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**ROLE OF PLANT LITTER
IN DEVELOPING THE CONTENT
OF PHENOLIC COMPOUNDS IN HUMIC SUBSTANCES**

**ROLA OPADU ROŚLINNEGO
W KSZTAŁTOWANIU ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH
W SUBSTANCJACH HUMUSOWYCH**

Abstract: The aim of the present paper was to determine the content of phenolic compounds in the extracts of fulvic acids and hydrolysates of humic acids depending on the properties of plant litter. The research involved sampling from organic and mineral horizons of forest soils located in the area of the Arboretum in Mlyniany in Slovakia. To identify and to determine the quantity of phenolic compounds the chromatographic method (HPLC) was used. The research demonstrated that the content of phenolic compounds in hydrolysates of fractions of humic acids was generally lower as compared with their content in the extracts of fulvic acids. The content of phenolic compounds both in the extracts of fulvic acids and in the hydrolysates of humic acids decreased with an increase in the degree of the organic matter transformation. It was also shown that the basic parameter which differentiated the properties of newly-formed humic acids under different tree species was the ratio of vanillyl, syringyl and cinnamyl compounds. The extracts of humic acids of O1 subhorizon on the oak stand demonstrated a similar share of vanillyl and syringyl compounds (40:42:18), while the extracts of humic acids of O1 subhorizon on the spruce and thuja stands showed a considerable advantage of vanillyl compounds.

Keywords: humic acids, fulvic acids, phenolic compounds, forest soils

An essential part of organic matter is made up of humus which is produced as a result of very complex processes of transformation of organic residue in soil. The main component of humus are humic substances, being the most common and, at the same time, one of the least known groups of organic compounds in nature.

In forest soils one of the basic factors determining the properties of not only the organic horizon but also deeper horizons is the species composition of the tree stand species composition [1, 2].

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The chemical composition of the plant litter, its decomposition rate and the humus resources have been known very well [1, 3–5], however, it is also essential to study the properties of humus substances which play an important role in soil operation.

The present study of the structure demonstrated that the molecules of humus acids include non-decomposed fragments of lignins [6–9]. Lignins, unlike proteins and carbohydrates, next to which they occur in plant cells, are more resistant to decomposition due to the effect of microorganisms and so they can accumulate temporarily in soil. The lignins accumulated can be included to humus acids or undergo chemical and biological transformations leading to the formation of humus substances [7, 9–12]. Therefore these compounds are considered as one of the main precursors of aromatic carbon in the molecules of humus substances [13].

The changes in the content of lignins and their degree of transformation in the plant material undergoing decomposition can be evaluated by the oxidation of plant materials or the soil samples with CuO or with acidic hydrolysis [7, 11, 13–16].

The methods facilitate the release of aldehydes and phenolic acids from lignins in a form of:

- vanillyl compounds (V – total content of vanillin and vanillic acid), derived from coniferyl alcohol,
- syringyl compounds (S – total content of syringaldehyde and syringic acid), derived from sinapyl alcohol,
- cinnamyl compounds (C – total content of ferulic acid, caffeic acid and coumaric acid), derived from coumaryl alcohol [7, 10].

The mutual proportions of coniferyl, sinapyl and coumaryl alcohol in lignins depend on the plant species [10, 17]. Lignins of angiospermous plants contain approximately the same amounts of vanillyl and syringyl compounds as well as little cinnamyl compounds (49:46:5), while the lignins of gymnospermous plants demonstrate a clear advantage of vanillyl compounds over the others (80:6:14).

Kögel [7] suggests that the indices of the degree of lignin decomposition can be changed in the content of vanillyl, cinnamyl and syringyl compounds and thus the total content of vanillyl, syringyl and cinnamyl compounds (V + S + C), released during the oxidation of plant materials, is applied as a measure of undisturbed uncondensed lignin structures [15, 16, 18]. In forest soils parameter V + S + C usually drops from subhorizon O1 to subhorizon Oh [18–20].

One of the state-of-the-art analysis methods for investigating humus substances is the high performance liquid chromatography (HPLC). The results provide much precious information on the processes of humification of organic matter as well as facilitate obtaining data on the degree of plant residue decomposition in soil and suggest the relationships between the chemical composition and the plant species. Therefore defining the proportions between phenolic compounds in humic acids facilitates determining the relationships between the properties of soil humus and its sources [14, 16, 19–26].

