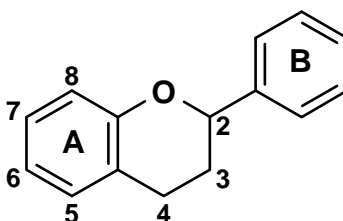


Condensed Tannin Structural Chemistry

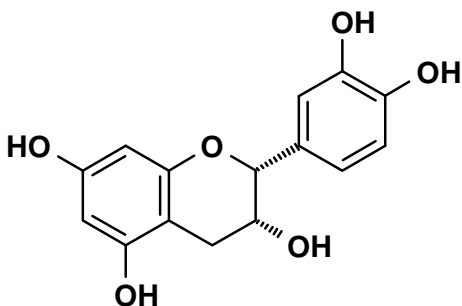
Ann E. Hagerman © March 28, 2002

Proanthocyanidins (condensed tannins) are polymeric flavanoids. The flavanoids are a diverse group of metabolites based on a heterocyclic ring system derived from phenylalanine (B) and polyketide biosynthesis (A). Although the biosynthetic pathways for flavanoid synthesis are

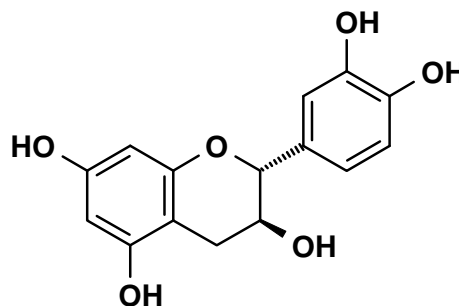


well understood, the steps leading to condensation and polymerization have not been elucidated. The flavanoid skeleton, the standard letters to identify the rings, and the numbering system are shown here.

The most widely studied condensed tannins are based on the flavan-3-ols (-)-epicatechin and (+)-catechin.



epicatechin

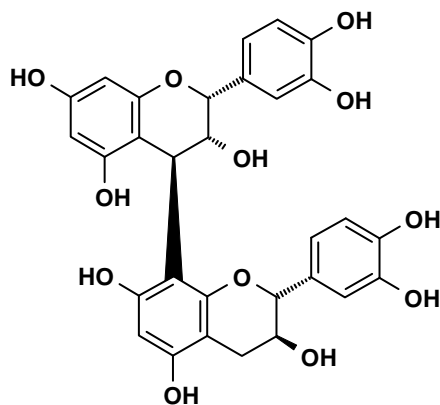


catechin

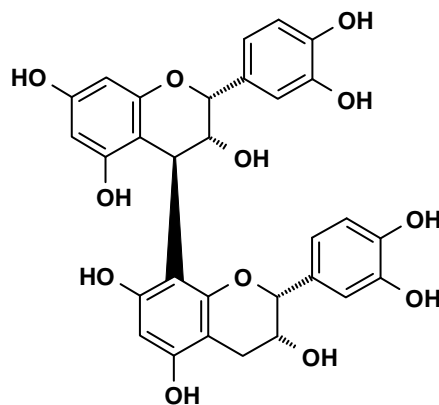
Flavan-3-ols

Addition of a third phenolic group on the B ring yields epigallocatechin and galocatechin. Much less common are flavan-3-ols with only a single phenolic group on the B ring, *para* to C-2 (epiafzelechin, afzelechin with stereochemistry corresponding to epicatechin, catechin respectively).

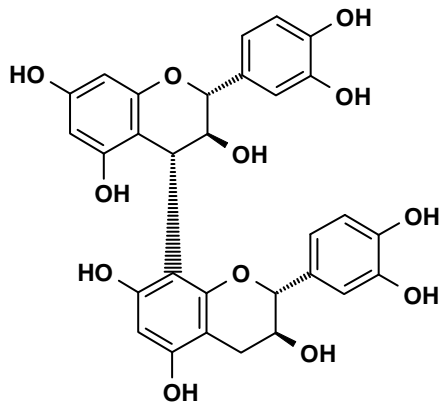
The best characterized condensed tannins are linked via a carbon-carbon bond between C8 of the terminal unit and C4 of the extender. The four common modes of coupling are illustrated by the dimers isolated by Haslam, and originally named B-1, B-2, B-3 and B-4. The more complete names specify the position and stereochemistry of the interflavan bond completely. In addition to these dimers, related dimers linked by C6 of the terminal unit and C4 of the extender have been isolated.



