Nujol mull spectrum indicated O–H stretching vibrations of intermolecular polymeric associations via hydrogen bonds.

The infrared spectrum of the OACP was, therefore, very similar to that obtained from the dichloromethane extract of a concentrated (0.5 *M*) malonaldehyde solution (Kwon and Van der Veen, 1968). Relative to their malondialdehyde spectrum prepared from a dilute solution, the spectrum of the concentrated reagent showed a decrease in carbonyl absorption and the appearance of O–H stretching vibrations.

In the presence of amines the proposed AOCP would be able to form enamine–imine type structures –N=CH—CH=CH—NH– and since enamine intermediates are operative in amine-catalyzed aldol condensations (Nielsen and Houlihan, 1968), further polymerization, shifts toward longer wavelength in light absorption, and higher fluorescent intensities might be expected. The slow loss of fluorescence of the OACP after removal of solvent from the TLC plates, i.e. direct contact with silicic acid or the gradual loss of fluorescence in dilute solutions of polar solvents such as water, ethanol, or dimethyl sulfoxide, at room temperature, are indications of the ease with which the equilibria of these condensation reactions can be altered.

These data also appear to be in agreement with the earlier work by Sawicki et al. (1963) who found that polar solvents inhibited the formation of fluorescence products between ethyl *p*-aminobenzoate and malonaldehyde while concentrated acid treatment and heating or the addition of amines enhanced it.

Herring muscle, containing at times up to 30% of lipids, generally showed a faint blue-white background fluorescence when fresh. However, with the onset of rancidity, storage for about 1 year at −12°, blotches of intensely yellow fluorescence were detectable particularly around the fins, the lateral line area, and in the regions of red muscle, metabolically active tissues which are high in lipids. At this stage it appeared as if the oxidized fluorescing lipids had permeated through the skin and butanol extracts of these muscle areas showed a distinct yellow fluorescence when examined under long-wavelength uv light. Marinaded products prepared from poorly stored herring also showed the bright yellow fluorescence. Applied to a Sephadex LH-20 column and eluted with absolute ethanol, the extracted fluorescing material from fish tissue appeared immediately after the void volume (Figure 1, cross hatched peak) and displayed two fluorescent Ex at 398 and 468 nm and respective Em at 470 and 550 nm, indicating the presence of two classes of fluorescing products with relatively large molecular weights up to 800. Due to some adsorption of the OACP to Sephadex LH-20, molecular weight estimates are uncertain; however, preliminary values for the OACP fractions I and II range from 190 to 310 mol wt units. Vapor pressure osmometer readings of the crude product in ethanol gave a mol wt of 200.

In conclusion, it would appear that the formation of nitrogen-free malonaldehyde polymers in biological tissue is possible under certain conditions; however, due to the omnipresence of amines, these polymers will probably exist predominantly in association with them.

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Cucurbit Root Starches: Isolation and Some Properties of Starches from *Cucurbita foetidissima* HBK and *Cucurbita digitata* Gray

Starches in potentially commercial amounts have been found in the roots of two species of feral xerophytic gourds, *Cucurbita foetidissima* and *Cucurbita digitata*. Commonly known as Buffalo gourd and Digitata gourd, these perennials are well adapted to marginal agricultural lands of semi-arid and arid environments. Starch can be readily isolated from the large storage roots. In each starch the granules resemble those of tapioca starch. Their average diameters are approximately 6 and 9 μ, respectively. Iodine affinity values of 4.07 and 4.42 suggest typical composition with respect to amylose and amylopectin content.

Curtis (1946) originally proposed that the wild perennial gourds of western and southwestern United States be investigated as possible seed oil and protein crops. Jacks et al. (1972) have reviewed subsequent work and concluded that certain xerophytic species do have such potential value. The feral xerophytic Buffalo gourd, *Cucurbita foetidissima*, has evolved in the semi-arid regions of western North America. A group of four closely related species

