Oxidative Stability of Wax Esters by Thermogravimetric Analysis

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ABSTRACT

Relative oxidative stabilities of sperm whale oil and eight wax ester preparations were determined by comparing oxygen uptake profiles that had been corrected for ester volatility. Wax esters with unsaturation near the ester bond, even though more volatile, are as stable toward oxidation as those with double bonds near the center of each aliphatic chain.

INTRODUCTION

Research aimed at saving an endangered species, the sperm whale, has involved the preparation of numerous wax esters as potential sperm whale oil replacements. To qualify for consideration, each candidate must possess good oxidative stability. Accordingly, we have sought a quick micro method by which to initially screen products that might be obtained from unusual seed oils.

Most laboratory procedures that measure oxidative stability are designed for use with triglyceride fats and oils for cooking and frying. Two common methods, the active oxygen method (AOM) (1) and the ASTM oxygen bomb test (2,3), measure oxidative degradation in terms of peroxide formation or oxygen uptake. These methods require rather large amounts of sample. In recent years, thermal analysis techniques have gained in popularity (4-6) because they conserve sample and offer additional advantages of shorter testing times and improved objectivity.

Dynamic thermogravimetric analysis (TGA) (5), seemed suitable for use with the wax esters, but sample volatilization, which was a much greater problem with the waxes than with triglycerides, precluded direct observation of oxygen uptake. Scanning samples thermogravimetrically in oxygen and nitrogen environments provided the means to cancel the adverse effects of volatilization and readily identify the onset and course of oxidation.

EXPERIMENTAL

Calibration of a Perkin-Elmer TGS-1 in conjunction with a DSC-1B differential scanning calorimeter and general experimental conditions were as described previously (5) with exception that temperature programming (5 C/min) was started at 60 C. Three runs were made for each wax in both oxygen and nitrogen with an average sample size of ca. 1.6 mg (2 μl) of liquid wax. For data interpretation, a line was drawn through the stabilized baseline at 60 C to represent the weight of the sample at the beginning of temperature programming. The weight gain or loss from this extrapolated baseline was measured at intervals of 10, 5, or 2 C, depending on the rate of weight change, and the weight change was reduced to a percentage of sample weight. The average percent of weight change at each measured temperature was calculated to give an average weight change curve over the temperature range from 60 C to ca. 200 C. The nitrogen curve was then subtracted from the oxygen curve at each temperature to give a difference curve or a more accurate representation of the reaction with oxygen. Rates of oxygen uptake were determined by measuring the slope of a tangent to the rapidly rising portion of the difference curve.

Several wax esters were obtained and tested by the described method. Crambe wax esters A and B represent small and large batch preparations (7) from the acids of *Crambe abyssinica*. Three different waxes were prepared from the acids of *Limnanthes douglassi* (unpublished information); mixed esters, from the total acids of the oil; diene wax esters, from monoene-rich acids; and tetraene wax esters, from diene-rich acids. Jojoba oil A was raw untreated oil, which is a natural wax ester. Jojoba sample B was oil that had been heated in the presence of activated charcoal to 300 C and filtered hot to remove caramelized material (8). Jojoba oil B was mixed with butylated hydroxyltoluene (BHT) at 0.1 and 1% (w/w) to test the effect of an antioxidant. Behenyl arachidate was purchased from Nu Chek Prep, Elysian, MN. Sperm whale oil was obtained from Ashland Chemical Company, Mapleton, IL.

