Thermochimica Acta, 212 (1992) 39–49
Elsevier Science Publishers B.V., Amsterdam

Characterization of tropical oils by DSC [1]

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(Received 2 September 1991; accepted 27 February 1992)

Abstract

The Harmonized Tariff System names specific tropical oils for classification, for example, palm, palm kernel and coconut. This study has characterized several different tropical oils using differential scanning calorimetry (DSC). The melting of the components of the oil matrix was profiled by heating from 230 to 380 K. A series of thermal variables for each oil was determined for the temperature region between 240 and 340 K. These variables included the total heat of melting, the peak temperature of the largest peak, and partial area slices taken at 10° intervals across the DSC curve. The variables were evaluated by canonical discriminant analysis and the resulting plots were correlated to oil type.

INTRODUCTION

The classification of tropical oils has been an analytical challenge for the laboratories of the US Customs Service. Prompted by the Harmonized Tariff System which classifies the various oils by name, i.e. coconut, palm, palm kernel, and by the difference in value between the oil fractions derived from distillation or fractionation, a means for identifying the oil or fraction is necessary. Even for those tariff classes for which the duty is free, classifications must still be made for trade statistics.

The use of DSC has been previously identified as a useful tool for the characterization of vegetable oils. For example, Busfield and Proschogo recently used DSC in their examination of the characteristics of palm stearins [1,2]. The procedures used for this study are modeled on those of Dyszel for characterizations of pistachio and macadamia nut oils [3,4].

EXPERIMENTAL

The tropical oils in this study were characterized using a DSC profiling technique which compared the thermal curves obtained from the oils under the conditions of heating from subambient through the melt. One hundred

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[1] Presented at the 20th Annual NATAS Conference, Minneapolis, MN, 20–26 September 1991.

0040-6031/92/$05.00

and seventy samples of palm, palm kernel and coconut oils, and fractions thereof, were characterized by this method. These oil samples were analyzed in two sets, containing 97 and 73 samples, respectively.

Tropical oil samples were obtained from actual imported shipments. The oil name assigned to the oil sample was based on the information provided by the importer. The oils had been stored in a freezer to prevent degradation. Prior to sampling, each oil was allowed to return to room temperature. A few oils that were obviously inhomogeneous at room temperature were gently heated until they became liquid and then sampled. The sample mass was in the range of 5–10 mg, which fits conveniently into the Perkin-Elmer (PE) aluminum volatile sample pans.

The DSC (DSC-2, Perkin-Elmer, Norwalk, CT) was programmed from 230 to 380 K at 5°C min^{-1}. Each encapsulated sample was introduced into the sample cell at the lower temperature under flowing nitrogen; the DSC signal baseline was allowed to stabilize and the heating begun. The thermal curve was recorded and stored using the thermal analysis data station (TADS, PE, Norwalk, CT). The sample was then cooled at 25°C min^{-1} to 230 K and allowed to equilibrate. A second heating run under the same conditions was then initiated. The results of the second run were used for comparisons between oils.

Characteristic variables were calculated for each of the 170 samples using the PE partial areas software. These included the following: Jgram, the heat of melting; Earea, the total thermal energy change; T_{max}, the peak temperature of the major transition; A250–A340, partial areas for 10° temperature intervals.

The heat of melting, designated Jgram, was calculated from the area under the curve between the designated partial area limits, corrected for sample mass. In some samples, this temperature region included an exothermic event, recorded as a valley amongst the peaks, that dropped below the baseline constructed for the partial areas calculation. A second parameter is the entered area, Earea. Earea, calculated by the partial area program, takes the total area of the thermal events, both positive and negative, into account. Earea is equal to Jgram only when the thermal curve does not drop below the partial areas baseline. Using partial areas, the thermal curve was subdivided into 10° intervals. Each of these values then becomes a variable in the linear and canonical discriminant analyses.

The values for these variables were loaded into a Quattro Pro Spreadsheet (Borland International Inc., Scotts Valley, CA) which facilitated transfer into a SAS Statistical Program (SAS Institute Inc., Cary, NC). Characteristic DSC thermal curves for palm oil, palm stearin, palm kernel oil, palm kernel stearin, and coconut oil are shown in Figs. 1–5, which indicate the partial area segments, the peak temperatures and the heats of melting. Three types of statistical analysis, available in the SAS program, were performed on the tabulated variables.

