

Tannins: Classification and Definition

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1 Introduction

The name 'tannin' is derived from the French 'tanin' (tanning substance) and is used for a range of natural polyphenols.¹

Since ancient times it is known that certain organic substances have tanning properties and are able to tan animal skins to form leather. Prehistoric tribes already knew about the tanning of protective animal hides with brain material and the fat of the killed animals.² However, precisely what happens to the skin during the tanning process was only elucidated during the twentieth century with the help of modern analytical techniques.² Real tanning is understood as the crosslinking of the skin's collagen chains, while false tanning entails the filling of hollow spaces between the skin's collagen chains. The traditional tanning of animal skins by means of plant tannins has been replaced gradually by mineral tanning, as represented by alum tanning (or glacé tanning, a variant of alum tanning) and more recently, since the end of the nineteenth century, by chromium tanning.² In nature the tannins are found worldwide in many different families of the higher plants such as in chestnut and oak wood, Divi-Divi, Sumach, Myrobalaen, Trillo, Valonea or plant galls; depending on their origin, their chemistry varies widely, having a molar mass of up to 20000 D. High tannin concentrations are found in nearly every part

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of the plant, such as in the bark, wood, leaves, fruit, roots, and seed. Frequently an increased tannin production can be associated with some sickness of the plant. Therefore, it is assumed that the biological role in the plant of many tannins is related to protection against infection, insects, or animal herbivory.^{3,4} The tannins appear as light yellow or white amorphous powders or shiny, nearly colourless, loose masses, with a characteristic strange smell and astringent taste.⁵

The tannins are applied widely, with uses ranging from tanning, known over millennia (Mediterranean since ca. 1500 BC), through medicinal uses to uses in the food industry. In medicine, especially in Asian (Japanese and Chinese) natural healing, the tannin-containing plant extracts are used as astringents, against diarrhoea,⁶ as diuretics,^{7,8} against stomach and duodenal tumours,⁹ and as anti-inflammatory, antiseptic, and haemostatic pharmaceuticals.³ As tannins can precipitate heavy metals and alkaloids (except morphine), they can be used in poisonings with these substances. It is also becoming clear that tannins often are the active principles of plant-based medicines.¹⁰

Tannins are used in the dyestuff industry as caustics for cationic dyes (tannin dyes), and also in the production of inks (iron gallate ink). In the food industry tannins are used to clarify wine, beer, and fruit juices.¹¹ Other industrial uses of tannins include textile dyes, as antioxidants in the fruit juice, beer, and wine industries, and as coagulants in rubber production.⁵

Recently the tannins have attracted scientific interest, especially due to the increased incidence of deadly illnesses such as AIDS and various cancers. The search for new lead compounds for the development of novel pharmaceuticals has become increasingly important, especially as the biological action of tannin-containing plant extracts has been well documented. During the last twenty years many representatives of this class of compounds have been isolated and characterized.^{6-8,12-73} Currently known tannins with unambiguously determined structures already number far more than 1000 natural products.⁷⁴ In extensive biological tests many representatives of this class were found to have antiviral, antibacterial, and, especially, antitumour activity.^{10,75-83} For example, certain tannins can selectively inhibit HIV replication.²¹

The nomenclature of the tannins is full of misunderstanding, erroneous interpretations, and changes caused by advances in this field.⁸⁴ Not all tanning substances can be called tannins, and on the other hand many tannins do not possess tanning properties but are counted with the tannins because of their structural characteristics. So *what* are tannins?

Bate-Smith and Swain defined the plant tannins as water soluble phenolic compounds with a molar mass between 300 and 3000, showing the usual phenol reactions (*e.g.* blue colour with iron(III) chloride), and precipitating alkaloids, gelatins and other proteins.⁸⁴ However, this definition does not include all tannins, since, more recently, molecules with a molar mass of up to 20000 D have been isolated that should also be classified as tannins on the basis of their molecular structures. Griffith defined tannins as "macromolecular phenolic substances" and divided them in two major groups, the 'hydrolysable' and 'condensed' tannins.⁸⁵ This definition of the tannins ignores the low molecular and monomeric tannins with a molar mass below 1000 D. Haslam^{86a} classified the plant polyphenols into two broad structural themes: (i) Galloyl and hexahydroxydiphenyl esters and their derivatives. (ii) Condensed proanthocyanidins. Galloyl and hexahydroxydiphenyl esters and their derivatives have been further classified into several broad categories: (1) Simple esters. (2) Depside metabolites (*syn*-gallotannins). (3) Hexahydroxydiphenyl and dehydrohexahydroxydiphenyl esters (*syn*-ellagitannins) based upon: (a) ⁴C₁ conformation of D-glucose; (b) ¹C₄ conformation of D-glucose; (c) 'open-chain' derivatives of D-glucose. (4) 'Dimers' and 'higher oligomers' formed by oxidative coupling of 'mono-

mers', principally those of class (3) above. While in Haslam's article^{86a} complex tannins have not been mentioned, in the newly published review by Ferreira *et al.* only two classes of tannins, namely: (i) condensed tannins and (ii) complex tannins, are treated exhaustively.^{86b} Gross adopted the classical definition of tannins that was formulated by Freudenberg in 1920 cited therein.^{86c} According to Freudenberg and Gross tannins are usually divided into the flavonoid derived condensed tannins, and into hydrolysable tannins. The former are divided into two groups, namely: (i) gallotannins, which include also *meta*-depsids, and (ii) ellagitannins. Also, the definition of tannins as a mixture of 'flavolanes of varying structure'¹¹ at best only covers some tannins and does not include the hydrolysable tannins which form a considerable portion of the tannins. An organic chemistry textbook⁸⁷ defines tannins as: "C- and O-glycosidic derivatives of gallic acid (3,4,5-trihydroxybenzoic acid)". This definition also describes only some of the tannins and does not include the condensed tannins based on flavan-3-ol (catechin) units. It is therefore necessary, as a result of the recently greatly expanded structural range of the tannins, to formulate a definition that includes all tannins.

