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ANHYDRORUTARETIN, A NEW FURANOCOUMARIN AND OTHER MINOR CONSTITUENTS OF *APIUM LEPTOPHYLLUM* SEEDS

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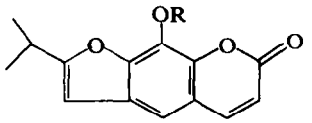
Key Word Index—*Apium leptophyllum*; Umbelliferae; anhydrorutaretin; *trans*-khellactone; rutaretin; sitosterol-D-glucoside; marmesinin; skimmin.

During earlier investigations on the seeds of *A. leptophyllum* [1–3] the presence of several minor components was indicated. Isolation and characterization of six of these are now described.

Ethyl acetate and alcoholic extracts on chromatography yielded anhydrorutaretin (**1**), mp 220–221°, a new furanocoumarin, in addition to five other components (see Experimental). On the basis of spectroscopic evidence, **1** has been characterized as 2-isopropyl-9-hydroxy-7*H*-furo[3,2-g] [1] benzopyran-7-one. The assigned structure was confirmed by direct comparison of its methyl ether with the P_2O_5-dehydration product (**3**) of methyl rutaretin (**5**). It is thus an isomer of closely related dihydrofuranocoumarin, leptophyllidin (**6**) from this plant material as described earlier [2, 3].



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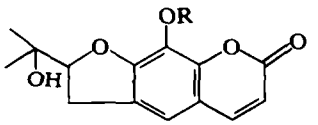
3 R = Me



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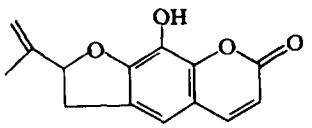

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EXPERIMENTAL

Melting points are uncorr. UV spectra were recorded in EtOH, IR in KBr disc and ^{1}H NMR with TMS as int. standard.

Isolation. Petrol-extracted finely powdered seeds (5 kg) of *A. leptophyllum* were further extracted with EtOAc, followed by EtOH. The latter was fractionated with C_6H_6 and EtOAc. The EtOAc solubles were pooled and separated into individual constituents by repeated CC followed by PLC over Si gel. The EtOAc-insoluble alcoholic extract was also chromatographed in the same manner. Known compounds were identified by their IR, UV, ^{1}H NMR and MS, and all except khellactone were confirmed by direct comparison (TLC, mmp, IR) with authentic samples.

Identification of EtOAc *extract constituents. Anhydrorutaretin* (**1**). Eluted with EtOAc (40 mg), PLC, CH_2Cl_2–MeOH (9 : 1), cream-coloured needles (EtOAc–petrol) mp 220–221°, M^+, 244; $C_{14}H_{12}O_4$; *IR* ν_{max} cm^{-1}: 3400, 3305, 2960, 1726, 1600, 1585, 1480, 1450, 1395, 1365, 1185, 1155, 860, 830, 758. UV λ_{max} nm (log ε): 254 (4.22), 262 (4.12), 268 (4.11), 314 (3.95). ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 1.27, 1.37 (3H each, 2*s*, $Me_2C<$), 3.17, (1H,*m*, CH—), 6.17 (1H, *d*, *J* = 9.5 Hz C-6), 6.29 (1H, *d*, *J* = 1. 1 Hz, C-3), 7.0 (1H, *s*, C-4), 7.39 (1H, *d*, *J* = 9.5 Hz, C-5), 9.95 (1H, *brs*, C-9, OH, exchanged with D_2O). MS 70 eV, *m/e* (rel.int.): 244 (M^+, 56), 229 ($M^+ - 15$; 100), 201 ($M^+ - 43$; 7), 149 ($M^+ - 95$; 6).

Acetate (**2**) (Ac_2O–Py). Colourless needles (EtOAc–petrol), mp 153–154°. UV λ_{max} nm (log ε): 215 (4.32), 250 (4.73), 296 (4.04) ^{1}H NMR (60 MHz, $CDCl_3$): δ1.30, 1.41 (3H each, 2*s*, $Me_2C<$), 3.07 (1H, *m*, >CH—), 2.51 (3H, *s*, OAc), 6.33 (2H, *d*, *J* = 9.5Hz, C-6; C-3 merged with it), 7.41 (1H, *s*, C-4), 7.75 (1H, *d*, *J* = 9.5Hz, C-5).

Methyl ether (**3**) (Me_2SO_4–K_2CO_3–Me_2CO). Lemon-yellow needles (MeOH), mp 90–1° (lit. [4] 90°, obtained by P_2O_5 dehydration of rutaretin methyl ether). IR ν_{max} cm^{-1}: 2920, 1720, 1618, 1600, 1582, 1460, 1370, 1180, 1148, 1060, 870, 840, 760. UV λ_{max} nm (log ε): 219 (4.52), 252 (4.60), 302 (4.05) ^{1}H NMR (90 MHz, $CDCl_3$); δ1.32, 1.40 (3H each, 2*s*, $Me_2C<$), 3.13 (1H, typical *m*, >CH—), 6.32 (2H, *d*, *J* = 9.5Hz, C-6; C-3 merged with it), 7.20 (1H, *s*, C-4), 7.72 (1H, *d*, *J* = 9.5Hz, C-5). It corresponded with anhydrorutaretin methyl ether (TLC, mmp, IR) obtained as in ref. [4].

