Quantitaive and Qualitative Changes Associated with Heat Treatments in the Carotenoid Content of Paprika Oleoresins

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Quantitative changes in the red and yellow carotenoid pigment fractions of four paprika oleoresins were studied at four storage temperatures. At all four temperatures, there was an overall loss of pigmentation, which was more marked with increasing temperature. However, pigmentation loss was not qualitatively uniform. At temperatures below 60 °C, the rate of destruction of the yellow pigment fraction was higher than that of the red pigments. Above 60 °C, the order of lability of the two fractions was inverted and the red pigment fraction became the more unstable. Thus, treatments above this temperature increase the proportion of yellow pigments. Any heat treatment results in a decrease in the total pigment concentration, with the initial proportion of red and yellow pigments switching in favor of one or the other depending on the temperature used.

Keywords: *Paprika; oleoresin; carotenoids; kinetic; degradation*

INTRODUCTION

The commercial quality of an oleoresin of sweet paprika depends almost entirely on three basic characteristics: a high concentration of pigments, the correct proportions of these pigments, and a sufficient stability to guarantee that the initial chromatic characteristics last throughout its useful life. In simple terms, an oleoresin can be denominated of quality when its color can.

The color of the oleoresin is due mainly to nine major carotenoid pigments, naturally present in multiple forms of esterification (Mínguez-Mosquera and Hornero-Méndez, 1993). Esterification does not modify the chromatic properties of the pigment, but it does alter the physicochemical properties, particularly the polarity (Mínguez-Mosquera and Hornero-Méndez, 1994).

Up to thirty different pigments are involved in the physicochemical and chromatic properties of the pigments of paprika oleoresin, although in fact these are esterification isomers of the eight major xanthophylls. This apparently unimportant detail is determinant for the extraction of paprika oleoresin and for its use as colorant. When polyhydroxylated pigments are deesterified, only a low percentage is recovered in oleoresin extraction. The major carotenoid pigment in the pepper fruit is capsanthin, which, because of its structure, would show low affinity for lipid media (Goodwin, 1976), but due to the fact that capsanthin is mostly esterified, it is highly liposoluble, and therefore almost 100% extractable.

The oleoresin has different characteristics and properties depending on the type of fruit from which it is obtained (Mínguez-Mosquera et al., 1993; Mínguez-Mosquera et al., 1994). Fruit variety is the main factor determining the quantitative pigment composition of the oleoresin. With regard to qualitative composition, the genus Capsicum is very uniform in all its species; no exclusive pigments have been detected, except those of the genus itself, and pigments inconsistent with those of a ripe fruit appear only sporadically, usually as a result of indiscriminate harvesting.

Besides pigments, the fruit may contribute other types of compound directly affecting oleoresin quality (Rajpoot and Govindarajan, 1981; Jinpin et al., 1994). The pepper contains a certain amount of fatty material, generally glycerides, and polyphenolic liposoluble antioxidants, which can act as efficient protectors against oxidative loss of carotenoid pigments. The type of fruit used is thus a decisive factor in the initial and lasting quality of the oleoresin.

The oleoresin extraction process can be divided into three basic steps: drying of the fruit, extraction with organic solvents, and elimination of the solvent. The process is standardized but admits variation in temperature and time of drying, the extraction system used, and the conditions of solvent elimination. These variables can be altered to achieve minimum operation costs with maximum extraction of the sample. As in any high-temperature process, thermolabile compounds can be affected. In the case of paprika oleoresins, carotenoids are precisely the most affected compounds and are also the most responsible for the quality.

Because of their polyenic nature, carotenoid pigments are readily oxidized (Isler, 1971); in addition, their individual structure makes them react differently to environmental factors (Mínguez-Mosquera and Jarén-Galán, 1995). Carotenoids with a high degree of oxygenation have a high polarity and therefore a lower affinity for lipid media. The oleoresin is a lipophilic matrix so that the highly polar carotenoid pigments immersed in it are more readily exposed to the outside medium and a rapid oxidation to colorless products. However, the greater oxygenation enables a greater electron delocalization, which in energy terms can be understood as a better capacity to resist oxidative attack.

With appropriate fruit variety and extraction system, a high initial quality of the oleoresin can be achieved.

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10.1021/jf981105c CCC: $18.00
Published on Web 09/18/1999

However, product quality will deteriorate progressively from the beginning of storage, with the state and range of quality at any moment being unknown.

