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VEGETABLE TANNING AGENTS

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The distribution and structure of hydrolyzed tannins, the separation of tanning agents and their quantitative determination, methods for preparing tanning extracts, methods for increasing the efficiency of extracting raw material, and the chemical processes during tanning of hides are discussed. The literature from 1950 to 1999 is reviewed.

Key words: tannin, structure, determination, tanning.

GALLO- AND ELLAGOTANNINS AND THEIR DISTRIBUTION

Vegetable substances that can convert animal skin into leather are called tanning agents or tannins. According to the generally accepted nomenclature of Freudenberg [1], tannins are subdivided into hydrolyzable and condensed (nonhydrolyzable).

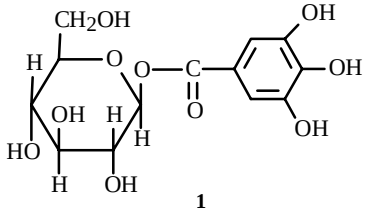
Hydrolyzable tanning agents are classified into gallotannins, ellagotannins, and mixed groups.

Gallotannins can be hydrolyzed by acids and bases into glucose or other compounds related to it and gallic acid.

Ellagotannins are esters of glucose and ellagic acid or compounds related to it, for example, chebulic, brevifolincarboxylic, and other acids.

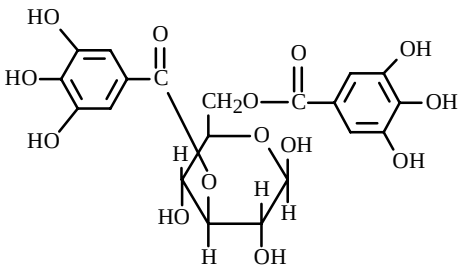
Vegetable tanning extracts usually have complicated compositions and contain compounds of both groups. The most important hydrolyzable substances are gallotannins, esters of gallic acid.

Mono-, di-, tri-, tetra-, penta-, and polygalloyl esters are known. The β-D-glucogallin **1**, a typical monogalloyl ester, was isolated in 1903 from the roots of *Rheum tanguticum* Max. Later this compound was observed in the tanning extract of *Mirobalans* [2].



1

Acertannin, which has been isolated from *Acer gunkala*, is an example of a diester. It was assigned for a long time the structure 3,6-di-O-galloyl-1,5-anhydro-D-sorbite (**2**). However, spectral investigations have rather recently identified this compound as 2,6-di-O-galloyl-1,5-anhydro-D-sorbite (**3**) [3].



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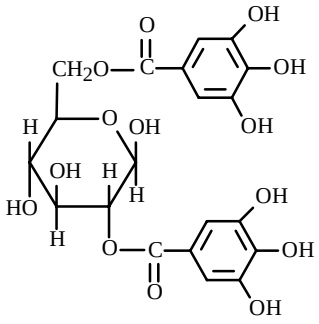

3

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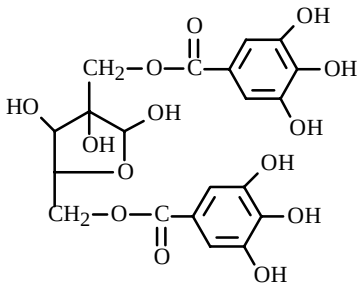
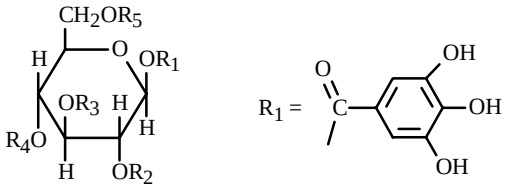
Hamamelitannin (**4**), which has been isolated from the roots of *Hamamelis virginian* [4], is also a diester. It was also detected in the phenolic compounds from red oak (*Quercus robur*) [5] and fruit of *Castanea sativa* [6].



4

Fruit of *Terminalia chebula* yielded the trigalloyl ester **5**, tri-O-galloyl-D-glucose [7]. Tetra- and pentagalloylglucoses 2,3,4,6-tetra-O-galloyl-D-glucose (**6**) and β-penta-O-galloyl-D-glcose (**7**) were isolated from *Rhus semialata*, *Rh. typhina*, and *Rh. coriaria* [7,8]. The leaves of *Arctostophylosuva-ursi* (L.) *spreng* gave 2,3,6-trigalloyl-D-glucose [9].

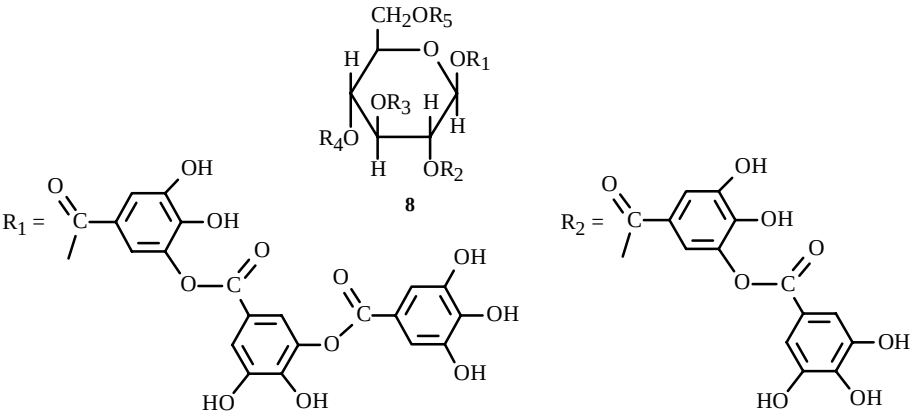


5: $R_1 = R_3 = R_5$ - galloyl groups, $R_2 = R_4 = H$
6: $R_2 = R_3 = R_4$ - galloyl groups, $R_1 = H$
7: $R_1 = R_2 = R_3 = R_4 = R_5$ galloyl groups

Chinese and Turkish tannins are the most studied polygalloylglucoses.

The structure of Chinese tannin isolated from galls of *Rhus semialata* was first proposed in 1914-1919 by Fisher and Freudenberg. The glucose:gallic acid ratio was shown to be 1:9 or 1:10. Fisher proposed the structure β-penta-*m*-digalloyl-D-glucose for Chinese tannin. Then, it was confirmed by other researchers [4, 7, 8, 10, 11]. It was found that Chinese tannin is a mixture of penta-, hexa-, hepta-, octa-, and nonagalloylglucoses and that one of the tannins of sumac (*Rhus typhina, Rhus coriaria*) is identical to Chinese tannin.

The structure of Chinese tannin (**8**) was solved in detail in 1965 using elemental analysis, a molecular-weight determination, methanolysis, NMR spectra of the methylated derivatives, etc. Then Chinese tannin was isolated from leaves of *Rhus semialata* using high-pressure liquid chromatography (HPLC) [12].

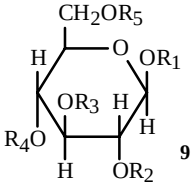


8

$R_2 = R_4$, $R_3 = R_5$ - galloyl groups

Fisher and Freudenberg found that the glucose:gallic acid ratio in Turkish tannin isolated from oak *Quercus infectoria* is 1:5 or 1:6. They also showed that methylation with diazomethane and subsequent hydrolysis of the methylated product gave 3,4,5-tri-O-methylgallic acid and a small amount of 3,4-di-O-methylgallic acid. It was proposed that one of the glucose hydroxyls in Turkish tannin is esterified with meta-digallic or tri-gallic acid and one hydroxyl is free.

It was later shown [4, 13] that Turkish tannin is a mixture of similar substances based on tetra-O-galloylglucose in which the 2 or 4 position is free. Tannin is formed by depside addition of two or three galloyls to this core (**9**).



9

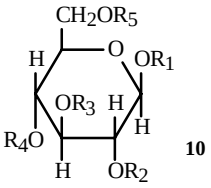
$R_1 = R_3 = R_4 = R_5$ - galloyl groups, R_2 = H
or
$R_1 = R_2 = R_3 = R_5$ - galloyl groups, R_4 = H

Later it was demonstrated [12] that the center of Turkish tannin is a pair of galloylglucoses, pentagalloylglucose and tetragalloylglucose in a 1:1 ratio.

Chemical (hydrolysis, acetylation, etc.) and spectral methods of analysis are used to determine the structures of gallotannins [14, 15].

The structures of Chinese and Turkish tannins were also studied by other groups [16-19].

Dhawa-tannin from leaves of *Anogeissus latifolia* [20] is a white, amorphous, and chromatographically pure substance. Chromatography, enzymatic hydrolysis by tannase, acetylation by acetic anhydride, methylation by diazomethane, and mild alkaline hydrolysis showed that this tannin consists of pentagalloylglucose with depside addition of 3-4 galloyls (**10**).



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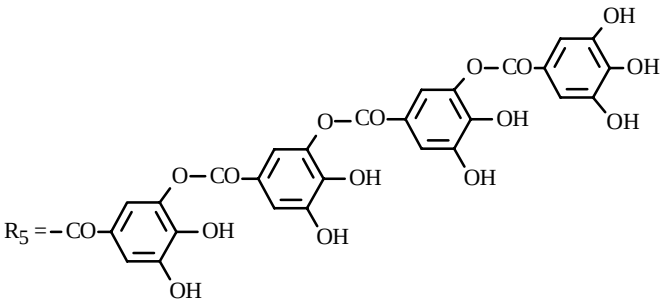
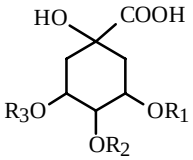
$R_1 = R_2 = R_3 = R_4$ - galloyl groups



Gallotannins are represented by taratannin, which was isolated from the pods of *Caesalpinia spinosa* [21]. This is 3,4,5-trigalloylquinic acid to which 2-3 galloyls are bound randomly through depside bonds (**11**).



