

## Chemistry and Utilization of Condensed Tannins from Tree Barks

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### Abstract

Chemical characteristics, protein-adsorbing capacity, chemical modifications and utilization of condensed tannins from tree barks were reviewed. Various aspects relating to the chemistry of these compounds and prospects for their utilization were discussed. Condensed tannins from *Quercus falcata*, *Salix sieboldiana* and most of the Japanese conifers consist mainly of procyanidins and those from *Acacia mearnsii* of pro robinetinidins. The protein-adsorbing capacity of condensed tannins is closely related to their molecular weights and the positions of phenolic hydroxyl groups in the B-ring. The most effective hydroxyl group is located in the *para*-position. In the reactions of catechin, the pyran ring is cleaved by alkaline treatment at 40°C or phenolation in the presence of BF<sub>3</sub>. The latter reaction can be effective for opening the pyran ring selectively. The tannins can be processed for utilization as cold-setting adhesives, polyurethane foams and adsorbents of heavy metal ions. Prospects for uses of condensed tannins include applications to biologically active compounds and functional materials.

**Discipline:** Forestry and forest products

**Additional key words:** catechin, proanthocyanidins, protein-adsorbing capacity, pyran ring, tannin-derived polyurethane foams

### Introduction

Vegetable tannins are widely distributed in plants and have been used as tanning agents, dyestuffs and drugs since older times. They can be divided into two major groups, condensed tannins and hydrolysable tannins. The former group consists of proanthocyanidins and the latter of polyesters based on gallic acid or hexahydroxydifenic acid and their derivatives. Condensed tannins are distributed in ferns and allied species, and both monocotyledoneae and

dicotyledoneae. They are present at very high concentrations in the bark of timber species such as conifers, eucalypts and leguminous hardwoods. Their molecular weights cover a wider range than those of hydrolysable tannins with the highest one being 20,000. Recently, many investigations on new forms of utilization and biological activities have been reported.

In this paper the classification, chemical characteristics, protein-adsorbing capacity and chemical modifications of condensed tannins, as well as several fields of utilization are reviewed. Furthermore, various aspects relating

to the chemistry of these compounds and prospects for their utilization are discussed.

## Classification

Condensed tannins belong to proanthocyanidins as plant secondary metabolites. Proanthocyanidins which are polymers of several kinds of flavan-3-ols are classified as shown in Fig. 1, according to the hydroxylation patterns of A- and B-rings of the monomer units<sup>8)</sup>. Procyanidins are widely distributed and prodelphinidins, profisetinidins and prorobinetinidins are also found frequently in many plants. As each flavan-3-ol has two asymmetric carbon atoms in the C-ring, there are four stereoisomers. Guibourtinidol, fisetinidol, robinetinidol, afzelechin, catechin and galocatechin are the monomer units with a (2R, 3S) absolute stereochemistry corresponding to progibourtinidin, profisetinidin, prorobinetinidin, propelargonidin, procyanidin and prodelphinidin, respectively. The corres-

ponding (2R, 3R) isomers are designated by the addition of the prefix 'epi' to the beginning of each monomer name, and (2S, 3R) or (2S, 3S) isomers are indicated by the addition of the prefix *ent* to the beginning of the appropriate monomer name.

## Chemical characteristics

### 1) *Quercus falcata*

*Q. falcata* (southern red oak) is the most important species of red oak in the forests of the southern United States. Related compounds of condensed tannins isolated from the bark of the southern red oak are listed in Fig. 2<sup>9)</sup>. The bark of southern red oak is a rich source of quercetin-3-rhamnoside (1) and it contains only low concentrations of catechin (2). The three major dimeric proanthocyanidins are epicatechin-(4 $\beta$ -8)-catechin (3), catechin-(4 $\alpha$ -8)-catechin (5) and the 3-gallate ester of epicatechin-(4 $\beta$ -8)-catechin (4). The acetone-water soluble tannins with a higher molecular weight consist of polymeric procyanidins predominantly made up of 2,3-*cis* chain extender units with a 2,3-*trans* catechin terminal. The polymers contain only small amounts of 2,3-*trans* procyanidin chain extender units and only traces of prodelphinidin units.

