

stant with time, despite the reduction in the flow rate that occurred.

Having demonstrated the feasibility of transport of strongly adsorbed pesticides on mobile colloids during leaching, it is important to indicate under what field conditions such transport might occur and contribute to edge-of-field loss. DDT or paraquat may reach the soil following foliar application and will be strongly adsorbed close to the soil surface. Other soil-applied herbicides such as the s-triazine group and other organochlorine pesticides have high K_D values and will not be transported much in solution. Hartley and Graham-Bryce (1980) point out the potential hazard in lateral runoff for such pesticides but consider vertical transport unimportant. However, if soils are leached with rainwater, or with sodic water and subsequently with low EC water, dispersion and release of clay can occur [e.g., Shainberg et al. (1981)]. Under such conditions, when release of soil colloids occurs, pesticides adsorbed in the surface soil may be transported to drainage water. Pesticides applied as wettable powders may also be transported in suspension form if leaching conditions occur soon after application.

The extent to which this type of transport occurs depends on the amount of clay or organic matter released by the surface soil on dispersion, the mobility of these colloids in the soil profile, the rate at which soil clogging occurs, the K_D value, and the kinetics of desorption of pesticide from the mobile colloids.

Registry No. Paraquat, 4685-14-7; Li-montmorillonite, 67034-72-4; DDT, 50-29-3.

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Further Investigations on "Polysugars" Derived from Poly(vinyl alcohol)

"Polysugars" derived from poly(vinyl alcohol) have recently been reported in the literature. The organoleptic properties of these polysugars ranged from sweet to extremely bitter. The syntheses of both sweet and bitter polysugars were repeated. The resultant polysugars were found by high-performance liquid chromatography analyses of reaction mixtures and by ¹H NMR and ¹³C NMR analyses of separated reaction products to be unreacted mixtures of poly(vinyl alcohol) and sucrose.

Recently two papers have appeared in the scientific literature (Usmani and Salyer, 1979, 1981) reporting the preparation of "polysugars" by heating sucrose with poly(vinyl alcohol) in the presence of 3A molecular sieves in dimethyl sulfoxide. Since the authors, without supporting data, went on to speculate that these polysugars "may prevent caries formation and function as noncaloric artificial sweeteners", these reports have received considerable attention in the lay press.

We were intrigued by several aspects of these reports. First, the authors claimed intermolecular etherification between sucrose and poly(vinyl alcohol), but the only data presented on the possible extent of etherification are titrimetric hydroxyl determinations. Aside from the removal of the molecular sieves and dimethyl sulfoxide the "slightly syrupy reaction products" were not further characterized. Second, the authors reported that the polysugars possessed organoleptic properties ranging from sweet to extremely bitter. Introduction of sweetness into a polymeric structure has been a long sought goal (DuBois and Crosby, 1977;

Brown et al., 1978; Wingard et al., 1978). So it is somewhat surprising that simple ethers of sucrose and poly(vinyl alcohol) were found to be sweet.

With these issues in mind the most favorable experiment for the generation of a sweet polysugar described by Usmani and Salyer [polysugar sample 204249, in Usmani and Salyer (1979)] was repeated several times as closely as the published experimental description allowed. A 1:1 weight ratio of sucrose and poly(vinyl alcohol), 37-42% residual poly(vinyl acetate), was heated in dimethyl sulfoxide with 3A molecular sieves at 100 °C for 7 h. The reaction mixture was worked up as reported by Usmani and Salyer and the crude reaction product was subjected to analysis. High-performance liquid chromatography (HPLC) of the reaction mixture showed only a mixture of poly(vinyl alcohol), sucrose, and dimethyl sulfoxide, Figure 1. Within the experimental error, the poly(vinyl alcohol) and sucrose were present in the same 1:1 weight ratio as the starting materials, Figure 2. Preparative gel permeation chromatography separated the poly(vinyl alcohol) and sucrose.

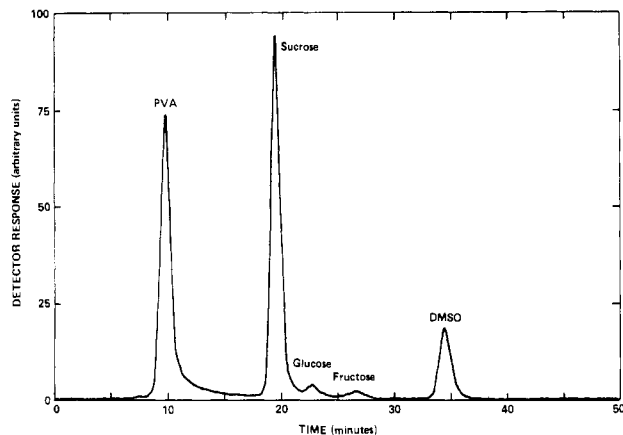


Figure 1. HPLC of polysugar prepared by the procedure described by Usmani and Salyer.