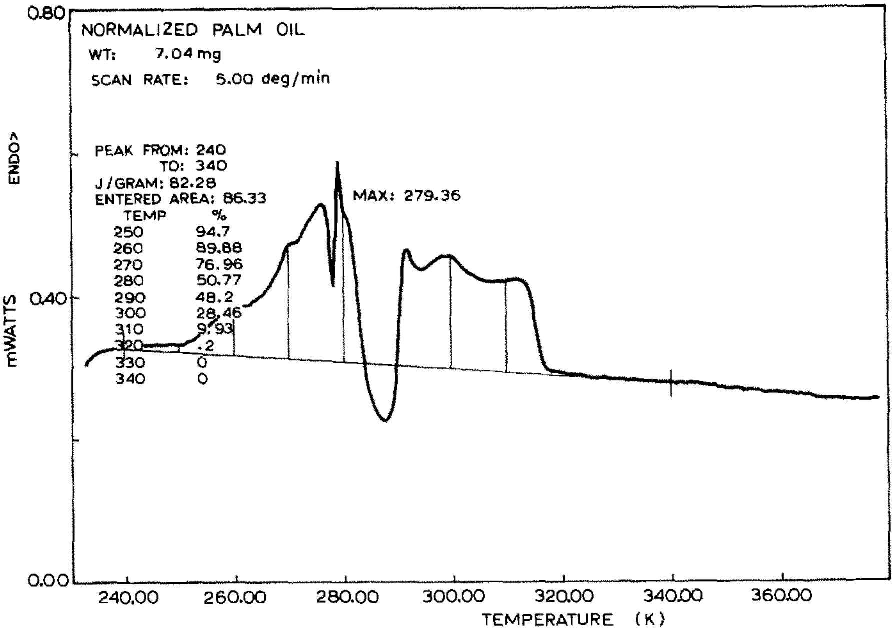

Fig. 1. DSC thermal curve of a typical palm oil: heating conditions, 230–380 K, 5°C min^{-1}; variables T_{max}, Jgram and Earea, and partial areas A250–A340 shown.

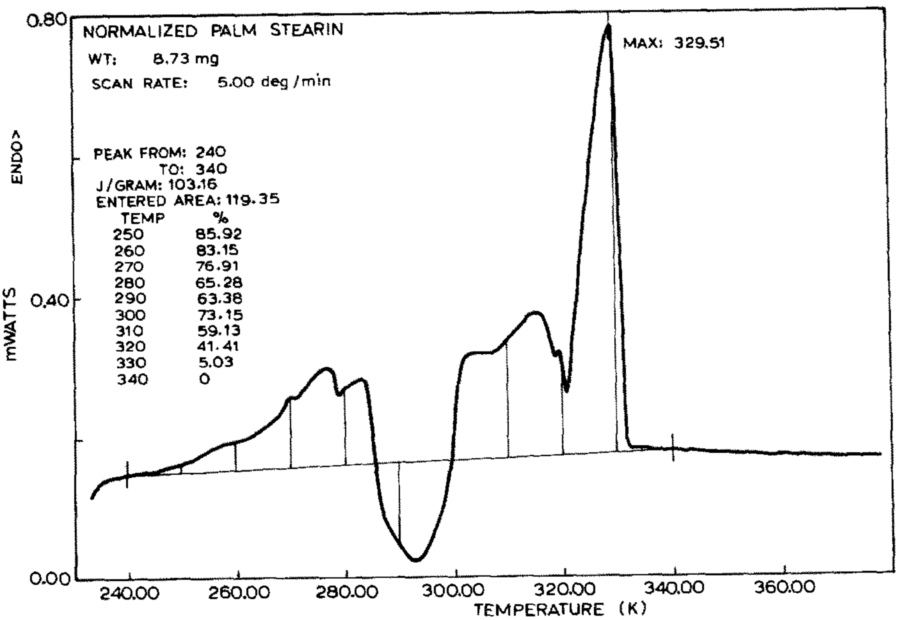

Fig. 2. DSC thermal curve of a typical palm stearin: heating conditions, 230–380 K, 5°C min^{-1}; variables T_{max}, Jgram and Earea, and partial areas A250–A340 shown.