Tannins are polyphenolic secondary metabolites of higher plants. Corresponding polyphenolic natural products have not yet been isolated from lower plants such as algae, or from the animal kingdom. The polyphenolic structure of the secondary metabolites from higher plants is a necessary but not sufficient requirement for membership of the tannin class. When the structural characteristics of the currently known tannins are analysed, the relatively low occurrence of C- and/or O-glycosidic derivatives of gallic acid is noteworthy. However, the characterized tannin structures show that, apart from the galloyl glycosides, the galloyl residues can be linked to each other or to other residues through their aromatic carbon and/or phenolic oxygen atoms. By these and similar couplings of two or more natural products to each other, nature provides a nearly inexhaustible store of highly diverse structures. It should be mentioned, however, that not all tannins must necessarily contain a galloyl unit or derivative. Examples of this type are found in the so-called condensed tannins that are built up from flavanoid precursors. The condensed tannins, constructed from at least two linked catechin units (C-4 with C-8 or with C-6, *see* Fig. 1 below, compound 4), can alternatively be linked through the hydroxy group of C-3 of each catechin unit to a galloyl unit. To formulate a definition which would do justice to all structural characteristics of the tannins, their origins and their importance in the plant, is *a priori* not so simple. This paper derives such a definition based on the molecular structures of the hitherto characterized tannins (Section 4).

2 Classification of the tannins based on their structural properties

Due to the enormous structural diversity of the tannins a systematic classification system based on specific structural characteristics and chemical properties would provide a convenient framework for further study. The observation that many tannins can be fractionated hydrolytically into their components, for example by treatment with hot water or with tannases, led to the classification of such tannins as 'hydrolysable tannins'. Non-hydrolysable oligomeric and polymeric proanthocyanidins were classified as condensed tannins.¹¹ Therefore, the term 'hydrolysable tannins' includes both the gallotannins and the ellagitannins.^{78,88} It should also be mentioned here that there are ellagitannins that are not hydrolysable, because of a further C-C coupling of their polyphenolic residue with the polyol unit, but are nevertheless for historical reasons classified as hydrolysable tannins [see Fig. 6, vescalagin (70)]. In 1985 the first tannins were described that contained, in addition to the hexahydroxydiphenyl (HHDP) units (the characteristic structural element of the monomeric

Tannins

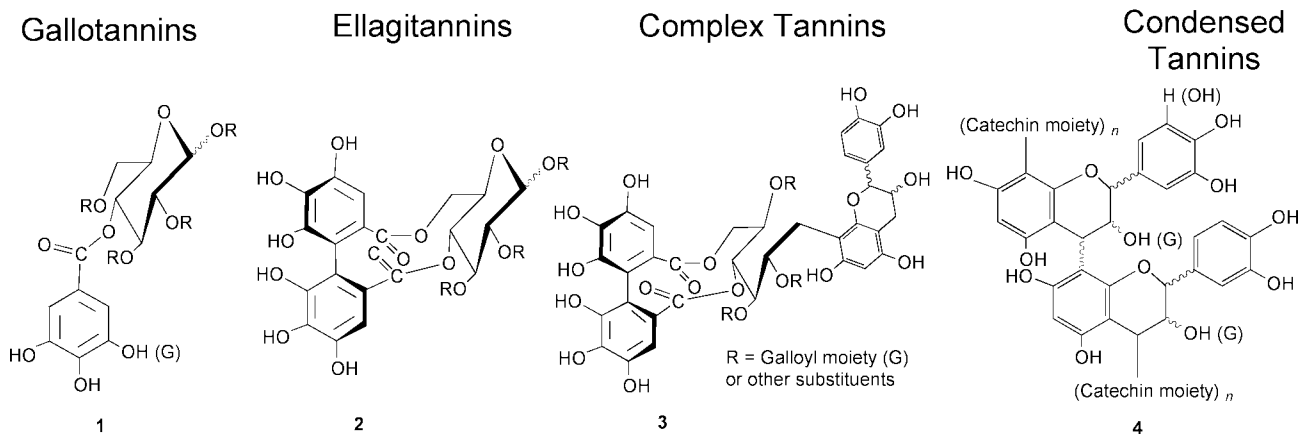


Fig. 1 Classification of the tannins.

ellagitannins), also *C*-glycosidic catechin units [see Fig. 9, acutissimin A (**76**)].⁸⁹ These tannins were originally classified as ‘non-classified tannins’, because they are only partially hydrolysable due to the C–C coupling of their catechin unit with the glycosidic part.⁹⁰ To properly place these ‘non-classified tannins’ in some scheme, the terms ‘complex tannins’^{3,4,77} and flavanoellagitannins^{78,91} were established over the following years. These examples clearly show that the division of the tannins into two groups, *viz.* hydrolysable and non-hydrolysable or condensed tannins,^{11,85} cannot do justice to the structural diversity of the tannins. The terms ‘flavanotannins’ or ‘condensed flavanoid tanning substances’⁸⁸ that are occasionally found in the literature denote tannins consisting of catechin units. The polymeric flavanotannins, constructed from coupled flavan-3-ol (catechin) units, belong to the condensed tannins (oligomeric and polymeric proanthocyanidins).

