

Hydrolyzable Tannin Structural Chemistry

Ann E. Hagerman

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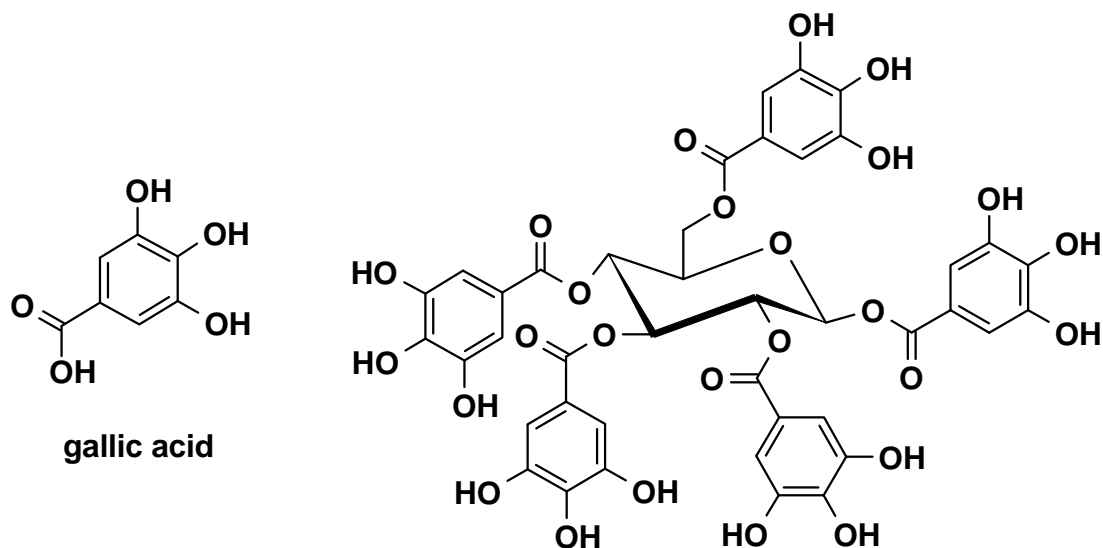
Introduction

Hydrolyzable tannins are derivatives of gallic acid (3, 4, 5-trihydroxyl benzoic acid). Gallic acid is esterified to a core polyol, and the galloyl groups may be further esterified or oxidatively crosslinked to yield more complex hydrolysable tannins.

Early work on hydrolyzable tannins included Haslam's significant elucidations of the structures of the simple gallotannins (Haslam, E. *Plant polyphenols. Vegetable tannins revisited*, ed.; Cambridge University Press: Cambridge, U. K., 1989). More recently, Okuda et al. (Okuda, T.; Yoshida, T.; Hatano, T. Hydrolyzable tannins and related polyphenols. *Progress in the Chemistry of Organic Natural Products* **1995**, *66*, 1-117) have been particularly active in characterization and classification of complex hydrolyzable tannins. Feldman's synthetic work (Feldman KS, Lawlor MD, and Sahasrabudhe K Ellagitannin chemistry. Evolution of a three-component coupling strategy for the synthesis of the dimeric ellagitannin coriariin A and a dimeric gallotannin analogue. 2000; 8011-9) has provided useful insights into likely biosynthetic routes for the complex hydrolyzable tannins. A limited survey of structures and their relationships is provided here.

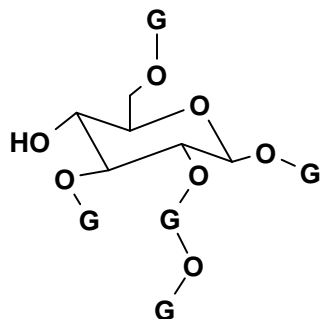
Gallotannins

The simplest hydrolyzable tannins, the gallotannins, are simple polygalloyl esters of glucose. The prototypical gallotannin is pentagalloyl glucose (β -1,2,3,4,6-Pentagalloyl-*O*-D-Glucopyranose). Pentagalloyl glucose, or PGG, has five identical ester linkages that involve aliphatic hydroxyl groups of the core sugar. The alpha anomer is not common in nature.