$R_1 = R_2 = R_3$ - mono-, di-, trigalloyl groups

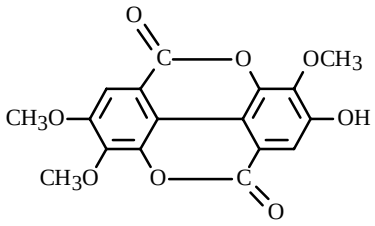
11

Several new gallotannins were recently isolated from various plants: 1,2,4-tri-O-galloyl-α-D-glucopyranose, 1,2,3,4,6-penta-O-galloyl-β-D-glucopyranose, 2,3,4,6-tetra-O-galloyl-D-glucose, 6-O-galloyl-D-glucose from *Nuphar japonicum* [22, 23] and *Euphorbia hirta* L. [24]; 1,2,3-tri-O-galloyl-α-D-glucose from plants of the Rosaceae family [25]; 1,4,6-tri-O-galloyl-β-D-glucose from the leaves of green tea [26]; 3-O-digalloyl-1,2,4,6-tetra-O-galloyl-β-D-glucose from *Quercus dentata* [27]; and 3,6-bis-O-digalloyl-1,2,4-tri-galloyl-β-D-glucose from *Rhus typhina* L. [28].

As noted above, hydrolysis of ellagotannins produces ellagic acid or acids related biologically to it, chebulic,

bravifolincarboxylic, dehydrodigallic acids and the dilactone of valonic acid. Ellagic acid is present in tanning agents as hexahydroxydifenic acid [29]. However, it is unstable and is isolated as ellagic acid after hydrolysis of ellagotannins.

Ellagic acid crystallizes from pyridine as pale yellow needles with a melting point >360°C. It settles on the surface of hides as a yellow residue when ellagotannins are used. Ellagic acid is found in plants as methyl esters and glycosides. Thus, 3,4,3′-tri-O-methylellagic acid (**12**) was isolated from *Euphorbia tirucalli* Linn. [30] as colorless crystals with a melting point of 288-291°C. It is practically insoluble in organic solvents.

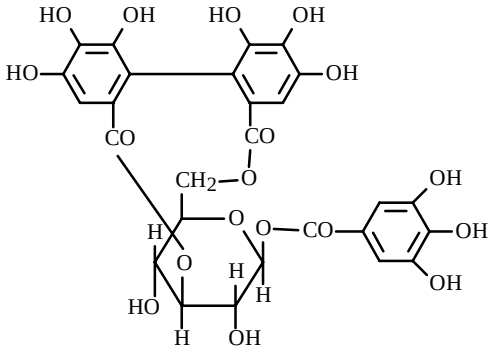


12

Euphorbia ferganensis B. Fedtsch yields 3-O-methylellagic and 3,3′-di-O-methylellagic acids [31]; *Euphorbia acaulis*, 4′-rutinosides of 3,3′-di-O-methylellagic and 3,3′,4-tri-O-methylellagic acids [32]; *Tellima grandiflora*, bihexahydroxydifenoylglucose [33].

Blazej and Suty proposed on the basis of their own data [34] and those of other researchers [35] a scheme for the biogenetic bonding of certain ellagic-acid derivatives.

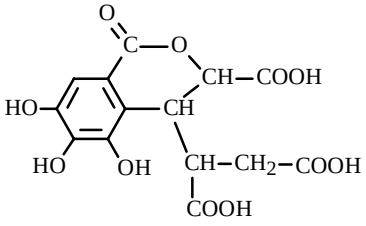
The first ellagotannin, corilagin (**13**), was isolated from the beans of *Caesalpinia coriaria* [36]. It crystallizes from water as long colorless needles with a melting point of 204-205°C (dec.). It is very soluble in acetone, slightly soluble in methanol, and poorly soluble in water and acetic acid. Partial hydrolysis of corilagin produces gallic acid. Total acid hydrolysis of **13** gives ellagic and gallic acids in addition to glucose in equimolar amounts.



13

Corilagin in the free state or as a hydrolysis product is also isolated from *Anogeissus latifolia* [20], *Geranium thunbergii* [37], and plum seeds [38]. Its structure and configuration were established by Schmidt et al. [39, 40].

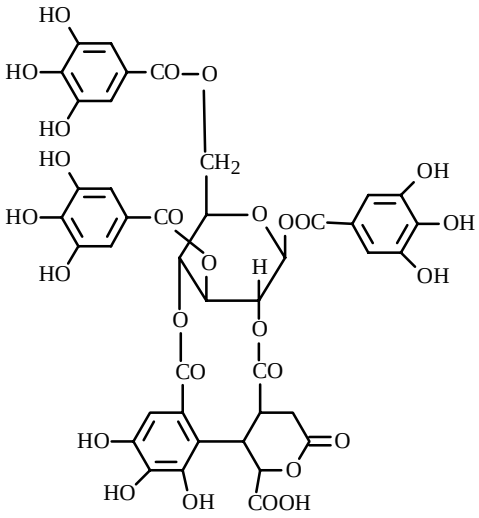
Chebulic acid was isolated from myrobalans and is a trihydroxytricarboxylic acid for which structure **14** was proposed [2, 41-44].



14

Schmidt et al. [2, 41] proposed on the basis of the structure of chebulic acid the existence of a biogenetic link between this compound and hexahyhdroxydifenic acid. Chebulic acid in the bound form is an amorphous, optically active compound.

Chebulinic acid (**15**) was isolated from myrobalans [45]. Acid hydrolysis produces chebulic acid and three molecules of gallic acid; partial hydrolysis, 1,3,6-trigalloylglucose and chebulic acid. Hydrolysis of chebulinic acid in neutral medium at 60°C forms neochebulinic acid (**16**) [46]. These acids differ only in the number of esters in the molecules.



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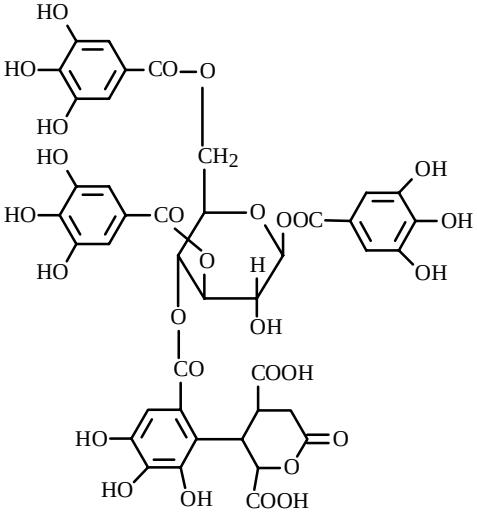
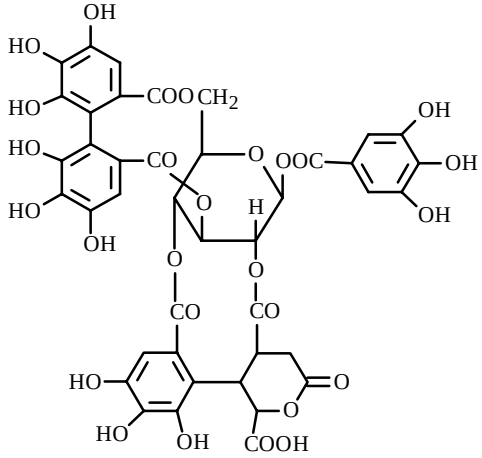


16

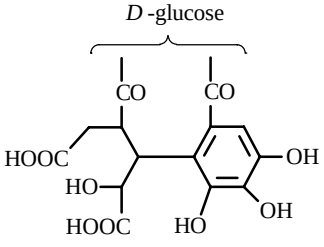
Stepwise hydrolysis of neochebulinic acid forms first trigalloylglucose and chebulic acid, then gallic and 3,6-digalloylglucose, and finally glucose and gallic acid.

Chebulagic acid (**17**) was also isolated from myrobalans (*Terminalia chebula*) [47-49]. It crystallizes from water with 10 water molecules. It darkens without melting at 240°C and higher temperatures. It is soluble in methanol, ethanol, acetone, ethyl acetate, and hot water; poorly soluble in cold water, and insoluble in petroleum ether and benzene. The optical rotation $[\alpha]^{20}_{D}$ is -57.2+2° (ethanol, c 2,6). Total hydrolysis gives glucose, ellagic, gallic, and chebulic acids in equimolar amounts.

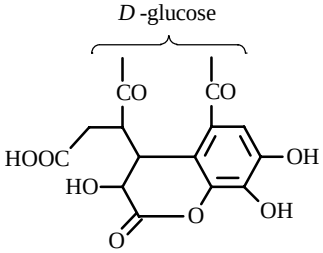


17

The structures of chebulinic (**15**) and chebulagic (**17**) acids have recently been refined [50, 51] and established as **18** and **19**. These data were reconfirmed using ^{13}C NMR and IR spectroscopy of the methylated product. Structures **20** and **21**, respectively, were proposed for these [52].

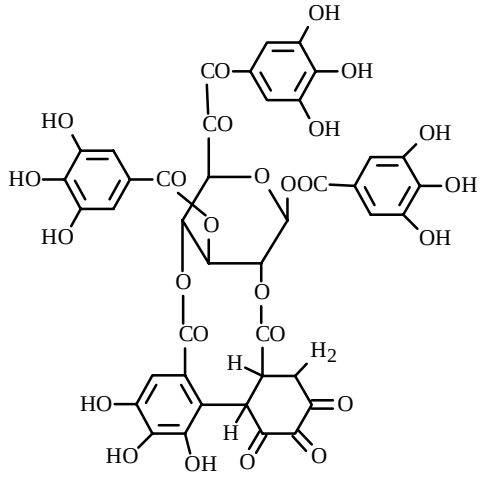


18, 19



20, 21

Terchebin, which has been isolated from the extract of *Terminalia chebula* fruit [53], is a crystalline substance without free hydroxyls in the sugar. The molecular formula is $C_{41}H_{30}O_{26}$. It can be written as 1,3,6-trigalloylglucose with one molecule of isohexahydroxydifenic acid in the 2 and 4 positions (**22**). Terchebin in solution behaves as a mixture of two equimolar isomeric compounds. The stereochemistry and absolute configuration of terchebin (**23**) were proved by Okuda et al.