On the basis of their structural characteristics it is therefore possible to divide the tannins into four major groups: *Gallotannins*, *ellagitannins*, *complex tannins*, and *condensed tannins* (Fig. 1).

(1) Gallotannins are all those tannins in which galloyl units or their *meta*-depsidic derivatives are bound to diverse polyol-, catechin-, or triterpenoid units.

(2) Ellagitannins are those tannins in which at least two galloyl units are C–C coupled to each other, and do not contain a glycosidically linked catechin unit.

(3) Complex tannins are tannins in which a catechin unit is bound glycosidically to a gallotannin or an ellagitannin unit.

(4) Condensed tannins are all oligomeric and polymeric proanthocyanidins formed by linkage of *C*-4 of one catechin with *C*-8 or *C*-6 of the next monomeric catechin.

2.1 Different polyol units of the tannins

The standard metabolism for the biosynthesis of tannins in higher plants uses various building blocks that are coupled to each other. For example, the gallotannins are biosynthesized by the different coupling possibilities of a polyphenolic building block such as gallic acid with diverse polyols such as *D*-glucopyranose. A complete listing of the structures of all known tannins falls outside the scope of this article; however, the

structures of the currently known tannins are summarized by way of a fractionation of their components. The following are some of the polyalcoholic components of the tannins: *D*-Glucopyranose (**5**), *D*-hamamelose (**6**), sucrose (**7**),⁹² shikimic acid (**8**), quinic acid (**9**), *scyllo*-quercitol (**10**)⁹³ and *proto*-quercitol (**11**),⁹⁴ salicin or 2-hydroxymethylphenyl β -*D*-glucopyranoside (**12**),⁹⁵ *D*-fructopyranose (**13**), 6-cinnamoyl-*D*-glucopyranose (**14**), 1,5-anhydro-*D*-glucitol,⁹⁶ 3,5-dihydroxyphenyl β -*D*-glucopyranoside (**15**),⁹⁷ 2-coumaroyl-*D*-glucopyranose (**16**), 4-hydroxy-2-methoxyphenyl β -*D*-glucopyranoside (**19**),⁹⁸ 4-hydroxy-3-methoxyphenyl β -*D*-glucopyranoside (**20**),⁹⁸ 3,4,5-trimethoxyphenyl β -*D*-glucopyranoside (**21**),⁹⁸ 2,6-dimethoxy-4-hydroxyphenyl β -*D*-glucopyranoside (**22**),⁹⁸ 4-carboxy-2,6-dihydroxyphenyl β -*D*-glucopyranoside (**23**),⁹⁹ 3-carboxy-5,6-dihydroxyphenyl β -*D*-glucopyranoside (**24**),⁹⁹ 4-(3-oxobutyl)phenyl β -*D*-glucopyranoside (**25**),⁹⁹ triterpenoid **26**,^{77,78} salidroside (**27**),^{89,92,100} methyl β -*D*-glucopyranoside (**28**),⁹² maclurin *C*- β -*D*-glucopyranoside (**29**),⁹² maclurin 2'-*O*-(*p*-hydroxybenzoyl)-*C*- β -*D*-glucopyranoside (**30**),⁹² mangiferin *C*- β -*D*-glucopyranoside (**31**),⁹² iriflophenone *C*- β -*D*-glucopyranoside (**32**),¹⁰¹ isomangiferin *C*- β -*D*-glucopyranoside (**33**),⁹² *D*-gluconic acid (**34**),¹⁵ *D*-glucitol (**35**),⁸⁹ glycerol (**36**), glycosidically bound catechins **37**, catechins, epicatechins, gallo-catechins, and epigallocatechins **38**^{80,88} *etc.* (Fig. 2).

The hydroxy functions of the tannin polyol residues may be linked fully or only partly with galloyl units or their derivatives, in which case they may be linked to several other residues.^{3,4,77,78} The diversity of tannin structures is further enriched by the capability of the anomeric centre of the glycosidic components to form *C*- and/or *O*-glycosidic, ester or acetal bonds, in the β or α form with a great variety of building blocks.

2.2 Different galloyl derivatives of gallotannins, ellagitannins, and complex tannins

In many tannins two galloyl units are linked to each other through their aromatic carbon atoms to form an axially chiral *hexahydroxydiphenyl* (HHDP) unit (**39**, **40**), which is the characteristic structural element of the monomeric ellagitannins. Linking the galloyl unit of the tannins, for instance *via* the phenolic oxygen atom, to a further galloyl unit leads to