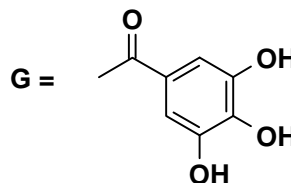


β -1,2,3,4,6-pentagalloyl-*O*-D-glucose

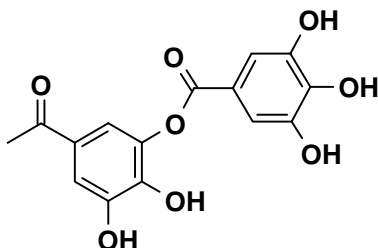
Like all of the gallotannins, PGG has many isomers. The molecular weights of all the isomers of PGG are the same (940 g/mol), but chemical properties such as susceptibility to hydrolysis and chromatographic behavior; and biochemical properties such as ability to precipitate protein; are structure-dependent.



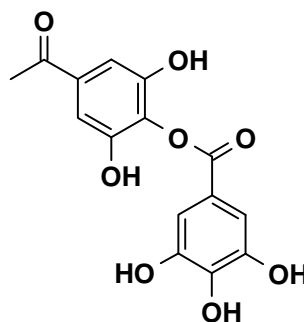
β -1,2,2,3,6-Pentagalloyl-O-D-Glucose



galloyl ester



**GOG = digalloyl ester,
meta-depside bond**



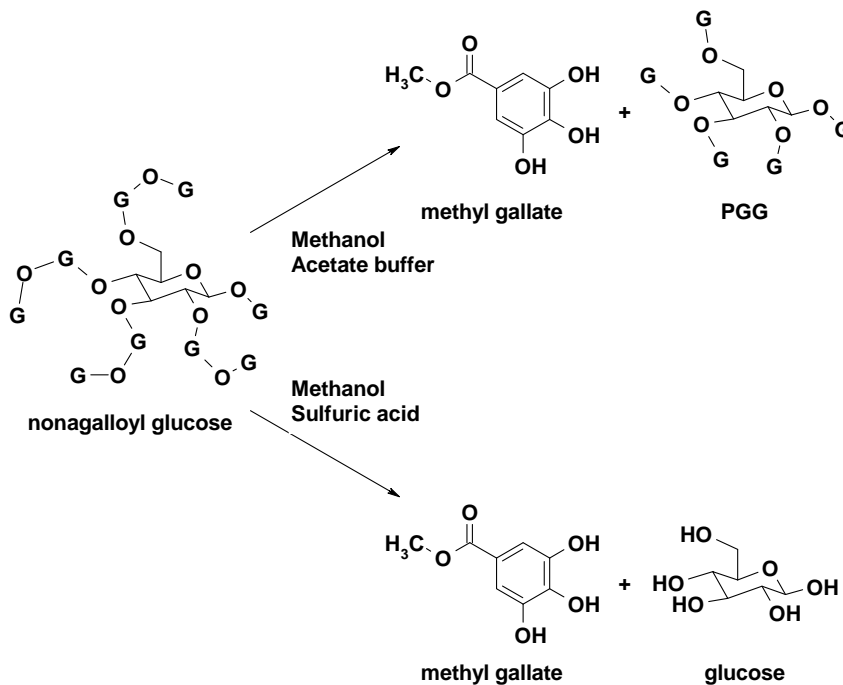
**GOG = digalloyl ester,
para-depside bond**

The polygalloyl ester chains found in gallotannins are formed by either *meta*- or *para*-depside bonds, involving a phenolic hydroxyl rather than an aliphatic hydroxyl group. The depside bond is more easily hydrolyzed than an aliphatic ester bond. Methanolysis in weak acid in methanol breaks depside but not ester bonds. Thus the core polyol with its esterified galloyl groups can be produced from complex mixtures of polygalloyl esters by methanolysis with acetate buffer. Strong mineral acid, heat and methanol can be used to methanolze both despide and ester bonds yielding the core polyol and methyl gallate. Hydrolysis with strong acid converts gallotannins to gallic acid and the core polyol.