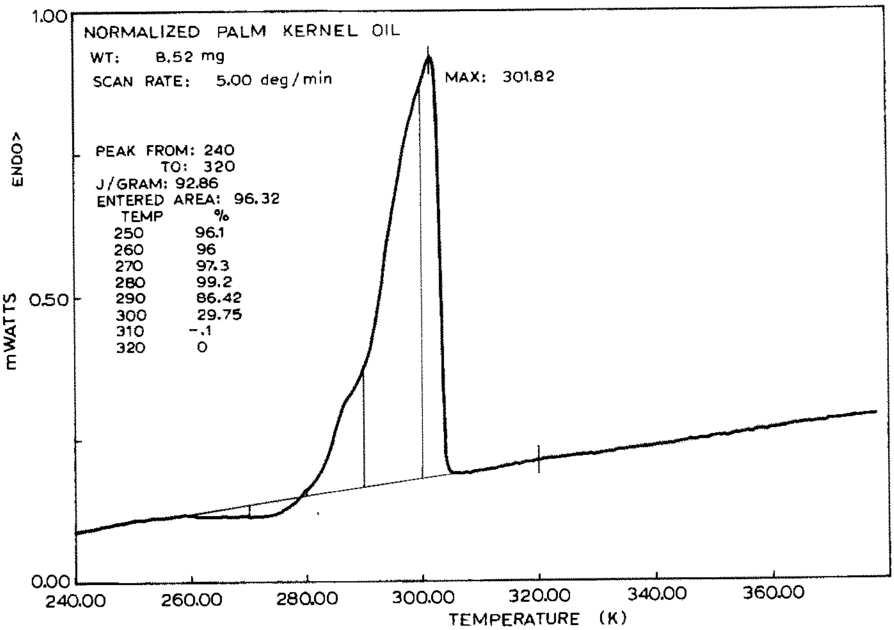

Fig. 3. DSC thermal curve of a typical palm kernel oil: heating conditions, 230–380 K, 5°C min^{-1}; variables T_{max}, Jgram and Earea, and partial areas A250–A320 shown.

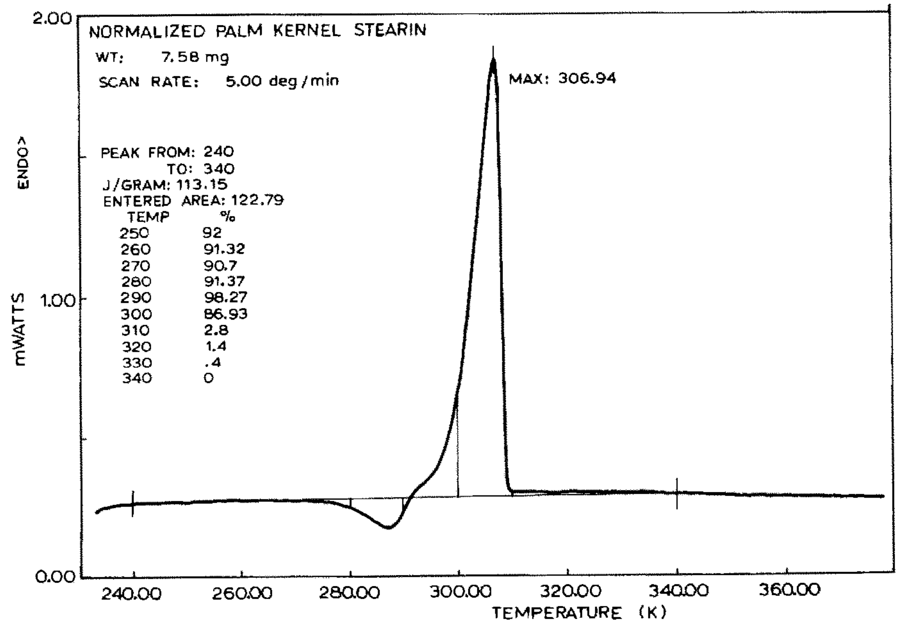

Fig. 4. DSC thermal curve of a typical palm kernel stearin: heating conditions, 230–380 K, 5°C min^{-1}; variables T_{max}, Jgram and Earea, and partial areas A250–A340 shown.

