Agrimoniin and Potentillin, an Ellagitannin Dimer and Monomer having an α-Glucose Core

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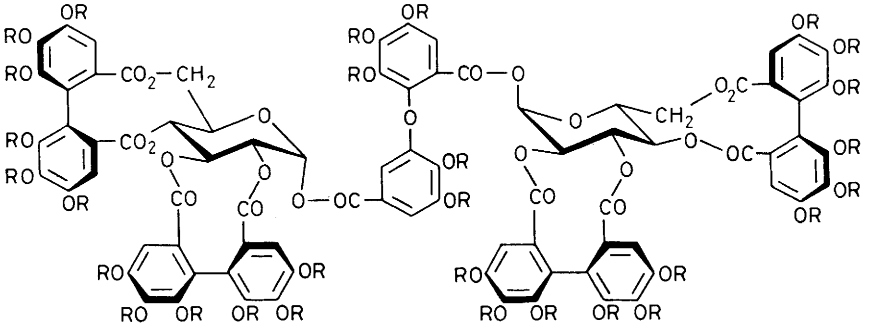
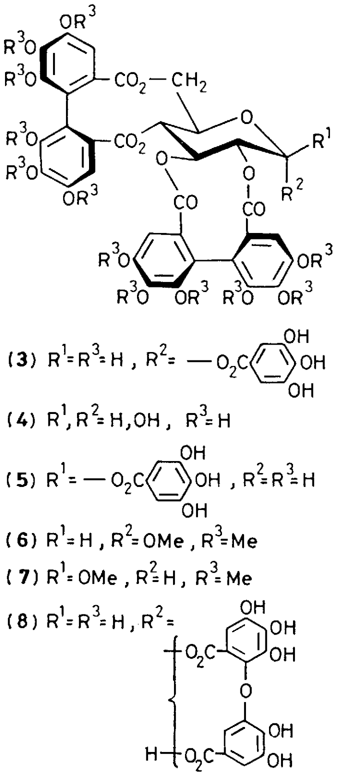
Potentillin (**3**), which has an α-glucosyl linkage, and its dimer, agrimoniin (**1**) have been isolated from *Agrimonia pilosa* Ledeb. and *Potentilla kleiniana* Wight et Arnott., and their structures elucidated.

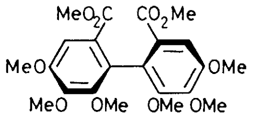
Hydrolysable tannins of known structures have a monosaccharide or a cyclic polyalcohol core which is esterified by polyphenolic acids. Although it was assumed that dimeric ellagitannins occurred in nature,[1,2] there was no clear structural evidence for this. We have now isolated a dimeric ellagitannin, which we have named agrimoniin (**1**), from two species of Rosaceae plants.

This tannin, and also potentillin (**3**) which is an α-glucosyl ellagitannin and is the monomer unit of (**1**), along with pedunculagin (**4**),[3] have been isolated from *Agrimonia pilosa* Ledeb. and *Potentilla kleiniana* Wight et Arnott., which have been used as antidiarrhoeics and styptics in Japan and China. Potentillin (**3**)† was obtained as an off-white amorphous powder, $C_{41}H_{28}O_{26}.5H_2O$, $[\alpha]_D$ + 108° (*c* 0.7, EtOH), λ_{max} (MeOH) 222 (log ε 4.81) and 258 nm (4.55). Its ^1H n.m.r. spectrum (200 MHz; CD_3OD) [δ 7.17 (2H, s, galloyl); 6.61, 6.53, 6.43, 6.38 (1H each, s, 2 × hexahydroxydiphenoyl); and 6.54 (1H, d, *J* 3.5 Hz, glucose anomeric H)], which is analogous to that of casuarictin (**5**),[3] except for the chemical shift and coupling constant of the glucose anomeric proton, indicates that (**3**) could be an α-isomer of (**5**). This assumption was confirmed by hydrolysis of (**3**) with tannase, which yielded pedunculagin (**4**) and gallic acid. Therefore, potentillin has the 1-*O*-galloyl-2,3;4,6-di-*O*-[(*S*)-hexahydroxydiphenoyl]-α-D-glucose structure (**3**).

