VEGETABLE TANNING SUBSTANCES. DEPENDENCE OF THE TANNING PROPERTIES OF EXTRACTS ON THEIR COMPOSITION

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Information is given on vegetable tanning substances, their classification, distribution in the plant world, and structure, and the dependence of their tanning properties on their composition, and also on methods of enriching tanning extracts. The review of literature sources includes publications from 1950 to 1989.

Vegetable tannins are finding wide use in various sectors of the national economy and medicine. Their astringent, bactericidal, hemostatic, and antiinflammatory properties are well known. In the textile industry, tannins are used for mordanting cotton fabrics in dyeing. They are used as colloidal stabilizers in industrial plants for boiling water, as setting retarders for ament slurries in the drilling of oil and gas wells, in the production of plastics and binders, in the oil-refining industry for the elimination of sulfur from petroleum, and also for the enrichment of low-quality ores by the flotation method. But, nevertheless, the basic consumer of tannins remains the leather industry. In spite of the wide use of syntans (synthetic tanning agents) in the preparation of various types of leather, natural tanning have not lost their importance. Their use is obligatory for the preparation of high-quality leather, and therefore the world production of vegetable tanning extracts amounts to several hundreds of thousands of tons per year.

Vegetable tannins consist of complex mixtures of phenolic compounds close in composition. They are subdivided into two large groups: hydrolyzable and nonhydrolyzable (condensed) tannins.

On acid hydrolysis, hydrolyzable tannins are split into phenolic and nonphenolic fragments. The former are usually represented by gallic and dihydroellagic acids and derivatives of cinnamic acid, and the latter by a hexose (usually D-glucose), an alicylic acid (such as quinic), hamamelose (2-C-hydroxymethyl-D-ribose), and the polyhydric alcohol sorbose. Depending on the nature of the acid formed as the result of hydrolysis, the hydrolyzable tannins are subdivided into two groups: gallic – which, on being decomposed forms glucose or a compound related to it and gallic acid – and ellagic – which decomposes into glucose and ellagic acid or a compound related to it.

The natural gallic tannins used in industry are polygalloylglucoses with molecular masses of the order of 1000.

Of the polygalloylglucoses, the most studied are the tannins of Chinese and Turkish galls (I and II), sumach tannin, Dhava tannin (III), and Tara tannin (IV). The structure of Chinese tannin, which is isolated from the galls of Rhus semialata Murr., was first suggested in 1914-1919 by E. Fischer and K. Freudenberg, who showed that the ratio of glucose and gallic acid in it amounted to 1:9 or 1:10 and proposed for it the structure of penta-m-digalloyl-β-D-glucose. This was subsequently confirmed in investigations by other workers [1-6] and, in particular, it was established that Chinese tannin was a mixture of penta-, hepta-, octa-, and nonagalloylglucoses. A detailed interpretation of the structure of Chinese tannin (I) was given in 1961-1963 on the basis of the results of elementary analysis, a determination of molecular mass, the methanolysis reaction, a study of the PMR spectra of methylated derivatives, etc. Sumach tannin is identical with Chinese tannin [7, 8].