The present work monitors the qualitative and quantitative composition of four oleoresins subjected to different heat treatments. Increase in temperature inevitably accelerates pigment loss, lowering the quality of the product, but the qualitative model of deterioration is not known. The degradation reaction of the carotenoid pigments could affect them all similarly so that with increasing treatment time the oleoresin shows a decrease in coloring capacity while the pigment profile is maintained. On the other hand, it might be that deterioration is selective, which would imply, besides a change in coloring capacity, an altered chromatic quality of the oleoresin.

MATERIALS AND METHODS

Starting Material. The study was conducted on four commercial oleoresins, obtained from dried peppers of varieties for paprika and extracted with hexane. Samples were identified throughout the work as O1, O2, O3, and O4.

Storage Conditions. The experiments were carried out in thermostated chambers at 40, 60, 80, and 100 °C. This range of temperature covers all the industrial processes in which paprika oleoresin can be used as food colorant. At each temperature, 20 aliquots of each oleoresin were placed in heat-resistant, inert, airtight flasks, which were filled completely to prevent an increase in internal pressure with rise in temperature and to minimize any possible interference of the headspace. A batch of 20 samples per oleoresin was placed in each thermostated chamber.

Sampling. A sample of each oleoresin was taken at intervals depending on the temperature used. For the experiments at 100 and 80 °C, 10 samples were taken whose concentration was within the range between 100 and 10% retention of the initial pigments concentration, while for those at 60 and 40 °C, five samples were taken. The total number of samples was thus 120. The intervals of sampling ranged between 1 and 2 days for the samples stored at 100 °C and more than 200 days for those at 40 °C.

Extraction of Pigments and Saponification of the Samples. In each sample taken from storage, the carotenoid pigment content was analyzed in quadruplicate. For each replicate, about 0.1−0.15 g of oleoresin was weighed exactly and transferred to a 500 mL decanting funnel containing 50 mL of ethyl ether and 10 mL of internal standard (β-Apo-8′-carotenal) solution in light petroleum ether at a concentration of around 75 mg/mL. The samples were saponified by adding 25 mL of 10% KOH−MeOH, which was left to act for an hour with periodic stirring. Saponification was interrupted by adding distilled water, when two phases separated. The ether phase, containing the carotenoid pigments, was washed to neutrality. The initial aqueous phase and the subsequent washings were discarded, except when they were colored, in which case they were treated with ethyl ether and the resulting ether phase was combined with the main one.

The ether phase was concentrated to dryness under vaccum in a rotary evaporator, and the pigments were taken to 50 mL with acetone. An aliquot (1 mL) of the sample was kept in an airtight flask at −20 °C until its analysis by HPLC.

Separation of Carotenoid Pigments by HPLC. The system of separation and quantification used was that described by Mínguez-Mosquera and Hornero-Méndez (1993). The method uses a reverse-phase column (Spherisorb ODS2) of 25 cm in length, 0.46 cm internal diameter, and with a particle size of 5 μm. Separation was performed using an acetone−water binary gradient with a flow of 1.5 mL/min. The volume of sample injected was 5 μL, and detection was performed at 450 nm using a fixed-wave UV−visible detector.

Pigment Quantification. The individual concentrations of the nine major carotenoid pigments of the oleoresin were determined using an internal standard technique (Mínguez-Mosquera and Hornero-Méndez, 1993). Kinetic calculations were made from the total carotenoid concentration, obtained by summing the individual pigment concentrations. In the same way, the pigments were grouped in isochromatic fractions of red and yellow pigments. As each oleoresin, treatment temperature, and sampling time was represented by four replicates, the experiment yielded a total of 1440 concentration data points for the kinetic study. For comparison purposes, the ratio of the two isochromatic fractions in each sample was also calculated.

Measurement of the Degradation Reaction Rate of Each Pigment Fraction. For total pigments and each isochromatic fraction of each oleoresin, and for all temperatures, the change in concentration was related to treatment time. The systems assayed follow theoretical kinetics of zero, first, and second order. The result showing the best multiple correlation coefficient (R^2) was selected. For all the oleoresins and temperatures assayed, 48 equations were obtained for the destruction rate of red and yellow pigments and 16 equations for the change in ratio of red and yellow pigments.