### 2) *Salix sieboldiana*

There is only one report on the chemical analysis of proanthocyanidins in the *Salix* species grown in Japan. Proanthocyanidins and their derivatives from the bark of *S. sieboldiana*, a shrub common in Japan, are shown in Fig. 3<sup>2)</sup>. This species contains a homologous series of acylated procyanidins (7), (9) and (11), together with the widespread procyanidin B-1(6), B-3(8) and trimer (10). Their structures are assigned to the 3-O-(1-hydroxy-6-oxo-2-cyclohexene carboxylic acid esters) of procyanidins B-1, B-3 and trimer. As 1-hydroxy-6-oxo-2-cyclohexene carboxylic acid is structurally related to saligenin, it is considered to be

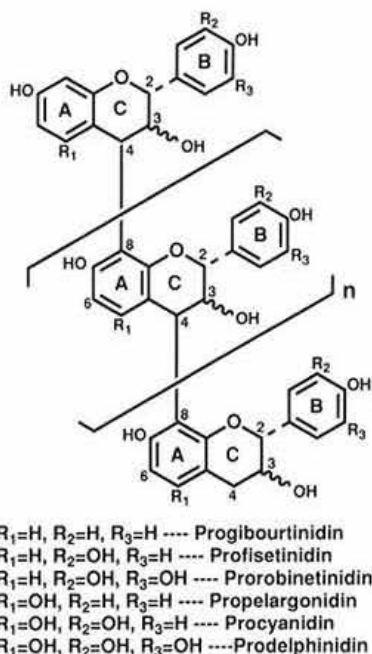


Fig. 1. Proanthocyanidin classification

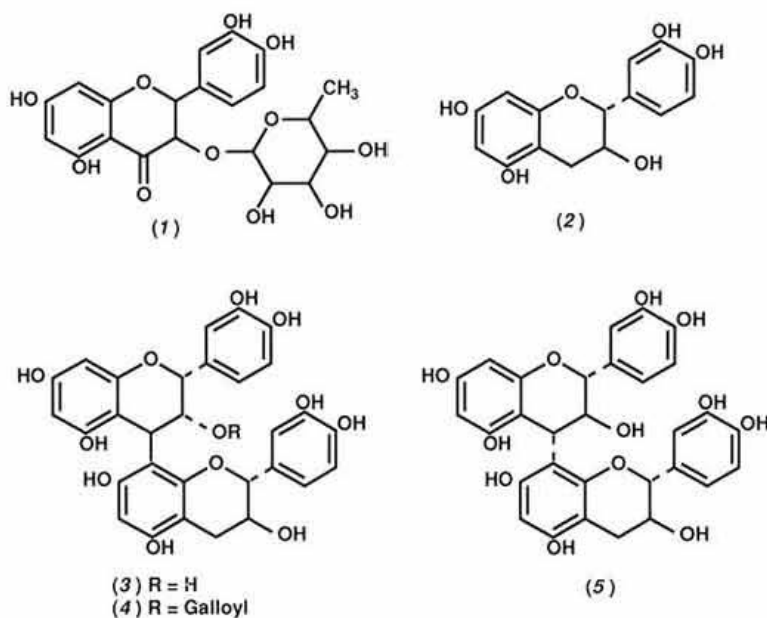


Fig. 2. Compounds isolated from the bark of southern red oak

a biosynthetic precursor of salicin which is a common constituent in the Salicaceae.

### 3) *Acacia mearnsii*

The bark of *A. mearnsii* is a good source of tannins (phenol content 38%, tannin content 24%<sup>7)</sup>). It contains a large amount of low molecular weight proanthocyanidins. About 30% of 70% acetone extracts from the bark are dimers or trimers. Major dimeric proanthocyanidins are robinetinidol-(4 $\alpha$ -8)-catechin (12) and robinetinidol-(4 $\alpha$ -8)-gallo catechin (13) (Fig. 3). The acetone-water soluble tannins with a higher molecular weight are proanthocyanidin polymers with a 2,3-*trans* heterocyclic ring, the extender units of which consist mainly of prorobinetinidin units.

### 4) *Conifers*

Many Japanese conifers contain a large amount of phenolic extractives in the bark, and proanthocyanidins are the main components of these phenolic extractives. Flavanol and tannin contents in the bark of the Japanese main

conifers amount to 5–18% and 2–7%, respectively<sup>9)</sup>. The composition of the polymeric proanthocyanidins from 9 species of conifers is shown in Table 1<sup>10)</sup>. Although polymeric proanthocyanidins from the bark are composed generally of polymeric procyanidins in many coniferous species, *Abies sachalinensis* and *Picea jezoensis* contain a certain amount of polymeric prodelfphinidins. The level of stereochemistry of the flavan-3-ol monomer units of the polymers varies considerably with the species. As for the extender units, the polymers from Cupressaceae and *Cryptomeria japonica* show nearly the same or higher ratios of 2,3-*trans* units to 2,3-*cis*. On the other hand, the polymers from Pinaceae show extremely high ratios of 2,3-*cis* units to 2,3-*trans*. In the terminal units, 2,3-*trans* units predominate and almost all the units consist of 2,3-*trans* in *P. jezoensis* and *Pinus densiflora*.