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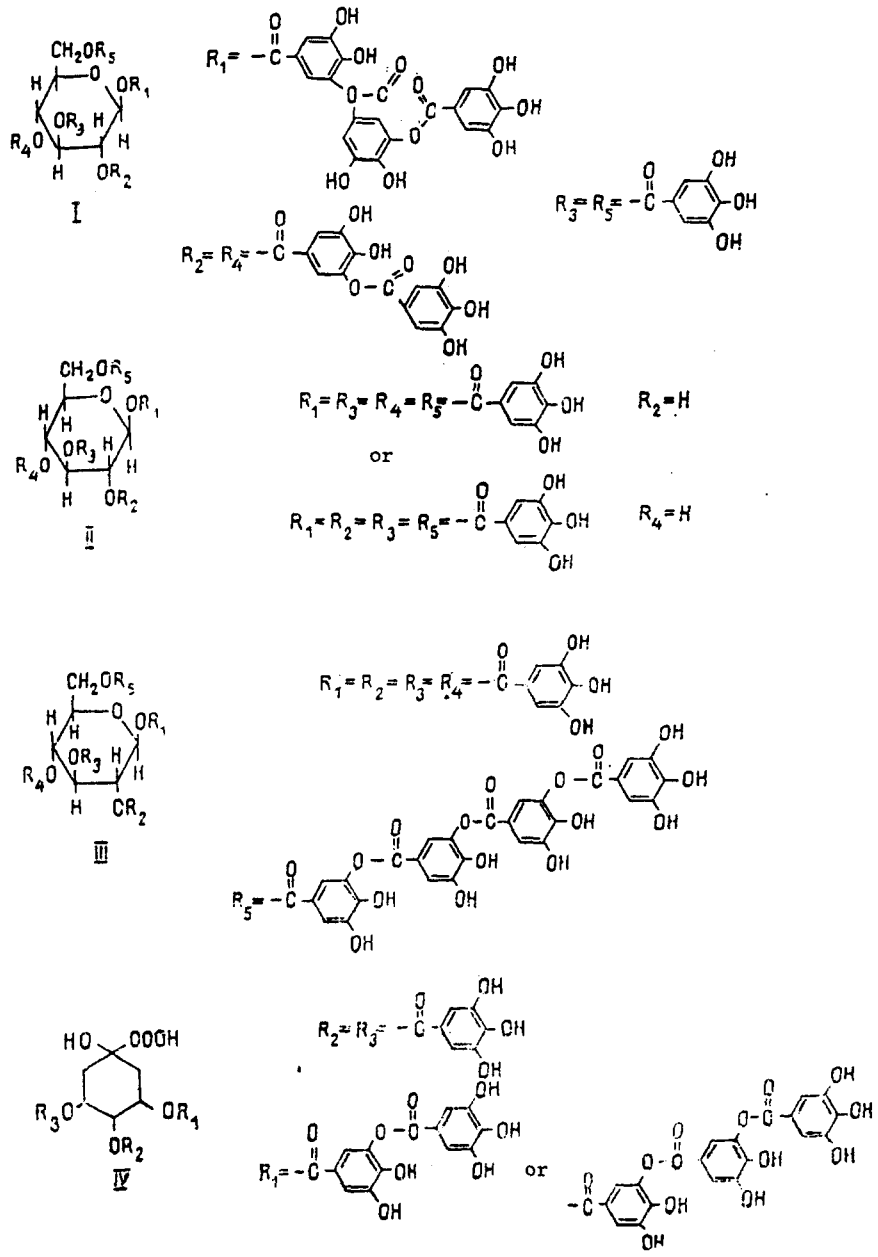
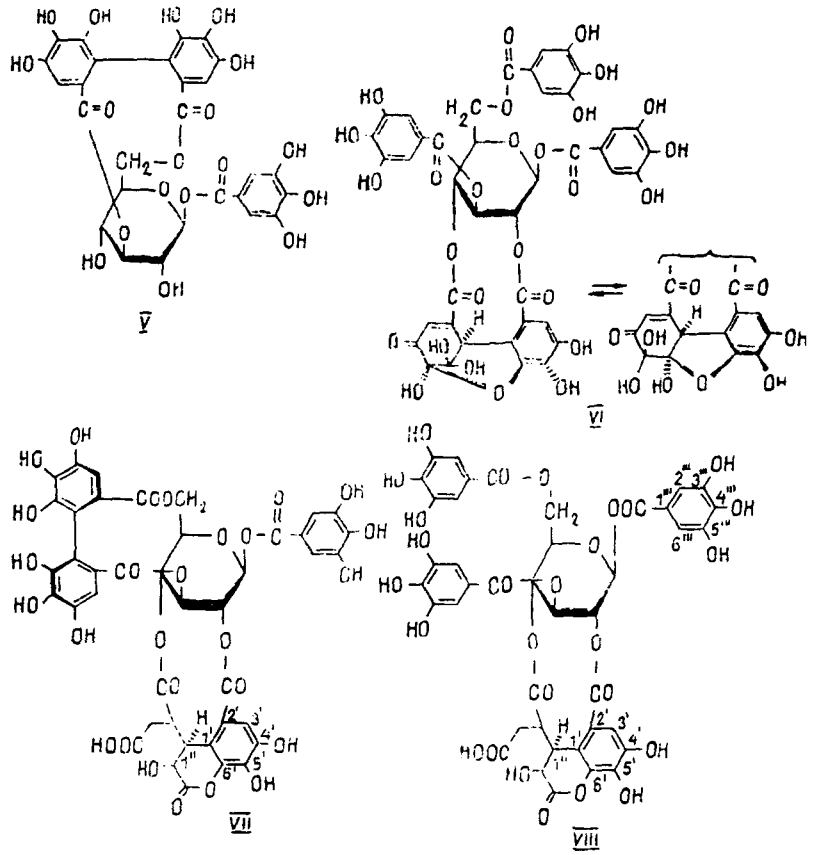


Turkish tannin is a mixture of substances close in composition: the main ones are tetra-O-galloylglucose fragments in which position 2 or 4 is free [3, 6, 9]. Dhava tannin consists of a pentagalloyl-β-glucose fragment to which 3 or 4 galloyl groups are attached in depside fashion (III) [10]. Tara tannin consists of 3,4,5-trigalloylquinic acid (IV) to which 2 or 3 galloyl residues are attached in unordered fashion by depside bonds [3, 11].