RESULTS

Data obtained for the waxes in oxygen and nitrogen

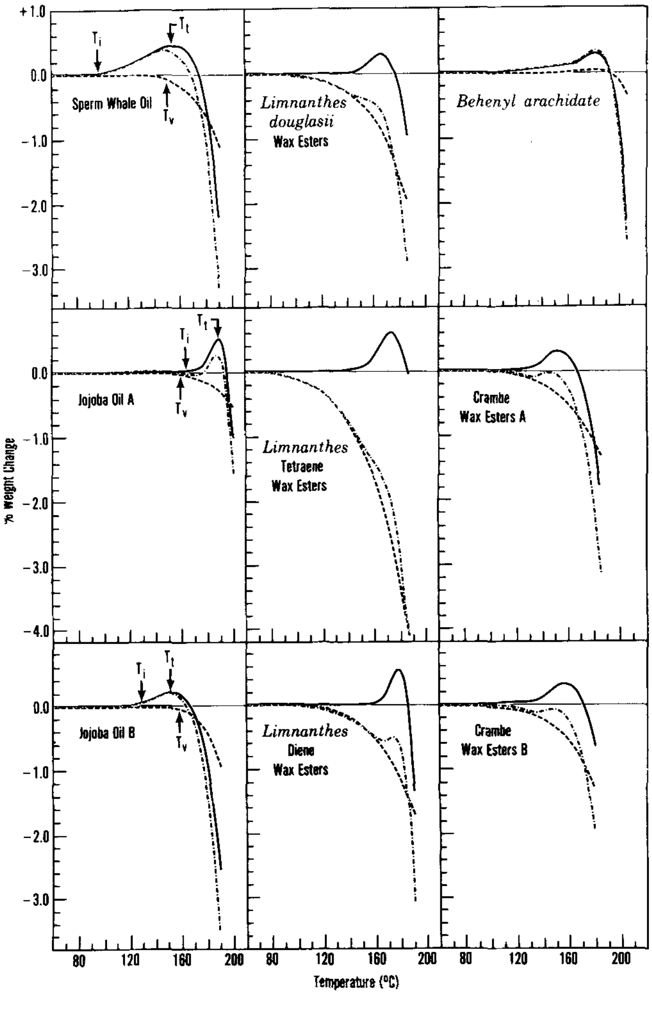

FIG. 1. Thermogravimetric curves of synthetic and natural waxes. Curves for oxygen and nitrogen are the average of three runs. —·—· O_2, – – – N_2, ——— O_2 minus N_2 (difference curve).

TABLE I

Thermogravimetric Parameters of Wax Esters

Sample	T_v[a] (C)	T_i[b] (C)	T_t[c] (C)	Weight gain (%)	Rate of O_2 uptake[d] (μg/C)
Sperm whale oil	145	100	150	0.44	0.15
Jojoba oil A	162	165	188	0.52	0.66
Jojoba oil B	158	128	152	0.24	0.17
Jojoba oil B with 0.1% BHT	110	132	158	0.64	0.42
Jojoba oil B with 1.0% BHT	100	151	164	0.48	0.67
Limnanthes wax esters	105	146	166	0.30	0.28
Limnanthes tetraene wax esters	88	142	172	0.61	0.53
Limnanthes diene wax esters	112	162	178	0.53	0.69
Behenyl arachidate	192	115	180	0.30	0.04[e], 0.19[f]
Crambe wax esters A	115	130	155	0.30	0.32
Crambe wax esters B	100	115	158	0.32	0.25

[a] Volatilization temperature.
[b] Initiation temperature.
[c] Transition temperature.
[d] Measured from difference curve (cf. Fig. 1).
[e] Rate from ca. 115-165 C.
[f] Rate from ca. 170-180 C.

environments and for the difference curves are shown graphically in Figure 1. Weight losses under oxygen or nitrogen were recorded continuously. Data points taken at 2-, 5-, or 10-degree intervals in constructing the difference curves have been omitted for clarity. Weight change measurements for any one wax at a particular temperature for the three runs in either oxygen or nitrogen had a mean deviation from the average of 0.04%.

Thermogravimetric parameters and temperatures for each wax are listed in Table I. The "initiation temperature," T_i, is that temperature where oxidation begins as evidenced by a positive change from the extrapolated baseline, Figure 1. T_t, the "transition temperature," is the point of maximum gain in sample weight. Both T_i and T_t were obtained from the difference data. The slope of the line between T_i and T_t on the difference curve is a measure, in μg/C, of the reaction rate with oxygen. T_v, the "volatilization temperature," is that temperature where weight loss begins in the nitrogen environment. The temperatures recorded for T_v and T_i were taken as those points where a cumulative change exceeded the mean deviation of 0.04%, even though the incremental change was often less than 0.01%.