The aim of the present paper was to determine the content of phenolic compounds in the extracts of fulvic acids and hydrolysates of humic acids depending on the plant litter properties in the Arboretum at Mlynany (Slovakia).

Materials and methods

The research involved the use of forest soil sampled in the Arboretum at Mlynany (Slovakia). The Arboretum is found in the northern end of the Poddunajska Lowland, in the left-bank part of the Žytawa valley, between 48°21' of the northern latitude and 18°21' of the eastern longitude. The above-sea-level height ranges from 160 to 208 m. The area morphology and the existing formations are created considerably by the river valley. The soils which occur here have been considered to represent Stagnic Luvisols. The Arboretum covers an area of 67 ha, and the entire collection takes about 2500 of woody plant species [27, 28]. The vegetation period at Mlynany takes about 240 days.

Table 1

Description of soil samples

Sample	Depth [cm]	Horizon	Sample	Depth [cm]	Horizon	Sample	Depth [cm]	Horizon
Oak stand			Spruce stand			Thuja stand		
MD01	5–4	OI	MS01	6–4.5	OI	MT01	4–3	OI
MD02	4–0	Ofh	MS02	4.5–2	Of	MT02	3–1	Of
MD1	0–3	A	MS03	2–0	Oh	MT03	1–0	Oh
MD2	3–15	AE	MS1	0–5	A	MT1	0–5	A
MD3	15–50	E	MS2	5–20	Bt ₁	MT2	5–18	AE
			MS3	20–30	Bhs	MT3	18–45	E
			MS4	30–50	Bt ₂			
Soil type	Stagnic Luvisols		Stagni-Albic Luvisols			Stagnic Luvisols		

The forest soil was sampled according to the scheme given in Table 1 under the following tree stands:

– oak (*Quercus cerris* L.); the trees about 90 year-old, 65 % tree layer cover, 25 % shrubby layer cover and 15 % herbaceous layer cover,

– spruce (*Picea abies* L. Karsten), the trees about 90 year-old, 75 % tree layer cover, 50 % shrubby layer cover, 10 % herbaceous layer cover and 5 % of Bryophytes layer cover,

– thuja (*Thuja plicata* D. Don. ex. Lamb.) the trees about 90 year-old, 70 % tree layer cover, 20 % shrubby layer cover and 10 % herbaceous plant layer cover.

The extraction of phenolic compounds was made following the pattern given in Fig. 1. The chromatographic division of solutions containing phenolic compounds was performed with the use of flow chromatograph HPLC Series 200 by Perkin-Elmer equipped with DAD detector. The analytical column by Waters X-Terra C18 of the molecule size of 5 µm and the size of 250 × 4.6 mm I.D. The filling of the pre-column was identical with the filling of the analytical column.

The mobile phase consisted of: eluent A: H₂O : CH₃CN : CH₃COOH (84:14:2) and eluent B: CH₃CN. The injection was 20 mm³. The detection was made at

the wavelength $\lambda = 254$ nm. The gradient division program was applied at the rate flow of $1 \text{ cm}^3/\text{min}$. The initial composition of the mobile phase accounted for 100 % of eluent A, the concentration of eluent B was increasing linearly during the analysis. The gradient was completed after 49 min when the content of eluent B was 10 %.