The gallic tannins also include platyacanthin (dehydrotrigalloyl-α-D-glucose) isolated from Rosa platyacantha Sch. [12], and 1,2,4-tri-O-galloyl-α-D-glucopyranose and 1,2,3,4,6-penta-O-galloyl-α-D-glucopyranose from the rhizomes of Nuphar japonicum DC [13], the structures of which were established on the basis of spectral characteristics and were confirmed by chemical transformations.

Representatives of the ellagic tannins are corilagin (V) [14], terchebin (VI) [15], and chebulagic and chebulinic acids (VI and VIII, respectively) from myrobalans (the fruit of Terminalia chebula Retzius) [16-20], granatin B (IX) isolated from the fruit of Punica granatum L. [21], and geranin (X) from Geranium thunbergii Sieb. and G. rectum Trautv. [22-25].

A special group of ellagitannins consists of castalagin (XI), vescalagin (XII), castalin (XIII), and vescalin (XIV) [26, 27]. They differ from other ellagitannins by the fact



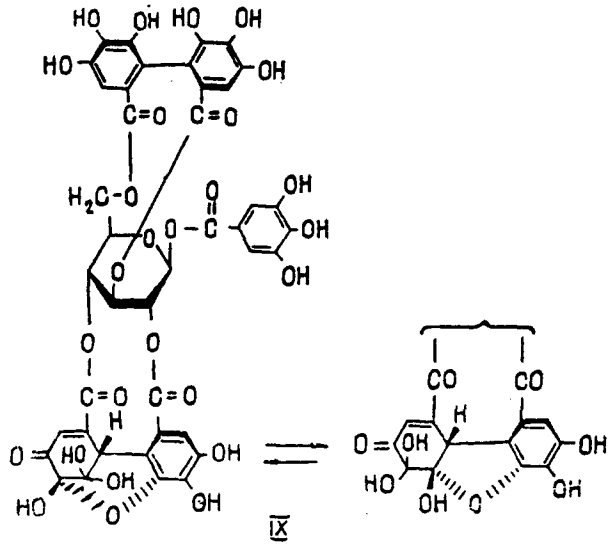
that they contain D-glucose in the form of an open chain and are C-glucosides.

The ellagic tannins also include myrilagin (1,2,3-dehydrotrigalloyl-4,6-hexahydroxydiphenoyl-α-D-glucose) from Myricaria alopecuroides Schrenk. [28, 29], colinin (2,3-digalloyl-4,6-(+)-hexahydroxydiphenoyl-α-D-glucose) from Geranium collinum Staph. [30], brevilagin 1 (XV), brevilagin 2 (XVI), and algarobin (glucose-4,6-brevifolincarboxylic acid) [31-33], pedunculagin (2, 3, 4, 6-(−)-dihexahydroxydiphenoylglucose) [34-36]), and mallotusic acid (XVII) from Mallotus japonicus Muel. et Arg. [37], and also tannins isolated from the leaves of Hippophae rhamnoides L. and consisting of 1-O-galloyl-4,6-O-hexahydroxydiphenoyl-β-D-glucose, 1-O-galloyl-2,3-O-hexahydroxydiphenoyl-β-D-glucose, and 6-O-galloyl-1,3-O-hexahydroxydiphenyol-β-D-glucose [38]. In addition, recently another series of ellagitannins isolated from various plant sources has been studied: the euphorbins A (XVIII) and B (XIX) from the epigeal part of Euphorbia hirta L. [39]; isorugosins A — 2,3-di-O-galloyl-4,6-O-(s)-valoneoyl-D-glucose-, B — 1-O-galloyl-4,6-O-(S)-valoneoyl-D-glucose-, and D (XX) from Liquidambar formosana [40], ellagitannins from the roots of European alder [41], 1,4,6-tri-O-galloyl-2,3-(R)-hexahydroxydiphenoyl-β-D-glucose, 4,6-di-O-galloyl-2,3-(R)-hexahydroxydiphenoyl-β-D-glucose, and 4,6-(S)-hexahydroxydephenoyl-D-glucose from Cercidiphyllum japonicum and C. cuspidata [42], and the diastereoisomeric ellagitannins nupharins A and B and their homologues from Nuphar japonicum DC [43].

