The DSC Thermal Analysis of Crystallization Behavior in Palm Oil, II

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ABSTRACT

Polymorphic behavior of palm oil crystals was investigated by means of a differential scanning calorimeter under isothermal and constant cooling conditions. Constant cooling conditions produced β_1' crystals mixed with α, and β_2' crystals. All underwent the typical transformations to the more stable forms; i.e., $\beta_2' \rightarrow \alpha \rightarrow \beta_1' \rightarrow \beta$. Isothermal conditions produced: (a) α crystals mixed with β_1', (b) transformation from them to β_1, and (c)β_2 and β_3 crystals. In palm oil crystals, sorbitan tristearate retarded the transformation of the unstable α and β' forms to the stable β form. This retardation, however, was greatly influenced by the cooling and heating conditions. Using that property of sorbitan tristearate, the polymorphic behavior of palm oil crystals could be studied in detail.

INTRODUCTION

This paper attempts to define the polymorphism of palm oil crystals with a differential scanning calorimeter (DSC), and follows up a previous paper by the author (1). Differential scanning calorimetry seems to be better suited for investigating fast polymorphic changes than does X-ray crystallography. For example, very systematic studies of the polymorphic transition of some pure triglycerides have been reported by Lovegren, et al. (2,3).

The crystallographic properties of plam oil have been investigated by Deroanne et al. (4), Persmark et al. (5) and Jacobsberg et al. (6). The unique crystallization behavior of palm oil is caused by the composition of the triglycerides and related compounds, e.g., fatty acids and partial glycerides (6–8). In this experiment, sorbitan esters were used to control the polymorphism in the oil under different cooling, heating and isothermal modes with a DSC. It is said that sorbitan esters possess the ability to stabilize α form crystals or to prevent the transformation from β' form to β form (9–11). Sorbitan tristearate, which was found to be the most effective among the esters, could greatly retard this transformation in palm oil crystals.

The present study is based on the information obtained from the work of Persmark, et al. (5) with palm oil, and the designation of the α and β' crystal forms describing the polymorphism is due to their investigations. The following knowledge, however, is newly added to their information, namely: (a) the discovery of crystal forms with higher melting point than Persmark's β' form; (b) the study of isothermal and constant cooling crystallizations; (c) the demonstration of the effect of sorbitan esters on crystal transformation.

EXPERIMENTAL PROCEDURES

Materials

The oil sample was a commercially available whole palm oil from Malaysia. It was the same oil used in work reported previously (1).

The literature (9,10) suggests that sorbitan esters retard crystal transformations; of these esters four were selected. Food grade sorbitan tristearate was obtained from KAO-Atlas Chemical Ltd., Japan. Reagent grade sorbitan monostearate, sorbitan trioleate and polyoxyethylene sorbitan trioleate were obtained from Wako Pure Chem. Ind., Japan.

Analytical Method

The DSC used was a Perkin-Elmer Model DSC-2. The reference material was 12.0 mg of polyethylene terephthalate sealed in a hermetically sealed aluminum sample pan. About 9 mg of each oil sample was weighed into aluminum sample pans; the covers were crimped in place. The sample and reference pans were placed in the DSC and held at 393 K for more than 5 min to destroy crystal nuclei before each scan.

To record the DSC cooling and heating curves, the samples were cooled to a given temperature and then heated at a constant rate. The cooling and heating rates were 1.25 and 10 K/min, respectively. The temperature was also rapidly reduced at a rate of ca. 80 K/min and held at the desired temperature (e.g., 295 K) under supercooled conditions for the DSC isothermal crystallization. The crystals thus generated were immediately heated at rates ranging from 1.25 to 10 K/min to obtain the DSC heating