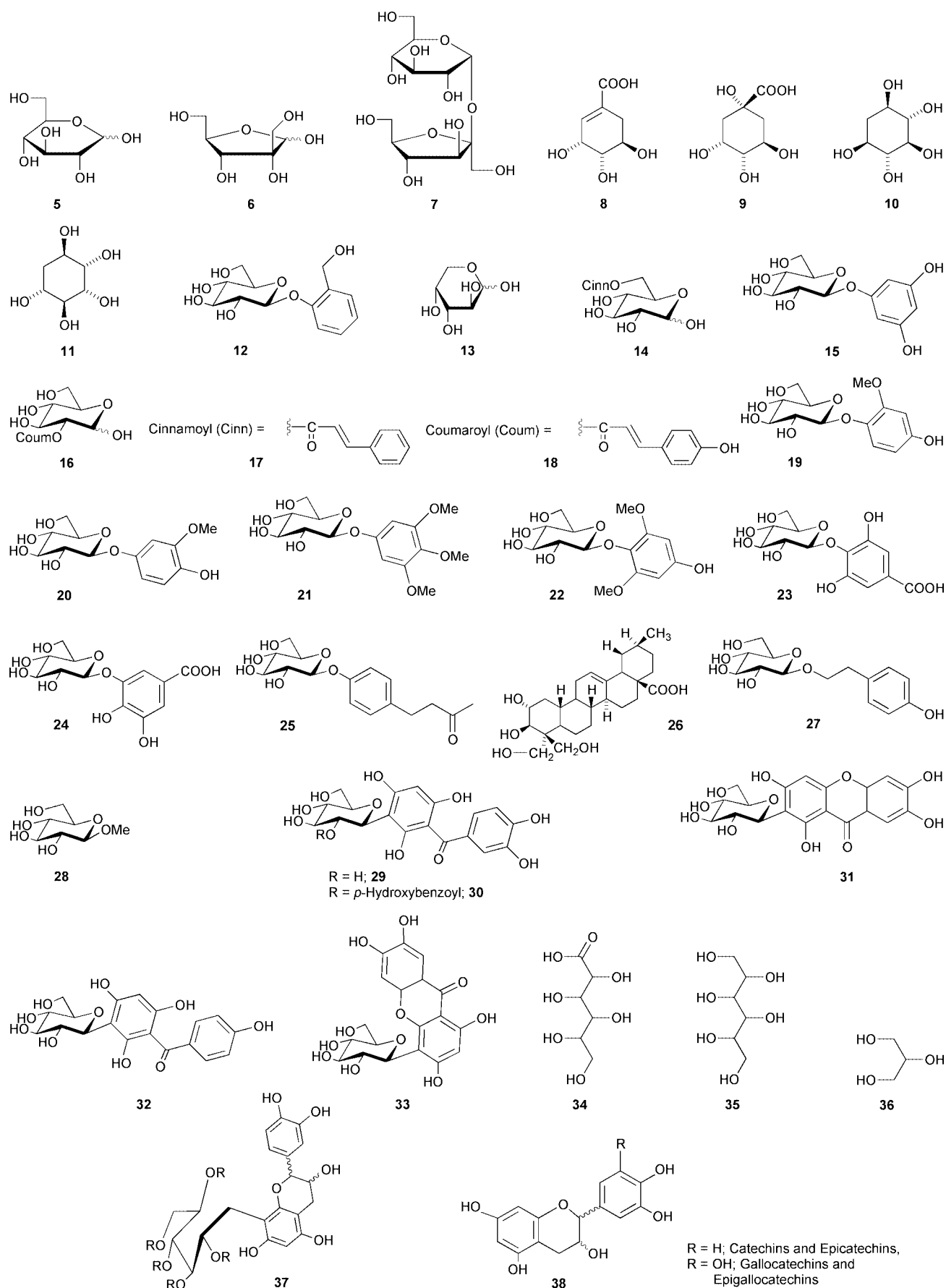


Fig. 2 Polyol residues of the tannins.^{3,4,77,92-95,97,100-103}

formation of a *meta*-digalloyl unit (50), the characteristic structural element of the *meta*-depsides which are also reckoned with the gallotannins.

Other important galloyl derivatives found in many tannins

are: HHDP (39, 40), flavogallonyl (41), valoneoyl (Val) (42), sanguisorbonyl (San) (43), dehydrohexahydroxydiphenoyl (DHHDP) (44, 45 and 46), gallagyl (Gal) (47), elaeocarpusoyl (Ela) (48), dehydrodigalloyl (49), *meta*-digalloyl (50), chebuloyl