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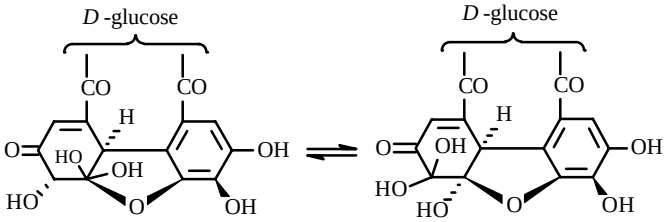
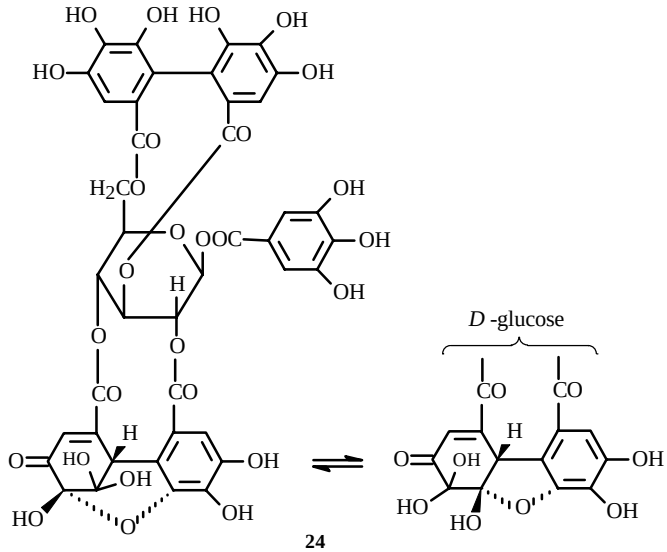


23

Counter-current dropping chromatography isolated from the ethylacetate fraction of *Punica granatum* fruit a new ellagotannin, granatin B, which is a yellow crystalline substance (from water) that is optically active with a mutarotary angle ($[\alpha]^{28}_{D}$ 109-123°, 4 h, acetone—water, 9:1). The empirical formula is $C_{14}H_{28}O_{27}\cdot 8H_2O$.

Okuda et al. [54] proved the stereochemistry and absolute configuration of granatin B (**24**). Granatin B was also isolated from other sources [55].



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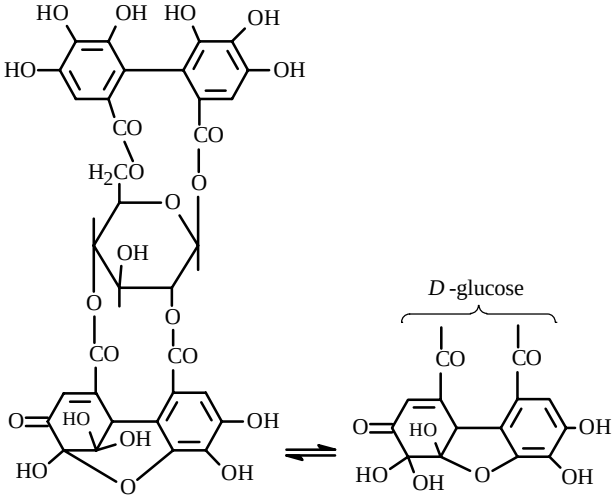
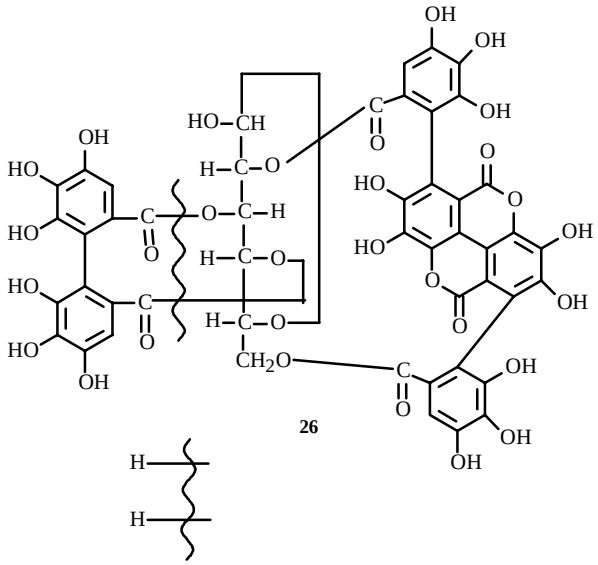


25

Granatin A (**25**), punicafolin [1,2,4-trigalloyl-3,6(R)-hexahydroxydifenoyl-β-D-glucose], and other hydrolyzed tanning agents (punicalagin **26** and punicalin **27**) were later isolated from *Punica granatum* [56].

Two more ellagic tanning agents, brevilagins 1 and 2 were isolated from *Algarobilla* [57-59].

Brevilagin 1 (**28**) is a yellow crystalline substance that is optically active ($[\alpha]^{20}_{D}$ +159.5°, ethanol). Elemental analysis showed that it has the empirical formula $C_{34}H_{24\text{-}28}O_{24}$. The uncertainty of the H content is due to the hygroscopicity of the compound. In fact, the molecular weight of brevilagin 1, which was determined by ebullioscopy in acetone, corresponds to $C_{34}H_{24\text{-}28}O_{24}$ (MW 816.5-820.6). Hydrolysis of brevilagin 1 by dilute H_2SO_4 forms ellagic acid; by conc. HCl, crystalline chloroellagic acid (**29**).



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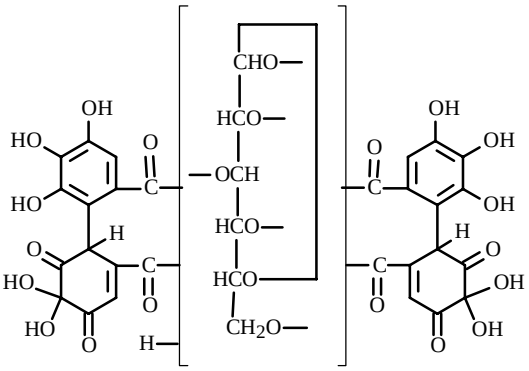

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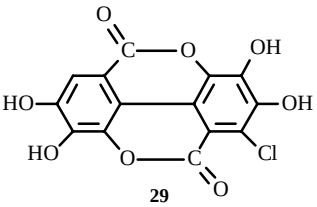
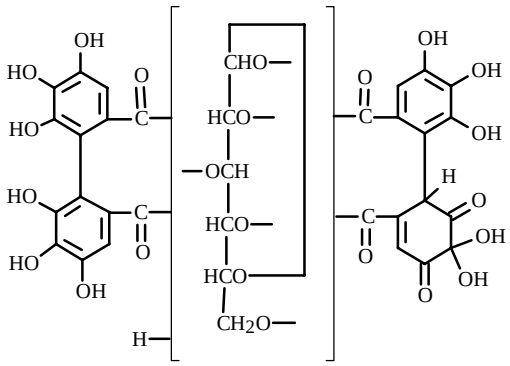


29

Brevilagin 2 is also crystalline and optically active ($[\alpha]^{20}_{D}$ +81°, ethanol). The molecular formula is $C_{34}H_{24}O_{23}$ but there are sometimes more H atoms. The melting point is not distinct.

Brevilagin 2 (**30**) consists of one molecule of hexahydroxydifenic acid and one molecule of dehydrohexahydroxydifenic acid bound to glucose. Hydrolysis by conc. HCl gives ellagic and chloroellagic acids.



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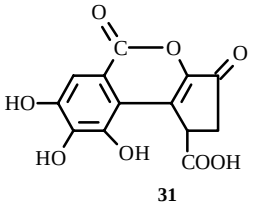

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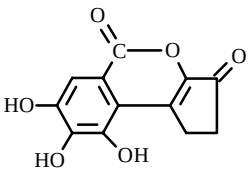

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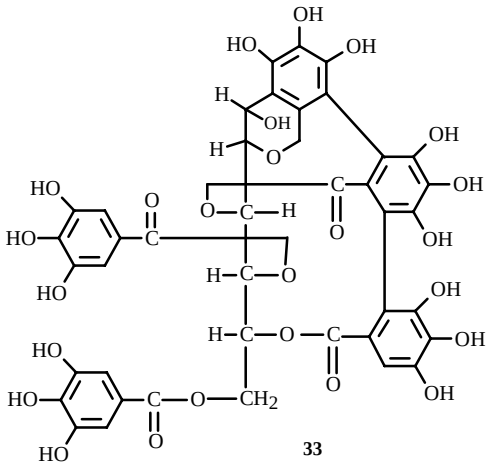


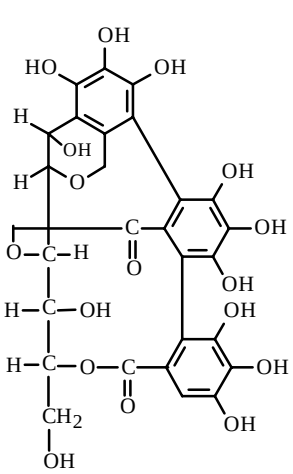
33

A new phenolcarboxylic acid, brevifolincarboxylic, $C_{13}H_8O_8$ (**31**), was isolated together with brevilagins from *Algarobilla* [29, 60, 61]. It forms phenylhydrazone, tetra-O-methylderivatives with dimethylsulfate and base, and the brevifolintri-O-methylderivative with diazomethane. Heating in water leads to decarboxylation and production of brevifolin (**32**).