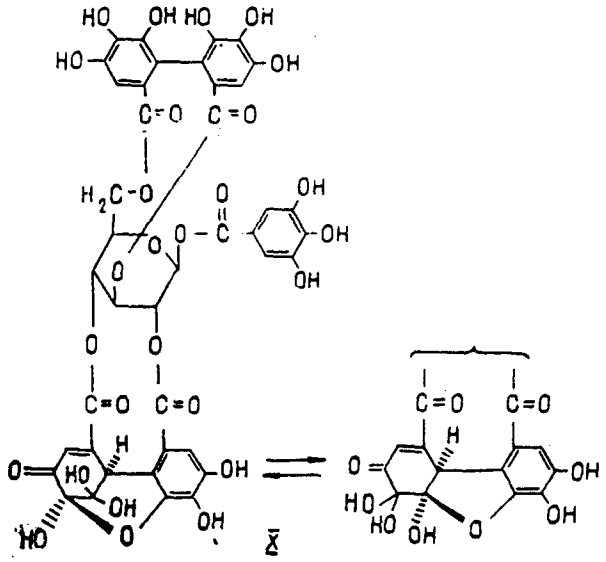
Usually, plant tanning extracts containing hydrolyzable tannins have a complex composition including compounds of both subgroups.

Tannins of the condensed series consist of mixed oligomers or polymers all the fragments of which are bound to one another by C—C bonds. The immediate biogenetic precursors of the condensed tannins are also such polyhydroxyflavans as flavan-3-ols (catechins) and flavan-3,4-diols (leucoanthocyanidins) [44-52].

The term "proanthocyanidins" introduced by K. Feudenberg and K. Weinges [50] is frequently used to denote condensed tannins. However, it must be mentioned that tanning properties are shown only at the level of the trimeric proanthocyanidins and appear more strongly with a rise in the degree of condensation up to definite dimensions of the molecule [46].



IX

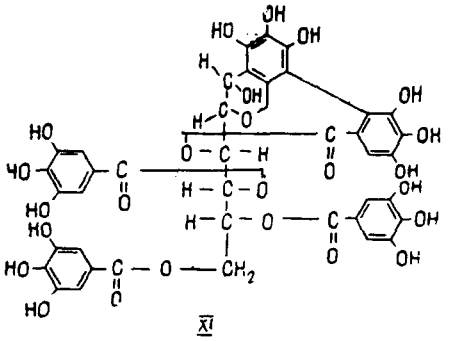


X

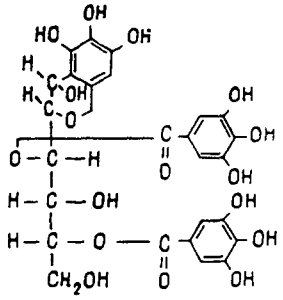
One and the same plant may contain different proanthocyanidins, i.e., proanthocyanidins constructed of different flavan components [46, 53-55].

Proanthocyanidins in the formation of which only leucoanthocyanidins participate are also known [56-59]. Very frequently plants contain not only dimeric but also trimeric, oligomeric, and polymeric proanthocyanidins [60-70]. An example of a trimeric proanthocyanidin is leucofisetinidin-(4 → 6)-leucofisetinidin-(4 → 6)-(+)-catechin (XXI) [71], and a tetrameric one is leucofisetinidin-(4 → 6)-leucofisetidinin-(4 → 6)-leucofisetinidin-(4 → 6)-leucofisetinidin-(+)-catechin (XXII) [72].

Some proanthocyanidins have very complex compositions. Their molecules are formed of various flavan units. Thus, for example, a polymeric proanthocyanidin with a very complex structure has been isolated from the carob (Ceratonia siliqua L.) [73]. (−)-Epicatechin gallate, (−)-epigallocatechin gallate, gallic acid, delphinidin, cyanidin, and pelargonidin have been detected in the products of its hydrolysis. A complex polymeric proanthocyanidin giving on acid hydrolysis delphinidin, cyanidin, pelargonidin, robinetinidin, and physetinidin has been isolated from unripe fruit of the sapodilla (Achras sapota L.) [74]. Complex polymeric proanthocyanidins have also been isolated from the roots of knotweed (Polygonum cariarium Grig.) in the products of the hydrolysis of which under various conditions (−)-epigallocatechin gallate, (−)-epigallocatechin, (±)-gallocatechin, (−)-epicatechin, delphinidin, and cyanidin were detected [46].