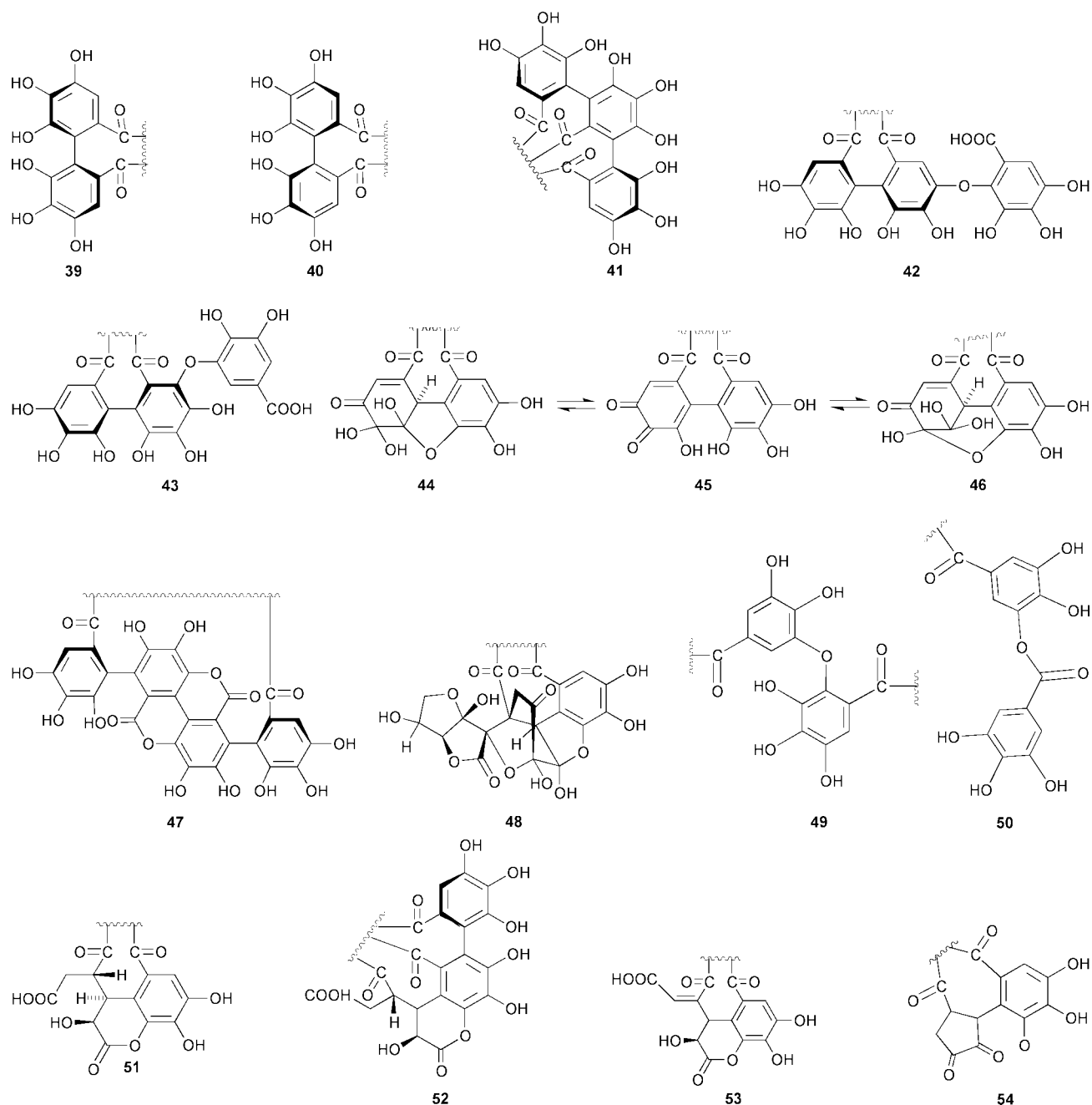


Fig. 3 Different galloyl derivatives of the tannins.

(Che) (51), trilloyl (52), dehydrochebuloyl (DHChe) (53), brevifoloyl (54) etc. (Fig. 3).^{3,4,77,78,104–106}

3 Single tannin classes

For clarity the four major groups of the tannins are briefly discussed by way of some selected examples.

3.1 Gallotannins

Gallotannins are the simplest hydrolysable tannins, containing a polyphenolic and a polyol residue. Although a great variety of polyol residues are possible, most of the gallotannins isolated from plants contain a polyol residue derived from D-glucose. The hydroxy functions of the polyol residues may be partly or fully substituted with galloyl units. In the case of partial substitution with galloyl residues the remaining hydroxy groups may be either unsubstituted or substituted with various other residues. For example, the anomeric centre of the glycosidic residues of the gallotannins may be unsubstituted (α, β mixture)

or substituted, in α or β form, as ester or acetal. The *meta*-depsides (or ‘*syn*-gallotannins’)¹⁰ also belong to the gallotannin group. Their galloyl residues are esterified with the polyol residue and also with one or more linked galloyl units in the *meta* position relative to the galloyl units’ carboxyl groups. The gallotannins 2,3,4,6-*tetra-O*-galloyl-D-glucopyranose (TGG) (55) and 1,2,3,4,6-*penta-O*-galloyl- β -D-glucopyranose (β -PGG) (56), found in many plant families, are key intermediates in the biosynthesis of nearly all hydrolysable plant polyphenols.^{107–110} Gallotannins in which the polyol residues are coupled to cinnamoyl (17) or coumaroyl (18) groups (e.g. 57 and 58) are relatively scarce.^{97,102,103}

Most of the gallotannins substituted with a galloyl unit at the anomeric centre of their D-glucosyl unit have the β configuration at the anomeric centre. There are, however, also some natural products such as 1,4-di-*O*-galloyl- α -D-glucopyranose (59),¹⁷ where the anomeric centre of the D-glucopyranose has the α configuration.^{111–113} The structural diversity of the gallotannins is demonstrated by some selected examples (Fig. 4).

