T1978TECH06

# EXTRACTION, CHARACTERISTICS AND MODIFICATION OF SUNFLOWER PECTINS

By

F.W. Sosulski
Crop Science Department
University of Saskatchewan, Saskatoon, S7N 0W0
and
S.J. Campbell
Research Station, Agriculture Canada
107 Science Cres., Saskatoon, S7N 0X2

## Abstract

Recent studies of the development, isolation and characteristics of sunflower head and stalk pectins are reviewed.

An aqueous acid precipitation procedure for isolation of pectin from sequestered extracts was developed with only minimal (10%) losses of sunflower head or stalk pectins. The low methoxyl pectin fraction obtained had a more uniform, but lower, methoxyl composition and higher gel power than pectin prepared by an alcoholic precipitation method. Sunflower pectins extracted from a 1:1 mixture of head and stalks contained 98.5% galacturonic acid of molecular weight 122,200 with pH 4.3, 22.5 mg $Ca^{2+}$/g pectin, 1% standardized pectin and 30% sucrose were optimal for gel firmness and strength. The sunflower pectin gels were particularly sensitive to pH and $Ca^{2+}$ concentration which decreased pectin solubility and increased pregelation, brittleness and granularity. Demethylation of the sunflower pectins by ammonia-ethanol treatments improved pectin solubility, eliminated pregelation and improved gel smoothness, elasticity, uniformity and stability in head samples. The ammonia-demethylation treatment was less effective in improving the gelation characteristics of stalk pectins.

The potential for commercial extraction of sunflower pectin as a byproduct of oilseed production has been investigated by several workers since Colin and Lemoyne (1940) first reported the presence of pectin-related substances in sunflower. Sunflower pectins are naturally occurring low-ester pectins because of their low contents of methoxyl groups in the water-soluble head pectins (34.3 - 66.8%), oxalate-soluble head pectins (30.0 - 44.1%) and stalk pectins (15.9 - 21.4%) (Lin et al, 1975). Lin et al (1975) reported that only one-quarter of the head pectins were water-soluble, the principal fraction being bound in the plant tissues and requiring a sequestrant such as ammonium oxalate or hexametaphosphate for extraction. The neck and stalk of the sunflower plant contained only bound pectins. The total pectin contents in four sunflower cultivars varied between 15-24% of the heads and 4-7% of the stalks. However, the water-soluble pectins are contaminated with pigments (Lin et al, 1976) and have low gel powers (Campbell et al, 1978).

The objective of this paper is to review the results of recent studies pertaining to the development of pectins in sunflowers, extraction procedures and the chemical and functional characteristics of native and ammonia-demethylated sunflower pectins.

## Pectin Synthesis

Sequential harvesting studies have demonstrated that most of the oxalate-soluble head pectin fraction is synthesized after physiological maturity (Campbell et al 1978). Between physiological maturity (about 120 days) and the final harvest (146 days), the oxalate-soluble pectin contents in dry, threshed heads of Outlook and Krasnodarets sunflowers increased from 6.2 to 22.8% (Table 1).

TABLE 1. Percentages of oxalate-soluble pectin in sunflower plants harvested at six dates.[a]

| Plant part and cultivar | Days from seeding to harvest | | | | | |
|---|---|---|---|---|---|---|
| | 55 | 77 | 90 | 116 | 131 | 146 |
| Early flowering Outlook and Krasnodarets | | | | | | |
| Stalk | 4.4 | 5.4 | 7.1 | 5.6 | 5.9 | 8.2 |
| Head | - | 3.5 | 5.4 | 6.2 | 13.1 | 22.8 |
| Late flowering Sundak and Sputnik | | | | | | |
| Stalk | 4.4 | 4.8 | 5.4 | 4.4 | 5.4 | 7.6 |
| Head | - | 3.2 | 5.4 | 4.8 | 7.6 | 17.2 |

[a] Campbell et al, 1978.

The increase in gel power occurred simultaneously with the reduction in methoxyl content in the pectin (Campbell et al, 1978). In addition to maturity influencing gel power, oven-drying of mature, threshed heads at temperatures of 70 and 85 degrees C resulted in higher gel power than drying at lower temperatures of 65 and 55 degrees C (Table 2).