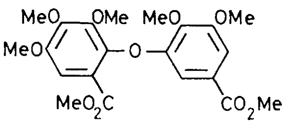


(**1**) R = H
(**2**) R = Me





(**9**)



(**10**)

Agrimoniin (**1**), $C_{82}H_{54}O_{52}\cdot 13H_2O$, $[\alpha]_D$ + 162° (*c* 1.0, EtOH), λ_{max} (MeOH) 232 (log ε 5.20) and 270 nm (5.05), was isolated as an off-white amorphous powder, which is chromatographically homogeneous [h.p.l.c. (normal phase and gel permeation) and t.l.c. (cellulose)]. Its ^1H n.m.r. spectrum (200 MHz; CD_3OD) exhibits nine singlets at δ 6.36, 6.37, 6.38, 6.41, 6.44, 6.54, 6.60, 6.71, and 7.27, and two doublets (*J* 2 Hz) at δ 6.85 and 7.39 in the aromatic region, together with two doublets (*J* 3.5 Hz) due to the sugar anomeric protons at δ 6.50 and 6.61, the latter overlapping that at δ 6.60. Methylation of (**1**) with CH_2N_2 gave a product which we regard as the nonacosamethyl derivative (**2**), which yielded upon methanolysis dimethyl (*S*)-hexamethoxydiphenate (**9**),[3] $[\alpha]_D$ − 34° (*c* 1.0, EtOH), dimethyl penta-*O*-methyldehydrodigallate (**10**),[4,5] and glucose. The molar ratio (3.9:1) of (**9**) to (**10**) was shown by g.l.c. (1% OV-1; column temp. 240 °C). These data indicate that agrimoniin is composed of a dehydrodigalloyl group, four hexahydroxydiphenoyl groups, and two glucose residues. This assumption was also supported by the

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† Satisfactory analytical and spectral data have been obtained for all new compounds.

^{13}C n.m.r. spectrum and by molecular weight estimation using h.p.l.c. (gel permeation).

Treatment of (**1**) with Me_2SO_4 and K_2CO_3 in acetone afforded the α-anomer (**6**) and the β-anomer (**7**) of trideca-*O*-methylpedunculagin,[3] along with (**10**). Another partial hydrolysate (**8**) [^1H n.m.r. (CD_3OD) δ 6.43, 6.50, 7.18 (1H each, s); 6.68 (2H, s); 6.80, 7.31 (1H each, d, *J* 2 Hz); and 6.43 (1H, overlapped by the signal at δ 6.43, anomeric H)] was also obtained by treatment of (**1**) with tannase. The α-configuration at C-1 of the two glucose moieties in (**1**) was determined by the coupling constants (*J* 3.5 Hz) in the ^1H n.m.r. spectrum and the chemical shifts (δ 91.9 and 91.5) of the anomeric carbon signals in the ^{13}C n.m.r. spectrum.

These data indicate that argimoniin has the structure (**1**), the first example of a dimeric ellagitannin which has been confirmed to occur in nature.

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References

1 M. K. Seikel and W. E. Hillis, *Phytochemistry*, 1970, **9**, 1115.
2 E. C. Bate-Smith, *Phytochemistry*, 1972, **11**, 1153.
3 T. Okuda, T. Yoshida, and M. Ashida, *Heterocycles*, 1981, **16**, 1681.
4 W. Mayer, *Liebigs Ann. Chem.*, 1952, **578**, 34.
5 T. Ozawa, K. Haga, D. Kobayashi, T. Kamiyama, and Y. Takino, *Agric. Biol. Chem.*, 1977, **41**, 1249.