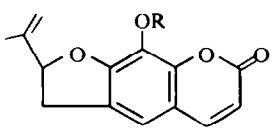
(*Received* 14 *April* 1978)

Key Word Index—*Apium graveolens*; Umbelliferae; apiumetin; rutaretin; furanocoumarins; structural determination

Since a number of coumarins have already been identified in the seeds of *A. graveolens* [1–3] it was considered worthwhile to carry out a further investigation of the seeds in search of related minor components. From the cold ether extract of the seeds two dihydrofurocoumarins were isolated using column chromatography and preparative TLC. These compounds were identified by chemical and spectroscopic methods as rutaretin (**1**) and its dehydrated derivative apiumetin (**2**). Rutaretin has earlier been isolated from *Ruta graveolens* [4] but apiumetin is a new compound.



(**1**) R = R_1 = H
(**3**) R = R_1 = Ac



(**2**) R = H
(**4**) R = Ac

EXPERIMENTAL

UV spectra were recorded in MeOH and NMR on a Varian A-60 instrument using TMS as internal standard. All compounds were crystallized from EtOAc–petrol.

Extraction and isolation. Dried *A. graveolens* seeds (4.0 kg) were extracted successively with petrol, C_6H_6 and cold Et_2O. The Et_2O extract was coned and chromatographed on Si gel (400 g) using C_6H_6 and C_6H_6–EtOAc as eluents. The fractions eluted with C_6H_6–EtOAc (19:1) on prep. TLC (Si gel, $CHCl_3$–MeOH, 19:1) gave compound E_1 and the fractions eluted with C_6H_6 on prep. TLC (Si gel; C_6H_6–Me_2CO, 6:1) yielded compound E_2.

Identification. Compound E_1 crystallized as long pale yellow needles (40 mg) mp 198°; $[\alpha]_D^{19}$ − 30.4 (*c* = 0.790, $CHCl_3$); R_f 0.80 ($CHCl_3$–MeOH, 23:2); 0.62 ($CHCl_3$–MeOH, 19:1); (Found: M^+ 262; C, 64.0; H, 5.1. $C_{14}H_{14}O_5$ requires: C, 64.1; H, 5.4%); UV λ_{max} log (ε) 265 (3.86), 280 (3.60). 335 (4.30); NaOAc, 265, 280, 335; IR (KBr) *v*, 3400, 1684, 1584, 1244 and 862 cm^{-1}. It gave a positive Gibb's test. Methylation with CH_2N_2 gave the partial methyl ether, mp 148°; (Found: C,

65.3; H, 6.0. $C_{15}H_{16}O_5$ requires: C, 65.2; H, 5.9%); UV λ_{max} log (ε) 260 (3.80), 335 (4.30); IR (nujol) ν, 3580, 1700, 1620, 1267 and 835 cm^{-1}; NMR ($CDCl_3$, δ): 1.33 and 1.45 (*s*, 3H each, gem dimethyl), 2.5 (*s*, 1H, —OH, D_2O exchangeable), 3.2 and 3.36 (*s*, 1H each, Ar—$\underline{CH_2}$—CH<), 4.08 (*s*, 3H, —OCH_3), 4.8 (*t*, 1H, Ar—CH_2—$\underline{CH}$<), 6.14 (*d*, J = 10 Hz, 1H, H-3), 6.92 (*s*, 1H, H-5), 7.7 (*d*, J = 10 Hz, 1H, H-4). Acetylation with Ac_2O and *p*-$CH_3.C_6H_4.SO_3H$ gave the diacetate, mp 162–4°, (Found: C, 63.0; H, 4.9. $C_{18}H_{18}O_7$ requires: C 62.4; H, 5.2%), UV λ_{max} log (ε), 225 (3.65), 245 (3.35), 290 (3.40), 320 (3.76); IR (KBr) ν, 1715, 1625, 1575, 1247 and 950 cm^{-1}. The diacetate (**3**) was kept on a pre-heated block at 330° for 75 sec and the product purified by prep. TLC (C_6H_6–Me_2CO, 24:1). The pyrolysed product was identical with the acetate of E_2 (see later). The mp and spectral values of compound E_1 were found to be identical with the reported values for (−)-2,3-dihydro-9-hydroxy-2(1-hydroxy-1-methylethyl)-7H-furo[3.2 g] [1]-benzopyran-7-one (rutaretin) [4]. Compound E_1 is therefore, rutaretin (**1**).