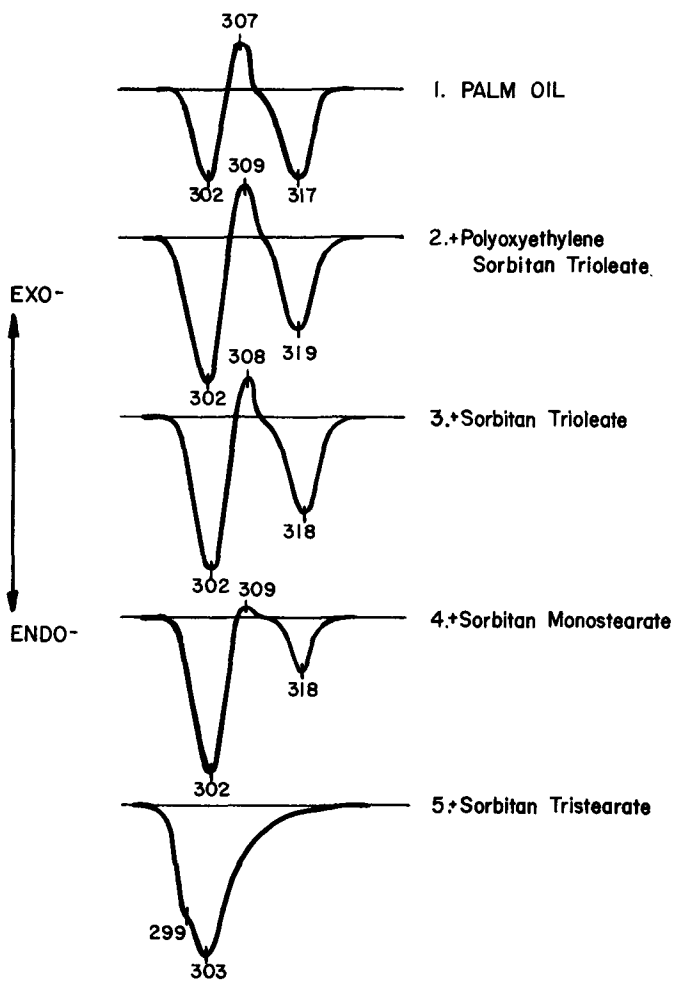

FIG. 1. DSC heating curves of palm oil and palm oil with 1.5% sorbitan esters. Samples crystallized as the first exothermal peak isothermally at 295 K, then heated at 10 K/min.

curves. The crystals were also heated at 10 K/min to investigate polymorphic transition at the different stages of the crystallization curve corresponding to the development of exothermal peaks. The exo or endothermal peak temperatures (K) were obtained from DSC curves and used for the determination of crystal forms.

As has been described in a previous paper (1), an unstable crystal form (the "A" form) in palm oil has been identified under isothermal condititions. These unstable crystals were used in investigating the retarding effect of sorbitan esters on the transformation of that "A" to a more stable form.

RESULTS AND DISCUSSION

Effect of Sorbitan Esters on Crystal Transformation

In order to determine which ester was the most effective in retarding the transformation of various crystal forms, four sorbitan esters were individually added to palm oil at the 1.5% level and thermograms obtained in the cooling-heating mode. Sorbitan tristearate appears to be the most effective retardant of crystal transformation in palm oil as shown by Figure 1. The sorbitan tristearate-palm oil blend shows neither a recrystallization peak of transformation nor a fusion peak of stable crystals; i.e., a peak at 317–319 K in a heating curve. Also, for sorbitan tristearate, the minimum effective concentration was determined for the levels between 0.1 and 2.0%. That ester showed the complete effect at concentrations greater than 1.5% in palm oil. Hereafter, sorbitan tristearate at a 1.5% level will be used to retard these transformations.

It is also known that the heating rate influences crystal transformation. The palm oil sample with 1.5% sorbitan tristearate was scanned with the DSC at heating rates ranging from 1.25 to 10 K/min to investigate the effect of the rate on retarding crystal transformation. At a heating rate of 1.25 K/min, the addition of sorbitan tristearate has no effect on the transformation, as shown in Figure 2. As the heating rate is increased from 1.25 to 10 K/min, the effect becomes more obvious, and the retardation is complete at rates greater than 5 K/min (Fig. 2). This crystallization behavior may be explained by the steric hindrance of sorbitan tristearate (10). At faster heating rates, the crystals may be restricted by the sorbitan tristearate in their transformation to a more stable form. At relatively slow heating rates, the crystals may have enough time to repack into the stable crystal form despite the steric hindrance effect of the sorbitan ester.