TABLE 2. Effect of oven-drying temperatures and harvest date on gel power of sunflower pectin.[a]

| Drying temp. Degrees C | Days from seeding to harvest | | |
|---|---|---|---|
| | 116 | 131 | 146 |
| 55 | 54 | 72 | 70 |
| 65 | 55 | 74 | 78 |
| 75 | 54 | 88 | 119 |
| 85 | 56 | 95 | 118 |

[a] Campbell and Sosulski, unpublished.

## Pectin Extraction

After preliminary washing of the ground sunflower plants, the residues are extracted with sequestering agents such as dilute oxalate or polyphosphate solutions to solubilize the bound LM pectin (Sabir et al, 1976). Polyphosphate extractants, however, can result in higher ash levels in the isolated pectins than dilute oxalate extractants. The common procedure for precipitation of the pectin with 55% ethanol at pH 2.0 was found to require 30 liters of 95% ethanol per kg of head material when the final washing and dehydration was completed (Lin et al, 1978). This total volume could be reduced to 12 liters by use of 25% ethanol at pH 1.0 at the initial precipitation step. To further reduce the costs of the isolation procedure on aqueous acid precipitation procedure was devised for which only 2.2 liters of alcohol were required for the final washing and dehydration steps.

TABLE 3. Yield, composition and gelatin of sunflower and citrus pectin.[a]

| Pectin characteristics | Sunflower precipitation method | | | Citrus pectin |
|---|---|---|---|---|
| | 55% ETOH | 25% ETOH | Acid | |
| Pectin yield, % | 13.0 | 11.6 | 10.2 | - |
| Moisture, % | 6.3 | 5.2 | 6.6 | 3.5 |
| Ash, % | 0.6 | 0.5 | 3.0 | 3.9 |
| Galacturonic acid, % | 98.7 | 97.9 | 98.0 | 82.9 |
| Degree of methylation, % | 36.8 | 34.5 | 31.0 | 30.3 |
| Degree of amidation, % | 0.4 | 0.4 | 0.4 | 17.8 |
| Gel power, units | 105.0 | 108.5 | 122.5 | 129.0 |
| Jelly unit yield[b] | 13.9 | 12.6 | 12.5 | - |
| Hunter color values L for gels | 44.1 | 39.6 | 32.7 | 43.5 |
| a | 1.4 | 2.4 | 3.4 | -0.6 |
| b | 15.3 | 15.9 | 13.7 | 12.5 |

[a] Lin et al, 1978.

[b] Jelly unit yield = $\frac{\text{pectin yield x gel power}}{100}$

The yield of pectin from acid precipitation was only 77% of that recovered by the 55% ethanol procedure (Table 3). However, the gel power of the acid-precipitated fraction was 17.5 units higher, so that the jelly unit recovery was 90% of the ethanol method. The chemical characteristics of the sunflower pectins compared favorably with those of a commercial citrus LM pectin (Sunkist Growers Ltd.) except for the low degree of amidation. Citrus pectins which have been demethylated by ammonia treatment show high levels of amidation of the carboxyl groups. The "L" values obtained with the Hunter Color Difference Meter show that the alcohol-precipitated pectin had reduced brightness, being slightly more grey in appearance (Table 3). Differences among the gels in "a" and "b" values were small. Ash level of the acid-precipitated pectin was higher than those of the alcohol precipitated-pectins but could have been higher with further washing and hydraulic pressing of the filtered gel.

## Gel Characteristics

The acid-precipitated head pectins with a methoxyl content of 31% (Table 3) gave stable gels over a wide range of pH (2.5-4.5) when the sucrose level was maintained at 30%, and calcium concentration of 25 mg/g of pectin (Figure 1). (Sosulski et al, 1978). Optimum gel formation of the commercial LM citrus pectin (Genu LM-15AB) was more dependent on specific conditions of pH, soluble solids content and calcium ion concentration than was required for sunflower pectin. However, the gel power test measured only firmness or percent sag of