Compound E_2 crystallized as shining needles (50 mg), mp 198°; $[\alpha]_D^{19}$ − 68.29° (c = 0.41, $CHCl_3$); R_f: 0.33 (C_6H_6–Me_2CO, 9:1); 0.85 ($CHCl_3$–MeOH, 19:1); (Found: M^+ 244; C, 68.5; H, 5.2. $C_{14}H_{12}O_4$ requires: C, 68.9; H, 4.9%); UV λ_{max} log (ε) 265 (3.86), 280 (3.65), 335 (4.30); NaOAc, 265, 280, 335; IR (KBr) ν; 3340, 1675, 1425, 1065 and 900 cm^{-1}; NMR (DMSO-d_6, δ): 1.7 (*s*, 3H, —$\underline{CH_3}$), 3.2 (*m*, 2H, Ar—$\underline{CH_2}$—CH<), 5.0 and 5.17 (*s*, 1H each, =$\underline{CH_2}$), 5.41 (*t*, 1H, Ar—CH_2—$\underline{CH}$<), 6.3 (*d*, J = 10 Hz, 1H, H-3), 7.1 (*s*, 1H, H-5), 8.03 (*s*, J = 10 Hz, 1H, H-4), It gave a positive Gibb's test and a negative ferric reaction. Methylation with CH_2N_2 gave a Me ether, mp 84°; (Found: C, 69.6; H, 6.0. $C_{15}H_{14}O_4$ requires: C, 69.8; H, 5.5%); UV λ_{max} log (ε) 260 (3.48), 330 (3.96); IR (KBr) ν: 1730, 1622 1412, 1085 and 891 cm^{-1}; NMR ($CDCl_3$, δ): 1.8 (*s*, 3H, —OCH_3), 3.28 (*m*, 2H, Ar—$\underline{CH_2}$—CH<), 4.12 (*s*, 3H, —OCH_3), 5.05 and 5.2 (*s*, 1H each, =CH_2), 5.43 (*t*, 1H, Ar—CH_2—$\underline{CH}$<), 6.29 (*d*, J = 10 Hz, 1H, H-3), 6.8 (*s*, 1H, H-5), 7.72 (*s*, J = 10 Hz, 1H, H-4). Compound E_2 on hydrogenation with Pd–C gave the tetrahydro-derivative, a pale yellow semi-solid which failed to crystallize UV λ_{max} 285, 315; IR (KBr) ν, 1725, 1625, 1475, 1078 and 952 cm^{-1}; NMR ($CDCl_3$, δ) 0.82 and 0.96 (2*d*, 3H each, gem dimethyl), 2.98 (*m*, 6H, Ar—$\underline{CH_2}$—CH<, Ar—$\underline{CH_2}$—$\underline{CH_2}$—), 5.1 (*t*, 1H, Ar—CH_2—$\underline{CH}$<), 7.14 (*s*, 1H, H-5). The acetate (**4**) prepared by the Ac_2O–C_5H_5N method crystallized as white needles, mp 110–2°; (Found: C, 67.50; H, 5.2. $C_{16}H_{14}O_5$ requires: C, 67.1; H, 4.9%); UV λ_{max} log (ε), 245 (3.86), 330 (4.37); IR (KBr) ν; 1725, 1620, 1415, 1062 and 897 cm^{-1}. It was found to be identical (mmp, UV, IR) with the pyrolysed product of the diacetate (**3**) of compound E_1. Compound E_2 is, therefore (−)-2,3-dihydro-9-hydroxy-2-isopropenyl-7H-furo [3.2 g] [1]-benzopyran-7-one (**2**).

Acknowledgements—The authors are grateful to Dr. O. P. Goel and Mr. R. B. Scott, Warner-Lambert/Parke-Davis, Michigan, U.S.A. for recording the mass spectra.

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Phytochemistry, 1978, Vol. 17, pp. 2136–2137 © Pergamon Press Ltd. Printed in England. 0031-9422/78/1201-2136 $02.00/0

C-GLYCOSYLFLAVONES FROM THE GENUS *ACHILLEA*

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(*Received* 7 *June* 1978)

Key Word Index—*Achillea*; Anthemideae–Compositae; chemotaxonomy; *C*-glycosylflavones; swertiajaponin; swertisin; vicenins 2 and 3; schaftoside; isoschaftoside.

INTRODUCTION

Recent studies on the distribution of flavonoids in *Achillea* indicate that most species contain *C*-glycosyl-flavones [1]. Earlier publications on *A. fragrantissima* (Forsk.) Sch.-Bip. [2] report the isolation of vitexin 7-*O*-glucoside but this could not be detected in another specimen examined [1]. Orientin and vitexin have been detected in *Achillea nobilis L.* by comparison with authentic samples [3]. Furthermore, *C*-glycosylation has also been noted in two other genera of the Anthemideae: *Artemisia* [4] and *Otospermum* [5]. The endemic Anatolian genus *Leucocyclus* which is closely related to *Achillea* also contained *C*-glycosyl-flavones [1]. Apart from the mono-*C*-glycosylflavones vitexin, isovitexin, orientin and isoorientin, the 7-methyl ethers of isoorientin and isovitexin respectively and di-*C*-glycosylapigenins are characteristic of the genus *Achillea*. The identification of the latter substances is the subject of the present communication.