Polymorphic Behavior under Constant Cooling Mode

Both the pure palm oil and the sorbitan tristearate-palm oil blend were cooled at constant rates of 1.25 and 10 K/min in order to reproduce the experimental conditions of Persmark et al. (5). The cooling curves thus obtained were essentially the same in shape as shown by Figure 3. At 10 K/min, the thermograms were nearly identical for both samples. At 1.25 K/min, however, the thermogram of the sorbitan tristearate-palm oil blend has a smaller peak at 296 K than does the pure palm oil sample as shown in Figure 3.

If Persmark et al. (5) are correct, the first sharp peak in palm oil at 293 K (Fig. 3-1) should correspond to the generation of the β_1' form. That peak, however, may also include a transformation from an unstable form to a stable form, since that peak is greatly reduced, becoming a smaller peak at 296 K, as a result of the addition of sorbitan tristeaarate (Fig. 3-2). The second large peak in palm oil at 276 K (Fig. 3-1) should also correspond to the crystallization of the β_2' form.

The crystals generated by cooling at 1.25 K/min were

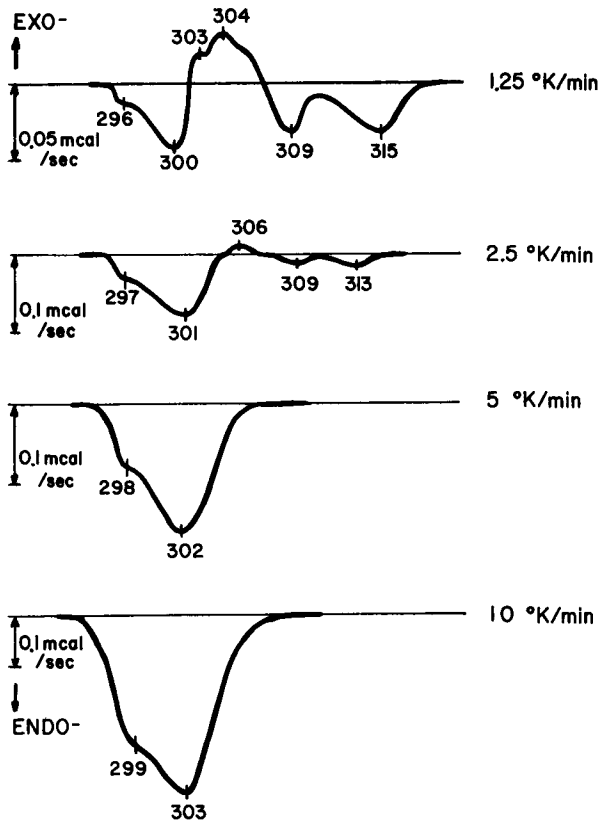

FIG. 2. DSC heating curves of palm oil with 1.5% sorbitan tristearate at rates ranging from 1.25 to 10 K/min. Samples crystallized as the first exothermal peak isothermally at 295 K.

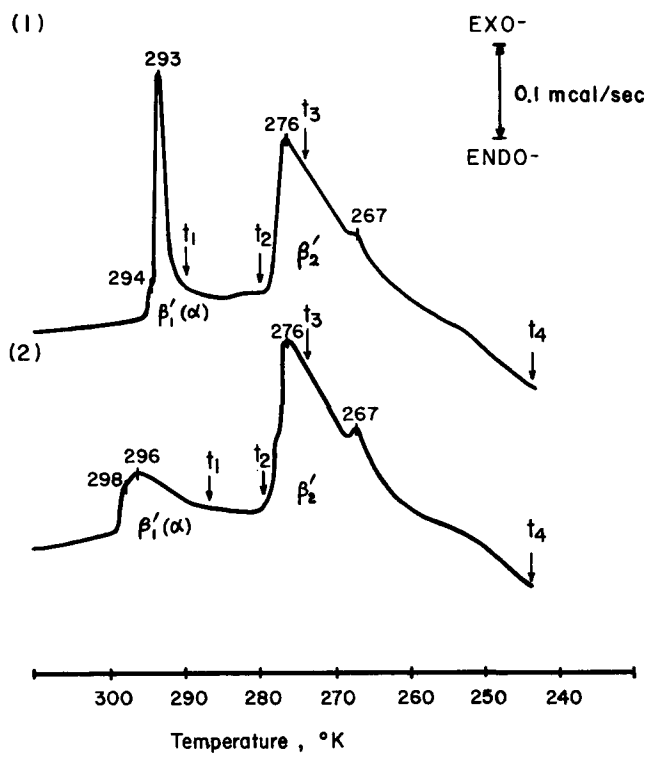

FIG. 3. DSC cooling curves at a rate of 1.25 K/min. 1) Palm oil and 2) palm oil with 1.5% sorbitan tristearate.

