Analytical Critique of Hexitols Used as a Cooking Medium

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ABSTRACT

Analysis by differential scanning calorimetry and gas liquid chromatography of hexitol blends used as a roasting medium for peanuts demonstrated that there was no significant deterioration of the hexitol components due to prolonged repetitive heating. Small decreases in the hexitol content of the roasting medium, which were found after 72 hr at a temperature of 330 F, closely corresponded to the increases in the hexitan content. Furthermore no evidence could be found of any significant oxidative degradation products in any of the polyol samples analyzed.

INTRODUCTION

Edible vegetable oils have been the accepted medium for cooking food products for countless years. Immersion of the food in the oil facilitates uniform and rapid heat transfer. However the necessity of prolonged heating of oils at temperatures approaching 200 C prompted the concern of many researchers regarding the degradation products that could develop in such oils (1-3). Even though there is evidence that in commercial processing the level of degradation of the heat transfer agent is insignificant (4-6), commercial processes for the roasting of nut products in a blend of hexitols (mannitol and sorbitol), which are disclosed in two recently issued patents (7,8), could be expected to be challenged in a similar manner as the vegetable frying oils. The two processes (7,8) result in some pick-up of the heat-exchange medium by the food itself. In this respect, the operation simulates the use of frying oils in processing foods. However the hexitols would be expected to be far more resistant to degradation changes, particularly in the presence of oxygen, since they do not contain the oxygen-susceptible double bonds of the vegetable oils.

This study was undertaken to determine the extent of degradation of hexitols when utilized as a roasting medium. Biological investigations of the safety of this medium used in frying operations are summarized in a separate report by Alfin-Slater et al. (9).

EXPERIMENTAL PROCEDURES

A blend of 80% mannitol and 20% sorbitol was prepared from fresh (virgin) material supplied by Atlas Chemical Industries Inc. (now a division of ICI America Inc.). A portion of the blend was utilized as a roasting medium for peanuts. Roasting was done by submersion of raw peanuts in the hexitol blend in a deep fat fryer at a temperature of 330 F until the proper roast level was obtained. A sample of the medium was drawn from the fryer after 72 hr of repetitive use. A portion of this sample (used for 72 hr) was decolorized as a 40% solution in water by addition of an activated charcoal, Darco-S-51, at 2% by weight of the hexitols present. After filtering, the solution was dried and evaluated along with the other sample.

Differential Scanning Calorimetry

All samples were ground with mortar and pestle to a fine powder of ca. 100 mesh in order to insure a representative aliquot and proper contact with the instrument sample holder. A sample of ca. 8 mg was accurately weighed in an aluminum sample cup and an aluminum lid was crimped on to the cup. This was then placed into the sample holder of the instrument (Perkin Elmer Differential Scanning Calorimeter Model DSC-1), and compared to an aluminum cup with three lids in the reference holder.

The instrument sensitivity was set at 4 mcal/sec for full

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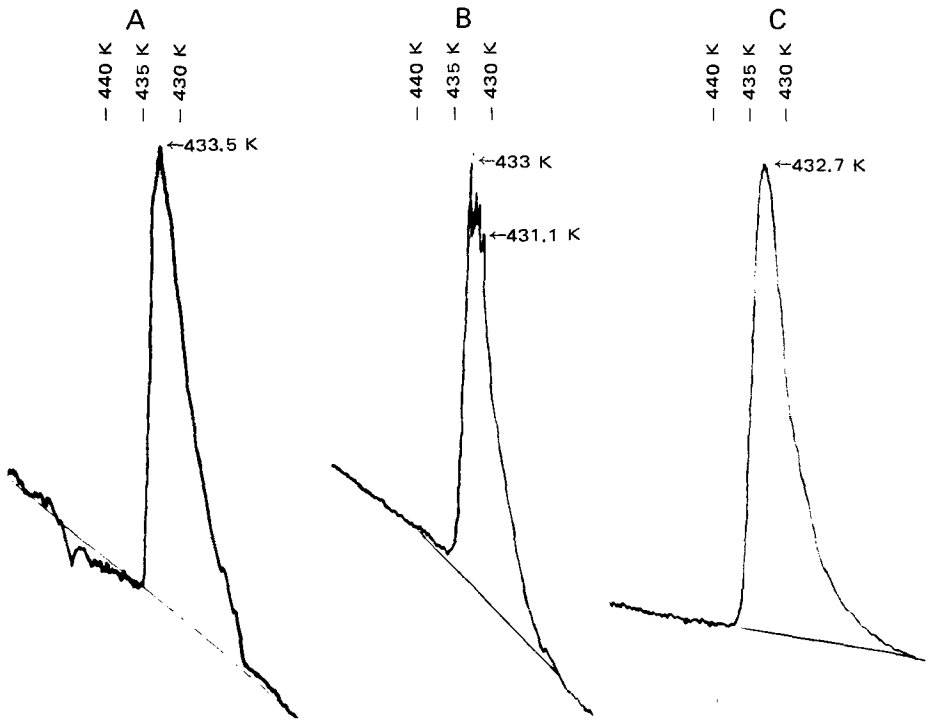