XI



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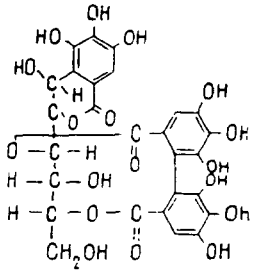

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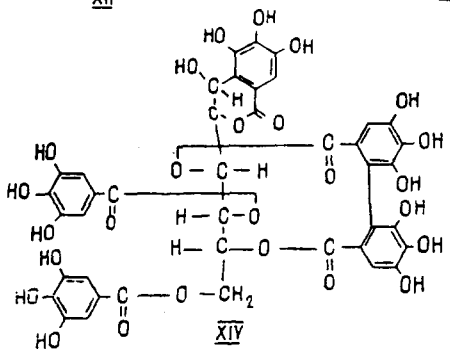


XIV

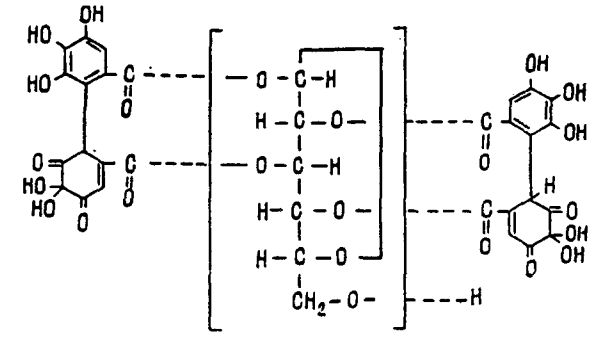
In some plants, the tannins are represented by both groups. Thus, the leaves of Quercus robur have yielded not only ellagic tannins but also oligomeric and polymeric proanthocyanidins [75]. Together with catechins and proanthocyanidins, green tea also contains hydrolyzable tannins [76].

COMPARATIVE STUDY OF THE COMPOSITION OF INDUSTRIAL TANNING EXTRACTS OF KNOTWEED, WILLOW, AND QUEBRACHO AND A SEARCH FOR METHODS OF IMPROVING DOMESTIC TANNINS

As is well known, tanning is not a purely physical process. The concluding stage of tanning from the chemical point of view is the formation of a stable cross-linked structure through the appearance between collagen molecules and the phenolic groups of tannins of, mainly, hydrogen bonds [77-86], and, possibly, covalent and electrovalent bonds [87-89].

The result of the binding of the tannins with the rawhide is the formation of leather, which, in comparison with rawhide, is more elastic, possesses a higher welding temperature (an index of the quality of the leather) and is more resistant to the action of water and microorganisms. However, it must be mentioned that such bonds can be formed only in those cases where the tannin molecules are large enough to link neighboring collagen chains and have a sufficient number of phenolic groups for the formation of cross-linkages at several points. At the present time it has been established that if the tannin molecule is too large (20,000 and above) it cannot penetrate or penetrates poorly into the hide during the tanning process and, consequently, does not bind with the collagen or does so only very weakly.

The phenolic substances in tanning extracts most responsible for the tanning process are those with molecular masses of from 500 to 3000 and, particularly 1000 [90, 91].



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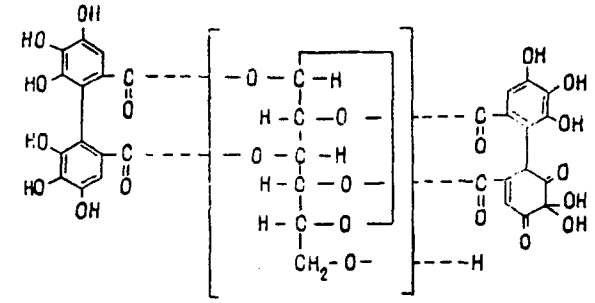