RESULTS

The same qualitative pigment profile was maintained throughout the heat treatments in all the oleoresin samples. This profile was that described for pepper, paprika, or oleoresin and comprising mainly capsorubin, violaxanthin, capsanthin 5,6-epoxide, capsanthin, cis capsanthin, capsolutein, zeaxanthin, β-cryptoxanthin, and β-carotene. The pigments were grouped in two pigment fractions for the study of change in concentration with heat treatment. The fraction of red pigments comprised capsorubin, capsanthin, cis capsanthin, and capsanthin 5,6-epoxide; the remaining pigments were in the yellow fraction of carotenoid pigments.

Characteristics of the Original Oleoresins. Externally, the four oleoresins differed above all in their degree of viscosity. Oleoresins O1 and O4 were fluids, while O2 and O3 were much thicker. This may seem unimportant for pigment stability, but in fact it shapes the different physicodynamic characteristics of the medium where the carotenoid degradation reaction takes place.

Table 1 shows the initial pigment concentration in the four oleoresins studied. All the oleoresins had an initial variability in total pigment content of around 5%. Certain pigments, such as violaxanthin or capsolutein, showed higher variability, but as their contribution to the total pigments is in practice insignificant, the measured concentrations can be considered reliable. The initial carotenoid content of the oleoresins was, in decreasing order, O4, O1, O2, and O3. Taking oleoresin O4 as a reference, and assigning it a value of 100 in pigment richness, the sequence was 100, 97, 54, and 41%.

In all the oleoresins, the major pigment was capsanthin, between 41 and 38% of the total. When the carotenoid pigments were grouped by fraction, the red pigments contained capsanthin in an absolute majority with around 60−75%. The yellow pigments were more uniform; no pigment predominated, although there seemed to be a certain trend for zeaxanthin and β-carotene to be major and violaxanthin and capsolutein to be minor. With regard to the predominant isochromatic fraction, the red fraction comprised around 60−70% of the pigmentation in all the oleoresins, as seen in the ratio between red and yellow pigments, which ranged between 1.4 for oleoresin O1 and 1.9 for O3 and O4.

Table 1. Carotenoid Composition of the Oleoresins Used as Raw Material in the Thermoxidation Experiment

	concentration (g/kg)			
pigment	oleoresin 1	oleoresin 2	oleoresin 3	oleoresin 4
capsorubin	3.90 ± 0.72	3.66 ± 0.42	2.97 ± 0.42	5.99 ± 0.62
violaxanthin	3.82 ± 0.44	1.59 ± 0.84	1.52 ± 0.84	4.25 ± 0.98
capsanthin epoxide	3.01 ± 0.56	1.97 ± 0.35	1.66 ± 0.27	3.78 ± 0.67
capsanthin	32.51 ± 1.13	18.66 ± 0.78	14.61 ± 1.48	36.99 ± 2.24
cis-capsanthin	10.44 ± 0.67	4.18 ± 0.53	4.34 ± 0.42	10.39 ± 0.68
capsolutein	4.66 ± 0.19	2.77 ± 0.22	1.90 ± 0.74	5.51 ± 0.19
zeaxanthin	10.11 ± 1.01	4.67 ± 0.63	3.39 ± 0.64	8.80 ± 0.12
cryptoxanthin	6.70 ± 0.80	4.27 ± 0.37	2.42 ± 0.27	5.07 ± 0.17
β-carotene	9.87 ± 0.45	5.44 ± 0.13	3.39 ± 0.15	6.63 ± 0.30
total reds	49.85 ± 1.53	28.55 ± 1.48	23.58 ± 2.19	57.15 ± 2.88
total yellows	35.36 ± 1.30	18.58 ± 1.38	12.62 ± 2.28	30.26 ± 0.32
total pigments	85.23 ± 2.48	47.13 ± 1.85	36.21 ± 3.87	87.41 ± 2.85
ratio R/Y	1.41 ± 0.05	1.54 ± 0.16	1.89 ± 0.33	1.89 ± 0.10

The fact that each oleoresin has a specific carotenoid content and *R*/*Y* ratio demonstrates that they have been obtained from distinct varieties of fruit or by using a specific extraction procedure.

Kinetics of Degradation of the Total Carotenoid Content. The pigment concentration decreased progressively with time in all the oleoresins and more markedly as temperature increased. Relating the total pigment concentration to sample treatment time, the pattern of change in concentration with time gives a better mathematical fit when the first-order kinetics model is used. Table 2 shows the kinetic parameters for the degradation of the total carotenoid pigments in the four oleoresins at the four storage temperatures.