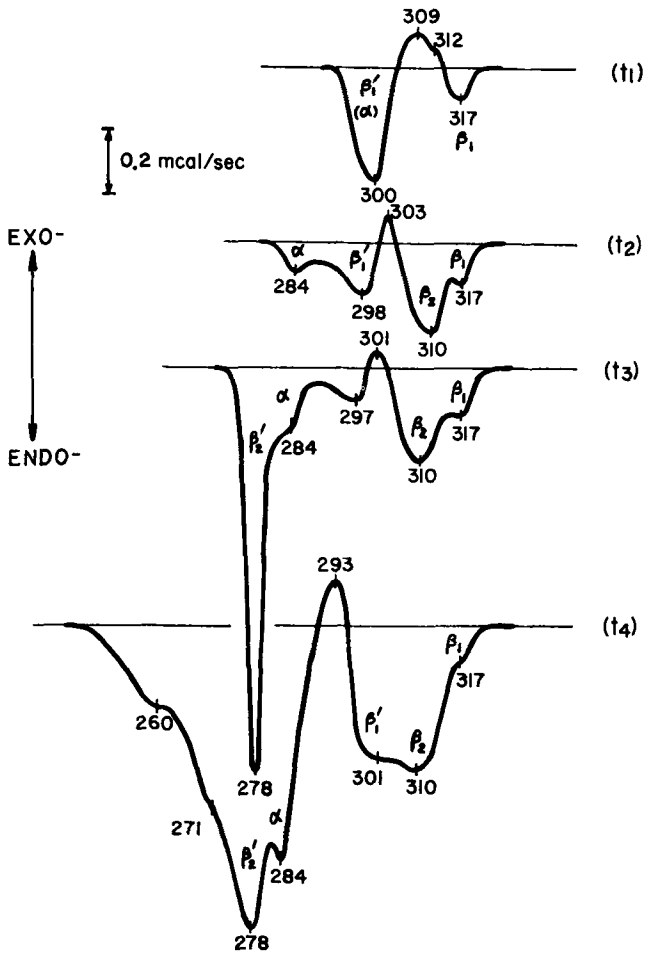

FIG. 4-1. DSC heating curves of palm oil 10 K/min., initiated at different stages (t_1–t_4) in crystal development after cooling at 1.25 K/min. (Fig. 3-1).

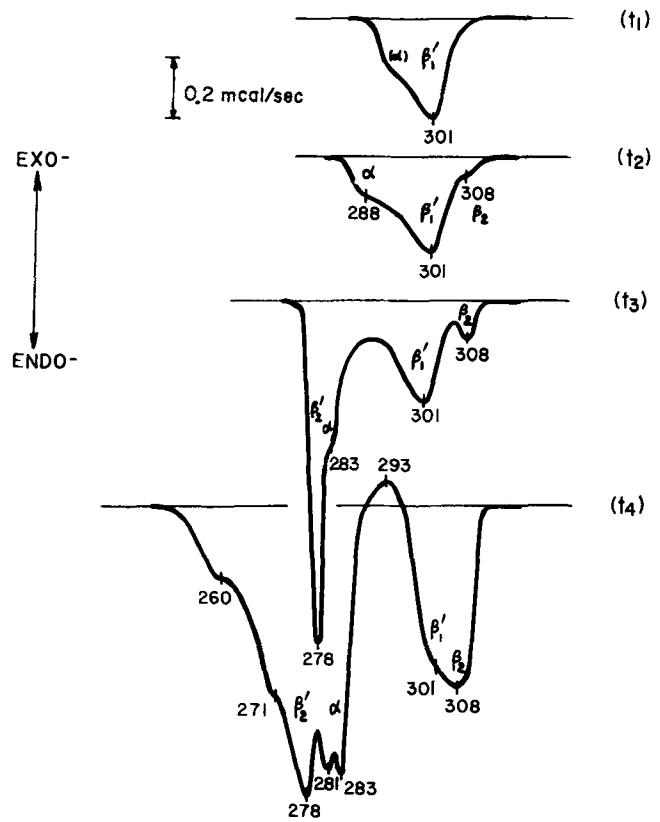

FIG. 4-2. DSC heating curves of palm oil with 1.5% sorbitan tristearate 10 K/min, initiated at different stages (t_1–t_4) in crystal development after cooling at 1.25 K/min. (Fig. 3-2).