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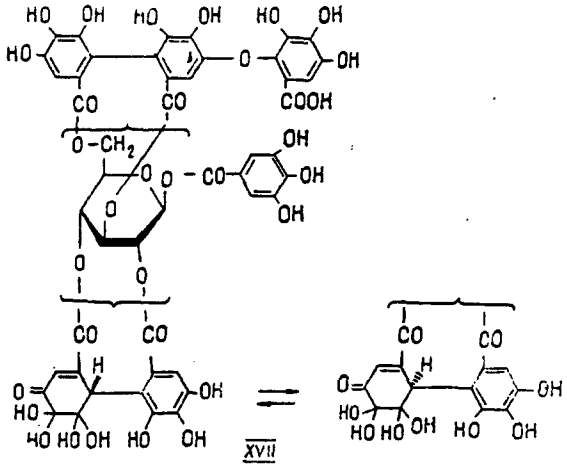
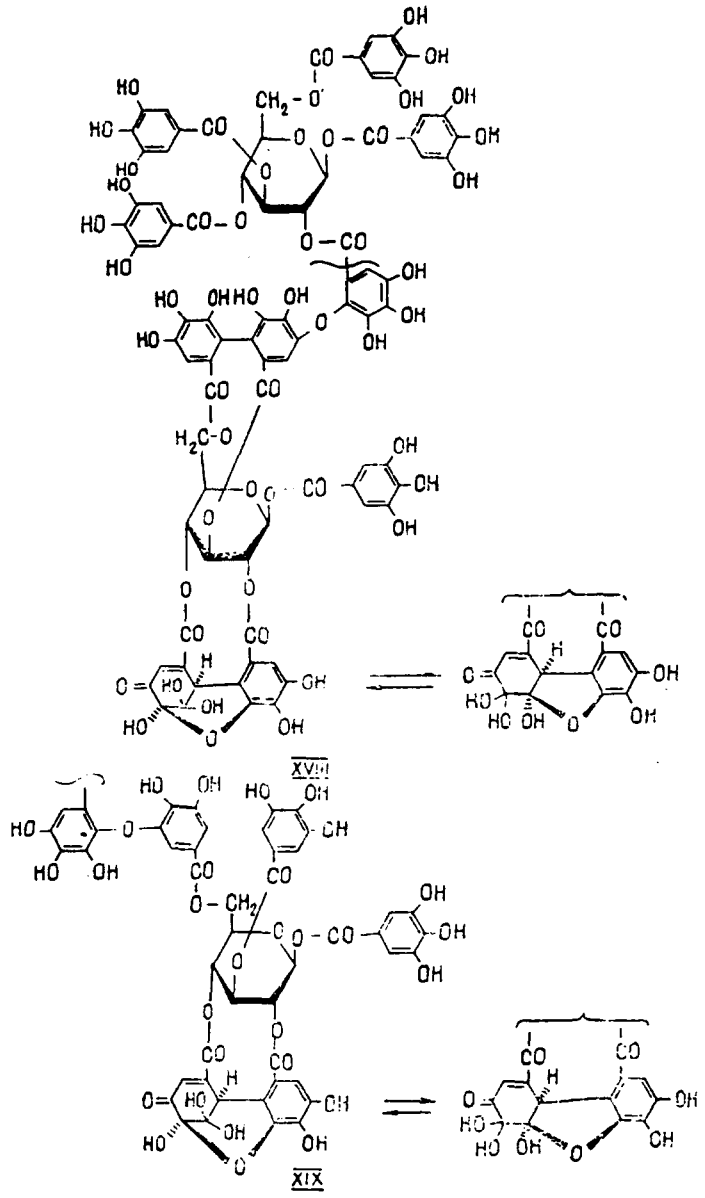


XVII

We have investigated the dependence of the tanning properties of some industrial tanning extracts (domestic – knotweed and willow – and an imported extract – quebracho) on the composition of their polyphenolic complexes. The aim of the work was to improve domestic extracts.

Quebracho extract – one of the best vegetable tannins in the world – contains about 75% of tannins. In samples of quebracho extract of the "Corona" brand and of knotweed and willow extracts that were investigated the amounts of tannins found were 72, 54, and 51%, respectively. Quantitative determination was performed by a colorimetric method that we have developed and have proposed as an express method of analyzing vegetable tanning materials containing tannins of the condensed series, and by the standard (VEM) method [92, 93].

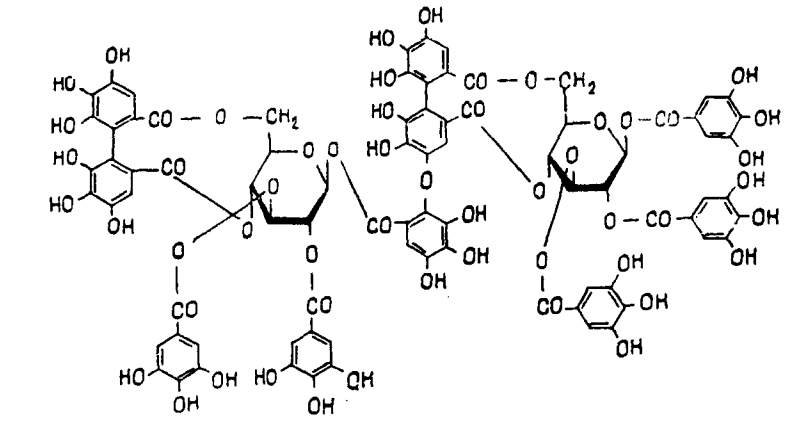
To determine the composition of the polyphenols of these tanning extracts, their aqueous solutions and ethyl acetate and other extracts were chromatographed on paper in the solvent system butan-1-ol-acetic acid-water (40:12:28). The visualizing agent was a 1% solution of vanillin in concentrated hydrochloric acid. It was established that the bulk of the polyphenols of the aqueous solutions of extracts of knotweed (Polygonum coriarium Grig.) and willow (Salix sp) consisted of tannins with a high degree of condensation appearing at the starting line, while the tannins of quebracho appeared in the form of a diffuse band extending from the starting line upwards to R_f 0.65, which is characteristic for oligomeric proanthocyanidins.