Unlike crambe oil, whose volatilization in nitrogen was negligible up to 200 C (5), the waxes under nitrogen (Fig. 1) showed appreciable weight loss at much lower temperatures. The one exception was the saturated wax, behenyl arachidate, which showed anomalous weight gain under nitrogen with an optimum at ca. 180 C. This weight gain under inert gas did not appreciably exceed the 0.04% mean deviation of the method. Of the unsaturated waxes, jojoba oils were the least volatile; limnanthes tetraene wax, the most. However, when BHT was added to jojoba oil B, the volatilization temperature was lowered considerably.

Under oxygen, only behenyl arachidate, sperm whale oil, and the jojoba oils registered weight gains above the extrapolated baseline. The weights of other waxes either leveled off or increased slightly, but any evidence of oxidation was recorded on the weight loss side of the extrapolated baseline. True points of maximum oxygen uptake (T_t) were not apparent from the oxygen curves alone. With the two crambe wax samples and sperm whale oil, T_t's from the difference curves were several degrees higher than those from the oxygen curves.

Except for behenyl arachidate and limnanthes tetraene wax esters (IV = 126.2) (S.P. Chang, private communication), all samples had IV's between 80 and 90, yet they exhibited rather different thermogravimetric behavior. Especially noteworthy is the large difference observed between untreated jojoba oil A and heat-treated oil B. Also, sperm whale oil, which consists of ca. 30% triglycerides and nonwax esters (9), took up much more oxygen at lower temperatures (0.2% at 125 C) than did any of the other waxes.

DISCUSSION

Recording the thermogravimetric behavior of wax esters in oxygen and nitrogen simplified their comparison and revealed subtle variations in volatility and oxidation characteristics that might otherwise have gone undetected by traditional tests for oxidative stability. The difference curves allowed precise discrimination between samples on the basis of initiation and transition temperatures and illustrated clearly that wax esters derived from seed oils are suitable sperm oil replacements as far as oxidative stability is concerned.

The constructed plots also made it easy to see the effects of a purification treatment on jojoba wax esters. It seems unlikely that heating with charcoal produced any significant chain shortening, because the treated oil, jojoba B, volatilized at about the same temperature as the untreated oil. Nevertheless, this treatment does reduce the natural oxidative stability of jojoba as evidence by 30-40 C reductions in the initiation and transition temperatures. Added antioxidant reversed the effect of heating and charcoal treatment, but even when jojoba oil B was supplemented with 1% BHT, its transition temperature still did not approach that of jojoba oil A. The oxygen uptake rate for the treated oil was much lower than that for the untreated oil, as if a certain portion of the oil had been destabilized by the treatment. Addition of BHT increased the rate of O_2 uptake. This result and the effect of BHT addition on initiation and transition temperatures suggest that heat treatment removed some natural oxidation inhibitors. Curiously, no such depressing effect of destabilized oil on the oxygen uptake rates of crambe oil mixtures is apparent in the data of Nieschlag et al. (5).

Even though the jojoba wax esters and the synthesized esters all had comparable molecular weights and (except the tetraene wax) all possessed the same level of unsaturation, they each exhibited rather novel thermal behavior. Like behenyl arachidate, the crambe wax esters followed a biphasic oxidation path; unlike the saturated wax, they seemed to be affected adversely, low T_v, by the initial low-level oxidation, which complicated the identification of an initiation temperature. It remains to be seen if the biphasic oxidation is due to saturated waxes in the crambe wax samples.

Structural effects on properties were most obvious in the volatility of waxes made from Limnanthes acids. Their tendency to volatilize at lower temperatures without affecting oxidative stability, Table I, was rather unexpected, but in retrospect, it is not illogical for these esters made from Δ5 or Δ5,Δ13 acids (10) to have different boiling points than those made from Δ11 or Δ13 acids.

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