Brevifolin is a pale yellow crystalline substance that is freely soluble in pyridine, very soluble with heating in methanol and ethanol, and slightly soluble in hot water. It crystallizes from 90% methanol as a yellow trihydrate. Brevifolin is optically inactive and has no distinct melting or decomposition point. Acid converts tetra-O-methylbrevifolin to tri-O-methylbrevifolin, which proves the presence of a lactone ring. The structure of brevifolin was confirmed by synthesis [62].

A special group of ellagotannins contains castalagin (**33**), vescalagin (**34**), castalin (**35**), and vescalin (**36**). These compounds were isolated from the wood of *Castanea sativa* and *Quercus sessiflora* [6, 63]. They differ from other ellagotannins in that they contain the D-glucose radical as an open chain and they are also C-glycosides. Castalagin is transformed on heating its aqueous solution to 100°C into vescalagin; castalin, into vescalin. It was shown that **33** is isomeric with **34** [64-66]. Hydrolysis by acid under mild conditions produces ellagic acid. In the first instance, vescalin appears after a certain time along

with castalin. Acid hydrolysis of **35** and **36** under forcing conditions forms glucose and flavogallic acid (**37**) [67]. Later these compounds were also isolated from other plants [68, 69].



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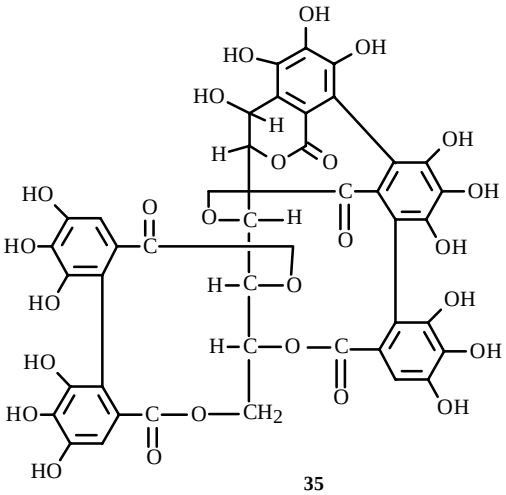

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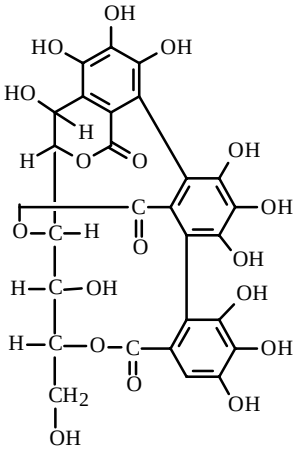

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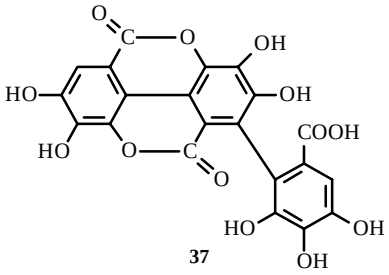

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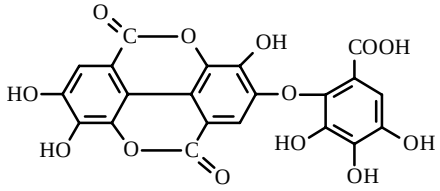
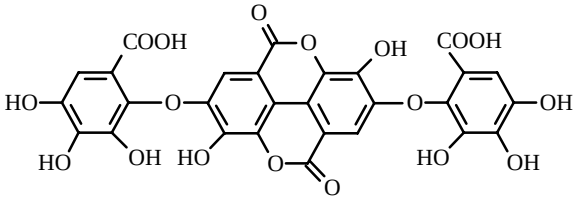


38

Flavogallic acid, which was isolated from the acid-hydrolysis products of tanning agents from *Castanea sativa*, *Quercus sessiflora* [6, 63], and *Q. valonea* [70], was synthesized in 1955 [71]. It appears in tanning agents as the cleaved lactone and is bound to the sugar by three carboxyls.

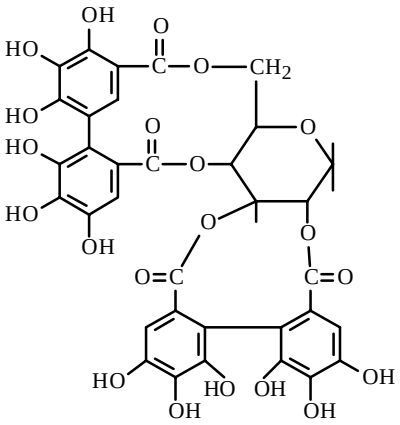
The dilactone of valonic acid (**38**) was isolated after hydrolysis of the acetone extract of tanning agents from *Q. valonea* [72, 73]. It crystallizes from 90% aqueous dioxane as thin white needles that are optically inactive. It is soluble in acetone much better than ellagic acid and crystallizes as fine prisms that have no distinct melting point. It is stable toward dilute acids and freely soluble in basic solution, which quickly darkens in contact with air. Methylation by diazomethane forms the pentamethylderivative $C_{28}H_{24}O_{13}$, which saponifies with heating in basic solution to the colorless hexamethylderivative $C_{27}O_{13}H_{22}$.

The hydrolysis products of tannins from *Chamaenerium angustifolium* yielded chamaeneric acid as white crystals of composition $C_{28}H_{14}O_{18}$ (**39**) with melting point >300°C [74]. The PMR spectrum of chamaeneric acid is similar to that of valonic acid.



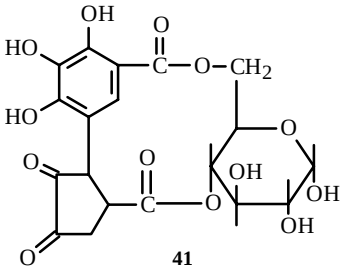
39

Galls of *Quercus pedunculata*, *Q. sessiflora* [75], and then the wood of *Eucalyptus delegateusis* [76] yielded 2,3,4,6-(-)-dihexahydroxyfenoylglucose and pedunculagin (**40**). NMR spectroscopy showed that the sugar has conformation C1 [51].



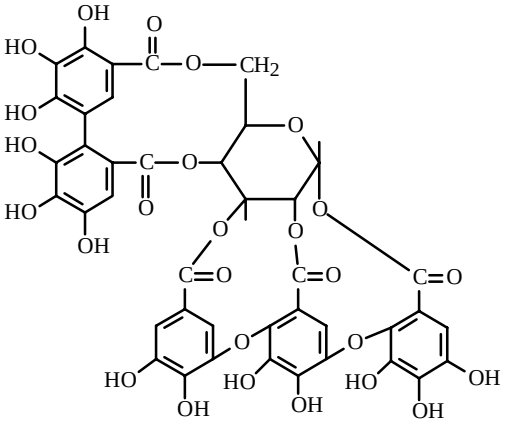
40

The ellagotannin algarobin (**41**), which is a glucose, 4,6-brevifolincarboxylic acid, was isolated from *Algarobilla*. Substitution at the 4 and 6 positions and the C1 conformation of the sugar were confirmed by NMR spectroscopy.



41

The ellagotannin 1,2,3-dehydrotrigalloyl-4,6-hexahydroxydifenoyl-λ-D-glucosamyrilagin (**42**), which was isolated from *Myricaria alopicuroides* [77, 78], is a colorless crystalline substance. The melting point is 270°C (dec.). It is soluble in acetone and alcohols, moderately soluble in ethyl acetate, and insoluble in water. Aqueous and acid hydrolysis of myrilagin produces glucose, gallic, ellagic, dehydrodigallic (**43**), and dehydrotrigallic (**44**) acids.



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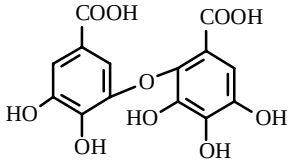

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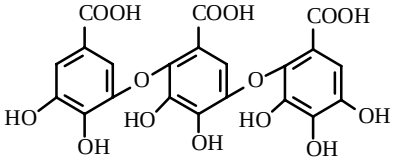
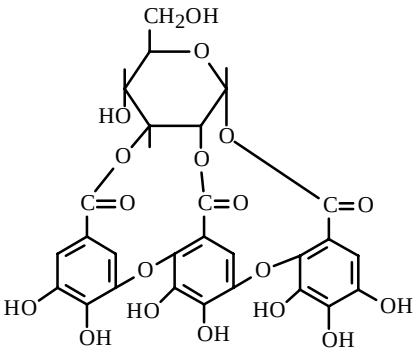


44

The structure of myrilagin was established by studying the hydrolysis products of **42** and its permethyl derivative and by IR and NMR spectroscopy.

Myrinin-1,2,3-dehydrotrigalloyl-α-D-glucose (**45**), which was isolated from the decomposition products of myrilagin, is an orange substance with melting point 230°C. It is soluble in alcohols and moderately soluble in ethyl acetate. The structure of myrinin was established by studying the products from acid hydrolysis, oxidation of the permethyl derivative with periodate, and basic hydrolysis of the methylated derivative and was confirmed by NMR spectroscopy.