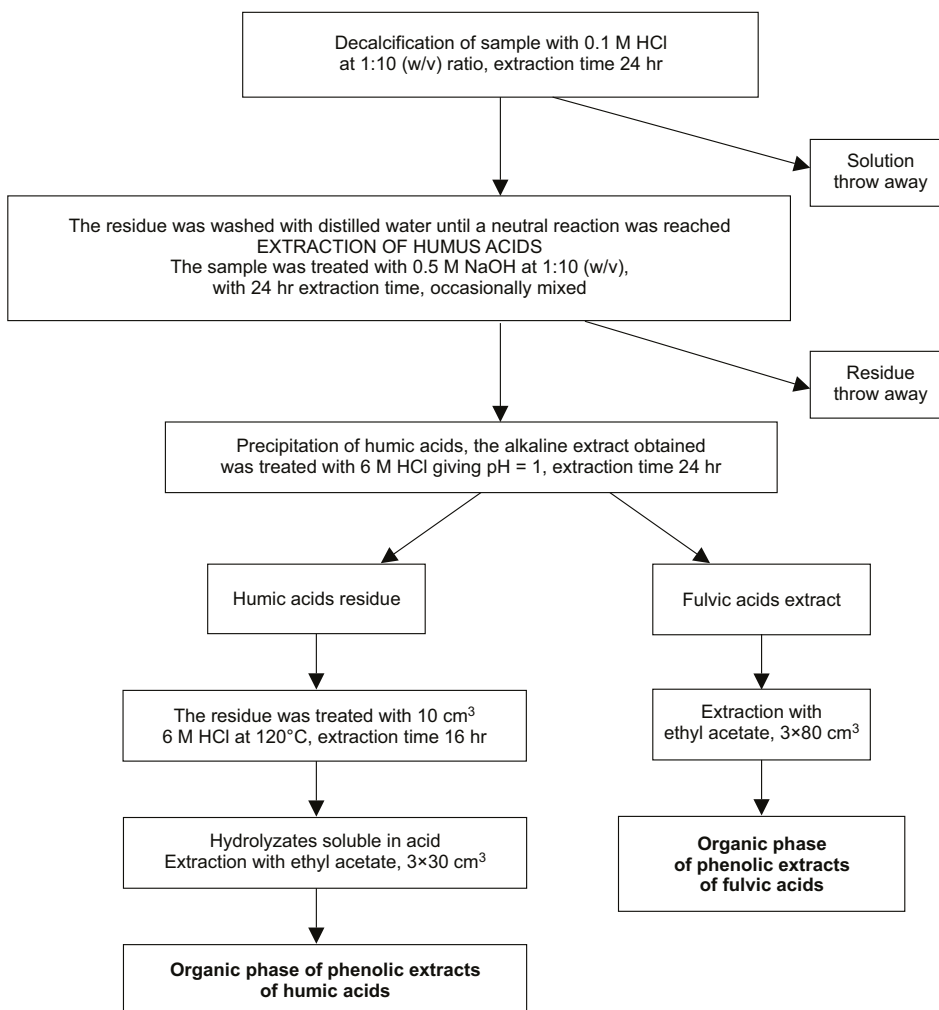


Fig. 1. Scheme of extraction procedure of phenolic compounds

The identification and the quantitative determination of phenolic compounds were performed based on the model solutions of phenolic compounds at the concentration of $0.6 \text{ g}/\text{dm}^3$. The list of the models applied is given in Table 2.

Table 2

List of models applied in qualitative and quantitative analysis of phenolic extracts

No.	Compound	Symbol
1.	Gallic acid (3,4,5-trihydroxybenzoic acid)	GA
2.	Protocatechuic acid (3,4-dihydroxybenzoic acid)	PA
3.	Vanillic acid (4-hydroxy-3-methoxybenzoic acid)	VA
4.	Syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid)	SYA
5.	<i>p</i> -Hydroxybenzoic acid (4-hydroxybenzoic acid)	p-HBA
6.	Caffeic acid (3,4-dihydroxy-trans-cinnamic acid)	CA
7.	Vanillin (4-hydroxy-3-methoxybenzaldehyde)	VAN
8.	Syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde)	SYAL
9.	2,4-Dihydroxybenzoic acid	DHBA
10.	Ferulic acid (4-hydroxy-3-methoxy-trans-cinnamic acid)	FERA
11.	Salicylic acid (2-hydroxybenzoic acid)	SA
12.	<i>p</i> -Coumaric acid (4-hydroxy-trans-cinnamic acid)	p-CA

The model curves plotted were used to calculate the phenolic compounds content ($\mu\text{g}/\text{cm}^3$) in the extracts of fulvic acids and hydrolysates of humic acids [14, 21, 24, 25]. The content of vanillyl (V), syringyl (S) and cinnamyl compounds (C) was calculated:

– V – total content of vanillin (VAN) and vanillic acid (VA), (VAN + VA),
 – S – total content of syringaldehyde (SYAL) and syringic acid (SYA), (SYAL + SYA),

– C – content of ferulic acid (FERA) and caffeic acid (CA), coumaric acid not determined and the following parameters were calculated:

V + S + C – sum of phenols of vanillyl, syringyl and cinnamyl type,

V : S : C – ratio of the share of respective compounds [7, 8, 29].