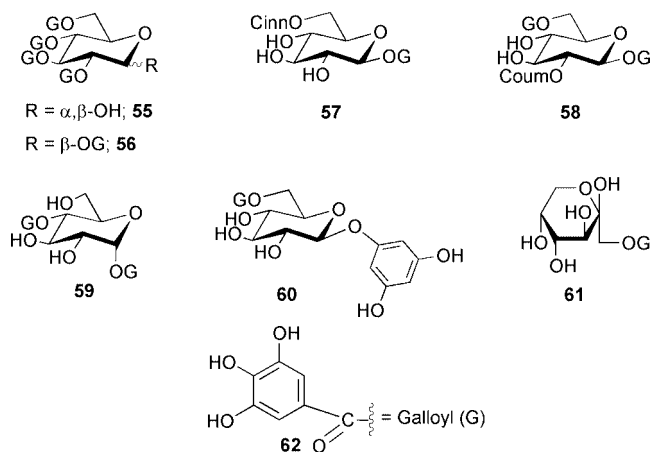


Fig. 4 Structures of some of the gallotannins.^{3,4,77,78}

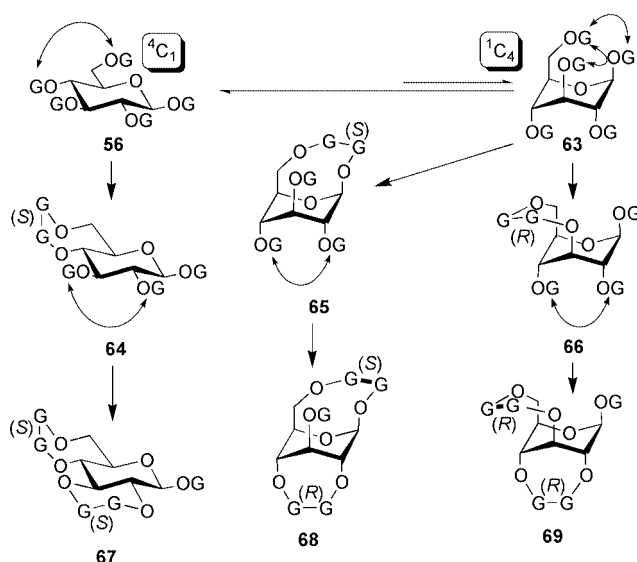


Fig. 5 Some of the coupling possibilities of D-glucopyranose in the 1C_4 or 4C_1 conformation with (*R*)- or (*S*)-configured HHDP units.^{77,78}

3.2 Ellagitannins

With more than 500 natural products characterized so far, the ellagitannins form by far the largest group of known tannins.¹¹⁴ Ellagitannins are formed from the gallotannins by the oxidative coupling of at least two galloyl units (**62**) (Figs. 4 and 5), yielding an axially chiral HHDP unit (**39** or **40**). The chirality is caused on the one hand by the bulky *ortho* substituents to the biaryl axis, and on the other hand by the atropisomerism caused by the inhibition of free rotation around the axis. This is caused by the esterification of both *ortho* carboxy groups with the polyol (usually D-glucopyranose, Fig. 3).^{3,4,77,78,104–106} Remarkably, all ellagitannins with HHDP units linked *via* the 4,6 or the 2,3-positions of their D-glucosyl unit have an (*S*)-configured HHDP unit, while linkage *via* the 3,6-positions seems to lead only to an (*R*)-configured HHDP unit.^{77,78,115}

Esterification to other positions of the sugar molecule, for example a 1,6-coupling^{20,74} is rarely found in nature. In the majority of ellagitannins with an axially chiral glucose-bound HHDP unit, both the configuration of the biaryl unit and the conformation of the D-glucosyl unit are determined by their linkage positions. An HHDP unit bound to the 2,3- or 4,6- or 1,6-positions of D-glucopyranose in the natural products always has the (*S*)-configuration, while most 2,4- or 3,6-coupled HHDP units favour the (*R*)-configuration. Thermodynamics govern the resulting D-glucose conformation, which again is determined by the coupling positions of the HHDP unit to the glucopyranose ring. While the glucopyranosyl

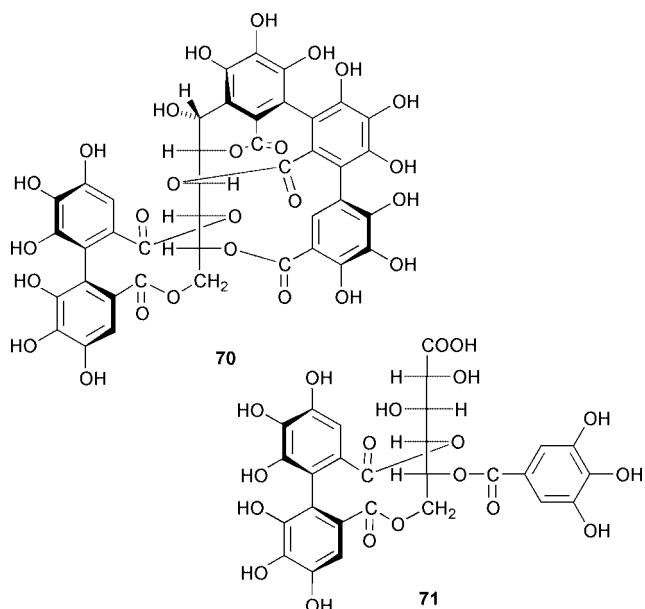


Fig. 6 Typical ellagitannins with a C-glycosidic bond^{77,78} and with a D-gluconic acid unit.¹⁵

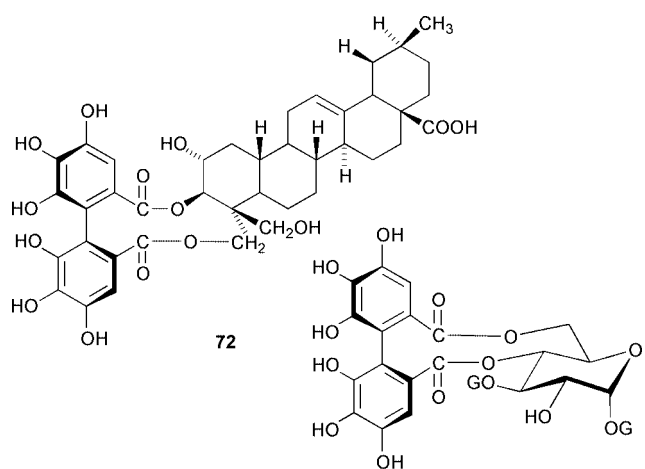


Fig. 7 The structure of a rare ellagitannin with a triterpenoid structural unit, and of a rare α -configured ellagitannin.

assumes a 4C_1 conformation in the case of 2,3- or 4,6-HHDP coupling, a 1,6- or 3,6- or 2,4-HHDP coupling always favours the thermodynamically less stable 1C_4 conformation (Fig. 5).