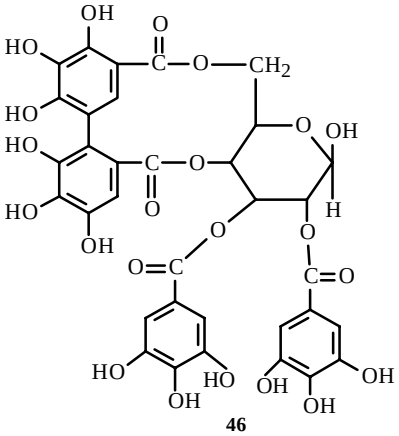


45

The hydrolysis product of myrilagin is dehydrotrigallic acid, which is a colorless crystalline substance with melting point 281-283°C (dec.). It is soluble in alcohols and moderately soluble in ethyl acetate.

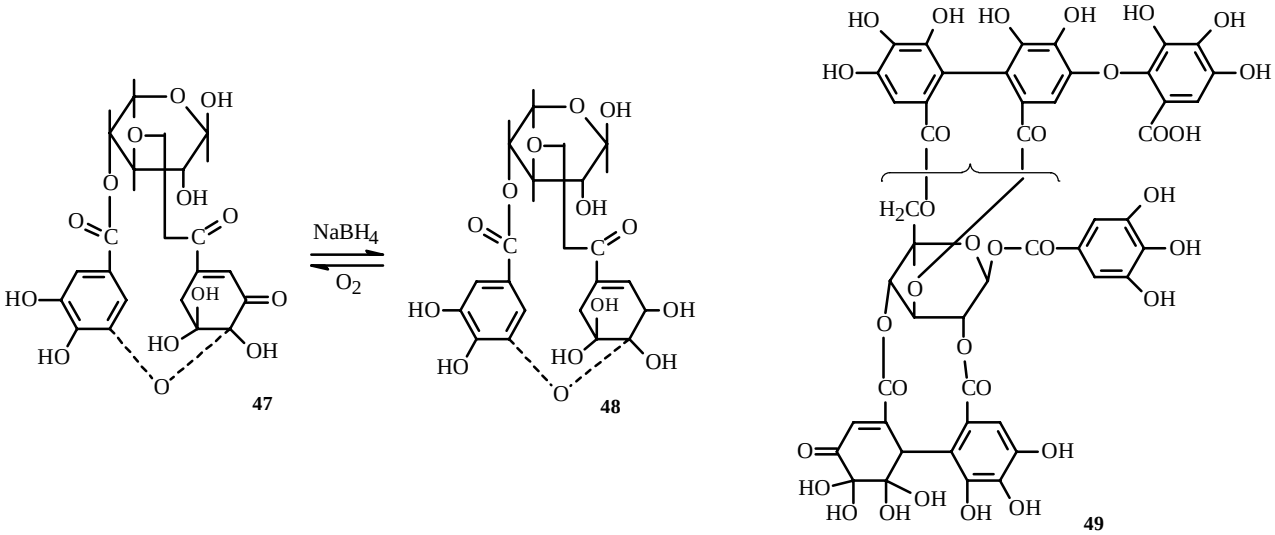
The structure of dehydrotrigallic acid was found by alkaline decomposition, methylation with diazomethane, and alkaline hydrolysis of the methylated product and was confirmed by NMR and IR spectroscopy of the starting compound and NMR and IR spectroscopy and mass spectrometry of the methylated product.

Collinin, 2,3-digalloyl-4,6-(+)-hexahydroxydifenoyl-β-D-glucose (**46**), was isolated from the leaves of *Geranium collinum* [79-82]. It is a crystalline substance with melting point 230°C.



46

Aqueous hydrolysis of **46** gives first ellagic acid and forms 2,3-digalloylglucose, which then cleaves to gallic acid and glucose and forms 3-galloylglucose as an intermediate. The structure of collinin was established by studying the products of methylation, hydrolysis, and periodate oxidation of the fully methylated product and was confirmed by IR spectroscopy.



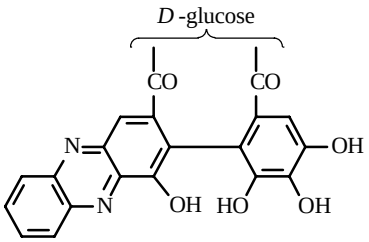
47 **48** **49**

The bark of *Alnus glutinosa* L. and *A. incana* L. Moench. yielded the tannins alnicortins 1 and 2 (**47**, **48**) [83] in addition to four alnicortins (1-4), which are hexahydroxydifenoyl-3-O-α,β-L-arabinosido-3-(O-α,β-D-xylopyranoside),

hexahydroxydifenoyl-1-(O-α-L-arabinosido)-1-(O-β-D-glucopyranoside), hexahydroxydifenoyl-1-(O-β-D-xylopyranosido)-1-(O-β-D-glucopyranoside), and hexahydroxydifenoyl-1-(O-α-L-arabopyranosido)-1-(O-β-D-xylopyranoside) [84].

The bark and leaves of *Mallotus japonicus* [85] yielded a new ellagotannin, mallotusinic acid (**49**). This compound is a brownish-yellow amorphous powder that is optically active ($[\alpha]^{15}_{D}$ -65.4°, *c* 0.5, MeOH). It gives a reaction characteristic of ellagotannins with sodium nitrite in acetic acid.

The PMR spectrum of mallotusinic acid contains signals for the sugar protons, the seven protons of the aromatic and vinyl rings, and two signals from the methine proton. The signal of each proton of the aromatic and vinyl rings splits into two peaks of approximately equal areas if measured in D_2O. The presence of a carbonyl was proved by reaction with o-phenylenediamine. This forms a yellow compound, phenazine 1 (**50**) with $[\alpha]^{15}_{D}$ -21° (*c* 0.5, MeOH). Hydrolysis of this compound precipitates the dark red phenazine 2 (**51**). Another ellagotannin, mallotinic acid (**52**) was isolated from the mother liquor of the hydrolysate by precipitation with $CHCl_3$.



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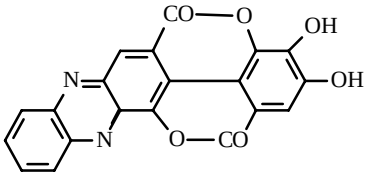
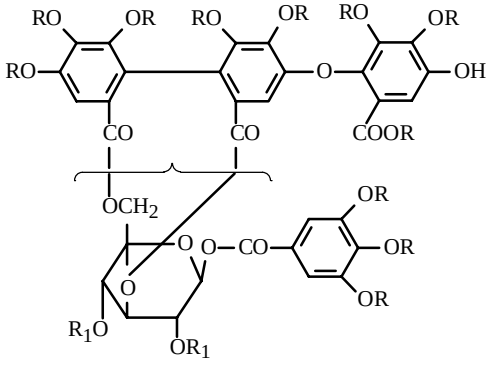
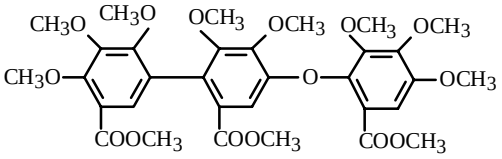


51

Methylation of mallotinic acid by diazomethane forms the dodecamethylderivative (**53**) with melting point 110.5-113°C. The methanolysis products of the dodecamethylderivative of malotinic acid yielded the methyltri-O-methylgallate with $[\alpha]^{20}_{D}$ +17° (*c* 10, acetone). Signals for protons in the PMR spectrum of this compound are identical to those of the trimethylocta-O-methylvalonate (**54**) with $[\alpha]^{20}_{D}$ -18.4°, which was isolated from tannin of *Q. valonea*. Therefore, these compounds are atropisomers.



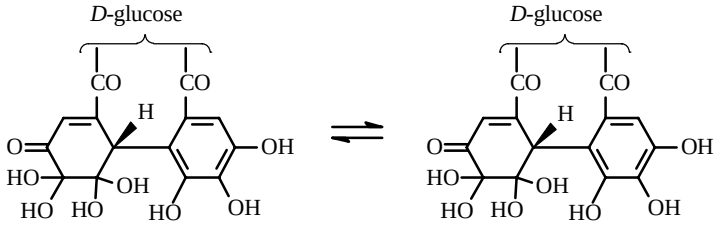
52: R = R_1 = H
53: R = CH_3, R_1 = H
55: R = R_1 = CH_3



54

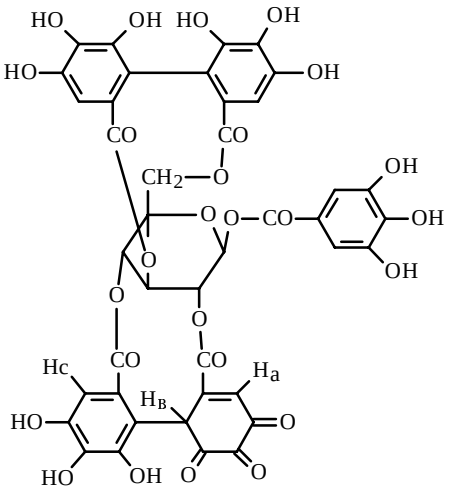
Methanolysis ($NaOCH_3$-CH_3OH) of methyltrideca-O-methylmallotinate (**55**), obtained from the reaction of the dodecamethylderivative and CH_3I—Ag_2O, proved that mallotinic acid contains free hydroxyl groups. The sugar fraction of the methanolysate contains 2,4-di-O-methylglucose.

An extensive study of the PMR and ^{13}C NMR spectra of mallotusinic acid and its derivatives (phenazines 1 and 2) revealed an equilibrium of the spatial structure of mallotusinic acid in the hydrated state (**56**) [86].