Results

The concentrations of the aldehydes and phenolic acids in hydrolysates of the fraction of humic acids and extracts of fulvic acids determined with the model curve method are given in Tables 3 and 5. Fig. 2 presents sample chromatograms of solutions containing phenolic compounds.

Table 3
Content of phenolic compounds in the extracts of fulvic acids. For symbols, see Table 2

Sample	Horizon (Depth) [cm]	GA	PA	VA	SYA	p-HBA	VAN	SYAL	DHBA	CA	FERA	SA
		µg/cm ³										
Oak stand												
MD01	O1	27.7	123	22.9	nd	37.4	8.02	16.9	nd	nd	24.5	8.70
MD02	Ofh	41.6	101	17.6	nd	14.0	5.41	7.01	nd	nd	7.31	6.46
MD1	A (0-3)	16.9	139	1.47	nd	1.23	0.477	0.597	nd	nd	0.529	nd
MD2	AE (3-15)	13.9	129	0.571	nd	0.863	0.219	0.153	nd	nd	0.100	nd
MD3	E (15-50)	9.56	nd	nd	nd	0.113	nd	nd	nd	nd	nd	nd
Spruce stand												
MS01	O1	22.3	14.7	0.682	0.600	39.7	10.3	6.20	24.0	nd	0.607	99.1
MS02	Of	14.0	8.29	0.119	0.413	40.7	8.36	3.93	11.5	nd	0.770	62.6
MS03	Oh	22.0	7.54	1.25	0.247	44.1	2.42	2.87	3.48	nd	nd	23.4
MS1	A (0-5)	4.40	5.23	2.17	0.161	45.8	0.242	0.339	5.36	nd	nd	17.6
MS2	Bt ₁ (5-20)	4.23	2.81	nd	nd	42.8	nd	nd	0.631	nd	nd	12.6
MS3	Bhs (20-30)	nd	7.03	1.38	nd	1.55	nd	nd	1.26	nd	nd	8.29
MS4	Bt ₂ (30-50)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Thuja stand												
MT01	O1	17.1	11.7	17.7	nd	nd	6.85	1.07	0.742	nd	4.14	15.1
MT02	Of	11.8	4.12	13.4	nd	nd	4.32	0.864	0.508	nd	3.82	12.2
MT03	Oh	2.49	1.15	4.75	nd	nd	1.68	0.497	0.366	nd	2.77	11.6
MT1	A (0-5)	0.891	0.411	2.79	nd	nd	1.16	0.304	nd	nd	0.059	10.8
MT2	AE (5-18)	0.472	0.171	1.07	nd	nd	0.438	nd	nd	nd	nd	3.84
MT3	E (18-45)	0.237	nd	0.419	nd	nd	0.229	nd	nd	nd	nd	1.23

nd – not detected

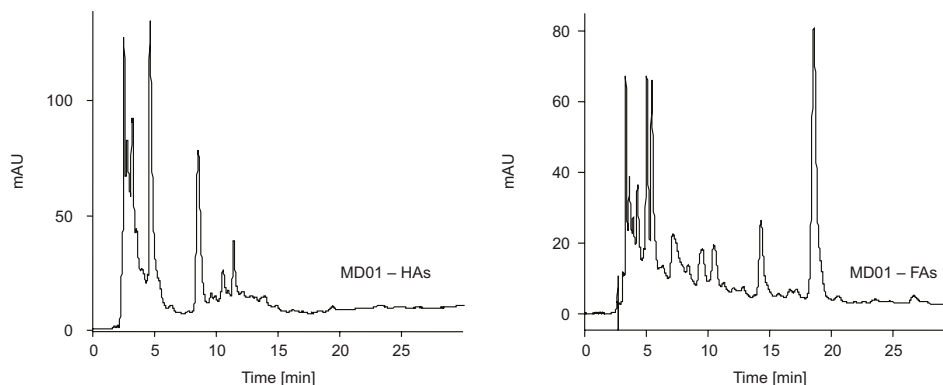


Fig. 2. Sample chromatograms of phenolic compounds which occurred in the extracts of fractions of humic acids (HAs) and fulvic acids (FAs)

Content of phenolic compounds in the fraction of fulvic acids

The extracts of fulvic acids isolated from the soil sampled from the organic horizon demonstrated a richer composition of phenolic compounds as compared with the extracts of fulvic acids of mineral horizons.