The polyphenols of the ethyl acetate fractions of the knotweed and willow extracts appeared in the form of diffuse bands beginning not far from the starting line and going up to R_f 0.30, while the polyphenols of the ethyl acetate extract of the quebracho extract gave a diffuse band from R_f 0.15 to 0.65. No highly condensed tannins were detected in the ethyl acetate fractions of the knotweed and willow extracts, unlike the aqueous fractions. Of monomeric catechins, (−)-epigallocatechin and (±)-gallocatechin were detected in the knotweed extract (ethereal fraction), (+)-catechin and (−)-epicatechin in the willow extract, and (+)-catechin and three unidentified catechins in the quebracho extract.

In order to study the tanning properties of these extracts, subfractions of tannins isolated from their ethyl acetate and butanolic fractions were obtained. Aqueous solutions of the subfractions isolated were treated with raw hide powder and the "tannide content" (content of tannins in the tanning material — crude, diffusion juice, concentrated extract, and powder expressed as percentages) and the "quality" (ratio of the content of tannins in the tanning agent to the total amount of water-soluble substances expressed as percentages) were determined by the standard method (VEM) [92]. The results are given in Table 1 with, for comparison, those on the total amount of tannins in the extracts and their yields into the butanolic and ethyl acetate fractions relative to the total amount.

The amounts of tannins — i.e., oligomeric proanthocyanidins (true tannins) — in the ethyl acetate fractions of the knotweed and willow extracts were 90.0 and 86.5%, respec-



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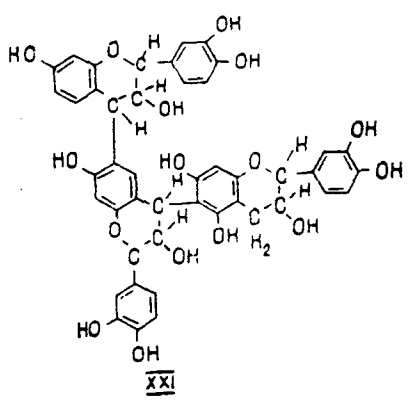

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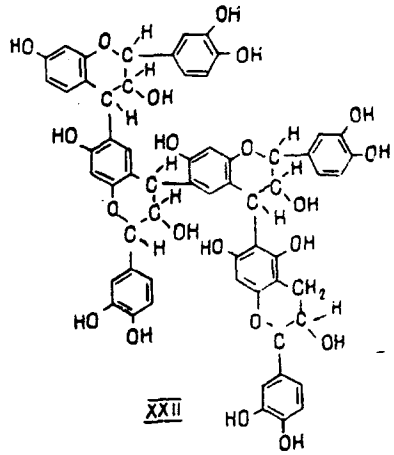

XXII

tively, and were close to the amounts of tannins in the ethyl acetate fraction of the quebracho extract (91.0%). However, the yields of tannins in the ethyl acetate fractions of the knotweed and willow extracts (20.4 and 24.5%, respectively) were considerably lower than in the analogous fraction of the quebracho extract (85.0%). Consequently, although the total amount of tannins in the knotweed and willow extracts were fairly high (53.5 and 51.0%, respectively), the true tannins made up only a small fraction of these amounts, while in the quebracho extract they were predominating. The amount of tannins in the butanolic fractions of the knotweed and willow extracts and their "quality" were considerably lower than those for the ethyl acetate fractions, although the total yields of polyphenols in the butanolic fractions were higher than in the ethyl acetate fractions. This fact can be explained by the assumption that not only oligomeric tannins but also highly condensed tannins, the tanning properties of which are considerably poorer than for the oligomeric ones, pass into the butanolic fractions.

Thus, it may be concluded that to obtain high-quality tannins from domestic raw material it is necessary to develop the technology of obtaining tanning extracts and, namely, to select those conditions for treating the raw material under which, simultaneously with extraction, no polycondensation of the oligomeric molecules of the tannins would take place but, conversely, the large molecules of tannins would be cleaved into smaller ones (1000-3000) possessing better tanning properties.

The results of our attempts to develop a technology for the production of a tanning extract from knotweed roots are being used in the Tarandubitel' Production Combine of the Uzbek SSSR Ministry of Light Industry.