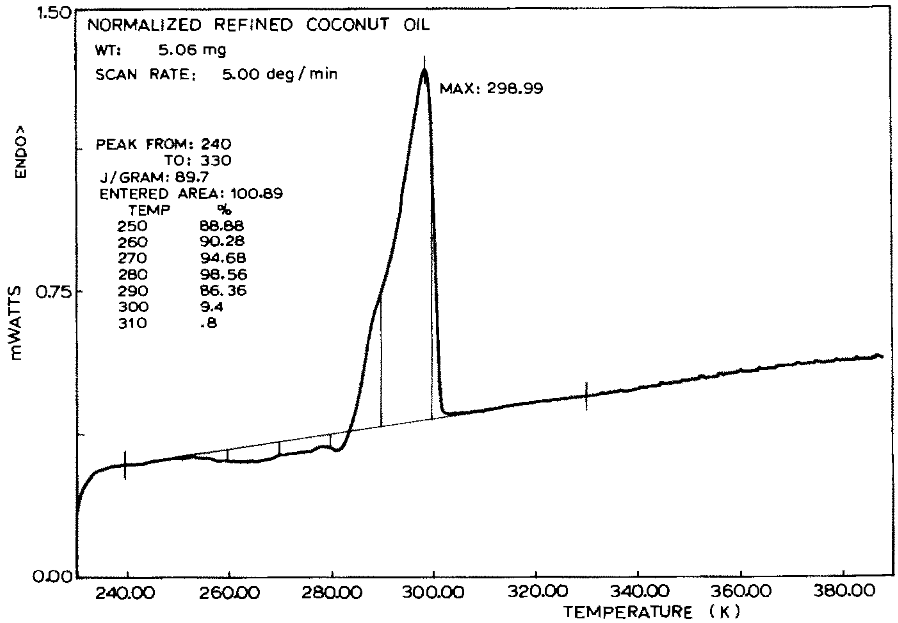

Fig. 5. DSC thermal curve of a typical coconut oil: heating conditions, 230–380 K, 5°C min^{-1}; variables T_{max}, Jgram and Earea, and partial areas A250–A310 shown.

(1) Linear discriminant analysis with probability of membership computes various discriminant functions for classifying observations. The performance of a discriminant function can be evaluated by estimating the probability of misclassification.

(2) Stepwise discriminant analysis uses forward selection, backward elimination or stepwise selection to try to find a subset of quantitative variables that best reveals differences among the classes.

(3) Canonical discriminant analysis finds linear combinations of the quantitative variables that best summarize the differences among the classes.

Linear discriminant analysis

First, linear discriminant analysis was performed on the sample variables, calculating the means, variance and standard deviations for each set of variables by class of oil. As seen in Tables 1 and 2, the mean and standard deviations for the values of T_{max} clearly indicate that some of the oil classes showed more diversity than others, a possible indication of misidentification of one or more of the oil samples attributed to that oil class.

As indicated, palm oil, palm stearin and palm kernel oil have T_{max} values which differed significantly within the family of palm oils and fractions. No

TABLE 1

Means and standard deviations for T_{max} by class of oil; Set 1 or 97 samples

No.	Oil	Mean	Standard deviation
31	Palm oil	289.9	±17.41
6	Palm olein	279.6	±2.78
21	Palm stearin	329.7	±7.24
25	Palm kernel oil	300.6	±4.82
1	Palm kernel olein	305.5	– [a]
7	Palm kernel stearin	306.6	±0.71
6	Coconut oil	298.9	±1.05

[a] Standard deviation not calculated for single value.

standard deviation was calculated for the palm kernel olein as there was only one sample of this type in the set.

Using the linear discriminant function and pairwise generalized squared distances between calculated group values, the linear discriminant analysis program then calculated a posterior probability of membership for each sample into an oil class. Of the 97 oil samples in Set 1, 19 were judged by this method to be misidentified. Table 3 lists the reclassified samples along with the calculated probability of membership in the new class. This tabulation can be summarized by type of classification change. For Set 1, the types of reclassification and the frequency of reclassification include the following: 9 samples, oil reclassified as oil fraction; 7 samples, different oil variety; 2 samples, fraction reclassified as oil; 1 sample, oil reclassified as fraction of different oil.

The linear discriminant analysis for Set 2 used Set 1 as its calibration model. Therefore the members of the second set were compared to the characteristics of the first. Table 4 lists the 26 of the 73 oil samples in this set which were reclassified. These were distributed as follows: 10 samples, oil reclassified as oil fraction; 16 samples, different oil variety; 0 samples, fraction reclassified as oil, 0 samples, oil reclassified as fraction of different oil.