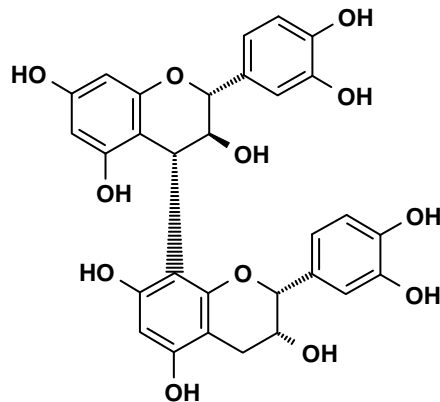
B-1
epicatechin-(4 β ->8)-catechin



B-2
epicatechin-(4 β ->8)-epicatechin

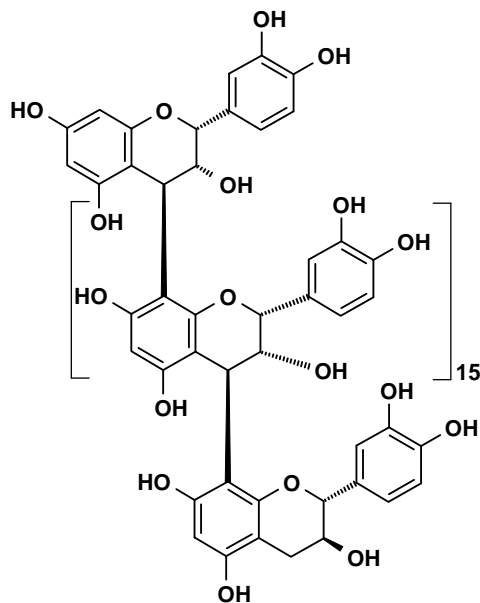


B-3
catechin-(4 α ->8)-catechin



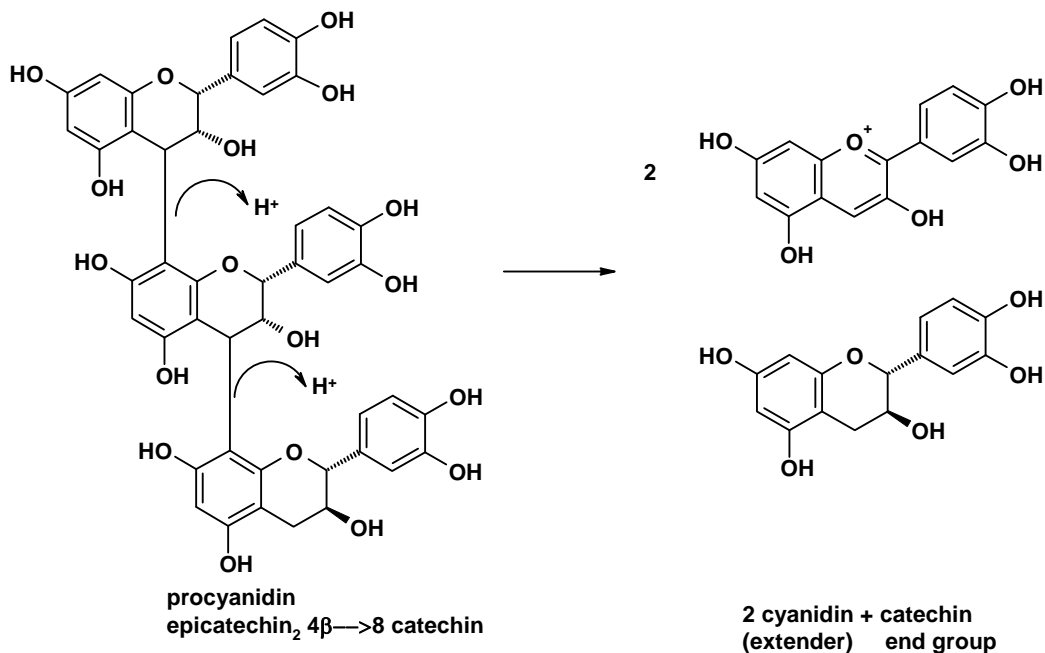
B-4
catechin-(4 α ->8)-epicatechin

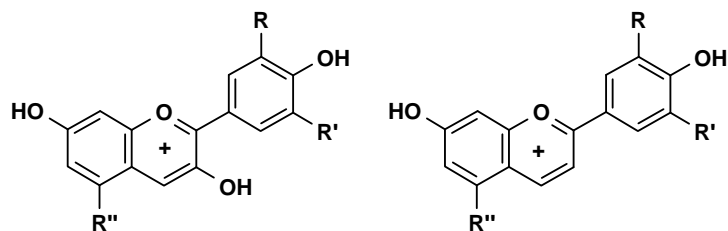
Further polymerization can yield the linear 4,8 polymers such as the Sorghum procyanidin. Linear polymers based on 4,6 dimers; and branched dimers containing both 4,6 and 4,8 linkages are less common.



Sorghum procyanidin
epicatechin-[(4 β ->8)-epicatechin]₁₅-(4 β ->8)-catechin

Although the term condensed tannins is still widely used to describe these flavonoid-based polyphenolics, the chemically more descriptive term “proanthocyanidin” is gaining acceptance. Proanthocyanidins are compounds that yield anthocyanidin pigments upon oxidative cleavage (NOT hydrolysis) in hot alcohols, e.g. via acid butanol chemistry.