heated at 10 K/min at different stages in the cooling curve as denoted by t_1, t_2, t_3 and t_4 in Figure 4-1 and 4-2. The heating curves at each stage indicate what crystals exist at that stage. In Figure 4-1, the heating curve at stage–t_1 shows that the β_1' form (probably mixed with α form crystals) melts at 300 K, recrystallizes and transforms to a more stable form, which finally melts at 317 K; this final form is tentatively termed the β_1 form because it has the highest melting point.

When the sample is heated at stage–t_2, before the crystallization of β_2', the fusion of α form can be identified as the endothermal peak at 284 K (Fig. 4-1). This melting point is substantially below that of the β_1' form at 298 K. Persmark, et al. (5) identified the α form in the crystals cooled to temperatures less than 263 K during a heating process at 0.5 K/min. It is difficult to separate α from β_1' crystals by heating from stage–t_1 since the heating at that stage starts at 291 K. The heating curve at stage–t_2 also shows two melting peaks at 310 and 317 K, which are higher than that of the β_1' form. The highest melting peak is probably due to the β_1 form; the crystal form at 310 K is tentatively termed the β_2 form.

The heating curves at stages t_3 and t_4 show endothermal peaks of β_2' crystal fusion at ca. 278 K as seen in Fig. 4-1. For the sorbitan tristearate-palm oil blend (Fig. 4-2), the heating curves at stages t_2 through t_3 show a small endothermal peak for β_2 crystal fusion that had a lower melting point (308 K) than did the β_2 form of pure palm oil (310 K), and no peaks for β_1 crystals. If a large amount of unstable β_2' from crystals are generated by cooling and then heated at stage–t_4, the thermogram shows a large peak of the β_2 form trnasformed from all these mixed crystals. The β_2 crystals seem to be aided in the transformation to this more stable β_2 form.

Table I shows the melting peak temperature for each crystal form from the DSC heating curves. There are also several unknown peaks in the DSC curves in this work which cannot be identified as yet.

Polymorphic Behavior under Isothermal Crystallization

Isothermal crystallization takes place in a super cooled sample, and seems to be a process similar to tempering and different from constant cooling crystallization. The isothermal crystallization curves at 295 K are shown for both the pure palm oil and the sorbitan tristearate-palm oil blend in Figure 5. The thermograms show two exothermal peaks for palm oil and three for palm oil with sorbitan tristearate. Sorbitan tristearate increases the exothermal rate of the

TABLE I

Melting Peak Temperatures of DSC Heating Curve for Crystal Forms of Palm Oil[a]

β_2'	Unstable	278 K
α		284 K
β_1'		298–301 K
β_2		310 K
β_1		317 K

[a]Palm oil samples cooled to 243 K at 1.25 K/min. as shown in Figure 3 and heated at 10 K/min.