TABLE 2

Means and standard deviations for T_{max} by class of oil; set 2 of 73 samples

No.	Oil	Mean	Standard deviation
43	Palm oil	282.7	±14.79
10	Palm stearin	327.8	±1.68
18	Palm kernel oil	300.3	±2.38
2	Palm kernel stearin	306.4	±0.73

TABLE 3

Reclassified oils of Set 1; linear discriminant analysis

Sample ID	Oil ID	Reclassification ID	Probability of membership (%)
PO187	P	O	99.11
PO171	P	K	98.52
PO175	P	K	97.75
PO097	P	K	98.84
PO177	P	K	96.85
PO185	P	K	95.87
PO173	P	M	99.99
PO091	P	S	99.91
PO159	P	S	100.00
PO095	P	S	99.98
PO143	P	O	99.98
PO027	P	S	99.97
PO039	O	P	92.60
PO041	O	P	69.83
PO069	K	O	98.13
PO119	K	C	99.97
PO073	K	M	99.99
PO133	K	M	100.00
PO117	C	K	96.18

Key: P, palm; O, palm olein; S, palm stearin; K, palm kernel; L, palm kernel olein; M, palm kernel stearin; C, coconut.

Linear discriminant analysis was performed on the combined data set composed of the thermal results of both Sets 1 and 2. The linear discriminant analysis results of reclassification of this combined set is given in Table 5. The following is a summary of the 35 designated reclassifications from this combined set of 170 samples: 19 samples, oil reclassified as oil fraction; 12 samples, different oil variety; 2 samples, fraction reclassified as oil; 2 samples, oil reclassified as fraction of different oil.

It was noted that the number of reclassified oils in the combined set is not the simple addition of the reclassifications of the two component sets. This difference is due to the manner in which the linear discriminant function was calculated. Set 2 results were calculated on the basis of the model established by Set 1. However, the combined set reclassification was the result of determining the linear discriminant function of the set without reference to any outside model, i.e. it formed its own model, as was done in the analysis of Set 1.

Seven samples from the combined list of reclassification did not appear on the reclassification lists of either individual set. However, with the exception of one sample with a 94% probability factor for reclassification, the other six all had probabilities of less than 90%, some less than 60%. It

TABLE 4

Reclassified oils of Set 2; linear discriminant analysis

Sample ID	Oil ID	Reclassification ID	Probability of membership (%)
PO237	P	C	100.00
PO251	P	O	65.97
PO253	P	S	99.93
PO227	P	K	95.03
PO229	P	S	100.00
PO233	P	O	88.27
PO235	P	O	99.96
PO187	P	O	99.11
PO223	P	S	100.00
PO216	P	O	80.60
PO218	P	C	100.00
PO286	P	C	99.35
PO297	K	C	100.00
PO325	K	C	100.00
PO313	K	M	100.00
PO327	K	P	93.51
PO317	K	C	100.00
PO319	K	C	100.00
PO339	K	L	77.53
PO321	K	C	100.00
PO323	K	C	100.00
PO314	K	C	100.00
PO329	K	P	96.54
PO331	K	P	55.39
PO333	K	P	84.33
PO337	K	P	57.85

Key: P, palm; O, palm olein; S, palm stearin; K, palm kernel; L, palm kernel olein; M, palm kernel stearin; C, coconut.

was noted that this group of samples was also split between three reclassifications of palm oil to palm olein and four of palm kernel oil to coconut oil.

Stepwise discriminant analysis

Next, stepwise discriminant analysis was carried out on the variables. Using the same significance criteria for each variable, the variables were evaluated to determine if they should be included in or excluded from the data set. No variables were excluded on the basis of this analysis and the full set of variables was carried into the canonical discriminant analysis.

Canonical discriminant analysis

Canonical discriminant analysis is a powerful technique which allows multiple variables to be evaluated by creating mathematical models utiliz-

TABLE 5

Reclassified oils; combined set, linear discriminant analysis

Sample ID	Oil ID	Reclassification ID	Probability of membership (%)
PO153 [a]	P	O	93.78
PO187	P	O	99.40
PO171	P	K	82.56
PO175	P	K	90.46
PO097	P	K	92.94
PO177	P	K	96.57
PO185	P	K	97.51
PO173	P	M	99.98
PO091	P	S	99.98
PO159	P	S	100.00
PO095	P	S	100.00
PO101 [a]	P	O	94.86
PO103 [a]	P	O	88.47
PO143	P	O	99.99
PO027	P	S	99.97
PO039	O	P	95.85
PO041	O	P	94.65
PO069	K	O	61.03
PO119	K	C	98.54
PO125 [a]	K	C	65.73
PO121 [a]	K	C	53.81
PO131 [a]	K	C	71.88
PO073	K	M	99.98
PO133	K	M	100.00
PO117	C	M	57.97
PO237	P	O	53.72
PO253	P	S	99.87
PO227	P	K	64.32
PO229	P	S	99.98
PO235	P	O	98.81
PO187	P	O	99.40
PO223	P	S	99.93
PO216	P	S	72.31
PO317	K	L	90.14
PO299 [a]	K	C	61.63