For both the C-glycosidic ellagitannins and the ellagitannins with a D-gluconic acid unit the coupling of the HHDP unit *via* the 2,3- and 4,6-positions of the D-glucosyl is highly characteristic. The C-glycosidic bond between the open-chain sugar and the bidentate substituent is always formed at C-1 of the sugar. Typical examples of these groups of substances are vescalagin (**70**)^{77,78} with a C-glycosidic bond, and lagerstannin C (**71**)¹⁵ with a D-gluconic acid unit (Fig. 6).

Seemingly, for the routine biosynthesis of the tannins, nature does not use only D-glucopyranose for the esterification with gallic acid. For example, D-hamamelose (**6**) and complex triterpenoids such as **26** are also used in tannin biosynthesis. As example of an ellagitannin with a triterpenoid structural unit, which could be isolated only seldomly from natural sources, the natural product castanopsinin A (**72**)^{77,78} can be mentioned.

Also, the ellagitannin group contains few examples where the anomeric centre of D-glucopyranose has the α -configuration. Heterophyllin A (**73**)³⁶ is one of the rare examples of this type (Fig. 7).

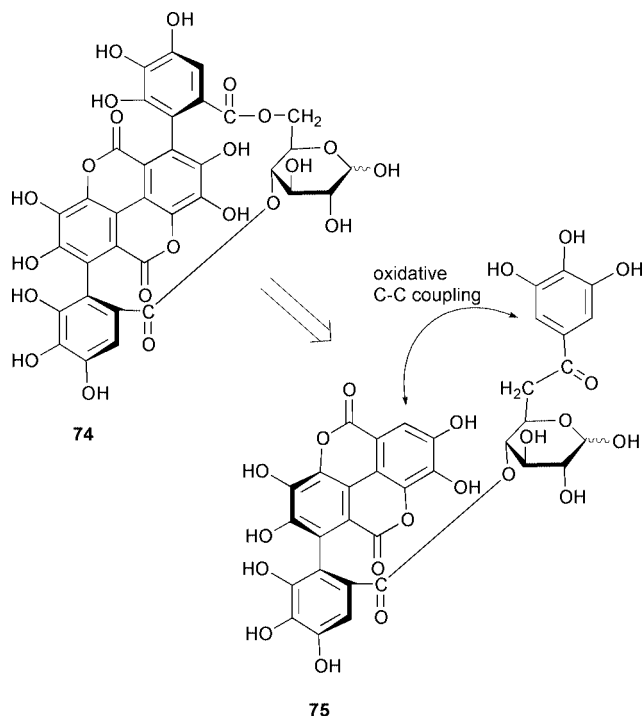


Fig. 8 The structures of punicalin (74) and terflavin B (75).

As early as 1977 Mayer *et al.* published the isolation of the ellagitannin punicalin (74) from the fruit husks of *Punica granatum* L.¹¹⁶ However, the correct structure was published only in 1986 by Nishioka *et al.*²⁴ Punicalin [4,6-(*S,S*)-gallagyl-D-glucopyranose] (74) contains the so-called gallagyl unit as characteristic structural element. The gallagyl unit itself is constructed from a lactonized HHDP nucleus which is C-C coupled with two galloyl (3,4,5-trihydroxybenzoyl) residues.²¹ The punicalin structure is completed with a D-glucosyl unit which is linked *via* two hydrolytically cleavable ester bridges to the gallagyl building block. Little is known about the biosynthesis of punicalin (74). It is known, however, that terflavin B (75), also isolated from *Punica granatum* L., is a key intermediate in the biosynthesis. Terflavin B can be transformed directly into punicalin (74) by oxidative coupling (Fig. 8).^{21,117}

3.3 Complex tannins

The structures of the complex tannins are built up from a gallotannin⁴³ unit or an ellagitannin⁹¹ unit, and a catechin unit.^{4,77,78,91} One example from this substance class is acutissimin A (76), having a flavogallonyl unit (nonahydroxytriphenyl unit) bound glucosidically to C-1, and linked *via* three further hydrolysable ester bridges to the D-glucose derived polyol (Fig. 9).^{77,78}

3.4 Condensed tannins

One of the striking properties of the monomeric catechins and leucoanthocyanidins, that have no tanning properties, is their ability to be converted into oligomers and polymers that do have tanning properties, by the action of acids or enzymes.^{3,4,77,78,88,91,118} Condensed tannins are oligomeric and polymeric proanthocyanidins consisting of coupled flavan-3-ol (catechin) units (oligomeric or polymeric proanthocyanidins = condensed proanthocyanidins = condensed tannins). Biosynthetically the condensed tannins are formed by the successive condensation of the single building blocks, with a degree of polymerization between two and greater than fifty blocks being reached. The coupling pattern of the catechin units in condensed tannins can vary considerably. For example, many con-