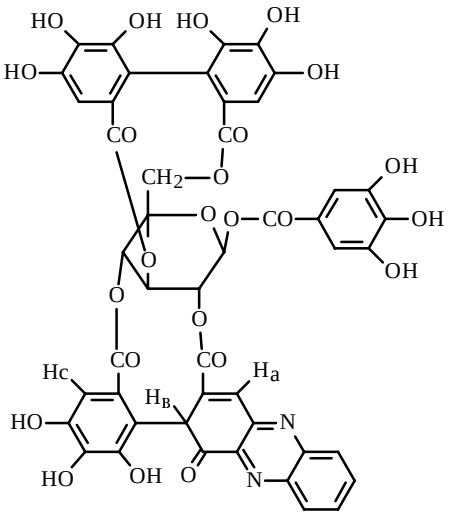
56

The aerial part of *Geranium thurberii* [38, 86-90] yielded the new compound geraniin. Crystallization from a CH_3OH—H_2O mixture produces yellow crystals of molecular formula $C_{41}H_{28}O_{27}\cdot H_2O$ with optical activity $[\alpha]^{15}_D$ -141° (hexahydrate, *c* 0.5, CH_3OH) and melting point >360°C. Hydrolysis of geraniin in boiling water forms ellagic and gallic acids and glucose. Hexahydroxydifenic acid and corilagin are observed as intermediates in the hydrolysis. Geraniin was characterized as a corilagin derivative in which the D-glucopyranose is esterified at the O-2 and O-4 positions (**57**) by determining the products of aqueous hydrolysis with 5% H_2SO_4, methylation of the hydrolysis products with diazomethane, and UV and PMR spectroscopy and mass spectrometry of the starting compound and the methylated hydrolysis products.



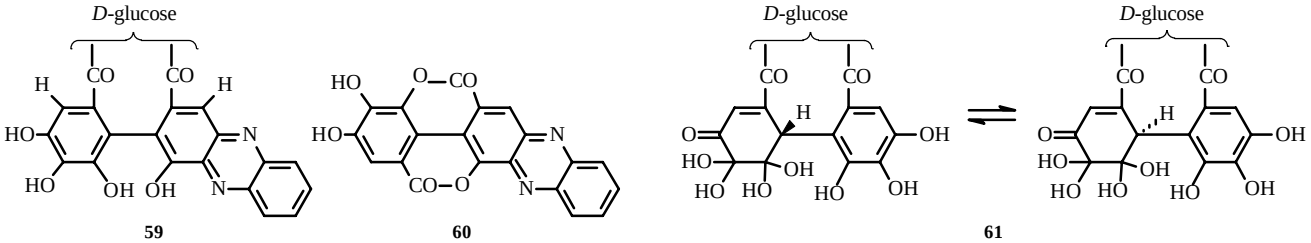
57

Reaction of geraniin with o-phenylenediamine in acidic medium (15% CH_3CO_2H) produces a pale yellow precipitate called phenazine A (**58**) with empirical formula $C_{47}H_{30}N_2O_4\cdot 6H_2O$, optical activity $[\alpha]^{15}_D$ -163° (*c* 0.5, CH_3OH), melting point >360°C, and R_f = 0.48 (*n*-butanol—acetic acid—water, 4:1:5).

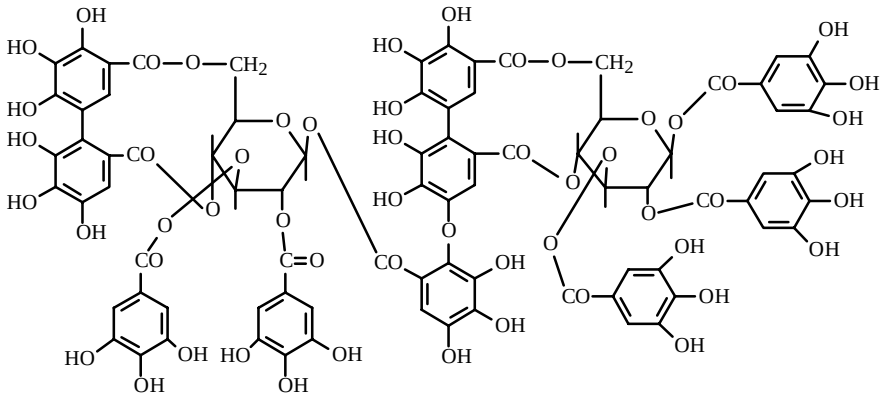


58

Reaction of geraniin with o-phenylenediamine in 50% CH_3CO_2H produces another compound, phenazine B (**59**) with empirical formula $C_{47}H_{30}N_2O_4\cdot 5H_2O$. It is an orangish-yellow powder with melting point >360°C, R_f = 0.48 (butanol—acetic acid—water, 4:1:5, upper phase), and optical activity $[\alpha]^{15}_D$ -90° (*c* 0.5, dioxane). If **59** is left in the reaction mixture for another day, the precipitate is treated with CH_3CO_2H, and the insoluble part is recrystallized from THF, dark orangish-yellow crystals with melting point >360°C and empirical formula $C_{20}H_8N_2O_6\cdot H_2O$, phenazine C (**60**), are formed. Geraniin was also isolated from other *Geranium* species [91, 92].



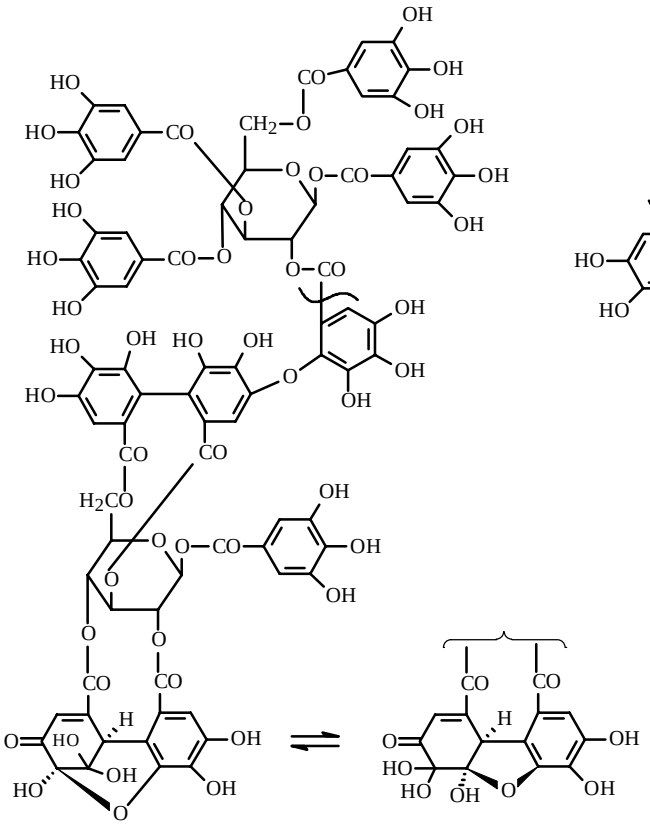
59 **60** **61**



62

It was also discovered that two of the three ketones of geraniin in the equilibrium mixture are hydrated (**61**).

Okuda et al. [93] studied the distribution of geraniin and mallotusinic acid in plants of the *Geranium* genus (Geraniales) and demonstrated that geraniin is the main component of the tannin in the studied *Geranium* species. The *Geranium* species lack mallotusinic acid. Geraniin was observed in most species of the subfamily *Euphorbiaceae* but in much smaller quantities than in *Geranium*.



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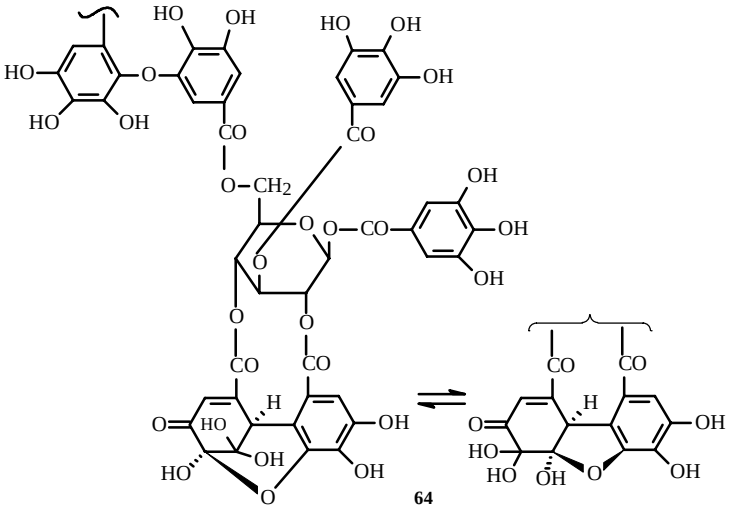

64

Leifertova et al. [94] isolated from the subterranean part of *Geranium purenaicum* and identified ellagic, gallic, and chlorogenic acids and quercetin and observed in the extract by paper chromatography 16 free amino acids. The free sugars included sucrose, glucose, and fructose; the bound sugars, galactose, arabinose, and xylose.

Several ellagotannins that were isolated from various sources have recently been studied. These include 1-O-galloyl-2,3-O-hexahydroxydifenoyl-β-D-glycose, 1-O-galloyl-4,6-hexahydroxydifenoyl-β-D-glucose, 6-O-galloyl-1,3-O-hexahydroxydifenoyl-β-D-glucose (hipporhamine) from leaves of *Hippophae rhamnoides* L. [95], 1,2,3-tri-O-galloyl-4,6-hexahydroxydifenoyl-β-D-glucose from leaves of *Geranium sanguineum* [96-98], and isorugosins A, 2,3-di-O-galloyl-4,6-O-(S)-valonyl-D-glucose, B, 1-O-galloyl-4,6-O-(S)-valonyl-D-glucose, and D (**62**) from *Liguidam-bar formosana* [99].