No caffeic acid (CA) was identified in any extracts of fulvic acids.

As for the quantitative characteristics, one shall consider that the concentration of phenolic compounds determined in respective fractions does not only result from the amount of these compounds which occur in the molecules of fulvic and humic acids but it is also connected with the content of FAs and HAs fractions in soils. With that in mind, one cannot directly refer the amount of the phenolic compounds obtained in FAs and HAs extracts to the amount of these compounds which occur in the molecules of fulvic and humic acids.

The extracts of fulvic acids, in general, demonstrated a decrease in the concentration of phenolic compounds deep in the soil profile (Table 3).

Similarly, it was observed that the highest content of GA, PA, SYAL and FERA was noted for FAs extracts on the oak stand. The other phenolic compounds identified, except for vanillic acid, occurred in greatest amounts in the FAs extracts in soil on the spruce stand.

Changes in the content of phenolic compounds in the extracts of fulvic acids of vanillic (V), syringic (S) and cinnamyl (C) type are given in Table 4.

The extracts of fulvic acids of the organic horizon of soils demonstrated higher contents of phenolic compounds V, S and C type and, as a result, V + S + C, as compared with FAs extracts of mineral horizons of soils. Besides, these contents decreased with the sampling depth. One shall stress that the extracts of fulvic acids from the soil sampled on the spruce stand contained the phenolic compounds C type (cinnamyl compounds) only in horizons O1 and Of.

Table 4

Content of vanillyl, syringyl and cinnamyl compounds and the values of parameter V + S + C in the extracts of fulvic acids

Sample	Horizon (Depth) [cm]	V	S	C	V + S + C
		$\mu\text{g}/\text{cm}^3$			
Oak stand					
MD01	O1	30.9	16.9	24.51	72.31
MD02	Ofh	23.0	7.01	7.31	37.35
MD1	A (0–3)	1.95	0.597	0.529	3.08
MD2	AE (3–15)	0.790	0.153	0.100	1.04
MD3	E (15–50)	nd	nd	nd	nd
Spruce stand					
MS01	O1	11.0	6.20	0.607	17.8
MS02	Of	8.48	4.34	0.770	13.6
MS03	Oh	3.67	3.12	nd	6.79
MS1	A (0–5)	2.17	0.339	nd	2.41
MS2	Bt ₁ (5–20)	0.242	0.161	nd	0.40
MS3	Bhs (20–30)	1.38	nd	nd	1.38
MS4	Bt ₂ (30–50)	nd	nd	nd	nd
Thuja stand					
MT01	O1	24.5	1.07	4.14	29.7
MT02	Of	17.7	0.864	3.82	22.4
MT03	Oh	6.43	0.497	2.77	9.68
MT1	A (0–5)	3.95	0.304	0.059	4.31
MT2	AE (5–18)	1.51	nd	nd	1.51
MT3	E (18–45)	0.647	nd	nd	0.647

Content of phenolic compounds in the hydrolysates of HAs fractions

The content of phenolic compounds in the hydrolysates of fractions of humic acids is given in Table 5.

Hydrolysates of humic acids fractions of organic horizon of soils showed higher contents of phenolic compounds as compared with the hydrolysates of HAs fraction of mineral horizons. It was observed that the spruce and thuja stands, in general, identified the highest contents of phenolic compounds for the humic acids fractions hydrolysates of subhorizon Of (Table 5).