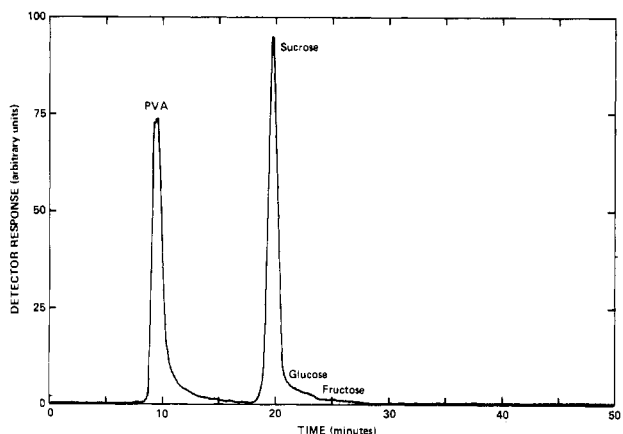


Figure 2. HPLC of a 1:1 mixture of poly(vinyl alcohol) and sucrose.

The ^1H NMR and ^{13}C NMR spectra of the isolated poly(vinyl alcohol) and starting poly(vinyl alcohol) were identical, indicating that there was no sucrose bound to the poly(vinyl alcohol).

Since we could not produce a sweet polysugar, an attempt was made to produce a bitter polysugar [polysugar sample 204257, Usmani and Salyer (1979)]. In our hands, we again produced a mixture of starting materials using Usmani and Salyer's reaction conditions of 24 h at 100 °C. The reported bitter taste of polysugar sample 204257 could have been from trans-acylation of the sucrose from the poly(vinyl acetate) giving various sucrose acetates, some

of which are reported to be intensely bitter (Kononenko and Kestenbaum, 1961).

These results suggest that Usmani and Salyer did not effect an etherification of poly(vinyl alcohol) with sucrose, unless critical experimental detail omitted from their reports prevented duplication of their results. Their sweet product could have been the same as ours and sweet because of the presence of the unreacted sucrose.

EXPERIMENTAL SECTION

The poly(vinyl alcohol), 75% hydrolyzed, M_n 3000, was purchased from Scientific Polymer Products, Inc. Crystalline sucrose was purchased from Revere Sugar Co. The Me_2SO and 3A molecular sieves were purchased from Fisher Scientific Co. and Alfa Product Division of Ventron, respectively. The chemicals were used as purchased without further purification. HPLC analysis was done by using an Aminex HPX-42 300 mm \times 7.8 mm carbohydrate analysis column operated at 85 °C with a refractive index detector. Integration of the detector responses was done by using a Bascom-Turner Model No. 4120 data center. ^1H NMR spectra were determined on a Bruker WM-250 spectrometer with $\text{Me}_2\text{SO}-d_6$ as the solvent and Me_4Si as an internal standard. ^{13}C NMR spectra were also determined on a Bruker WM-250 spectrometer with $\text{Me}_2\text{SO}-d_6$ as the solvent and internal reference.

Registry No. Sucrose, 57-50-1; poly(vinyl alcohol), 9002-89-5.

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Inhibitory Effect of Poly(2-methyl-5-vinylpyridine *N*-oxide) on Tobacco Mosaic Virus Multiplication in Tobacco Leaf Protoplasts

Tobacco mosaic virus (TMV) multiplication was markedly inhibited when tobacco mesophyll protoplasts infected with TMV in vitro were incubated in poly(2-methyl-5-vinylpyridine *N*-oxide) solution. No remarkable decrease in the infectivity of TMV occurred by mixing with the polymer.

In animal cells, it was suggested that an interaction occurred between monosilicic acid and poly(2-vinylpyridine *N*-oxide) and that certain of these oxides inhibited fibrogenesis normally associated with the presence of quartz in the lungs and the cytotoxic actions of silica in cultures of phagocytic cells (Holt et al., 1967; Holt, 1971). When administered to animals by injection, the polymer pre-

vented the pathological effects normally associated with inhaled silica dust. In the rice seedling grown with nutrient solution containing the polymer, the particular epidermal cells of leaves took on the ability of accumulating great amounts of silica (Parry, 1975).

We have examined whether or not poly(vinylpyridine *N*-oxide) and related polymers possess additional biological