Cercidins A, 1,4,6-tri-O-galloyl-(R)-hexahydroxyfenoyl-β-D-glucose, B, 4,6-di-O-galloyl-(R)-hexahydroxydifenoyl-β-D-glucose, and cuspinin-4,6-(S)-hexahydroxydifenoyl-D-glucose were isolated from *Cercidiphyllum japonicum* and *Castanopsis cuspidata* [100] whereas *Nuphar japonicum* yielded diasteromeric tannins nupharins A, 1,2,4-tri-O-galloyl-3,6-(S)-hexahydroxydifenoyl-α-D-glucopyranose, and B, 1,2,4-tri-O-galloyl-3,6-(R)-hexahydroxydifenoyl-α-D-glucopyranose [23].

The dimeric ellagotannins euphorbins A (**63**) and B (**64**) were isolated from the aerial part of *Euphorbia hirta* L. [24].

Dimeric and oligomeric ellagotannins of very complicated composition were isolated from *Quercus robur* L. [5], *Rosa davurica* [101], plants of the Melastomataceae family [102], *Oenothera erytrosepala* [103], *Euphorbia hirta* [104], *E. watanbei* [105, 106], *E. heterophylla* [107], *E. tirucalli* [108], *Oenothera laciniata* [109], and others [110].

Thus, gallo- and ellagotannins are some of the most widely distributed natural compounds and are represented by a significant number of compounds of various structure.

SEPARATION AND ISOLATION OF TANNING AGENTS

Paper and thin-layer chromatography are common methods for determining the qualitative composition of tanning agents, like for other types of natural compounds.

Labels are needed to identify tannins that contain many galloyl groups during chromatography in acidic systems because the tannins mentioned above appear as broad bands under these conditions.

Chromatography of tanning agents on thin layers of polyamide or silica gel is performed using benzene—ethanol (1:1), benzene—methanol—pyridine (80:10:5), benzene—ethanol—pyridine (9:3:1), and acetone—water—pyridine (100:20:5) [111, 112].

It is noteworthy that the reproducibility and resolution of these methods are generally rather poor.

The composition of vegetable tannins is known to undergo seasonal variations [113, 114]. The chemical composition definitely changes upon storage of tanning materials and during extraction. A method with higher resolution and good reproducibility is needed to characterize these variations in tannin composition.

Recently HPLC has been used to determine the composition of vegetable tanning agents [115-126]. This method was first used by Okuda et al. [37, 87, 90] to study hydrolyzable tanning agents. The researchers used a chromatograph equipped with a gradient-elution system, a UV detector, and a thin steel column packed with a hydrocarbon polymer. The working pressure was 30-100 kg/cm^2. The mobile phase was a mixture of 0.5 M KH_2PO_4, ethanol, and ethylacetate in various ratios.

A characteristic feature of HPLC is the use of small solution volumes (1-6 mL) and low concentrations (0.1-0.5 mg/mL) to give rapid determinations (20-30 min). The amount of pure polyphenols is determined by estimating peak areas.

A drawback of HPLC is the inability to prepare pure compounds in appreciable quantities and the need for high-purity preparations that are used as internal standards at analyses.

Column chromatography continues to be the principal method for isolating pure compounds from mixtures of tanning agents despite its drawbacks. Column chromatography on Sephadex G-25 with elution by 50% aqueous acetone was used to separate condensed tannins [127]. It was found that tannins of molecular weight up to 900 can be separated on such a column whereas tannins of molecular weight ~1100 cannot penetrate the gel.

Identical data were obtained during fractionation of Chinese tannin components on Sephadex G-25 by aqueous acetone [128].

Gel filtration on Sephadex columns was also used by other research groups [75, 129-137].

Combination of gel filtration on Sephadex columns with preparative paper chromatography can be used to isolate pure dimeric proanthocyanidines [138, 139].

Silica-gel columns have been used successfully to separate and isolate catechols from Georgian tea [140] and cotton [141] and to separate and isolate catechols and leucoanthocyanidines from tanning knotweed [142-145] and other samples [146, 147]. Chumbalov and Pashinina [148, 149] proposed a method for separating phenolic compounds that is based on sorption of vegetable tannins by rawhide powder. The rawhide powder is first washed with water to remove various impurities that are sorbed together with the tannins. Then, the powder is treated with organic solvents and their mixtures with water to extract tanning agents.

Column chromatography on other adsorbents, e.g., cellulose [6, 12, 138, 139, 150-152] and polyamide [153-155] is also widely used to separate and isolate tanning agents.

Counter-current dropping chromatography (water—organic solvent) has recently been used for difficultly separated mixtures of phenolic substances. In particular, labile and complicated compounds such as mallotusinic acid and geraniin were isolated by this method [90, 85]. The pH of the aqueous layer can be varied in order to improve the separation.

QUANTITATIVE DETERMINATION OF TANNING AGENTS

Many different methods for quantitative determination of tanning agents are known. The standard method for determining their tanning properties is considered to be the Unit-Weight Method (UWM) [156]. The method consists essentially of first treating aqueous solutions of tanning agents with rawhide powder. Only tannins react with the rawhide powder whereas nontannings remain in solution. In general, the amounts of total water-soluble substances and nontannins are determined in the analytes. The amount of tannins is found by the difference between them. It was found [157] that rawhide powders that are used for standard analyses of tanning extracts differ markedly in chemical properties, degree of collagen branching, and ability to remove tanning agents depending on the method and site of preparation. Samples of rawhide powders that were manufactured in Freudenberg, Darmstadt, Lyon, and Vienna were examined. The differences in the determination of tannin content were 7%; in the quality, 5%.

The drawbacks of the standard method are its complexity and duration. The complexity sometimes leads to markedly differing results. For example, the discrepancies in one Czech laboratory reached 2.3%. They were even greater between different laboratories [158].

Therefore the use of intestinal membrane instead of rawhide powder was proposed [159].

A noteworthy biological determination method is based on aglutination of erythrocytes [160-161]. Biological methods are highly selective for tanning substances. The only phenolic compounds that usually accompany tannins and that exhibit a slight ability to coagulate human erythrocytes are pyrogallol and pyrocatechol. However, this property does not interfere in the determination of tanning agents. Drawbacks of this method are the sharp decrease in reactivity of erythrocytes upon storage and the dependence of the activity of these compounds on the pH and temperature of the medium.

The gelatin method gives results close to those of the standard method (UWM) [162]. The method consists of titration of tanning extracts with an aqueous solution of gelatin of known concentration. In this instance, gelatin tannate precipitates. Investigation of the electrophoretic mobility of the complexes obtained from reaction of tannin and gelatin showed [163] that the mobility of the complex at a certain pH is independent of the mass ratio of tannins to gelatin and is essentially the same as the electrophoretic mobility of the gelatin itself. Results from an electrophoretic-mobility determination of the charge on tannin and gelatin molecules can be used to calculate the amount of tannin bound to gelatin.

It should be noted that results of analyses that used gelatin were slightly lower than results obtained by the standard method because rawhide powder also adsorbs some nontannins.

One of the classical methods for determining tanning agents is the Loewenthal method [164], which is based on the facile oxidizability of phenolic compounds by $KMnO_4$ in acidic medium in the presence of indigocarmine indicator. Various modifications of this method were used in the tea industry during the production of vitamine P from tea leaves, during the determination of tanning agents in various materials [165-167], etc.

It was found that the largest amount of permanganate is consumed by oxidation of polyphenols with ortho- and para-dihydroxyls (pyrocatechol or hydroquinone derivatives) during the oxidation of phenols [168]. However, this method is nonetheless poorly suited for determining tanning agents because simple polyphenols that are not tanning agents also react.

A colorimetric method based on the formation of yellow tannins with 1% aqueous ammonium molybdic acid has this same drawback. It is used to determine tannins in wines [169] and plant materials [170, 171].

However, the experimental uncertainty of this method compared with the standard method (UWM) is 5-6% [171]. Folin (phosphotungstic reagent), Folin—Denis and Folin—Ciocalteu (phosphomolybdeno-phosphotungstic reagent) [172] and various modifications of them are widely used to determine tanning agents by the colorimetric method. The determination is based on measuring the degree of coloration of the resulting complex in saturated Na_2CO_3. Using Folin—Denis reagent in combination with preliminary preparative paper chromatography [173] or adding sodium molybdate to Folin reagent [174] have been proposed. Separate determination of simple phenols, flavans, and condensed and hydrolyzable tanning agents in each other's presence by combining selective separation into fractions with subsequent colorimetric determination with Folin—Ciocalteu reagent is also possible [175]. Drawbacks of these methods are the instability of the coloration of the complexes over time and the inaccuracy, which has been noted [173, 174]. Sadykov et al. [176] developed a colorimetric determination method for tanning agents in knotweed roots (*Polygonum coriarium*) and its extracts that is based on a color reaction between condensed tanning agents and vanillin reagent (1% vanillin in conc. HCl). This method was tested under industrial conditions and is used at "Tarandubitel′" PO as a rapid method for monitoring the production of tanning extract from knotweed roots.

The accuracy of the determination by another method, spectrophotometric [177-182], is 1%. However, combination of this method with preparative chromatography [183-185] significantly increases the accuracy. Electrochemical methods for determining tannins are also known, in particular, potentiometric [186] and voltammetric [187]. These methods make it possible to determine tannins in colored solutions and are convenient for monitoring the production of tanning agents, wines, etc. The experimental uncertainty of the first method is 3-7%; of the second, 5-6%. Other methods of note are a diazonium method [188] based on the ability to couple tannins with diazotized amines, a method based on the precipitation of tannins by copper acetate [189] followed by titration of the excess of acetate, a method for precipitating tannins with alkaloids [190], and a method for quantitative determination of tanning agents with a zinc complex [191].

