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藁稈類의 腐熟過程中 加水分解物中의 有機酸 含量 變化

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Changes in the Contents of Some Organic Acids in The Hydrolysates of Decomposing Straws of Rice, Barley, Wheat and Rye

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SUMMARY

Six low-molecular-weight organic acids from decomposing plant residues were analyzed, which were formic, acetic, succinic, malic, tartaric, and citric acids. Straws of rice, barley, wheat, and rye were put under acid-hydrolysis after decomposition for different periods of time. The contents of organic acids in the hydrolysates were determined.

1. The relative molarity of a low-molecular-weight organic acid varies with the passage of the time of decomposition.
2. In general, formic and acetic acids were the major low-molecular-weight oganic acids in all samples.
3. Malic acid was found to be only in a trace amount in rice and barley straws, and in their decomposed residues.
4. The relative molarities of total monocarboxylic acids(formic and acetic) increased with the progressing time of decomposition, far exceeding those of dicarboxylic and tricarboxylic acids combined together.
5. Formic and acetic acids were compensatory for each other and they were supposed to persist for a long time in soil environment.

INTRODUCTION

It has been well recognized that organic acids are common constituents in soil[2, 3, 8, 12, 13, 14]. They include a variey of aliphatic and aromatic acids with a wide range of molecular weight. Low-molecular-weight organic acids, such as formite, acetic, oxalic and butyric, are identified to be present in most mineral soils[1, 3, 13, 14]. Long-chain aliphatic acids are supposed to persist for considerable periods because of their low solubility and adsorption on clay and humus particles[9, 21]. Water-soluble low-molecular-weight organic acids on the other hand are likely to exist for transitory duration and their relative level in the soil solution may be at the highest when plant residues are subjected to active decomposition[13].

Low-molecular-weight organic acids play a signi-

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ficant role in solubilization of minerals, especially of plant nutrients, through chelation reactions. Weathering of rocks is also enhanced in the presence of these organic acids. The contribution of them to the mobilization and transport of mineral plant nutrients has drawn great attention[4, 5, 6, 7, 11, 12, 15, 18, 19, 20]. Evidences have been accumulated to prove their influence on the growth of higher plants. Observed are both favorable and unfavorable effects. Chelating abilities of low-molecular-weight organic acids can result in the increased plant availability of even insoluble phosphate, potassium and many micronutrients[13, 14, 19]. Under certain paddy conditions, however, root development and growth of rice are inhibited by a rather high concentrations of some organic acids, in particular, butyric acid[13, 16, 17].

There is considerable variation expected in the relative amounts of low-molecular-weight organic acids detected from plant residues when they are put under microbial attack for a period of time. The fluctuation in the level of organic acid contents may serve as a measure which reflects some aspects of the dynamic status of soil environment.

MATERIALS AND METHODS

1. Plant materials

Four crop residues, straws of rice, barley, wheat, and rye, respectively, were collected after harvest, air-dried, powdered, watered, and then allowed to decompose in an incubator at 30 ± 1℃ for 45 and 90 days. Undecomposed plant materials were also prepared in the same manner to be used as a check.

2. Method of Analysis

Contents of organic acids were determined following the method used by Oades et al[10]. An HPLC(Wates Model 201) instrument was employed for the analysis of 6 organic acids : formic, acetic, succinic, malic, tartaric, and citric acids.

RESULTS AND DISCUSSION

Contents of low-molecular-weight organic acids under investigation appeared to decrease with the progression of decomposition in all plant samples, rice straw being the only exception(Table 1). It is most likely that an active microbial activity is still undergoing even at the end of 90 days of humification in the residue of rice straw. Rice straw has been well known resistant to microbial decomposition. In Korea it has been widely used as a raw material for roofing, grain sacks, various kinds of ropes, shoes, and others. The level of total organic acids examined had the range of 0. 18m mol per 1g at the beginning of decomposition and 0.28m mol per 1g of dry matter in the end of 90days of decay of rice straw. The level of formic acid was the highest at all stages of decomposition of rice straw, followed by succinic, acetic, citric, and tartaric acid. Only a trace amount of malic acid was detected from residues of rice and barley straws.

In general formic and acetic acids steadily appeared in all samples. It has been suggested that they are fairly stable in soils as reported by many workers[12, 14, 15, 18]. A drastic reduction of the levels of succinic, malic, tartaric and citric acids was observed in the majority of samples. It might have the meaning that under present as well as under field conditions they are unstable compounds, easily decomposed by microorganisms.