Changes in the content of phenolic compounds of vanillic (V), syringic (S) and cinnamyl (C) type in the humic acids fractions hydrolysates are provided in Table 6. In mineral soil horizons, similarly as in the organic horizon, vanillyl compounds were dominant. The cinnamyl compounds in mineral horizons were observed only in the hydrolysates of HAs fraction of the layer adjacent to the organic horizon on the spruce stand.

Table 5
Content of phenolic compounds in the extracts of humic acids. For symbols, see Table 2

Sample	Horizon (Depth) [cm]	µg/cm ³										
		GA	PA	VA	SYA	p-HBA	VAN	SYAL	DHBA	CA	FERA	SA
Oak stand												
MD01	OI	43.5	33.6	20.2	21.5	38.6	13.1	27.4	nd	nd	4.79	nd
MD02	Ofh	9.36	13.8	23.1	1.35	2.92	3.77	3.40	nd	nd	0.699	nd
MD1	A (0-3)	1.70	0.281	3.21	nd	0.195	0.248	0.249	nd	nd	nd	nd
MD2	AE (3-15)	3.52	nd	0.674	nd	nd	nd	nd	nd	nd	nd	nd
MD3	E (15-50)	1.52	nd	0.283	nd	nd	nd	nd	nd	nd	nd	nd
Spruce stand												
MS01	OI	14.2	3.13	34.3	0.733	1.05	0.714	2.37	0.324	0.663a	1.49	4.10
MS02	Of	16.2	5.79	58.8	0.781	2.07	1.22	1.56	0.796	2.32c	1.73	7.23
MS03	Oh	10.9	5.23	54.8	0.789	1.52	1.11	1.11	1.63	0.667a	0.614	13.2
MS1	A (0-5)	5.61	2.10	0.871	0.341	2.67	0.833	2.72	nd	1.79b	nd	1.07
MS2	Bt ₁ (5-20)	4.30	1.76	0.336	0.098	1.22	0.380	0.412	nd	nd	nd	0.724
MS3	Bhs (20-30)	3.20	0.621	0.278	0.038	0.512	0.139	0.704	nd	nd	nd	nd
MS4	Bt ₂ (30-50)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Thuja stand												
MT01	OI	1.32	4.46	21.2	0.731	nd	0.778	0.147	nd	nd	nd	2.01
MT02	Of	2.09	6.31	27.0	1.03	nd	0.961	0.164	nd	nd	0.108	1.90
MT03	Oh	0.397	0.720	8.9	0.342	nd	0.511	0.092	nd	nd	nd	nd
MT1	A (0-5)	0.245	nd	1.02	0.103	nd	nd	0.057	nd	nd	nd	nd
MT2	AE (5-18)	nd	nd	0.384	nd	nd	nd	nd	nd	nd	nd	nd
MT3	E (18-45)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd – not detected

Table 6

Content of vanillyl, syringyl and cinnamyl compounds and the values of parameter V + S + C in hydrolysates of the fraction of humic acids

Sample	Horizon (Depth) [cm]	V	S	C	V + S + C
		μg/cm ³			
Oak stand					
MD01	OI	33.3	48.9	4.79	87.0
MD02	Ofh	26.9	4.75	0.699	32.3
MD1	A (0–3)	3.46	0.249	nd	3.71
MD2	AE (3–15)	0.67	nd	nd	0.674
MD3	E (15–50)	0.28	nd	nd	0.283
Spruce stand					
MS01	OI	35.0	3.10	2.15	39.6
MS02	Of	60.0	2.34	4.05	64.1
MS03	Oh	55.9	1.90	1.28	58.4
MS1	A (0–5)	1.70	2.82	1.79	6.31
MS2	Bt ₁ (5–20)	0.716	0.753	nd	1.47
MS3	Bhs (20–30)	0.417	0.742	nd	1.16
MS4	Bt ₂ (30–50)	nd	nd	nd	nd
Thuja stand					
MT01	OI	22.0	0.878	nd	22.8
MT02	Of	27.9	1.19	0.108	29.2
MT03	Oh	9.43	0.434	nd	9.87
MT1	A (0–5)	1.02	0.160	nd	1.18
MT2	AE (5–18)	0.380	nd	nd	0.384
MT3	E (18–45)	nd	nd	nd	nd

The values of V + S + C parameter recorded for HAs hydrolysates of organic horizons of soils were definitely higher than in the HAs extracts of mineral horizons (Table 6). The highest value of V + S + C parameter was noted for HAs fraction of subhorizon OI on the oak stand.