However, these methods do not give satisfactory results [192]. This is due mainly to the complex nature of the polyphenols that make up the bulk of plant tannins. All these methods cannot be used for selective determination of the content of only tannins. Phenolic compounds that are not tanning agents affect the results to one extent or another. Some of these methods do give results that agree with those of the standard method but only for certain tanning agents. Therefore, the standard method, despite its drawbacks, remains the most reliable and universal because the deviations are <3% if the analysis is carefully performed.

PREPARATION OF TANNING EXTRACTS

One of the most important problems of the tanning-extract industry is the search for ways to increase the yield of tannins from plant material. Production of the tanning agent involves three steps: extraction, evaporation, and drying. The efficiency of using the plant material is increased mainly in the first step, extraction, by selecting the appropriate conditions of temperature, cycles, ratio, use of additives, etc.

The raw material can be extracted using ultrasound [193, 194]. This partially lyses the plant cells, which enhances the transfer of tannins into the diffusion liquid and shortens the extraction time. Use of a rotary-pulse apparatus [195] and treatment of raw material with vibrations [196] have almost the same effect as ultrasound.

Other methods for increasing the extraction efficiency include UV irradiation of the raw material or the diffusion liquid [197, 198]. However, it should be noted that these methods have no significant advantages over the usual extraction methods and require specialized expensive equipment and large energy expenditures.

The principles of counter-current extraction are applied in order to produce a quality extract with a high density. Different extraction cycles, solid/liquid ratios, and temperatures are used depending on the raw material [195, 199-202].

The use of certain chemicals as additives is recommended in order to increase the degree of extraction of tanning agents as bound tannides. Thus, NaOH and $Na_3PO_4 \cdot 12H_2O$ are used as additives during extraction of oak [203]. NaOH up to 2% of the raw material mass was used during extraction of oak bark [204]. The tanning liquid was demineralized by passing it over cation-exchange resin.

Use of sulfanol [205], phenol [206], and syntan SL [207] has also been reported.

Literature data on the use of sulfite salts as additives are somewhat contradictory. Thus, it was shown that sulfites do not increase the tannin yield and decrease the quality during extraction of oak in general and the bark, sapwood, and heartwood

in particular [208]. Ekimov et al. [209] consider sodium sulfite to be unsuitable for extraction of oak wood but suitable for extraction of oak bark. Use of sodium sulfite to extract fir [210] and willow [211] bark and ammonium bisulfite and sulfite to extract oak chips [212, 213] gave positive results.

It was demonstrated [214] that sulfite salts not only improve the tannin yield in the diffusion liquid but also increase their solubility. Sulfiting the diffusion liquid dissolves tannins that have precipitated.

Kotasek et al. [215] noted that tanning agent obtained by sulfite extraction of fir bark has an advantage over ordinary fir extracts. It diffuses faster into the leather. Other researchers have produced the same results [216].

Several methods for clarifying tanning extracts are known. Thus, a method for precipitating hydroxides of alkaline-earth metals, lead salts, etc. was proposed [217]. Tannates and nontannates of the corresponding metals precipitate. Then, the precipitate is treated with dilute carbonate until the majority of the nontannins located in the precipitate are dissolved.

Treatment of roots with four times the amount of acetone was proposed for enriching the extracts [218]. The precipitate contains carbohydrates. The tannins remain in solution.

Nosacheva et al. [219] described almost the same method for clarifying solutions of tanning agents with ethanol.

BONDING OF VEGETABLE TANNING AGENTS TO COLLAGEN

The processes occurring during the interaction of tannins with collagen has drawn much attention for a long time.

The bonding of tannins to collagen produces leather, which is more elastic than rawhide and is more resistant to water, temperature, and microorganisms. However, such bonds are formed only if the tannin molecules are large enough to join neighboring collagen chains and have enough phenols to form crosslinks in several places. Thus, the gallotannins mentioned above, i.e., glucogallin, acertannin, hamamelitannin, tri-O-galloyl-D-glucose, and biogenetic precursors of condensed tanning agents, i.e., catechols, leucoanthocyanidines, and dimeric proanthocyanidines, have either no tanning ability or a small amount of it. Treatment of aqueous solutions of condensed tannins that contain a significant amount of monomers with slightly polar solvents, e.g., diethylether, transfers flavan-3-ols into the organic phase whereas the polyphenols of higher molecular weight remain in the aqueous. The tanning ability and quality of the aqueous solutions of tanning extracts, as a rule, increase after such treatment.

This also happens during treatment of tanning agent from certain type of raw material, e.g., leaves of *Uncaria gambir* and *Schinopsis lorentzii*. This is apparently due to oxidative condensation of catechols. Flavan units also condense in the plants themselves. For example, it was discovered during a study of *Polygonum coriarium* roots [220] that the monomeric flavan units flavan-3-ol and flavan-3,4-diol predominate in the polyphenol complex of roots of year-old plants whereas proanthocyanidines predominate in older ones. Therefore, the tanning ability and quality of roots from older plants is higher than that of year-old plants.

It was found that the tannin molecule cannot penetrate in the tanning process or poorly penetrates into the rawhide if it is too large. Therefore, it does not bind collagen or binds it very weakly. Tannins of molecular weight from 500 to 3000, especially 1000, are most responsible for tanning by phenolic compounds [221]. Natural galloylglucoses, which are used in industry, are polygalloylglucoses with a molecular weight of 1000 (Chinese and Turkish tannins).

It was found in the 1950s that part of the tannins can be adsorbed during the tanning process by the highly developed inner surface of collagen and are precipitated in the pores and capillaries. Adsorbed tannins and tannins that penetrated into the leather at the final moments of tanning and did not manage to react with the protein are easily washed out.

Some researchers consider [222] ionic bonds to be one of the bond types that can form between tannins and collagen. These bonds form between phenol hydroxyls of tannins that carry a negative charge and positively charged protein groups (amino groups etc.).

$$P - NH_3^+ + O^- - T > P - NH_3 - T$$

A series of experiments [223] on the extraction of rawhide powder tanned with willow extract by several solvents of increasing polarity was carried out to elucidate the nature of the bonding of tannins to collagen and the degree of reversibility of tanning. The extent of tanning was determined from the decrease of tanning coefficient (amount of bound tannins and decrease of binding temperature). Extraction by the solvents could wash out 97% of the initial tannins. It was concluded that tannins are comparatively weakly bound to collagen, i.e., via H-bonds. Covalent chemical bonds of tannins to collagen are not

required for a normal tanning effect.

Russel et al. [224, 225] continued the investigation of the binding mechanism of tannins and collagen. They determined that a small fraction of willow tannins, called "stable to solvents," consists of molecules of high molecular weight. Their structures are analogous to the basic components of tannins. These compounds were found in many natural condensed tanning agents. The tanning is completely reversible for hydrolyzable tannins upon treatment of leather with solvents at a certain pH. The existence of a fraction "stable to solvents" was explained by a special orientation of the high-molecular-weight tannin components on the collagen surface, which forms a large number of H-bonds that make this fraction stable toward organic solvents.

According to Russel et al., the binding mechanism of tannins to collagen can be explained by ionic bonds, dipole attraction, and formation of H-bonds. Such factors as the molecular dimensions and the accessibility of the collagen surface to them should be considered. It was thought that covalent bonds are not formed during normal tanning.

However, Endres [226] demonstrated that the tanning effect of commercial plant extracts (quebracho, mimosa, fir) arises owing to formation of crosslinking covalent bonds, i.e., tanning also includes formation of covalent bonds.

A study of the reaction of babul tanning agent with modified rawhide powder (deaminated, esterfied, acetylated, etc.) has found that methylation increases tannin fixation. According to the literature, this is due to the formation of additional H-bonds [227].

An investigation of the reaction of vegetable tanning agents with chromated normal and modified collagen demonstrated [228, 229] that the principal collagen groups play a significant role in the rate of absorption of vegetable tannins. These groups become more accessible after chromating. The tanning is irreversible owing to a coordination bond between the vegetable tanning agents and the collagen chromium complex.

Gustavson described the molecular structure of collagen during a determination of the tanning mechanism [230]. He studied the changes occurring in rawhide during formation of aldehydes, vegetable tanning, tanning with syntans, etc.

Santhanam et al. [231] studied the tanning mechanism using the binding of tannins of *Ceriops roxburghiana* with chemically modified collagen. They concluded that the peptide group, to which tannins are bound via H-bonds, plays the main role during collagen tanning. The remaining active groups of collagen (NH_2, COOH, and OH) play a secondary role in tanning. Furthermore, it was found that the collagen binding temperature and the amount of bound tannins are not directly related.

Other researchers have also concluded that collagen peptide groups are the main binding site of tannins [232].

It was found [233-235] that tanning by vegetable tanning agents is based on the formation of multifurcated H-bonds between collagen and tannins, i.e., noncovalent and reversible bonds. Covalent crosslinking between collagen moieties starts with reaction of NH_2 groups of lysine and arginine with tanning molecules in the quinoid form and finishes with formation of Schiff bases.

Modeling of tanning of modified rawhide powder revealed that removal of arginine guanidine groups has a noticeable effect on the leather properties. About 20% of the tannins are bound to arginine guanidines; the remainder, to collagen peptides.

The increased binding strength of part of the tannins to protein was explained [236] by several bonds on a single portion. In this instance, rings that are more energetically favorable are formed.

The data indicate that various research groups have reached the following conclusions about the nature of tanning-agent binding to collagen:

The reaction is reversible owing to the formation of H-bonds and ionic bonds between N atoms of amino and amide groups of the polypeptide and hydroxyls of the tanning agent.

Tanning-agent molecules are covalently bound to collagen. This ensures that the process is irreversible.

In both instances the size and shape of the tanning-agent molecule is very important. These properties guarantee that a sufficient quantity of crosslinking bonds is formed.

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