### Protein-adsorbing capacity

Condensed tannins are able to precipitate

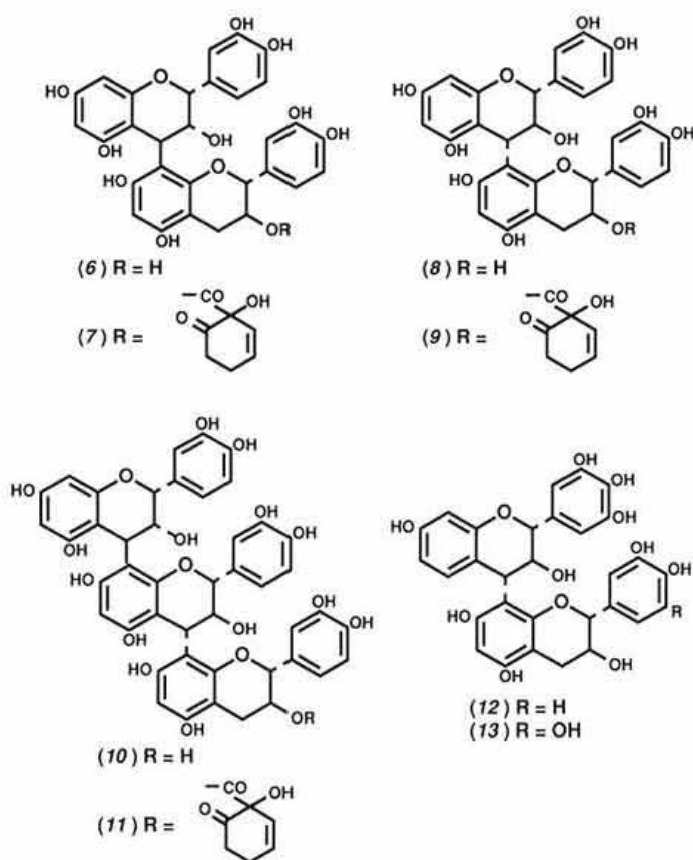


Fig. 3. Proanthocyanidins and their derivatives from the bark of *Salix sieboldiana* and *A. mearnsii*

Table 1. Composition of polymeric proanthocyanidins from coniferous bark

	Pcy:Pdp <sup>a)</sup>	Ratios of stereochemistry (2,3- <i>trans</i> :2,3- <i>cis</i> )	
		Extender units	Termination units
Cupressaceae			
<i>Chamaecyparis obtusa</i>	100:0	60:40	59:41
<i>Chamaecyparis pisifera</i>	100:0	54:46	64:36
Taxodiaceae			
<i>Cryptomeria japonica</i>	100:0	78:22	69:31
Pinaceae			
<i>Abies sachalinensis</i>	71:29	73:27	84:16
<i>Larix leptolepis</i>	100:0	11:89	80:20
<i>Picea jezoensis</i>	95:5	11:89	100:0
<i>Pinus densiflora</i>	100:0	7:93	97:3
<i>Tsuga sieboldii</i>	100:0	11:89	44:56
<i>Pseudotsuga japonica</i>	100:0	16:84	23:77

a): Pcy; Procyanidins, Pdp; Prodelphinidins.

proteins and it is assumed that they are involved in the chemical defense of some plants against predators such as insects and herbivores. In the tannin-protein interaction, phenolic hydroxyl groups in the A- and B-rings play important roles. Results of BSA-precipitating tests of synthesized condensed tannin oligomers with mono-, di-, and tri-hydroxylated B-rings are shown in Fig. 4<sup>3)</sup>. BSA-precipitating capacity of oligomers D and G accounts for 83 and 87% of that of oligomer F, respectively. These results indicate that the condensed tannins with only a 4'-hydroxylated B-ring show almost a similar capacity to that of the tannins with 3', 4'-dihydroxylated or 3', 4', 5'-tri-hydroxylated B-rings.

