# A Note on Ferulic Acid as a Constituent of the Water-Insoluble Pentosans of Wheat Flour

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Ferulic acid and other as yet unidentified compounds found previously in the water-soluble pentosans were detected in starch tailings. These compounds are liberated by alkaline saponification and therefore are probably bound by ester linkage to the insoluble pentosans.

About 75% of the pentosans, determined with the furfural method in a white wheat flour, are water insoluble. After washing out the starch, they are found predominantly in the starch tailings (1). The reasons for their water insolubility are

not completely understood; greater physical entanglement due to a higher degree of branching (2) has been suggested as a possible explanation. Ferulic acid has been found in the soluble flour pentosans (3) and it seemed of interest to also test the insoluble pentosans for the presence of this acid. Preliminary tests showed that solutions of starch tailings in alkali turn green-yellow and decolorize upon acidification. The same phenomenon was observed upon treatment of synthetic ferulic acid esters of polysaccharides (4). In further experiments with commercial starch tailings obtained from a wheat starch factory, the presence of bound ferulic acid could be confirmed by thin-layer and gas chromatography.

## MATERIALS AND METHODS

Wheat starch tailings were obtained from Blattmann & Co., Waedenswil (Switzerland) as a grayish powder. The sample had a protein content of 3%; monosaccharides found after hydrolysis were glucose (86%), xylose (8%), and arabinose (6%).

### Liberation of Ferulic Acid

Fifteen grams of starch tailings was ground in a mortar, moistened with ethanol, and dispersed in 200 ml. water. Eight hundred milliliters of 0.5N KOH solution was added to the slurry and the solution kept under nitrogen at 60°C. for 90 min. to liberate bound ferulic acid (3). The green-yellow solution was acidified to pH 3 with HCl whereby it turned almost colorless. The polysaccharides were precipitated with 1.5 liters of methanol and filtered off. The filtrate was concentrated to 200 ml. and extracted with ethylacetate. The extracts were evaporated to dryness and the residue taken up in methanol. The methanol solution was used for thin-layer and gas chromatography, as well as for polyphenol determination.

### Thin-Layer Chromatography

The following materials and reagents were used:

1. Merck silica gel Fertigplatten F-254
2. Benzene:dioxane:ethylacetate (90:25:4)
3. Benzene:ethylacetate (3:1) (5)
4. Diazotized benzidine (spray reagent) (5).

### Gas Chromatography

A Perkin-Elmer F-7, equipped with a stainless-steel column containing 1% SE-30 on Chromosorb G, AW-DMCS, 80 to 100, was used. The silylated sample was injected at 245°C. into the column and held at 200°C. at a flow rate of 32 ml./min. of $N_2$.

### Quantitative Determination of Phenols

Polyphenols were measured using the Folin-Ciocalteau reagent. The absorption was read at 720 nm.; ferulic acid was used as a standard.

## RESULTS AND DISCUSSION

The presence of ferulic acid in the extracts of the alkaline saponification products of the insoluble pentosans was established by thin-layer (TLC) and gas chromatography (GLC). TLC showed, besides the ferulic acid spot, an unidentified

slightly faster-moving one, which has also been found in soluble pentosans (6). A third, slower-moving spot had the same $R_f$ value as diferulic acid detected also in oxidized pentosan gels (4,6). GLC revealed only two peaks, one of which could be identified as ferulic acid using an authentic silylated sample of this acid as reference. The total content of phenolics was found to be 1.2 mg./g. starch tailings calculated as ferulic acid. Assuming that the phenols are bound to the pentosans only, this figure corresponds approximately to the degree of esterification of synthetic ferulic acid esters of guar gum capable of oxidative gelation (4).

The presence of ferulic acid and its oxidation product raises the question whether a part of the insoluble pentosans could have been formed by oxidation of soluble pentosans in the ripening wheat kernel. The presence of oxidases catalyzing this reaction is well established (7). This hypothesis is also supported by the fact that galactose is almost completely absent both in a pentosan gel and in the starch tailings (8,9). The oxidative gelation cross-links and insolubilizes mainly the arabinoxylan fraction, which contains no galactose. The cross-linking of part of the pentosans by diferulic acid formed upon oxidation (4) would also explain the insolubility of these pentosan fractions. The recent detection of ferulic acid in the cell walls of the aleurone tissue (10) shows that the presence of this acid is not restricted to the starch-containing endosperm cells.

## Literature Cited

1. KULP, K. Pentosans of wheat endosperm. Cereal Sci. Today 13: 414 (1968).
2. MONTGOMERY, R., and SMITH, F. A review of carbohydrates of wheat and other cereal grains. J. Agr. Food Chem. 4: 716 (1956).
3. FAUSCH, H., KUENDIG, W., and NEUKOM, H. Ferulic acid as a component of a glycoprotein from wheat flour. Nature 199: 287 (1963).
4. GEISSMANN, T., and NEUKOM, H. Vernetzung von Phenolcarbonsäure-estern von Polysacchariden durch oxydative phenolische Kupplung. Helv. Chim. Acta 54: 1108 (1971).
5. RANDERATH, K. Dünnschicht-Chromatographie. Verlag Chemie, Weinheim BRD (1965).
6. GEISSMANN, T. Untersuchungen ueber die oxidative Gelierung von Weizenmehlpentosanen und Phenolcarbonsaeureestern von Polysacchariden. Ph.D. thesis. Swiss Federal Inst. of Technol., Zurich, Switzerland (1970).
7. HONOLD, G. R., and STAHMANN, M. A. The oxidation-reduction enzymes of wheat. IV. Qualitative and quantitative investigations of the oxidases. Cereal Chem. 45: 99 (1968).
8. UPTON, E. M., and HESTER, E. E. Nonstarchy polysaccharides and proteins of soft wheat flour tailings. Cereal Chem. 43: 156 (1966).
9. COLE, E. W. Isolation and chromatographic fractionation of hemicelluloses from wheat flour. Cereal Chem. 44: 411 (1967).
10. FULCHER, R. G., O'BRIEN, T. P., and LEE, J. W. Studies on the aleurone layer. I. Conventional and fluorescence microscopy of the cell wall with emphasis on phenol-carbohydrate complexes in wheat. Aust. J. Biol. Sci. 25: 23 (1972).

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