"Tanning knotweed" (Polygonum coriarium Grig.) is one of the best tannide-bearing plants in the world, its roots containing about 35% of tannins. Monomeric polyhydroxyflavans present in the polyphenolic complex of knotweed roots are (−)-epicatechin gallate, (−)-epigallocatechin gallate, (−)-epicatechin, (±)-gallocatechin, (−)-epigallocatechin, and leucodelphinidin [47, 94-96]. Consequently, it may be assumed that the flavan derivatives mentioned are biogenetic precursors of the tannins of knotweed root. And, in actual fact, we established that the knotweed tannins are very complex in composition and are formed from

TABLE 1. Results of a Comparative Study of the Amounts of Tannins in Quebracho, Knotweed, and Willow Extracts and Their Fractions

Tanning extract	Material investigated	Moisture content	Tannins content	Quality	Yields of the fractions as percentages of the total tannins content in the extract
		%			
Quebracho	Factory extract	8.5	72.0	80.7	—
	Butanolic fraction	6.5	86.0	92.0	95.2
	Ethyl acetate fraction	6.5	91.0	97.3	85.0
Knotweed	Factory extract	8.0	53.5	60.0	—
	Butanolic fraction	5.5	67.0	71.2	42.6
	Ethyl acetate fraction	5.5	90.0	95.2	20.4
Willow	Factory extract	7.5	51.0	60.0	—
	Butanolic fraction	7.0	65.0	69.9	47.0
	Ethyl acetate fraction	7.5	86.5	92.2	24.5

TABLE 2. Quality Indices of the Diffusion Liquor, the Concentrated Extract, and the Tanning Powder Obtained with and without the Use of Sulfur Dioxide

Index	Extraction by water without sulfur dioxide			Extraction by water with sulfur dioxide		
	diff. liq., %	concentrated extract	powder, %	diff. liq., %	concentrated extract	powder, %
Dry powder	3.40	31.22	93.40	4.37	39.54	93.60
Total amount of water-soluble substances	3.12	29.27	89.35	4.14	37.48	90.25
Insoluble substances	0.28	1.95	4.05	0.23	1.86	3.35
Nontannides	1.28	12.05	37.17	1.36	12.37	30.63
Tannides	1.84	17.22	52.18	2.78	25.11	60.22
Quality	59.00	58.82	58.40	67.20	67.00	66.76

(−)-epigallocatechin gallate, (−)-epicatechin, (±)-gallocatechin, (−)-epigallocatechin, leucodelphinidin, and leucocyanidin [47, 96].

In spite of the high "tannide content" and "quality" of knotweed roots, the extracts prepared from them possess a comparatively low quality. With the aid of the chromatographic method, we therefore studied the change in the composition of the phenolic substances in the process of obtaining a tannin extract from knotweed roots.

For analysis we took samples from all the diffusers, the settling tank, the concentrated extract, and the final product — the tanning powder. The aqueous extracts themselves were chromatographed directly, and aqueous fractions from them were also chromatographed. As a result, it was established that the first diffuser retained the whole complex of catechins present in the roots; in the second diffuser the amount of (−)-epicatechin gallate and (−)-epicatechin was lower; in the third, (−)-epicatechin gallate and (−)-epicatechin were no longer present and the amount of (±)-gallocatechin had fallen; while in the fourth and fifth diffusers the composition of the catechins shown for the third was retained but with an appreciable decrease in the quantitative respect. Beginning from the sixth diffuser and up to the end of the process, including the final product, only a small amount of (−)-epigallocatechin and its gallic acid ester were retained. Together with the exhaustion of the monomeric catechins, the amount of highly condensed tannins appearing at the starting line increased. Their amount in the extract was considerably higher than in the roots. Their formation is apparently favored by the severe conditions of extraction and evaporation (high temperature and length of the process).

The capacity of sulfur dioxide for selectively cleaving the interflavan carbon-carbon bonds that are characteristic for tannins of the condensed series and forming fragments of lower molecular mass with retention of the basic flavan structure is well known [97]. This property of sulfur dioxide has been used in the extraction of knotweed roots [98]. Sulfur dioxide was passed through the diffusers during the first hour of extraction.

This principle was used to treat 60 kg of knotweed roots, giving 29 kg of a powdered tanning extract with a moisture content of 6.4%, a "tannide content" of 60.2%, and a "quality"

of 66.8%. For comparison, we obtained an extract from the same amount of knotweed roots by the known method. Its yield was 21 kg with a "tannide content" of 52.18% and a "quality" of 58.4%.

Table 2 gives comparative quality indices of the diffusion liquor, the concentrated extract, and the tanning powder obtained with the use of sulfur dioxide in the extraction process and without it.

As can be seen from Table 2, the use of sulfur dioxide ensures a considerable increase in the yield of tanning powder (by 40%) and of tannins (by 60%). The improvement in the "quality" of the tanning powder is connected not only with the increase in the yield of tannins but also with the antioxidant action of the sulfur dioxide, as a result of which no oxidative transformations of the tannins take place and, consequently, their losses are considerably decreased. The main effect is achieved, however, as mentioned above, by the cleavage of the large molecules of proanthocyanidins into smaller fragments possessing better tanning properties.

Thus, on generalizing literature information and the results of our own investigations it may be concluded that the true tannins of the condensed series are oligomeric proanthocyanidins. Effective methods of improving domestic tanning extracts have been shown.

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