The protein-adsorbing capacity of proanthocyanidin dimers, trimers, tetramers and polymers from the bark of *A. mearnsii* is shown in Fig. 5<sup>7)</sup>. The results indicate the following relationships between the degree of polymerization of proanthocyanidins and protein-adsorbing capacity: 1) Dimers hardly display a protein-adsorbing capacity. 2) The protein-

adsorbing capacity increases with the increase of the molecular weights. 3) Tetramers show a capacity nearly equal to that of polymers.

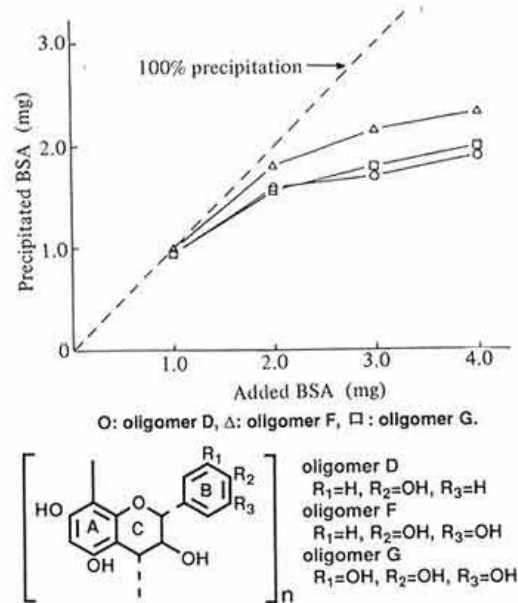


Fig. 4. BSA-precipitating capacity of synthesized condensed tannin oligomers

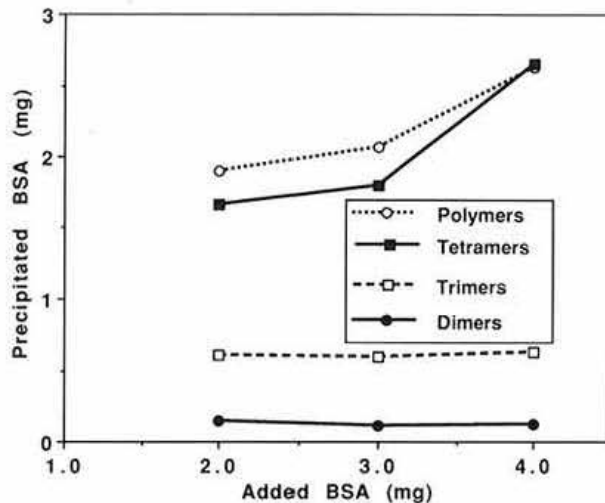


Fig. 5. Protein-adsorbing capacity of proanthocyanidin dimers, trimers, tetramers and polymers from the bark of *A. mearnsii*

