

ALKALOIDS AND COUMARINS OF *HERACLEUM WALLICHII*

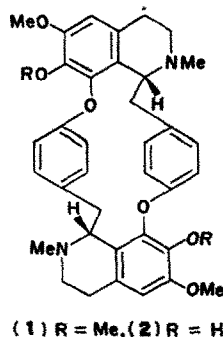
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Key Word Index—*Heracleum wallichii*; Umbelliferae; coumarins; alkaloids; sterol; bisbenzylisoquinoline alkaloids; stigmaterol; cycleanine; isochondrodendrine; columbianetin; marmesin; vaginidiol.

The genus *Heracleum* is rich in furanocoumarins. Isolation of four known furanocoumarins from the petrol extract of the roots of *H. wallichii* has already been reported [1]. From the roots of this plant, two bisbenzylisoquinoline alkaloids, cycleanine (1) and isochondrodendrine (2) have been isolated. This is first report of identification of alkaloids of the genus *Heracleum*. The petrol extract was also found to contain stigmaterol and the benzene extract yielded three dihydrofuranocoumarins, columbianetin, marmesin and vaginidiol (3). This is the second report of the occurrence of vaginidiol [2] in nature.



EXPERIMENTAL

Air-dried and milled roots of *H. wallichii* were exhaustively extracted with 95% EtOH in the cold. Solvent was removed (vac.) and the basic components separated from the residue in the usual way. The basic fraction was chromatographed on basic alumina. Elution with $C_6H_6-CHCl_3$ (8:1) afforded cycleanine, $C_{38}H_{42}O_6N_2$ (0.1%), mp 270–271° (needles from acetone), $[\alpha]_D^{25} -22^\circ$ (c, 1% in $CHCl_3$); M^+ 622; characteristic peak at m/e 265.5. NMR ($CDCl_3$): δ 2.55 (6H, 2 N-methyls), 3.41 and 3.82 (12H, 4 O-methyls), 2.64–3.40 (12H, m, methylene protons), 4.30 (2H, q, benzylic methine); 10 aromatic protons

appeared as 4 pairs of doublets at 5.81, 6.27, 6.61, 7.06—each for 2H, and 6.57 (2H, s). Picrate, mp 193° (dec.); methiodide, mp 306–307° (dec.). Elution with $CHCl_3-MeOH$ (8:1) yielded isochondrodendrine, $C_{36}H_{38}O_6N_2$ (0.01%), mp 296–299° (dec.) (needles from pyridine), $[\alpha]_D^{25} +112^\circ$ (0.1 N HCl), –ve $FeCl_3$ test. NMR (CD_3SOCD_3): δ 3.52 (6H, 2 O-methyls), more deshielded protons of the O-methyl around 3.8 in (1) are missing. Rest of the spectrum up to δ 8 was comparable with that of cycleanine. Dried milled roots were soxhletted successively with light petrol (60–80°) and C_6H_6 . The petrol extract on chromatography over alumina, (grade II) yielded stigmaterol, $C_{29}H_{48}O$ (0.02%), mp and mmp 167–168°, M^+ 412, acetate, mp 140°, and cycleanine. The C_6H_6 extract was chromatographed on neutral alumina (grade III) and eluted successively with C_6H_6 , $C_6H_6-CHCl_3$ (1:1), $CHCl_3$ and $CHCl_3-MeOH$ (20:1). C_6H_6 and $C_6H_6-CHCl_3$ eluates were combined and rechromatographed over Si gel. Elution with $C_6H_6-CHCl_3$ (1:1) gave successively columbianetin, $C_{14}H_{14}O_4$ (0.002%), mp 163–164°, $[\alpha]_D^{25} +18^\circ$ (c, 1% in $CHCl_3$) (IR and NMR), and marmesin $C_{14}H_{14}O_4$ (0.003%), mp 186–187°, $[\alpha]_D^{25} +25^\circ$ (c, 1% in $CHCl_3$) (IR and NMR). The $CHCl_3-MeOH$ eluate from alumina was rechromatographed over Si gel. Elution with $CHCl_3-MeOH$ (20:1) afforded vaginidiol, $C_{14}H_{14}O_5$ (0.01%), mp 168–169° (prisms from C_6H_6), $[\alpha]_D^{25} +231^\circ$ (c, 1% in EtOH). M^+ 262. NMR ($CDCl_3 + CD_3SOCD_3$): δ 1.47 and 1.54 (6H, gem dimethyl), 2.97 (1H, broad s, tert. hydroxyl), 4.33 (1H, d, J 6.5 Hz, H2'), 4.71 (1H, broad s, sec. hydroxyl), 5.76 (1H, d, J 6.5 Hz, H3'), 6.18 (1H, d, J 9.5 Hz, H3), 6.85 (1H, d, J 8.5 Hz, H6), 7.42 (1H, d, J 8.5 Hz, H5), 7.72 (1H, d, J 9.5 Hz, H4).

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ALCALOÏDES ARTEFACT DE *LASIANATHERA*
AUSTROCALEDONICA

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Lors de l'étude chimique de *Cantleya corniculata* (Becc.) Howard, Icacinacées, un alcaloïde de type pyridine, la cantleyine 1, a été isolée [1]. Il a été montré qu'elle prenait naissance au cours de l'extraction, en présence d'ammoniaque, à partir d'un précurseur hétéro-

sidique [2]. Il était intéressant d'étudier systématiquement d'autres plantes de la même famille afin de trouver le ou les précurseurs directs de cet alcaloïde artefact. *Lasianthera austrocaledonica* est un arbre de 8 à 15 m de hauteur. Dans la présente note, nous décrivons les alcalo-