FIG. 1. A. Virgin mixture: 80% mannitol-20% sorbitol. B. Used for roasting, 330 F, 72 hr. C. Used (330 F, 72 hr) decolorized from 40% aqueous solution.

TABLE I

Gas Liquid Chromatographic Analysis of Mannitol-Sorbitol Mixtures[a]

Sample	Area, %		Concentration, %	
	Mannitol	Sorbitol	Mannitol	Sorbitol
Reference standard: 80% mannitol-20% sorbitol	95.5	4.5	80.0	20.0
Virgin mixture	95.1	4.9	79.7	20.3
Used for roasting (330 F, 72 hr)	95.6	4.4	80.1	19.9
Used for roasting (330 F, 72 hr); decolorized from 40% aqueous sol.	95.6	4.4	80.1	19.9

[a]Method described by Boggs and Anderson (10) without the internal standard.

scale response on the 5 mv recorder, and the scanning temperature was set at 2.5 C/min for all samples.

Gas Liquid Chromatography

Two separate methods were utilized for preparation of the samples for gas liquid chromatography (GLC). One procedure was based on the preparation of the diisopropylidene derivatives, as reported by Boggs and Anderson (10). The second and preferred procedure was a modification of the procedure of Sawardeker et al. (11) such as follows: 200 mg of a sample or 100 mg of xylitol and 100 mg of a sample were weighed into a 50 ml Erlenmeyer flask with a ground glass joint. Four milliliters anhydrous pyridine and 4.0 ml acetic anhydride were added to the flask along with five glass beads. The flask was fitted with a water-cooled condenser, and the solution was refluxed for 4 hr and then cooled to room temperature.

A 1 μl portion of the derivatives prepared by either procedure was injected into an F&M Model 700 gas chromatograph with a flame ionization detector. The column utilized was that proposed by Boggs and Anderson (10): a 10 ft x 1/8 in. stainless steel column packed with 5% STAP on 60/80 mesh, acid-washed, DMCS-treated, Chromosorb W, maintained isothermally at a temperature of 220 C. All the peaks were measured with a compensating polar planimeter. The areas obtained were compared with previously determined standard curves if the internal standard xylitol was not included. When xylitol was included, calculation was made by the following formulas: wt of the hexitol (mg) = (peak area of derivative x 100)/(peak area of internal standard x K), where K is the response factor of the appropriate hexitol. K = (area of hexitol acetate x wt of internal standard)/(wt of hexitol x area of internal standard).

In order to establish reference retention times for the hexitans, mannitan and sorbitan standards were synthesized by the procedures reported by Fletcher and Diehl (12) and Soltzberg et al. (13).

Determination of the residual mannitol-sorbitol solution on roasted nuts was carried out by slicing the nuts into quarters, washing with hot water and evaporating the water extract to dryness. The mannitol-sorbitol in the dry residue was then determined by the internal standard GLC procedure.

As a part of this study, GLC analyses were also performed by the Chemical Research Department of Atlas Chemical Industries Inc. on samples of crystalline sorbitol, mannitol and blends of the two, heated for 30 hr at 350-360 F.