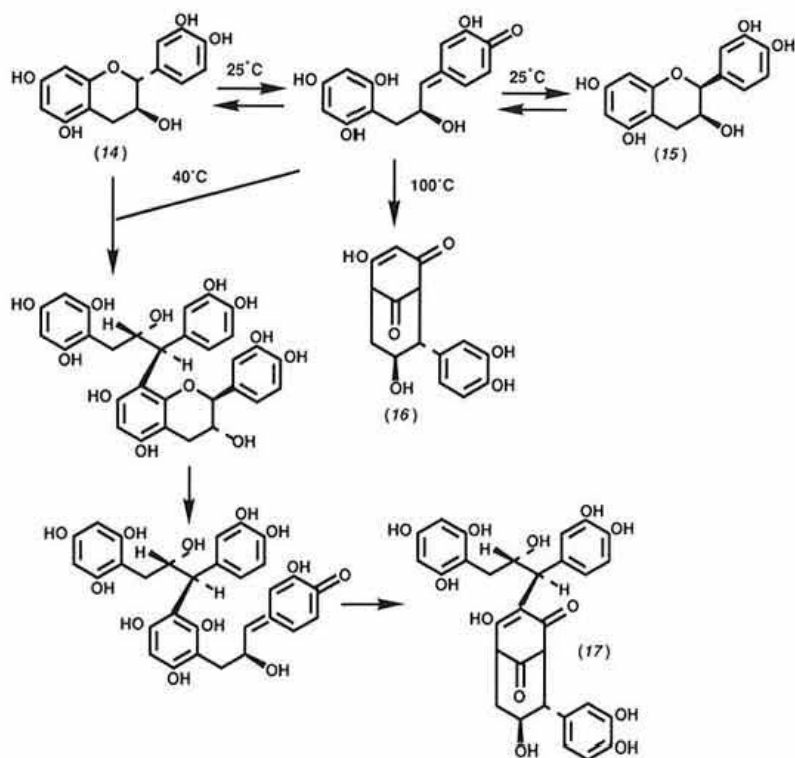


Fig. 6. Base-catalyzed reactions of (+)-catechin

## Chemical modifications

### 1) Alkaline rearrangement reaction

When condensed tannins are treated with alkaline media, a reduction of the phloroglucinol ring and appearance of carbonyl groups are observed. Therefore condensed tannins are considered to undergo some base-catalyzed rearrangement reaction. Reaction of catechin (14) at pH 12 is shown in Fig. 6<sup>6)</sup>. In reactions at 25°C, the principal reaction consists of the opening of the pyran ring to give the quinonemethide and reclosure of the pyran ring to give catechin and *ent*-epicatechin (15), with the former predominating in a ratio of about 3 to 1. When the same reaction is carried out at 100°C, catechinic acid (16) is obtained at a high yield. At 40°C, a dimeric product consisting of a 1-(3,4-dihydroxyphenyl)-

3-(2,4,6-trihydroxyphenyl) propane-2-ol substituted at C-1 with a catechinic acid moiety (17) is formed in a yield of about 20%.

### 2) Phenolation by Lewis acid catalyst

As the rotational degree of freedom of condensed tannins is considerably low due to the presence of a pyran ring, it is important to develop a method for opening the pyran ring selectively. Phenolation catalyzed by  $\text{BF}_3$  is a very promising method. The phenol modification of catechin (14) in the presence of  $\text{BF}_3$  is shown in Fig. 7<sup>4)</sup>. The reaction mechanism is as follows: 1) an unshared electron pair of oxygen atoms on the pyran ring coordinates with a  $\text{BF}_3$  molecule into an excess of phenol and (18) is formed via the  $\text{S}_\text{N}2$  reaction, 2) then, dehydration occurs between alcoholic and aromatic hydroxyl groups in the C-2 position and in the A-ring of (18) to form (19).

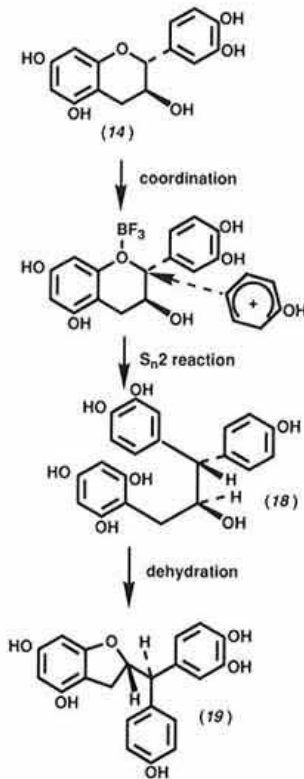


Fig. 7. Phenolation of (+)-catechin by BF<sub>3</sub> catalyst

## Utilization

### 1) Adhesives

Recently, it has been demonstrated that condensed tannins from conifer barks can be utilized as adhesive materials. As conifer tannins have a phloroglucinol type A-ring, they display a high reactivity to formaldehyde. Therefore, cold-setting adhesives can be produced from tannins from conifer barks. The optimum method of preparation of tannin-based cold-setting adhesives consists of a simple mixture of bark extracts and resorcinol resin without prereaction. The adhesives consisting of 50 parts of methanol extract from *Larix leptolepis*, 50 parts of resorcinol resin, 15 parts of paraformaldehyde at pH 9 exhibit a higher bonding ability than that of commercial phenol-