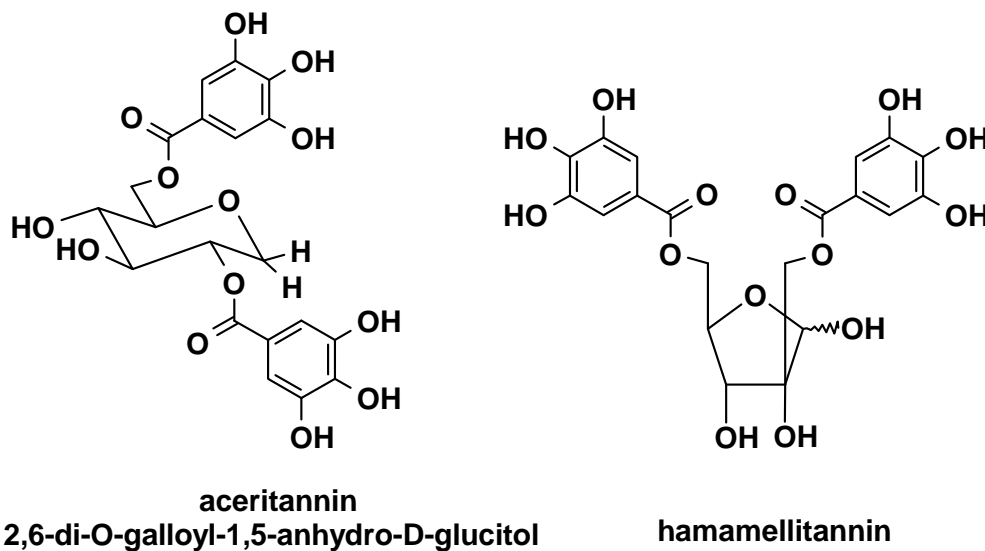
Simple gallotannins with up to 12 esterified galloyl groups and a core glucose are routinely found in tannins from sumac or oak galls. Commercial tannic acid is comprised of mixtures of gallotannins from sumac (*Rhus semialata*) galls (Chinese gallotannin); Aleppo oak (*Quercus infectoria*) galls (Turkish gallotannin); or sumac (*R. coriaria*, *R. typhina*) leaves (sumac gallotannin). Although commercial sources provide a nominal molecular weight for tannic acid (1294 g/mol), the preparations are heterogeneous and variable mixtures of galloyl esters. Tannic acid is not an appropriate standard for any tannin analysis because of its poorly defined composition.

PGG can be prepared from some commercial tannic acids by methanolysis in acetate buffer. For the preparation to be successful, the tannic acid must have PGG as its core ester, most likely in preparations of Chinese or sumac gallotannin. Turkish gallotannin is comprised of esters of 1,2,3,6-tetragalloyl glucose; or 1,3,4,6-tetragalloyl glucose.

Although for many gallotannins glucose is the alcohol, other polyols including glucitol;