RESULTS AND DISCUSSION

The use of the differential scanning calorimeter for the determination of purity is a well established technique (14-18), and the comparison of a thermogram of a blend of known composition to that of an unknown with respect to the range of melting, sharpness of melt and melting point can permit a close estimation of the purity of the unknown sample. This estimation of purity is in the order of ±1-2% when the component, as in this case, is present in a substantial amount (80%) (14,15,17).

As indicated in Figure 1A, which is a representation of the thermogram obtained of the melting of the virgin 80% mannitol-20% sorbitol blend, and 1B, the sample taken after 72 hr of use for the roasting of peanuts, neither the range of melting, the shape of the melting curves, nor the melting points are significantly different. The additional observed peaks superimposed on the melting curve coupled with the shift in the base line (change in specific heat) as noted in the latter thermogram indicate only the liberation of very small amounts of dissolved or trapped gases.

That this is the case is evident from Figure 1C, the thermogram of the decolorized and filtered sample, which indicates that the purity and composition of the blend remains relatively unchanged during the roasting process.

TABLE II

Gas Liquid Chromatographic Analysis of Mannitol-Sorbitol Mixtures

Sample	Normalized area, %		Average normalized area, %		Concentration, %	
	Mannitol	Sorbitol	Mannitol	Sorbitol	Mannitol	Sorbitol
Reference standard:[a]						
80% mannitol-	74.4	25.6				
20% sorbitol	74.1	25.9	74.3	25.7	80.5	19.5
Mannitol, as used in mixture	100	Trace	—	—	100	0
Sorbitol, as used in mixture	2.5	97.5	—	—	2.5	97.5
Test samples						
Virgin mixture	72.2	27.8				
	72.4	27.5	72.5	27.5	78.6	21.4
	72.8	27.2				
Used for roasting	73.1	26.9				
(330 F, 72 hr);	73.2	26.8	73.1	26.9	79.2	20.8
decolorized from 40% aqueous sol.						

[a]Prepared initially to contain an 80:20 ratio by weight of mannitol to sorbitol; mathematically corrected for component purity.

TABLE III

Gas Liquid Chromatographic Analysis of Trace Components in Mannitol-Sorbitol Mixtures

Sample	Relative retention time[a]	Normalized areas, %
Virgin mixture	0.42	0.05
	0.44	0.00
	0.47	0.00
	0.53	0.00
	0.69[b]	0.07
Used for roasting (330 F, 72 hr)	0.42	0.06
	0.44	0.03
	0.47	0.09
	0.53	0.34
	0.69[b]	0.06
Used for roasting (330 F, 72 hr); decolorized from 40% aqueous sol.	0.42	0.05
	0.44	0.00
	0.47	0.07
	0.53	0.25
	0.69[b]	0.08

[a]Retention times determined relative to mannitol for discernible peaks in high resolution studies.

[b]Only peak not corresponding to retention times obtained for mannitans and sorbitans.

The fact that this sample gives a comparable thermogram as that obtained for the virgin blend (within the precision of the method) indicates that only very small amounts of dissolved or entrapped gases and suspended peanut solids are responsible for the brown color and burnt sugar odor of the used sample before decolorization and filtration. Confirmation of these findings and conclusions were attained by the GLC evaluations.

Examination of the samples by the procedure of Boggs and Anderson (10), but without the internal standard they proposed, showed no other peaks on the chromatogram other than those attributed to the solvent or the isopropylidene derivatives of mannitol and sorbitol. Because the response of the instrument to these derivatives of the two different hexitols is not directly proportional to the amounts present in the test system, concentrations were determined (as shown in Table I) by normalizing the area per cents and relating them to those obtained for the reference standard.

