The Carbohydrate Composition of Almond Hulls

Several carbohydrates, fructose, glucose, sucrose, sorbitol, and inositol present in almond hulls were identified and quantitated by gas-liquid chromatography. Methods employed to confirm the presence of these carbohydrates are discussed.

Almond hulls, a byproduct of the California almond industry, are removed from the almonds after harvesting. Although the hulls are used as supplemental livestock feed, little information exists in the literature concerning their composition. The most complete analysis is that of Cruess *et al.* (1947), who determined general categories of constituents. These workers found the total sugar content of the hulls to be rather high (25.61%), but did not determine individual carbohydrates. In connection with other work in our laboratory concerned with the sugar content of various materials, it was therefore of interest to us to reinvestigate the distribution and establish the identity of almond hull carbohydrates.

Our results are presented herein.

EXPERIMENTAL

Two samples of ground almond hulls from Northern California were extracted in a Waring Blendor with hot distilled water, filtered, cooled, and made up to a known volume. Aliquots from these extracts were taken for the various determinations. Another extract, prepared by overnight Soxhlet extraction of ground hulls with methanol, gave essentially similar results.

The sucrose content of the hulls was determined by an isotope dilution method (Sibley *et al.*, 1965) which is specific for sucrose. Other sugars were identified by comparison of their glc retention times with known sugars.

TMS ethers of the sugars were prepared by adding 2 ml of a 2 mequiv/ml solution of trimethylsilylimidazole (Pierce Chemical Co.) in dry dimethylformamide to a previously dried sample containing 10–40 mg of carbohydrate and 10 mg of inositol as internal standard. The container was stoppered and warmed at 50° C for 10–20 min with occasional shaking to effect derivatization. Three microliter aliquots were injected into the chromatograph. A sample of extract without added inositol was also run to correct for the inositol present in the sample.

Gas liquid chromatographic analysis of TMS ethers of the carbohydrates was accomplished on a Varian 1520B chromatograph equipped with dual $^1/_8$" × 6 ft stainless steel columns packed with 3% SE-52 on 80–100 mesh Chromosorb W and dual FID. Injector and detector ovens were operated at 300° C, and the column oven was programmed from 150° C at 2° C/min for the first 12 min and at 15° C/min thereafter to a maximum temperature of 280° C. Peak areas were measured with a Vidar Autolab Model 6210 digital integrator. Retention times of the various TMS ethers under these conditions were:

Sugar	Time, Min
Fructose	7.32
α-Glucose	9.32
Sorbitol	10.60
β-Glucose	12.00
Inositol	14.10
Sucrose	18.50

RESULTS AND DISCUSSION

Previous isotope dilution studies by us had shown sucrose to be a constituent of almond hulls. The sucrose content, however, accounted for only a small portion of the carbohydrate content reported by Cruess. Our current results, obtained by the use of a glc method, confirm quantitatively the presence of sucrose. In addition, fructose, glucose, and two hexitols, sorbitol and inositol, were also identified and quantitated. Our results, reported in percentages based on hulls, and those previously found by Cruess are summarized in Table I.

Fructose and glucose in our extracts were identified by comparison of their glc retention times to those of standards.

Confirmation of sorbitol and inositol was more involved. Dilute hydrochloric acid was added to an aliquot of an extract to convert sucrose to fructose and glucose, followed by treatment with sodium hydroxide to destroy reducing sugars. Glc analysis of an aliquot of the resulting solution indicated the presence only of peaks attributable to the two hexitols. The remainder of the solution was dried and acetylated with acetic anhydride in pyridine. The resulting inositol and sorbitol acetates were separated by fractional crystallization

Table I. Composition of Almond Hulls, %

Carbohydrates	This Study	Literature[a]
Fructose	8.8	[b]
Glucose	10.4	[b]
Sucrose	5.25 5.20[c]	[b]
Inositol	2.5	[b]
Sorbitol	4.6	[b]
Total Carbohydrate	31.5	25.61
Copper Reducing Matter	22.4	18.55
Moisture	9.66[d]	7.54
Water Soluble Solids	52.4[d]	50.00
Methanol Soluble Solids	47.3	50.00[e]
Ash	5.58[f]	4.6–6.3

[a] Cruess *et al.* (1947). [b] Not determined. [c] Isotope dilution. [d] Vacuum oven, 70° C, 24 hr. [e] Ethanol solubles. [f] 650° C, 1.5 hr.

from methanol. Mixed melting points of each substance with authentic material were undepressed.

The carbohydrate present in the hulls correspond to what one might expect to find in this sort of material, both quantitatively and qualitatively. Strain (1937) reported amounts of sorbitol in fruits of several species of *Rosacae*, which averaged approximately 2.6%. Inositol occurs widely in the plant world, as do fructose, glucose, and sucrose. The latter have been recently determined in several plants and fruits by methods similar to ours (Davison and Young, 1969). Interestingly, pentosans and pentose sugars were not observed by us, although Cruess' work originally indicated large amounts (16.6%) of these materials to be present.

Of the higher sugars, no trisaccharides were observed in any glc runs. Raffinose, for example, would have been detectable at the 0.05% level under our experimental conditions.

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Received for review May 18, 1970. Accepted June 30, 1970.
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