Trans-*khellactone*. Eluted with EtOAc (50 mg), PLC, C_6H_6–EtOAc (1 : 1) colourless cubes (MeOH), mp 187–188° (lit. [5] 186°), M^+ 262, $C_{14}H_{14}O_5$. For IR, UV, ^{1}H NMR see ref. [5], MS 70 eV, *m/e* (rel.int): 262 (M^+, 15), 192 ($M^+ - 70$; 13), 191 ($M^+ - 71$; 100), 162 ($M^+ - 100$; 15), 134 (162 – 28; 15), 107 ($\overset{+}{C}H_2C_6H_4OH$; 8).

Acetate (Ac_2O–Py). Colourless needles (C_6H_6–petrol), mp 163–164° (lit. [5] 161–162°), IR ν_{max} cm^{-1}: 3000, 2925, 1753, 1735, 1610, 1565, 1490, 1430, 1390, 1372, 1230, 1220, 1145, 1065, 1040, 1015, 830, 820, UV λ_{max} nm (log ε): 244 (3.52), 255 (3.45), 323 (4.01), ^1H NMR (60 MHz, $CDCl_3$): δ1.35, 1.42 (3H each; 2*s*, *gem* dimethyl), 2.09, 2.11 (3H each, 2*s*, 2xOAc), 5.27 (1H, *d*, *J* = 4.5Hz, C-9), 6.19 (1H, *d*, *J* = 4.5Hz, C-10 [6]), 6.19 (1H, *d*, *J* = 9.5Hz, C-3), 6.75 (1H, *d*, *J* = 8.5Hz, C-6), 7.31 (1H, *d*, *J* = 8.5Hz, C-5), 7.54 (1H, *d*, *J* = 9.5 Hz, C-4).

Rutaretin (**4**). Eluted with EtOAc (30 mg) PLC, $CHCl_3$–MeOH (9 : 1), yellow needles (EtOH), mp (dry) 195–197° (lit. [4] 193°).

EtOH *extract constituents. Sitosteral-β-*D*-glucoside.* Eluted with EtOAc–MeOH (99 : 1), colourless crystalline solid (EtOH) (70 mg), mp 286–287° (decomp.) [7].

Marmesinin. Eluted with EtOAc–MeOH (99 : 1) (40 mg), PLC, CH_2Cl_2–MeOH (9 : 1), colourless solid (MeOH), mp 261–263° [8]. On acid hydrolysis, it yielded D-glucose (PC) and marmesin [9].

Skimmin. Eluted with EtOAc–MeOH (99 : 1) (40 mg), PLC, CH_2Cl_2–MeOH (9 : 1), colourless solid (MeOH), mp 208–210° [10] It yielded D-glucose (PC) and umbelliferone on hydrolysis with acid.

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REFERENCES

1. Atal, C. K., Sharma, B. R. and Qadry, S. M. J. (1973) *Indian J. Pharm.* **35,** 127.
2. Sharma, P., Sharma, M. and Rangaswami, S. (1978) *Indian J. Chem.* **16B,** 563.
3. Sharma, B. R. and Sharma, P. (1979) *Indian J. Chem.* (in press).
4. Schneider, G., Müller, H. and Pfaender, P. (1967) *Arch. Pharm.* **300,** 73.
5. Kapoor, S. K., Kohli, J. M., Sharma, Y. N. and Zaman, A. (1972) *Phytochemistry* **11,** 477.
6. Nielsen, B. E. (1970) *Dan. Tidsskr. Farm.* **44,** 198.
7. Swift, L. J. (1952) *J. Am. Chem. Soc.* **74,** 1099.
8. Starkowsky, N. A. and Badran, N. (1958) *J. Org. Chem.* **23,** 1818.
9. Chatterjee, A. and Mitra, S. S. (1949) *J. Am. Chem. Soc.* **71,** 606.
10. Shoeb, A., Kapil, R. S. and Popli, S. P. (1973) *Phytochemistry* **12,** 2071.

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LATIFOLONE IN *THAPSIA VILLOSA* ROOTS

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Key Word Index—*Thapsia villosa*; Umbelliferae; 3,4-methylenedioxy-5-methoxypropiophenone; latifolone; scopoletin; phenolic acids.

While continuing our studies on *Thapsia villosa* L., the roots were examined for their constituents. Scopoletin, 4-hydroxybenzoic, vanillic and ferulic acids were readily characterized. A major compound, purple in UV light, was detected on chromatograms. The substance gave a positive reaction with 2,4-dinitrophenylhydrazine, a pink–red color with vanillin–H_2SO_4, showed a UV maximum at 297 nm unchanged by alkali addition, and its M^+ and mp agreed with those of 3,4-methylenedioxy-5-methoxypropiophenone (latifolone, crocatone). Latifolone, first isolated from *Oenanthe crocata* [1], was later characterized in *Laserpitium latifolium* [2], *L. siler* (≡ *Siler montanum*) [3], *L. archangelica* [4], *Laser trilobum* [5], *Ligusticum hultenii* [6], *Ferula ugamica* [7], *F. rigidula* [8], *F. persica* [9] and *Anthriscus sylvestris* [10]. In all cases latifolone was isolated from the roots and could not be detected in the aerial parts. It now seems that the compound is characteristic of the Umbelliferae.

EXPERIMENTAL

Roots (3 kg) of *T. villosa* (voucher sample No. 4779, Herbarium of the Department of Botany, University of Salamanca, Spain) were collected in July in Ortigueira (Coruña), cleaned, chopped and homogenized with MeOH. The extraction was repeated twice, and the extracts were combined and concd *in vacuo*. The concentrate was continuously extracted overnight with Et_2O. The Et_2O soln was dried, evapd to a small vol. and chromatographed on Whatman 3 mm paper in *iso*-PrOH–NH_3–H_2O (10 : 1 : 1) (IAW). Bands with fluorescence or giving positive phenolic reactions were eluted with MeOH and the eluates rechromatographed.