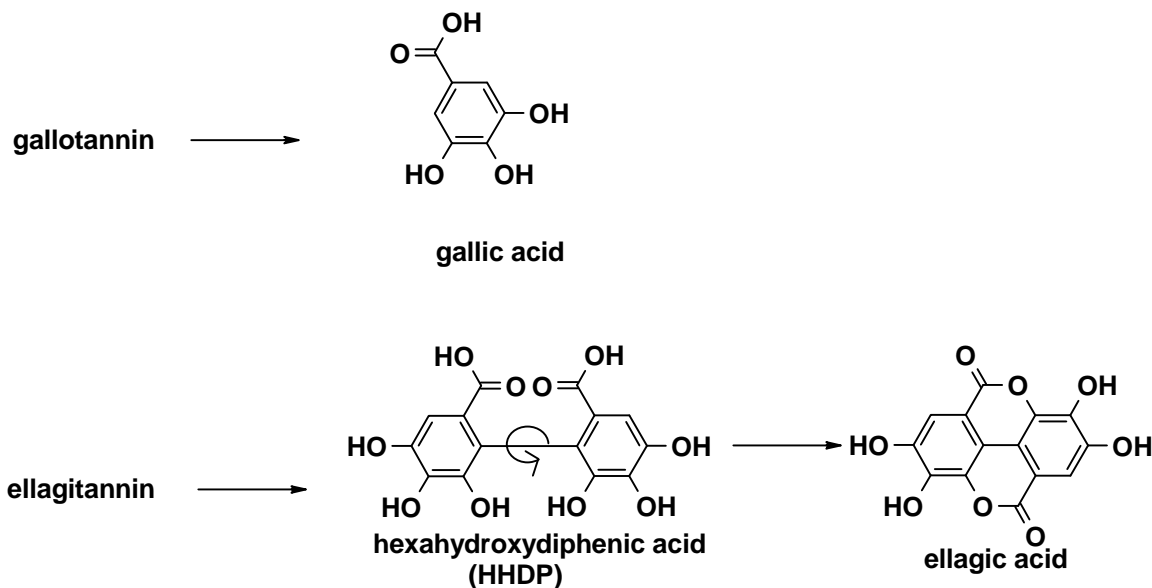
hamamelose; shikimic acid; quinic acid; and quercitol; have been reported as constituents of gallotannins from a few species. For example, aceritannin is found in leaves of several species of maple (*Acer*), and hamamellitannin is found in bark of witch hazel (*Hamamelis virginiana*), oak (*Quercus rubra*),



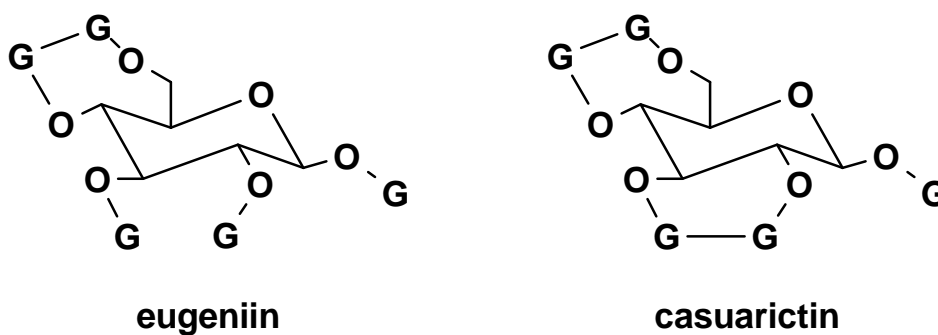
and several chestnut species (*Castanea* sp.).

Ellagitannins

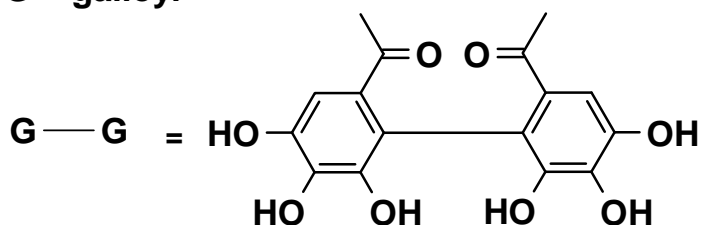
Oxidative coupling of galloyl groups converts gallotannins to the related ellagitannins. The simple ellagitannins are esters of hexahydroxydiphenic acid (HHDP). HHDP spontaneously lactonizes to ellagic acid in aqueous solution.