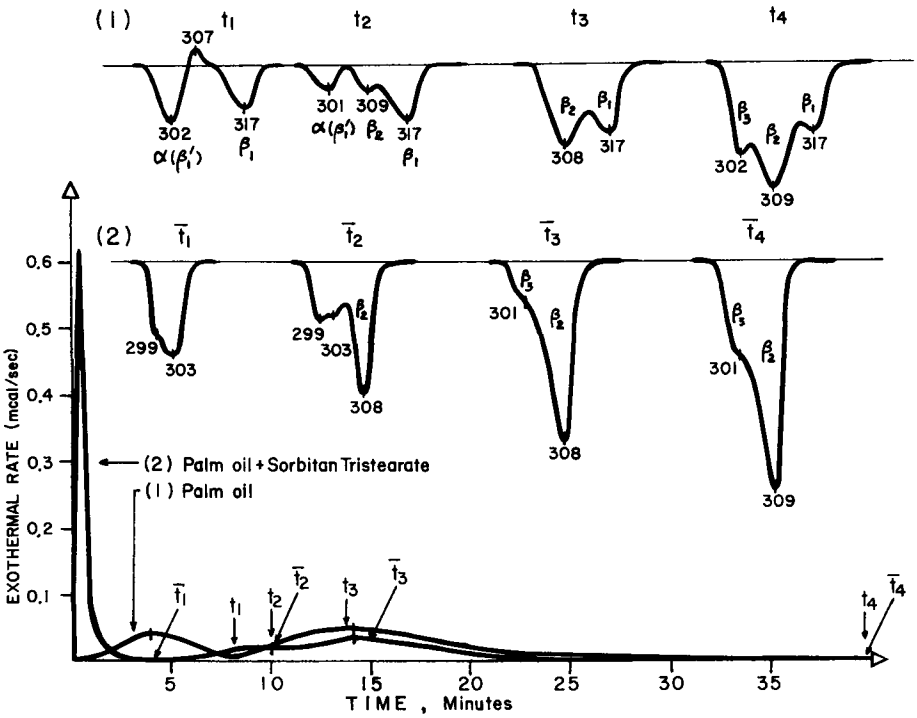

FIG. 5. DSC isothermal crystallization curves at 295 K (lower part), and heating curves (upper part) initiated at different stages (t_1–t_4) in isothermal crystal development. 1) Palm oil and 2) palm oil with 1.5% sorbitan tristearate.

first exothermal peak under the isothermal mode, but, under the constant cooling mode as shown in Figure 3, the exothermal rate of the first peak is depressed by the addition of sorbitan tristearate. This behavior suggests that the isothermal crystallization differs from the constant cooling crystallization.

If Persmark's tempering information is correct (5), it is reasonable to consider that the first exothermal peak under isothermal mode corresponds to the generation of the α form. These α form crystals, however, may be mixed with β_1' form, because of the higher melting peak temperature. In Figure 5-1, the heating curve at stage–t_1 shows that these α form crystals melt at 302 K, recrystalize at 307 K and transform to a more stable form which finally melts at 317 K. Those transformed crystals are presumed to be β_1, since they have the same melting peak temperature as the β_1 form in Figure 4-1.

When these α form crystals were heated at 10 K/min beginning at the apex of the first exothermal peak of isothermal crystallization, the melting peak of α crystals was the same size as both the recrystallization peak at ca. 307 K and the melting peak of β_1 crystals at ca. 317 K. As the heating stage is moved from t_1 to t_3, both the melting peak of α crystals and the recrystallization peak of α to β_1 decrease and ultimately disappear from the heating curves. Another endothermal peak at ca. 309 K begins to appear in the heating curve at stage–t_2 and becomes progressively larger at stages t_3 and t_4. This peak seems to be also coincident with that of β_2 form in Figure 4-1. The endothermal peak at 302 K does not appear at stage t_3 but does at t_4. The crystal form for this peak is tentatively termed β_3.

When sorbitan tristearate is added, the sample does not show the endothermal peak of the β_1 form in the heating curve at stage–$\bar{t}_1$ of Figure 5-2. At stage–$\bar{t}_2$, during the second exothermal peak of the crystallization, the endothermal peaks of fusion at 299 K and 303 K are decreased; the melting peak of β_2 crystals at ca. 308 K, however, is increased. This second exothermal peak produced by isothermal crystallization seems to be the transformation peak of those crystals producing endothermal peaks at 299 K and 303 K to the β_2 form. After the third exothermal peak of the isothermal crystallization at stage–$\bar{t}_4$, the sample shows only endothermal fusion peaks of the β_2 and β_3 forms. Sorbitan tristearate has no effect on the crystallization-transformation of the β_2 and β_3 forms but does on the transformation of the β_1 form.

Under the isothermal mode, these observations suggest for palm oil crystallization:

1. The α form crystals generate the first exothermal peak. The "A" form described in a previous report (1) is coincident with the α form (probably mixed with the β_1' form).
2. The α form crystals transform to β_1 form crystals at the beginning stages of the isothermal crystallization.
3. The transformation to β_2 and β_3 form crystals generates the second exothermal peak. The "B" form of a previous report (1), is coincident with these three β forms.