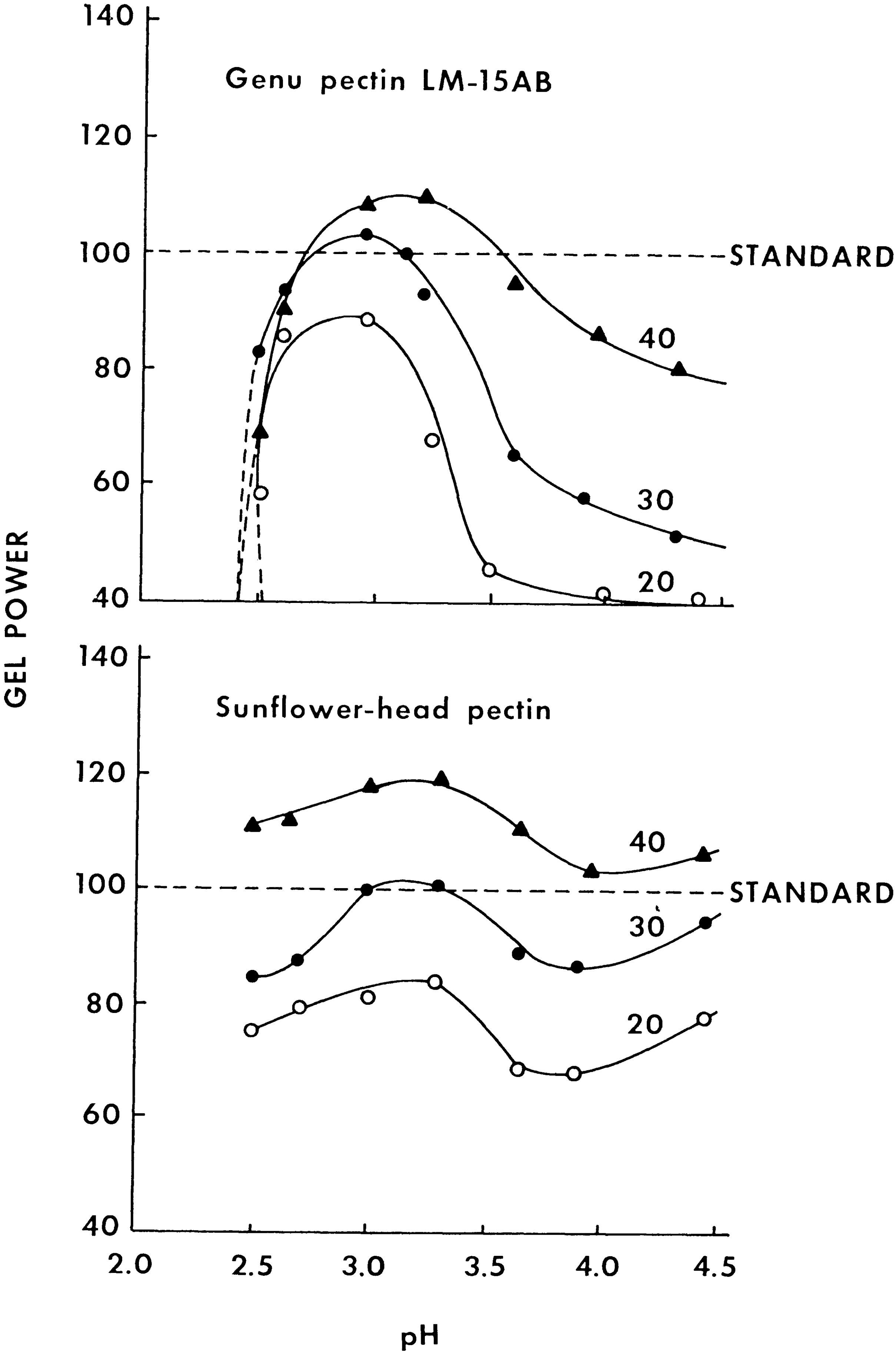


Fig. 1. Influence of pH on the gel power of sunflower-head pectin and a LM citrus pectin in gels mad with three levels of sucrose (%) and a calcium ion level of 25 mg/g of pectin (Sosulski et al., 1978).

Table 4. The changes of gel characteristics of sunflower pectin as pH, calcium, pectin and sugar concentration were increased

| Increase in | Solubility of pectin | Pregelation | Brittleness | Granularity | Clearness |
|---|---|---|---|---|---|
| pH | ↑↑* | ↓↓ | ↓ | ↓↓ | ↑ |
| Calcium level | — | ↑↑ | ↑↑ | ↑ | ↓ |
| Pectin concentration | — | ↑ | ↑ | ↑ | ↓ |
| Sugar concentration | — | ↑ | ↑↑ | ▲ | — |

* The number, direction and size of arrow indicate the degree of positive or negative change of gel characteristics.