[a] Entry does not appear on reclassification lists of Sets 1 or 2.
Key: P, palm; O, palm olein; S, palm stearin; K, palm kernel; L, palm kernel olein; M, palm kernel stearin; C, coconut.

ing all the variables for each observation. Unique linear combinations are created for each variable which can be used to define model characteristics for each oil type. Further manipulation of these values creates canonicals which are ranked so that the first canonical represents the greatest variance of the sample from the assigned model, the second canonical the next

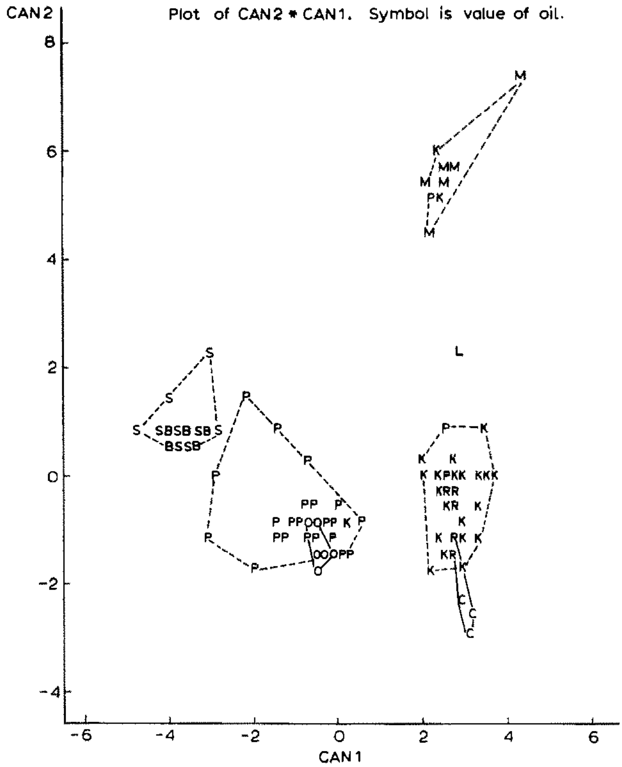

Fig. 6. Canonical discriminant analysis plot of Can2 vs. Can1 values for tropical oil data. P, palm; O, palm olein; S, palm stearin; K, palm kernel, L, palm kernel olein; M, palm kernel stearin; C, coconut. 72 sample points hidden. Other letters which may appear are the result of two or more letters in the same space.

greatest variance, and so forth. Plotting the first and second canonical values associated with each sample gives a two-dimensional representation of the grouping by characteristic types. Oils that are very similar in their characteristics will appear to be tightly grouped on the canonical plots. Conversely, dissimilar oils will appear to be far apart.

For our purposes, the canonical values for each sample were calculated and pairs of values were plotted. Figure 6 illustrates a composite of the individual canonical plots. Each sample in the combined sample set is marked by a letter representing its oil class. Some letters may appear on the plot which are not identified in the legends. These are artifacts of the plotting process and are caused by the direct overlay of two letters. For sample, a "P" over an "S" will appear as a "B". Likewise, the "R" is a result of a "K" and a "P".

The spatial region attributed to each oil is shown by the broken or solid lines. Letters different from the majority within the boundaries of a region represent samples which were reclassified as that oil type by the linear discriminant analysis calculations. The graphic placement of these oils within the assigned canonical region of an oil group reinforces the validity of the reclassification, as determined by the linear discriminant analysis. It can be seen that there is good spatial separation between the palm oil and the following other oil classes: palm stearin, palm kernel stearin, palm kernel olein and coconut. Moderate separation was achieved visually between the palm/palm olein and palm/palm kernel pairs. Palm kernel and coconut oils were also moderately separated using this technique.

CONCLUSION

DSC can be a useful technique for the identification of tropical oils. The use of canonical discriminant analysis enables a complex data set to be displayed in a readily understandable format and is useful in highlighting those individual samples which do not fall within the bounds of the predicted thermal behavior.

Further work will be necessary to determine whether the samples which are reclassified using the linear discriminant analysis are truly the type of oil which is indicated by the analysis. Additional samples of both palm and palm kernel oleins are required to determine the bounds of their canonical regions.

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