The combined level of formic and acetic acids greatly exceeded those of other organic acids. It was anticipated that microbial attack on organic acids would lead to further breakdown of them into lower-molecular-weight organics[2]. That this is in fact the case can be clearly demonstrated when molecular weights of organic acids are compared, and classified according to the number of carboxyl

Table 1. Contents of organic acids in the hydrolysates of decomposing plant residues of rice, barley, wheat, and rye straws

Plant material	Decay (d)	Organic acid(Mmol/g dry matter×10)						
		Formic	Acetic	Succinic	Malicc	Tartaric	Citric	Total
Rice straw	0	1029.7	237.4	417.4	tr	41.3	42.5	1768.3
	45	1385.2	490.7	743.1	tr	39.4	101.6	2759.9
	90	1846.8	305.0	548.9	tr	22.5	81.3	2804.5
Barley straw	0	1038.3	455.3	470.9	tr	31.8	59.1	2055.4
	45	1218.1	349.9	248.1	tr	21.2	51.5	1888.7
	90	756.2	315.2	99.5	tr	1.0	1.1	1172.9
Wheat straw	0	1845.8	487.1	543.9	110.5	38.3	40.2	3056.8
	45	313.2	792.6	83.3	37.5	0.5	26.9	1254.0
	90	255.1	690.3	66.8	32.4	0.2	26.3	1971.1
Rye straw	0	407.6	492.1	297.5	85.4	26.1	44.1	1352.8
	45	643.1	385.5	39.1	121.6	34.6	1.0	1224.9
	90	86.8	707.8	7.8	60.8	26.2	0.6	889.9

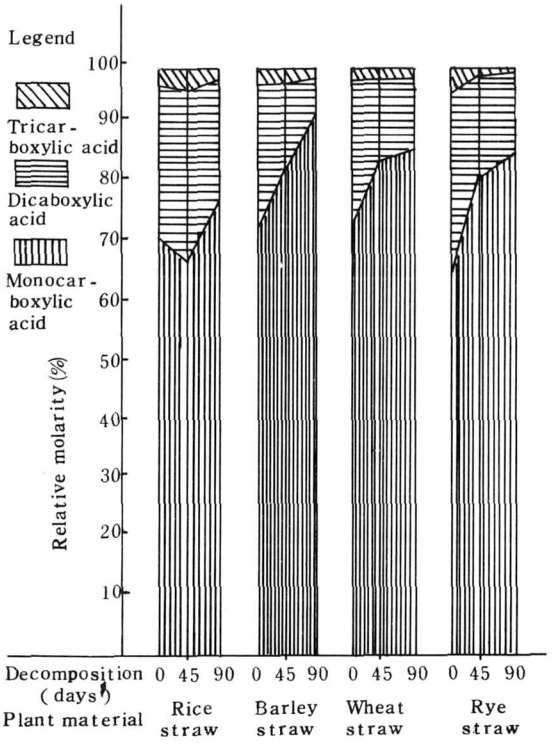

Fig. 1. Change of relative molarities of organic acids in the hydrolysates of decomposing rice, barley, wheat, and rye straws.

radicals. Formic and acetic acids are monocarboxylic, succinic, malic and tartaric acids are dicarboxylic, and citric acid is tricarboxylic. The relative level of monocarboxylic acids combined together increased with prolonged decomposition. On the contrary the relative molarities of dicarboxylic and tricarboxylic acids decreased during the same periods of decay(Fig. 1). It appeared that formic and acetic acids were compensatory as regards relative molarity. The increased relative molarity of the one with the passage of time took place at the expense of the other. Formic and acetic acids have been cited to be the common compounds in soils of different areas over the world[13]. The increases of these two organic acids shown in this experiment may explain in part their persistence and abundance found in soils. Accordingly their contribution to the physico-chemical properties of soil might be considerable[13].

摘　　要

低分子量을 가진 6個의 有機酸含量 變化를 測定하기 위하여 볏짚, 보릿짚, 밀짚과 호밀짚을 腐熟시키면서 經時的으로 試料를 採取하여 加水分解시킨후 分析한 結果는 다음과 같다.

1. 低分子量 有機酸含量은 腐熟期間이 經過함에 따라 變化했다.

2. Formic acid와 Acetic acid가 全試料中에서 가장 많은 量으로 檢出되었다.

3. Malic acid는 볏짚과 보리짚에서 極히 微量으로 檢出되었다.

4. Monocarboxylic acid의 molarity가 Dicarboxylic과 Tricarboxylic acid의 molarity를 合한 것보다 훨씬 많았다. 腐熟期間이 經過함에 따라 이런 경향이 더욱 뚜렷하였다.

5. Formic acid와 Acetic acid는 서로 보상관계가 있었으며 土壤에 잔유하는 기간도 상당히 오래일 것으로 추정된다.

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