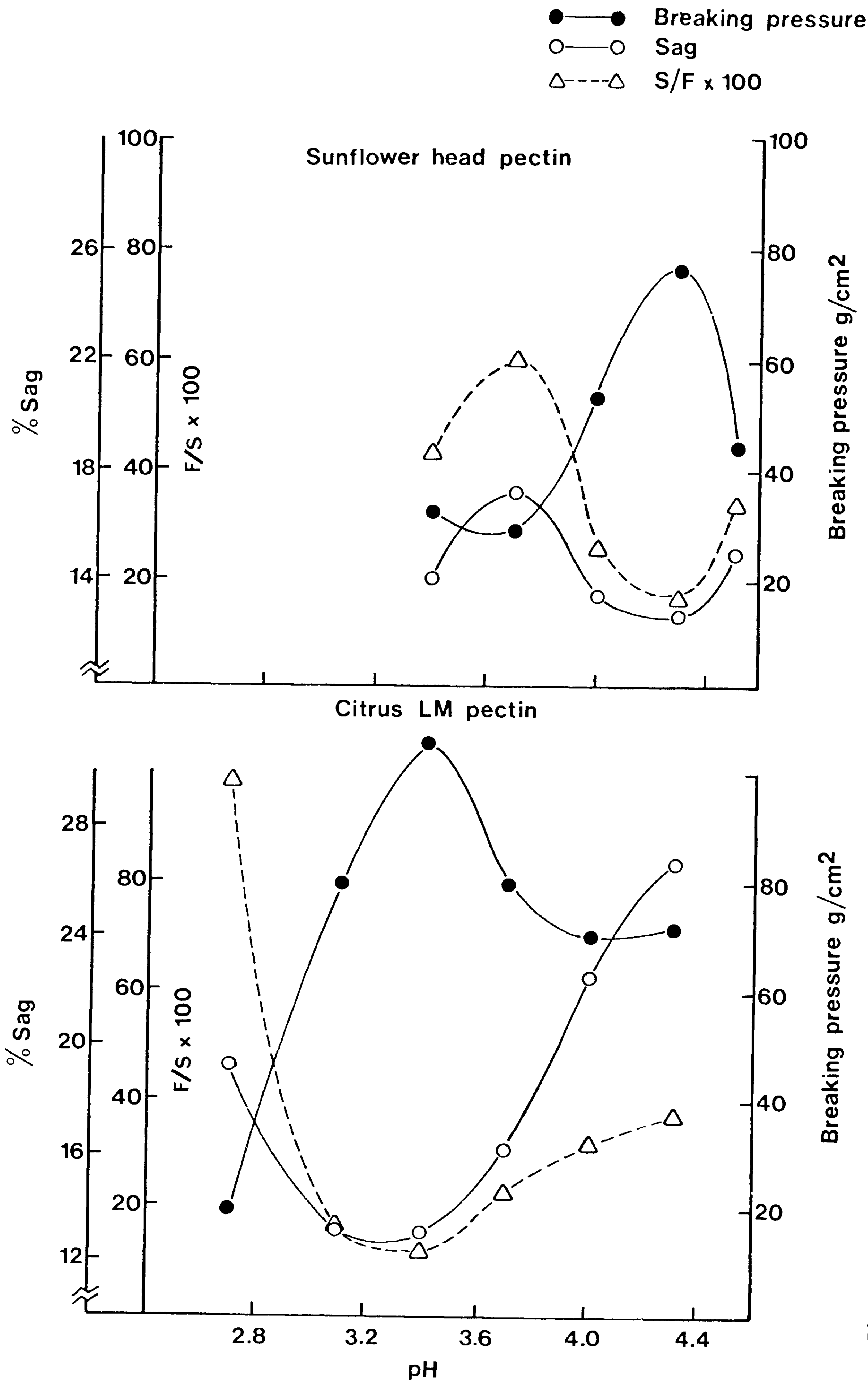


Fig. 2. The effects of pH on sag and breaking pressure of gels made from unmodified sunflower head pectin and on LM citrus pectin (from Kim et al., 1978b).

the gel. When the gels were cut into slices, characteristics of brittleness, poor elasticity and granularity were observed. The general relationships of pH, calcium level, pectin and sugar concentrations on pregelation and the preceding gel characteristics, determined on a blended, acid-precipitated pectin originating from both head and stalk material, are illustrated in Table 4 (Kim et al, 1978a).