X-ray diffraction studies will be described for these crystal forms of palm oil in a subsequent paper.

ACKNOWLEDGMENT

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Letters to the editor

Sir: We have recently evaluated two related procedures for quickly estimating the content of glucosinolates in rapeseed. In the first rapid procedure (1), commonly known as the "Tes-Tape procedure," a small sample of seed is crushed. The crushed seed is mixed with a quantity of activated carbon empirically determined to be the amount needed to absorb endogenous glucose. Water is added and, after the glucosinolates have been hydrolyzed by the seed enzymes, the excess glucose is estimated using a semiquantitative, glucose specific test paper containing glucose oxidase, peroxidase, and the chromogen o-tolidine. This method was reported to be relatively sensitive and accurate (1) and has been used, in various modifications, as a screening procedure for low glucosinolates rapeseed in plant breeding programs, at crushing plants and in quality monitoring programs.

The second procedure (described as the Tes-Stick Procedure (2)) is actually a simplification of the first procedure to a kit form. The kit consists of a plastic bag with a quick seal, two plastic tubes which are graduated for addition of seed and water, and a cardboard stick which has a wick, carbon and glucose test paper incorporated onto it. To estimate glucosinolates, a sample of seed (measured with the plastic tube) is crushed with a hammer in the plastic bag. Water is added and mixed with the crushed seed, and after the glucosinolate hydrolysis is complete the wick of the cardboard stick is placed in the liquid. The glucosinolate content is then estimated semiquantitatively as in the first procedure.

The two procedures were used to estimate the glucosinolate content of 115 samples of rapeseed from the Grain Research Laboratory's 1978 New Crop Survey (3). The samples had previously been analyzed for total glucosinolates by the method of Wetter and Youngs (4) which determines glucosinolates spectrophotometrically by the ultraviolet absorption of thiourea derivatives of the isothiocyanate split products. The samples tested included 48 samples of "Canola" seed (glucosinolates 3 mg/g as 3-butenyl isothiocyanate or less and erucic acid 5% or less) and 67 samples of rapeseed with glucosinolate contents ranging from 3.1 mg/g to 14.6 mg/g. Seventy-six of the samples graded No. 1 Canada Rapeseed (CR) while 39 of the samples were graded No. 2 CR or No. 3 CR. Correlations between the three procedures are shown in Table I. The correlations were reasonably high and not significantly different. Grade did not significantly effect the correlations.

The primary use for the two rapid procedures is to detect Canola types of rapeseed. For ca. 90% of the samples the rapid tests indicated correctly whether or not the sample was Canola (Table II). Examination of the data showed that in most of the cases where the test failed, the glucosinolate levels were close to the 3 mg/g cut-off level indicating that this error rate should not impose a severe penalty on the tester.

TABLE I

Correlation Coefficients (R) between Glucosinolates as Determined by Three Procedures fro 115 Samples of Rapeseed

	Wetter & Youngs	Tes-Tape
Test-Tape	0.805	
Tes-Stick	0.854	0.850

TABLE II

Effectiveness of Rapid Tests in Distinguishing Low-Glucosinolate Rapeseed

	Tes-Tape	Tes-Stick
No. of samples of Canola indicated as not Canola (n = 48)	6	4
No. of samples of high-glucosinolate seed indicated as Canola (n = 67)	5	6

Both rapid tests require between 7 and 9 min to complete a single sample. Overlapping of up to three samples is possible. The Tes-Stick procedure seems somewhat less sensitive than the Tes-Tape procedure with the cut-off for Canola being a color reading of 2 for the Tes-Stick and 3 for Tes-Tape. The major advantages to the Tes-Stick procedure are its simplicity and cleanliness relative to the Tes-Tape procedure. Some difficulties noted with the Tes-Stick procedure were: (a) difficulty in manipulation within the relatively small bag—especially for analysts with large hands; (b) tendency of certain seed lots to puncture the bag when crushed, (these punctures can be sealed with tape); (c) some sticks lose their wick action due to loss of adhesion with the cardboard (or sometimes for unexplained causes).

In summary, we have found that both the Tes-Tape and newer Tes-Stick procedures are suitable for distinguishing between types of rapeseed with high and low glucosinolates levels.

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