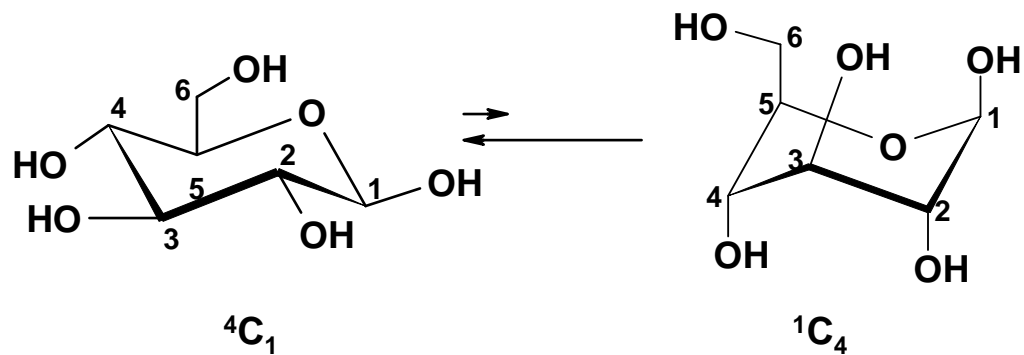


Intramolecular carbon-carbon coupling to form HHDP is most common between C-4/C-6 (e.g. eugeniin); and C-2/C-3 (e.g. casuarictin, also has C-4/C-6), as would be expected for polygalloyl glucoses in the more stable 4C_1 conformation. However, in a few plants intramolecular coupling occurs at C-3/C-6 (e.g. corilagin), C-2/C-4 (e.g. geraniin, also has C-3/C-6), or C-1/C-6 (e.g. davidiin), suggesting the



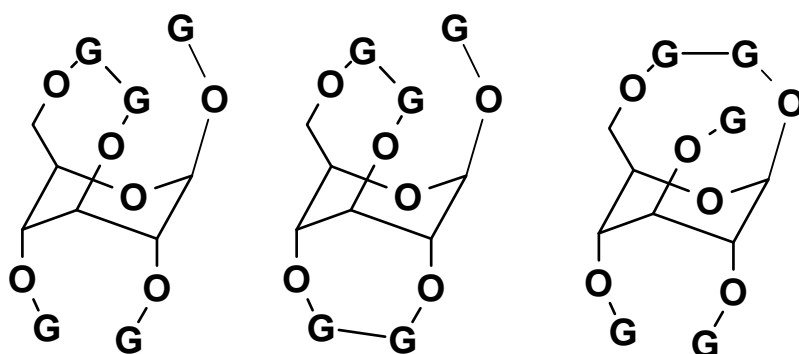
G = galloyl





β -D-glucose

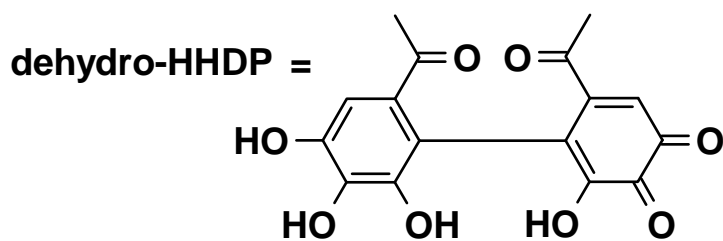
polygalloyl glucose starting material was in the less stable 1C_4 conformation. Geraniin is further characterized by partial oxidation of the C-2/C-4 HHDP to dehydro-HHDP, and in aqueous solution several forms of dehydro-HHDP can be detected in geraniin by nmr.