One shall stress that the content of phenolic compounds in the hydrolysates of humic acids fraction was generally lower, except or vanillic acid, as compared with their content in the extracts of fulvic acids. Vanillic acid, irrespective of the tree species and the sampling depth, occurred always in bigger amounts in the hydrolysates of humic acids.

Discussion

The source of much precious information on the humification processes of the organic matter inflow into soil can be phenolic compounds. As seen from the literature reports [14, 16, 19–26], both the qualitative and the quantitative composition of phenolic compounds depend on the type of the material researched and the decomposition degree of organic matter inflow to soil.

The present results demonstrate the differences in the qualitative and quantitative composition between hydrolysates of humic acids and extracts of fulvic acids. The hydrolysates of humic acids did not include dihydroxybenzoic acid (DHBA), and in the FAs extracts, in general, there was no syringic acid (SYA). Besides, it was shown that the content of phenolic compounds in the hydrolysates of humic acids was lower as compared with their content in the extracts of fulvic acids, except for vanillic acid.

Similarly, with the present results, it was noted that the content of aldehydes and phenolic acids identified in the extracts of fulvic acids and humic acids isolated from forest soils samples depended not only on the tree species but also the sampling depth (Tables 3 and 5). It is essential that in the extracts of humic and fulvic acids of mineral horizons the qualitative composition of phenolic compounds was changing, while the concentration of aldehydes and FAs present in the extracts were much lower than in the fractions of humus acids of the organic horizon.

The humification progress can be seen from the changes in the V + S + C parameter values determined as a measure of undisturbed uncondensed lignin structures. The present results (Tables 4 and 6) coincide with the literature reports [15, 16, 18–20] according to which the V + S + C parameter value decreases with soil profile depth, and thus it decreases with the increase in the degree of humification of the material researched. The values of V + S + C parameter obtained for the fraction of fulvic acids and the fraction of humic acids of subhorizon O1 were determined also by the plant litter properties. The highest content of V, S and C type compounds was found for the extracts of humus acids (HAs + FAs) of ectohumus on the oak stand.

The basic parameter differentiating the properties of newly-produced humus acids under different tree species is the ratio of vanillyl compounds (V), syringic (S) and cinnamyl (C) compounds. The proportions of these compounds obtained for a total of HAs + FAs, hydrolysates of humic acids and the extracts of fulvic acids are given in Table 7. The compounds discussed occur in lignins in specific proportions.

The reports by Higuchi et al [17] and Crawford [10] demonstrated that mutual proportions of coniferyl, sinapyl and coumaryl alcohols in lignins depend on the plant species.

The extracts of humus acids (HAs + FAs) of subhorizon O1 on the oak stand showed a similar share of vanillyl and syringyl compounds and a low share of cinnamyl compounds (Table 7), while the extracts on the spruce stand and thuja stand identified a considerable advantage of vanillyl compounds over the others. Therefore for the extracts being the sum: HAs + FAs, isolated from the soil sampled from subhorizon O1, there were reported similar values of the ratio of V, S and C compounds to the value of the ratio of these compounds in lignins [10, 17], which suggests a high share of lignins in the processes of humus acids formation in forest soils.

The proportions of the V, S and C type compounds in the extracts of humic acids isolated from the soil sampled from the organic horizon on all the stands showed, in general, a considerably greater share of vanillyl compounds over the others, except for the oak stand, subhorizon O1 (Table 7).