$R'' = \text{OH}$
 $R = R' = \text{H}$, pelargonidin
 $R = \text{H}, R' = \text{OH}$, cyanidin
 $R = R' = \text{OH}$, delphinidin

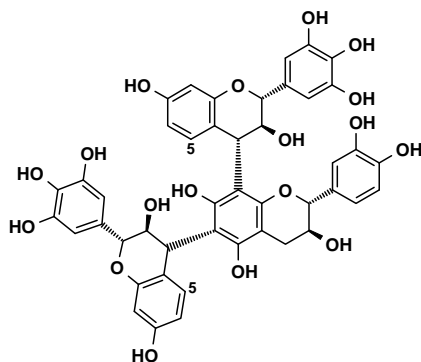
$R'' = \text{OH}$
 $R = R' = \text{H}$, apigeninidin
 $R = \text{H}, R' = \text{OH}$, luteolinidin

$R'' = \text{H}$
 $R = R' = \text{H}$, guibourtinidin
 $R = \text{H}, R' = \text{OH}$, fisetinidin
 $R = R' = \text{OH}$, robinetinidin

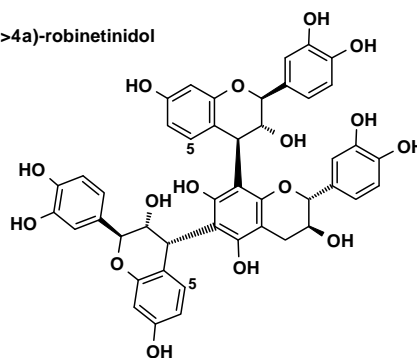
Anthocyanidins

The products of the acid butanol reaction are an unmodified terminal unit, and the colored anthocyanidins produced by the extender units. Catechin- and epicatechin-based polymers produce cyanidin, and thus are known as procyanidins. Gallicocatechin and epigallocatechin-based polymers yield delphinidin, and the rare mono-substituted flavan-3-ol based polymers yield pelargonidin.

An important group of condensed tannins are 5-deoxy-flavan-3-ols polymers. Branching is common in these tannins, because of the reactivity of the 5-deoxy A ring. Profisetinidins and



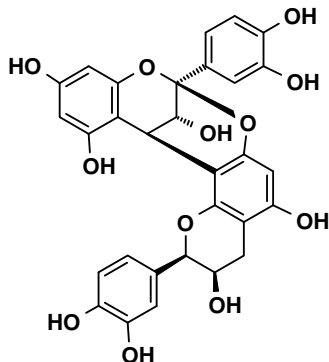
robinetinidol-(4 α ->8)-catechin-(6 α ->4a)-robinetinidol



profisetinidin

Another type of linkage that has been described but not studied extensively involves oxidative C-O coupling between the flavonoid rings to yield A2 and related proanthocyanidins.

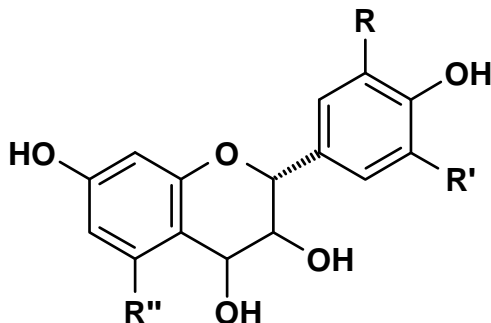
The flavan-3,4-diols, or leucoanthocyanidins, are sometimes confused with proanthocyanidins.



epicatechin-(2 β -->7,4 β -->8)-epicatechin

proanthocyanidin A-2

The flavan-3,4-diols are monomeric flavonoids that yield the anthocyanidins upon treatment with heat and acid. They thus have reactive chemistry similar to that of the condensed tannins, but they do not interact with protein to form precipitable complexes.



Flavan-3,4-diols

R'' = H (stable)

R = H, R' = OH, leucofisetinidin

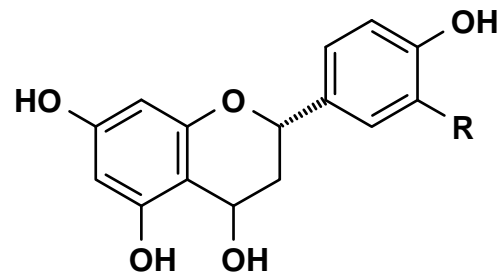
R'' = OH (unstable)

R = R' = H, leucopelargonidin

R = H, R' = OH, leucocyanidin

R = R' = OH, leucodelphinidin

The flavan-4-ols are also leucoanthocyanidins, but are unique in their lability. They yield the anthocyanidins upon treatment with alcoholic acid at room temperature.



Flavan-4-ols

R = H, apiferol (leucoapigeninidin)

R = OH, luteoferol (leucoluteolinidin)

Stafford has suggested that pro-3-deoxyanthocyanidins might exist in a few plants. Evidence to date is limited to spectroscopy and some chemical conversions that are consistent with the chemistry shown here. (Stafford, H.A. *Flavonoid Metabolism*; CRC Press: Boca Raton, FL, 1990, pages 65-83).