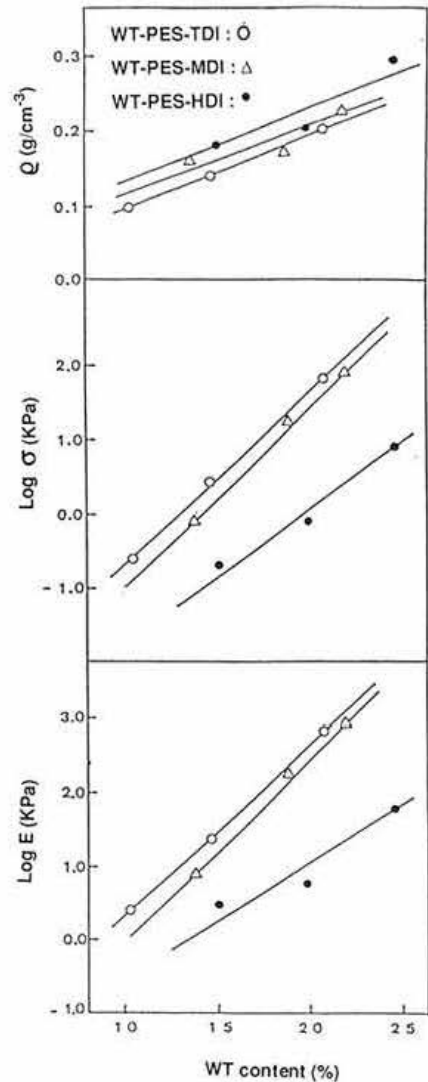


Fig. 8. Changes in density ( $\rho$ ), compression strength ( $\sigma$ ) and compression elasticity ( $E$ ) as functions of WT content of PU foams

WT: Wattle tannin,  
 PES: Polyester-polyol,  
 TDI: Toluene diisocyanate,  
 MDI: Diphenylmethane diisocyanate,  
 HDI: Hexamethylene diisocyanate.

resorcinol resin adhesives (Dainihon Ink Co., Ltd.)<sup>11)</sup>.



### 2) Polyurethane foams

Tannin-derived polyurethane (PU) foams can be readily prepared by the following procedure<sup>1)</sup>. A polyester-polyol (PES, hydroxyl groups 1.35 mmol/g, carboxyl groups 0.14 mmol/g, viscosity 3800 cp) solution of wattle tannin (WT) reacts with three kinds of diisocyanates in the presence of triethylene diamine catalyst, silicone surfactant and trimethylol propane as a crosslinking agent. Density and mechanical properties of the obtained foams are shown in Fig. 8<sup>1)</sup>. Properties generally vary directly with the tannin content. Density increases gradually, and compression strength and compression elasticity increase rapidly with the increase of the tannin content. Therefore, tannins seem to act as crosslinking agents and as hard segments in the PU foam structure. A form containing 25% WT is slowly degraded by wood-destroying fungi such as *Coriolus versicolor* and *Tyromyces palustris*.

### 3) Adsorbents of heavy metal ions

Condensed tannins can adsorb several heavy metal ions. The capacity for heavy-metal adsorption of spherical tannin resin prepared from commercial Mimosa tannin (MT) and MT with various pretreatments is shown in Table 2<sup>12)</sup>. Sulfonated MT (SMT) and trichloroacetic acid-pretreated MT (TMT) display a greater ad-

**Table 2. Adsorption of metal ions on pretreated tannin-resins**

Resin <sup>a)</sup>	Amount of adsorbed metal ions (mmol/g of resin)			
	Cr <sup>6+</sup>	Cd <sup>2+</sup>	Cu <sup>2+</sup>	Fe <sup>2+</sup>
MT	0.074	0.000	0.036	0.026
SMT	0.067	0.025	0.060	0.069
TMT	0.077	0.011	0.051	0.065
RMT	0.071	0.000	0.029	0.046

Metal solution: 20 ppm × 100 ml, pH = 5 (Cr and Cd), pH = 4 (Cu and Fe).

a): MT; Commercial Mimosa tannin, SMT; Sulfonated MT, TMT; Trichloroacetic acid treated MT, RMT; Resorcinolated MT.

sorption capacity than MT, presumably due to the cleavage of the pyran ring in the flavanol skeleton. On the other hand, resorcinolation is not very effective in enhancing adsorption, due to the increased steric hindrance.

### Prospects

Over the past ten years tannin chemistry has made progress due to the development of chemical analyses, and many new compounds and structures have been identified. However, since condensed tannins are widely distributed and their structure is very complicated, it is necessary to study plants containing tannins more extensively. The relationship between the stereochemistry and the protein-adsorbing capacity of condensed tannins must be clarified.

Application to biologically active compounds is one of the most promising areas for use of condensed tannins. Recently, various medicinal activities of condensed tannins have been reported. Antimicrobial activity, antibacterial activity, antitermite activity and germination- and growth-regulation activity against other plants are also very promising biological activities. As outlined previously, the rotational degree of freedom of condensed tannins is considerably low due to the presence of a pyran ring. Therefore if the selective cleavage of the pyran ring could be achieved, the biological activity of the tannins could be markedly improved.

Another area of promising utilization is probably the preparation of tannin-derived functional materials. As it is known that some species of fungi and bacteria can degrade condensed tannins, the materials derived from condensed tannins may be potentially biodegradable.

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