Table 7

Ratios of the share of vanillyl, syringyl and cinnamyl compounds
in humus, humic and fulvic acids

Sample	V : S : C		
	HAs + FAs	HAs	FAs
Oak stand			
MD01	40:42:18	38:56:6	43:23:34
MD02	72:17:11	83:15:2	61:19:20
MD1	80:12:8	93:7:0	63:20:17
MD2	85:9:6	100:0:0	76:15:9
MD3	100:0:0	100:0:0	nd
Spruce stand			
MS01	79:16:5	87:8:5	62:35:3
MS02	86:8:6	90:4:6	62:32:6
MS03	90:8:2	95:3:2	54:46:0
MS1	40:22:38	40:18:42	42:58:0
MS2	51:49:0	27:45:28	60:40:0
MS3	71:29:0	36:64:0	100:0:0
MS4	nd	nd	nd
Thuja stand			
MT01	88:4:8	96:4:0	82:4:14
MT02	88:4:8	95.6:4:0.4	79:4:17
MT03	81:5:14	96:4:0	66:5:29
MT1	90:8:2	86:14:0	92:7:1
MT2	100:0:0	100:0:0	100:0:0
MT3	100:0:0	nd	100:0:0

The extracts of fulvic acids isolated from soil sampled from subhorizon OI on oak stands were as follows: 43:23:34, while the extracts of fulvic acids of subhorizon OI on the spruce and thuja stands, just like the extracts of humus acids and humic acids, revealed a considerable advantage of vanillyl compounds over the others, 62:35:3 and 82:4:14, respectively. It was noted that the greater the depth, the greater the changes in the ratio of respective compounds present. Johansson et al [11] report on the spruce needle decomposition process involving an increase in the share of vanillyl compounds and a slight decrease in the share of cinnamyl compounds. Similar relationships for HAs and FAs were observed also by Banach-Szott [19] and Banach-Szott and Dębska [20] in earlier reports.

Conclusions

1. The qualitative and quantitative composition of phenolic compounds in humus acids were determined by the kind of plant litter and the soil sampling depth. The humus acids of organic horizon demonstrated a much higher content of phenolic compounds as compared with the humus acids of mineral horizons.

2. The highest contents of vanillyl, syringyl and cinnamyl compounds were found in humus acids of subhorizon OI on the oak stand. The lowest content of V, S and C compounds in organic horizons was recorded for humus acids on the thuja stand.

3. Humus acids of subhorizon OI on the oak stand showed a higher share of the total of syringyl and cinnamyl compounds to the share of vanillyl compounds, while humus acids on the coniferous tree stands (spruce, thuja) – a considerable advantage of vanillyl compounds. The values of the V : S : C ratio recorded suggest a high share of lignins in the processes of humus acids in forest soils.

4. The fraction of fulvic acids demonstrated, in general, a higher content of the aldehydes and phenolic acids identified as compared with the hydrolysates of humic acids fractions. Only the content of the vanillic acid was higher in the hydrolysates of humic acids as compared with its content in the extracts of fulvic acids.

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ROLA OPADU ROŚLINNEGO W KSZTAŁTOWANIU ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH W SUBSTANCJACH HUMUSOWYCH

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Abstrakt: Celem pracy było określenie zawartości związków fenolowych w ekstraktach kwasów fulwowych i hydrolizatach kwasów huminowych w zależności od właściwości opadu roślinnego. Do badań pobrano próbki z poziomów organicznych i mineralnych gleb leśnych zlokalizowanych na terenie Arboretum w Młynianach na Słowacji. Do identyfikacji oraz ilościowego oznaczenia związków fenolowych zastosowano metodę chromatograficzną (HPLC). Wykazano, że zawartość związków fenolowych w hydrolizatach frakcji kwasów huminowych była generalnie mniejsza w porównaniu z ich zawartością w ekstraktach kwasów fulwowych. Zawartość związków fenolowych zarówno w ekstraktach kwasów fulwowych, jak i hydrolizatach kwasów huminowych zmniejszała się wraz ze wzrostem stopnia transformacji materii organicznej. Wykazano również, że podstawowym parametrem odróżniającym właściwości nowo powstałych kwasów humusowych pod różnymi gatunkami drzew jest stosunek jednostek wanilinowych, syryngowych i cynamonowych. Ekstrakty kwasów humusowych podpoziomu surowinowego (OI) na stanowisku dębu cechowały się zbliżonym udziałem jednostek wanilinowych i syryngowych (40:42:18). Natomiast ekstrakty kwasów humusowych podpoziomu OI na stanowiskach świerka i tui charakteryzowały się znaczną przewagą jednostek wanilinowych.

Słowa kluczowe: kwasy huminowe, kwasy fulwowe, związki fenolowe, gleby leśne