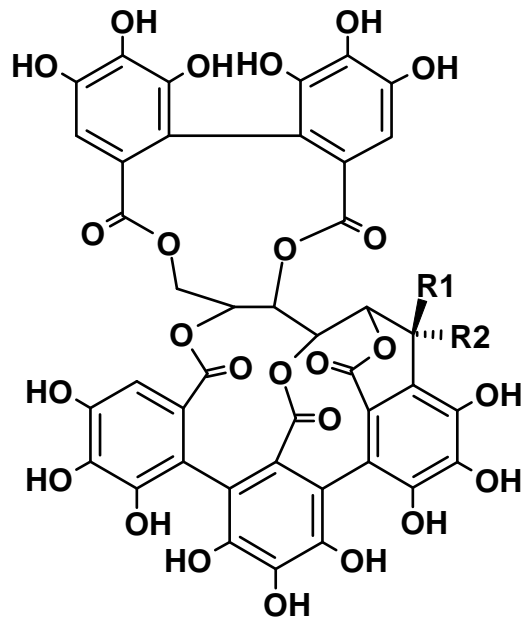
corilagin

geraniin

davidiin

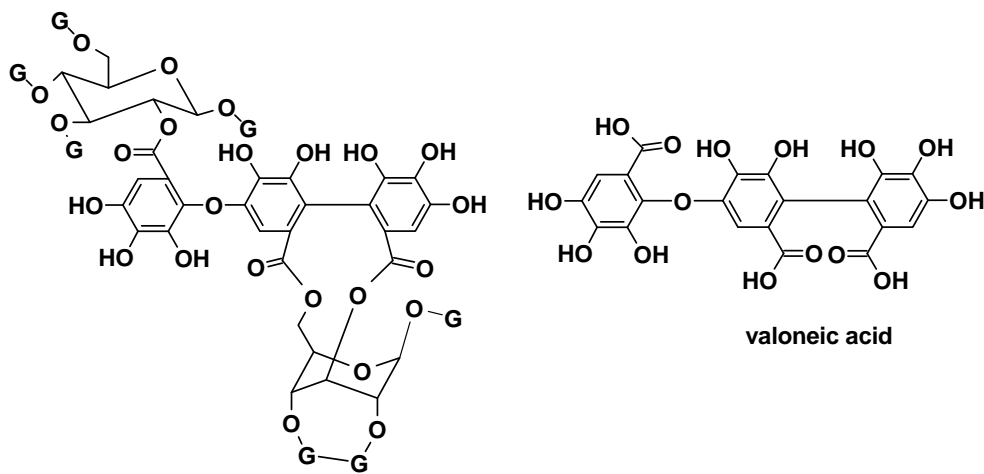


In some plants including oak and chestnut the ellagitannins are further elaborated via ring opening. Thus after conversion of casuarictin to pedunculagin, the pyranose ring of the glucose opens and the family of compounds including casuariin, casuarinin, castalagin, and castlin; stachyurin, vescalagin and vescalin forms.



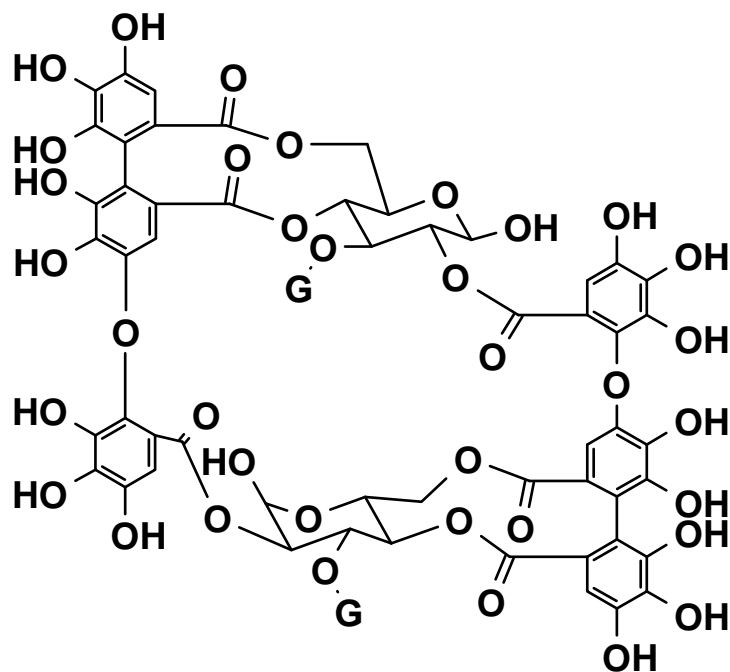
R1 = H, R2 = OH castalagin
 R1 = OH, R2 = H vescalagin

The ellagitannins can undergo intermolecular oxidative coupling with other hydrolysable tannins to yield dimers. For example, in several euforbs (e.g. *Euphorbia watanabei*) geraniin oxidatively condenses with PGG to yield various euphorbins, characterized by the valoneoyl group.



euphorbin A
 G-G is a partially oxidized HHDP

Oenethein B, Woodfordin C, Cuphiin D₁ and Eugeniflorin D₁ are macrocyclic dimers linked by two valoneoyl groups, and the nobotanins are macrocyclic trimers.



oenethein B