TABLE IV

Gas Liquid Chromatographic Analysis of Mannitol-Sorbitol Mixtures[a]

Sample	Concentrations found, %		
	Mannitol	Sorbitol	Total hexitols
Virgin mixture	80.2	19.4	99.6
	79.3	20.1	99.4
	79.8 Ave.	19.8 Ave.	99.5 Ave.
Used for roasting (330 F, 72 hr)	77.7	19.8	97.5
	79.0	23.1	102.1
	78.4 Ave.	21.5 Ave.	99.8 Ave.
Used for roasting (330 F, 72 hr); decolorized from 40% aqueous sol.	79.2	20.3	99.5

[a]Xylitol used as internal standard.

Better separation and instrument responses for the different hexitols, more in line with concentrations present, were obtained with the acetate derivatives separated on the same column (Table II). Whereas the mannitol used in preparing the samples and reference standard showed the presence of only a very small amount of sorbitol (less than 0.5%), the sorbitol used was estimated to contain 2.5% mannitol. The concentrations of the hexitols in the test samples were obtained by normalization of the area per cents and relating them to those obtained for the reference standard, following correction of the latter for the mannitol in the sorbitol component.

In order to detect trace quantities of substances other than mannitol and sorbitol, the sample size was increased and the instrument attenuation decreased to obtain a 50-fold increase in sensitivity. The retention times of the trace components relative to the retention time of mannitol are indicated in Table III, along with their normalized area per cents. Comparison of these retention times to those

TABLE V

Analysis of Hexitols[a]

Sample	Crystalline sorbitol before heating	Crystalline sorbitol heated at 340-350 F for 30 hr	Mannitol-sorbitol blend[b] (used for 24 hr at 330 F for roasting peanuts)
GLC separated components			
Glycerine	0.02	0.02	0.00
Erythritol	0.04	0.05	0.00
Hexitans			
1.4 Sorbitan	0.14	1.5	0.05
0.27[c]	0.13	0.16	0.00
0.91[c]	Trace	0.22	0.12
0.92[c]	Trace	0.17	0.00
0.96[c]	0.26	0.22	0.13
Mannitol	1.3	1.3	67.4
Sorbitol	95.7	93.0	28.5
Iditol	0.24	0.29	0.03
Other components			
Water	0.70	0.38	1.30
Total sugar (as maltitol)	1.06	0.92	0.57
Reducing sugar (as glucose)[d]	0.08	0.01	0.07
Peroxides[d]	0.00	0.16	0.00
Acid no.[d]	0.00	0.01	0.00
Saponification no.[d]	0.00	0.00	0.82
Total recovery	99.59	98.23	98.10

[a]Supplied by the Chemical Research Dept., Atlas Chemical Industries Inc. 5% (5 ft x .25 in.) XE60 on ABC Chromosorb W, 80/100 mesh column at 200 C, detector temperature of 250 C and injection port at 325 C in an F&M 810 with FI detector (private communication, Atlas Chemical Industries Inc.).

[b]In this case, a blend of 70% mannitol-30% sorbitol.

[c]Retention time relative to mannitol.

[d]Components not included in recovery value.

obtained for a preparation of mannitans and sorbitans confirmed the suspicion that the trace components developed on heating were only the anhydrides of mannitol and sorbitol.

In order to obtain a direct measurement of both the major and minor constituents of the heated mannitol-sorbitol blend and to preclude the possibility of other substances being present in the sample but not represented on the chromatogram (due to obscurance by the solvent peak or nonelution from the column), xylitol was incorporated as an internal standard into the acetate analytical procedure; the results are summarized in Table IV.

The weight per cents of the hexitols were obtained after adjustment by means of a response factor relating sorbitol and mannitol to the internal standard.

Because the area response can vary in repeated analysis of the same sample due to handling and instrumental conditions, a constant weighed amount of internal standard (xylitol) was added to the samples prior to the acetylation step of the procedure. A correction factor (K value) was obtained from the analysis of the reference standard containing known amounts of xylitol and approximately the same relative concentrations of mannitol and sorbitol as contained in the samples under study.

The true concentration of sorbitol and mannitol contained in the reference standard was calculated after individual analysis of the component hexitols established their respective purities.

The mannitol used again contained a very small amount of sorbitol, but the sorbitol by this procedure contains 2.1% mannitol. The concentration of the reference standard was adjusted accordingly to 80.4% mannitol and 19.6% sorbitol.