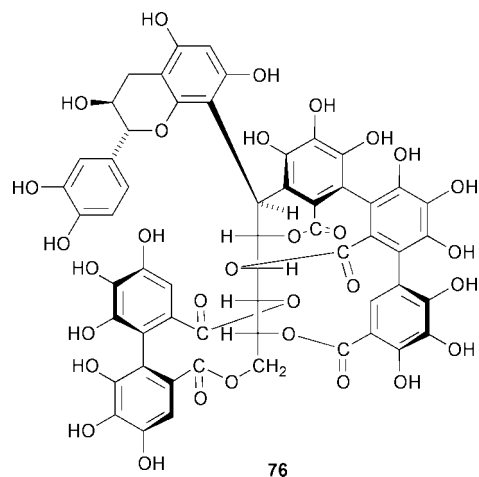


Fig. 9 Acutissimin A, the usual representative of the complex tannins.^{77,78}

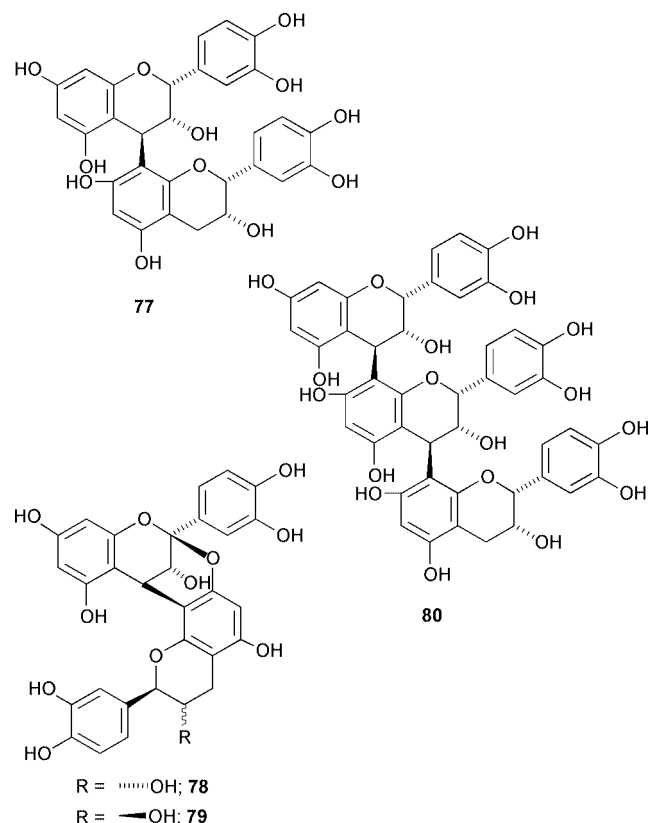


Fig. 10 Different linkage patterns of condensed tannins, for example procyanidin B₂ (77), proanthocyanidin A₁ (78), proanthocyanidin A₂ (79) and proanthocyanidin C₁ (80).

densed tannins are known where the coupling of the single units is by way of position C-4 of the first unit linked with C-8 (or C-6)^{4,119} of the second unit, which may have a different substitution pattern.^{4,120} The tannins found in red wine (and to a lesser extent in white wine) are this type of condensed tannins. The properties of these tannins, and especially their importance to winemaking, depend on their specific reaction with proteins, which in turn is directly related to their degree of polymerization. Oligomers and polymers consisting of two to ten catechin units are also known as flavolans.¹¹ Some typical condensed tannins with unsubstituted catechin units are procyanidin B₂ [epicatechin-(4β→8)-epicatechin (77)], proanthocyanidin A₁ [epicatechin-(4β→8,2β→O→7)-catechin (78)], proanthocyanidin A₂ [epicatechin-(4β→8,2β→O→7)-epicatechin (79)], and proanthocyanidin C₁ [epicatechin-(4β→8)-epicatechin-(4β→8)-epicatechin (80)] (Fig. 10).

4 Definition of the tannins

Based on the molecular structures of the currently known tannins, and their origin and role in plant life, the following definition of the tannins may be derived:

Tannins are polyphenolic secondary metabolites of higher plants, and are either galloyl esters and their derivatives, in which galloyl moieties or their derivatives are attached to a variety of polyol-, catechin- and triterpenoid cores (gallo-tannins, ellagitannins and complex tannins), or they are oligomeric and polymeric proanthocyanidins that can possess different interflavanil coupling and substitution patterns (condensed tannins).

5 Summary and perspective

Nature is a unique source of structures of high stereochemical diversity, many of them possessing interesting biological activities and medicinal properties. In the context of the worldwide spread of deadly conditions such as AIDS and a variety of cancers, an intensive search for new lead compounds for the development of novel pharmacological therapeutics is extremely important. The fact that the biological activity of tannin-containing plant extracts has been known for ages has led, especially during the last two decades, to the isolation and characterization of many representatives of this class. The group of unambiguously characterized tannins includes more than 1000 natural products. In extensive biological tests many representatives of the tannins exhibited antiviral and antibacterial properties, but especially prominent was the anti-tumour activity. Certain tannins, for example, are able to inhibit HIV replication selectively.

Comparison of the synthetically accessible natural products with the currently known natural tannins shows that synthetic chemistry still has a long way to go. Theoretically, considering all possible combinations of the polyphenols and polyalcohols introduced in this review, taking account of the stereochemistry, several thousand compounds can be constructed. Given the number of tannins isolated so far, nature must still have many more in store. With the advances in synthetic methodology and the development of more sophisticated isolation and analytical techniques, many more of these tannins should be identified. Indeed, new tannin structures are published almost weekly. However, nature has also set certain limits on the biosynthesis of tannins and certain imaginable and chemically feasible constructs have not yet been isolated as natural products, as we have reported previously.¹²¹

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The literature references with respect to the isolation and characterization of tannins selected for this paper represent merely a fraction of the available published material. This is a subjective selection necessitated by space constraints, and the reader's kind understanding is requested for any relevant articles on the isolation of tannins that are not mentioned.

Dedicated to Professor Joachim Thiem, Hamburg, on the occasion of his 60th birthday.

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