Pectins are evaluated for gel firmness and gel power using a Sunkist Exchange Ridgelimeter and for their strength with a Marine Colloids Gel Tester. The ratio of firmness (% sag or F) to strength (breaking pressure or S) was calculated to determine the optimal formulations for low-ester sunflower pectin gels (Kim et al, 1978a). The effects of pH on the F/S ratio of oxalate-soluble pectins was an S-curve with a maximum value at pH 3.8 and a minimum at pH 4.3 (Figure 2). If an F/S ratio of 10 could be taken as satisfactory for gel quality, then conditions of pH 4.3 and, at least, 22.5 mg $Ca^{2+}$/g pectin, 1% pectin and 30% sugar would be required in sunflower gel formulations for satisfactory firmness and strength.

### Ammonia-demethylation

Brittleness and the lack of smoothness of the sunflower gels have been attributed to the uneven binding of calcium among pectin molecules which has been attributed to the non-random distribution of free carboxyl groups in the pectin molecule arising from enzymatic cemethylation. Ammonium hydroxide treatment of the pectin was investigated with the objective to randomize the distribution of methoxyl and free carboxyl groups on the pectin molecules and improve the elasticity and other functional characteristics of the gels (Kim et al, 1978b). Sunflower head and stalk pectins were separately demethylated by ammonia-ethanol treatments over a range of concentrations, duration of treatment, and temperature conditions. Demethylation of the head pectins improved gel smoothness, elasticity, uniformity and stability. The ammonia-demethylation treatment improved but did not overcome the adverse characteristics of the stalk pectin relative to the citrus control. The modified sunflower head pectins exhibited the lowest F/S ratio for maximum breaking strength and minimum sag at pH 4.3 which was similar to that for unaltered head pectin.

## Conclusion

Low-methoxyl pectins do not require sugar for gel formation; divalent ions such as $Ca^{2+}$ are effective in cross-linking the gel structure. Up to 30% of sugar does impart desirable textural properties to LM-$Ca^{2+}$ gels. Markets for LM pectin in low sugar jams, jellies, dietetic desserts, pudding mixes, apple sauce and tomato aspec appear to be expanding. In addition, the greater freezer-thaw stability of LM pectins improves the characteristic of frozen food products. At the present time, all commercial LM pectins are obtained from the catalytic demethylation of high methoxyl citrus pectins.

Native sunflower pectins exhibit a number of properties which are distinct to the LM citrus pectins. These properties arise apparently as a result of the enzyme demethylation of the pectin after physiological maturity. The most recent studies suggest that sunflower head pectins could be modified by an ammonia-demethylation procedure to be functionally superior to available commercial products. Further studies are continuing on specific applications of the amidated sunflower head pectin in high pH dessert gels.

## Literature Cited


CAMPBELL, S.J., F.W. SOSULSKI, and M.A. SIBIR, 1978. Development of pectins in sunflower stalks and heads. Can. J. Plant Sci., In Press.

COLIN, H., and S. LEMOYNE, 1940. Uronic material from the pith of *Helianthus*. Compt. rend. 211:44-47.

KIM, W.J., F. SOSULSKI, and S.J. CAMPBELL, 1978a. Formulation and characteristics of low-ester gels from sunflower pectin. J. Food Sci. 43. In press.

KIM, W.J., F. SOSULSKI, and S.C.K. LEE, 1978b. Chemical and gelation characteristics of ammonia-demethylated sunflower pectins. J. Food Sci. In review.

LIN, M.J.Y., E.S. HUMBERT, and F.W. SOSULSKI, 1976. Extraction of pectins from sunflower. Can. Inst. Food Sci. Technol. J. 9:70-74.

LIN, M.J.Y., F.W. SOSULSKI, and E.S. HUMBERT, 1978. Acid isolation of sunflower pectin. Can. Inst. Food Sci. Technol. J. 11. In press.

LIN, M.J.Y., F.W. SOSULSKI, E.S. HUMBERT, and R.K. DOWNEY, 1975. Distribution and composition of pectins in sunflower plants. Can. J. Plant Sci. 55:507-513.

SABIR, M.A., F.W. SOSULSKI, and S.J. CAMPBELL, 1976. Polymetaphosphate and oxalate extraction of sunflower pectin. J. Agr. Food Chem. 24:348-350.

SOSULSKI, F., M.J.Y. LIN, and E.S. HUMBERT, 1978. Gelatin characteristics of acid-precipitated pectin from sunflower heads. Can. Inst. Food Sci. Technol. J. 11. In press.