Independent K values were determined for both mannitol and sorbitol relative to the internal standard, and these correction factors were then applied to subsequent sample runs on the same day for calculation of the weight per cent of the hexitols. The concentration of all determinations made was in good agreement with the theoretical concentration of 80% mannitol-20% sorbitol and showed over 99.5% recovery by weight of the hexitols from each of the three samples confirming the presence of only ca. 0.5% extraneous materials.

On the basis of the various independent assay procedures utilized, it is evident that the hexitols (mannitol and sorbitol) are not affected during use as a roasting medium for peanuts, with the exception of a very slight anhydride formation.

Additional support of this conclusion was supplied by Atlas Chemical Industries Inc., the supplier of the mannitol and sorbitol, by similar GLC evaluation of heat-treated samples of blends and the component hexitols. A summary of these data is shown in Table V, which indicates that the development traces of hexitans are the only measurable degradation products of the hexitols under the conditions of use. The saponifiable substances noted in very small amounts in a blend sample (supplied after 32 hr of use for roasting peanuts) are derived from the food components in the frying medium.

While the conditions of use reported here are equivalent or milder than those used for preparation of sorbitan esters such as sorbitan monostearate, an FDA approved food additive, and of sugarless hard candies made with the hexitols (Atlas Chemical Industries Inc., private communication), they are severe in comparison to those conditions in current use (8). Under the improved conditions of roasting (8) less of the hexitols are applied to the product (an average of 3% rather than the 6% formerly attained), and the repetitive use of the heated mannitol-sorbitol blend has been eliminated. The latter reduces significantly the exposure to heat of the hexitols as currently used in the commercial roasting of peanuts and tree nuts, such as cashews, filberts, almonds and pecans.

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REFERENCES

1. Artman, N.R., and J.C. Alexander, JAOCS 45:643 (1968).
2. Fioriti, J.A., and R.J. Sims, "Oxidation Products from Heated Vegetable Oils," AOCS Meeting, Chicago, September 1970.
3. Reddy, B.R., K. Yasuda, R.G. Krishnamurthy and S.S. Chang, JAOCS 45:629 (1968).
4. Nolan, G.A., J.C. Alexander and N.R. Artman, J. Nutr. 93:337 (1967).
5. Rathmann, D.M., J.R. Stockton and D. Melnick, CRC Crit. Rev. Food Tech. 1:331 (1970).
6. Poling, C.E., E. Eagle, E.E. Rice, A.M.A. Durand and M. Fisher, Lipids 5:128 (1970).
7. Wells, P.R., and D. Melnick, U.S. Patent 3,477,858 (1969).
8. Cooper, I., W.A. Parker and D. Melnick, U.S. Patent 3,671,266 (1972).
9. Alfin-Slater, R.B., P. Wells, L. Aftergood and D. Melnick, JAOCS 50:348 (1973).
10. Boggs, L.A., and G. Anderson, "Quantitative Analyses of Sugar Mixtures by Gas Chromatography of their Di-O-Isopropylidene Derivatives with Galactitol as an Internal Standard," 152nd ACS Meeting, New York, 1966, Abstr. E-18.
11. Sawardeker, J.S., J.H. Sloneker and A. Jeanes, Anal. Chem. 37:1602 (1965).
12. Fletcher, H.G., Jr., and H.W. Diehl, J. Amer. Chem. Soc. 74:3175 (1952).
13. Soltzberg, S., R.M. Goepp, Jr., and W. Freudenberg, Ibid. 68:919 (1946).
14. Thermal Analysis Newsletter, Vol. 6, Perkin-Elmer Corp., 1966.
15. Instrument News, Vol. 16, No. 3, Perkin-Elmer Corp., 1966, p. 9,15.
16. Industrial Res. 8:53 (1966).
17. Murphy, C.B., Anal. Chem. 44:513R (1972).
18. Redfern, J.P., in "Encyclopedia of Chemical Technology," Second edition, Vol. 20, Edited by Kirk-Othmer, Wiley & Sons, New York, 1969, p. 113.

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