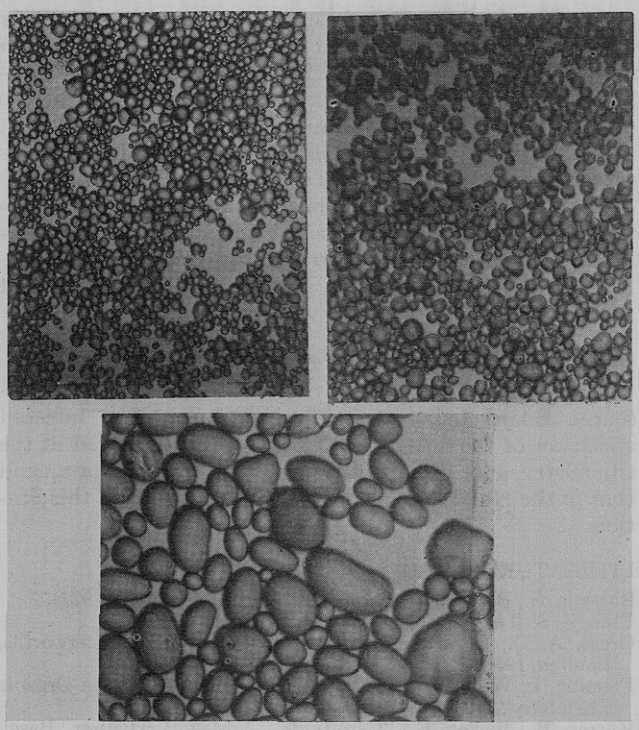

Figure 1. (Left) Starch from root of *C. foetidissima;* (right) starch from root of *C. digitata;* (bottom) starch from Idaho potato (156×).

known as the *C. digitata* group thrive in extremely hot arid deserts of southwestern United States and northwestern Mexico (Bemis and Whitaker, 1969).

The decorticated seeds of Buffalo and Digitata gourds contain approximately 50% oil and 35% protein (Jacks et al., 1972). These perennial plants develop large fleshy storage roots. *Cucurbita foetidissima* develops a particularly large and extensive system with root diameters of 8–12 in. and lengths of 4–6 ft being common (Dittmer and Talley, 1964).

A study has been undertaken to determine the nature of carbohydrate substances in cucurbit roots. The isolation of starches and some of their properties are reported here.

MATERIALS AND METHODS

Roots of plants in their second year of growth were peeled, sliced, and ground in 2 l. of 1% NaCl in a mechanical food blender in 300-g amounts for 2 min. The slurry was filtered through a 150 mesh screen. Residues of several operations were combined and reground in fresh salt solution. Filtrates were combined, filtered through fine muslin, and collected in a tall glass cylinder. Starch granules were allowed to settle for 2–3 hr. The supernatant was drawn off and discarded. The starch layer was dispersed in 1 l. of liquid as listed below and allowed to settle; the supernatant was drawn off and discarded. This procedure of dispersal, settling, and decantation was followed three times with 1% salt solution, three times with distilled water, and three times with methanol. After suction filtration the starch was dried in a vacuum oven at 40° and finally equilibrated with atmospheric moisture. Starch yields on a moisture equilibrated weight basis by this procedure were: *C. foetidissima,* 55%; *C. digitata,* 49%. Moisture contents of freshly collected roots were: *C. foetidissima,* 67–69%; *C. digitata,* 77–79%.

Table I. Analytical Values for Cucurbit Root Starches

Analysis, %	*C. foetidissima*	*C. digitata*
Moisture	6.18	8.78
Protein	0.85	0.45
Fat	0.57	0.50
Ash	0.12	0.17
Iodine affinity	4.07	4.42

Chemical and physical properties were determined by the procedures outlined in Whistler et al. (1964). Idaho potato starch was prepared by the method of Schoch (1957).

RESULTS AND DISCUSSION

Photomicrographs of the two cucurbit root starches and potato starch are presented in Figure 1. The granules of the cucurbit starches have a similar appearance. While predominantly round, there are some oval and some truncated granules present. They generally resemble tapioca starch granules although they are less truncated and have a smaller average diameter. Under a magnification of 700× a faint centric hilum is visible in larger granules. The granules of *C. foetidissima* root starch have a diameter ranging from 2 to 17 μ with an average of about 6 μ; those of *C. digitata* range from 3 to 17 μ with an average of about 9 μ.

The gelatinization temperature for each starch was determined by observation of staining with Congo Red. The value for *C. foetidissima* was 57.0–60.5° and the value for *C. digitata* was 65.5–68.0°. The root starch of *Trianosperma ficifolia,* a genus of the family Cucurbitaceae with a common granule diameter of 14 μ, is reported to have a gelatinization temperature of 58–60° (Reichert, 1913).

Certain analytical data are listed in Table I. The iodine affinity values indicate amylose–amylopectin ratios in the normal range. Both starches exhibit typical values for the other analyses listed.

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