The kinetic parameters of the rate equations correspond to prior observations: the rate constant is negative and increases in absolute value with temperature, in accord with a degradative reaction favored by increased temperature. As the kinetic model is first order, the ordinate at origin in the rate equation is the natural logarithm of the theoretical initial pigment concentration, which for a given oleoresin should in principle be identical at different temperatures, although experimentally it ranges within a band of variability similar to that of the raw material.

The high level of significance in the correlation coefficients yielded by the model used to calculate the kinetic parameters means that the calculated equations reliably represent what really happens during the degradative reaction. The rate constants at each temperature allow oleoresin stability to be ranked, revealing similarities and differences in behavior in the various treatments. Other kinetic models have been tried for the best fit; the results for the zero order model could be considered mathematically acceptable, but systematically it has always given lower correlation coefficients.

In storage at 40 °C, all the oleoresins showed relatively low rate constants. Oleoresin 3 was by far the most unstable, almost tripling the value yielded by the other samples.

At 60 °C, the rate constants increased in absolute value, although not uniformly. Oleoresins 2 and 3 were practically identical in lability, with identical degradation rates. Oleoresins 1 and 4 also behaved very similarly, maintaining the behavior pattern shown previously.

At 80 °C, the rate constant of degradation of the total pigments in each oleoresin increased considerably. Again, different groups of similar behavior appeared. Oleoresin 4 showed maximum stability and had become clearly differentiated from oleoresin 1, which began to approach oleoresin 2 in lability. The maximum degradation rate was shown by oleoresin 3.

Table 2. Kinetic Constants[a] for the Degradation of the Total Carotenoid Pigments in Paprika Oleoresins Subjected to Four Temperatures

sample	slope (k_v)	ordinate (ln C_0)	R^2
Temperature = 40 °C			
oleoresin 1	−0.003 ± 0.000	4.446 ± 0.018	97.78
oleoresin 2	−0.003 ± 0.000	3.836 ± 0.022	96.76
oleoresin 3	−0.008 ± 0.000	3.639 ± 0.044	97.97
oleoresin 4	−0.002 ± 0.000	4.442 ± 0.018	95.57
Temperature = 60 °C			
oleoresin 1	−0.006 ± 0.000	4.465 ± 0.010	97.83
oleoresin 2	−0.011 ± 0.000	3.854 ± 0.013	98.84
oleoresin 3	−0.013 ± 0.000	3.611 ± 0.020	98.30
oleoresin 4	−0.005 ± 0.000	4.454 ± 0.010	97.06
Temperature = 80 °C			
oleoresin 1	−0.033 ± 0.001	4.357 ± 0.027	97.29
oleoresin 2	−0.032 ± 0.001	3.669 ± 0.039	94.57
oleoresin 3	−0.066 ± 0.003	3.576 ± 0.070	93.59
oleoresin 4	−0.023 ± 0.001	4.288 ± 0.036	90.84
Temperature = 100 °C			
oleoresin 1	−0.069 ± 0.002	4.271 ± 0.028	95.60
oleoresin 2	−0.122 ± 0.004	3.774 ± 0.050	95.66
oleoresin 3	−0.097 ± 0.003	3.350 ± 0.036	96.42
oleoresin 4	−0.058 ± 0.003	4.196 ± 0.041	88.26

[a] Integrated equation for first-order kinetics of degradation: $C = C_0 \exp(k_v t)$ (C is pigment concentration in g/kg; t is time in days).

Finally, at 100 °C, the rate constants show that the degradation reaction was extremely quick in all the oleoresins. Once again, oleoresins 1 and 4 showed similar stability, as did oleoresins 2 and 3, although in this case, oleoresin 2 was considerably more unstable than oleoresin 3, which at the lower temperatures had always been the most unstable.

In summary, two groups of oleoresin can be distinguished. Oleoresins 1 and 4 were the most stable, with oleoresin 4 systematically showing at all temperatures the minimum rate constant of degradation. In contrast, oleoresins 2 and 3 were highly unstable, their order depending on temperature. Initially, oleoresin 2 was more stable than oleoresin 3, but as the temperature increased, this order inverted and oleoresin 2 was much more unstable at 100 °C. The grouping by stability coincides with that by pigment concentration. The oleoresins with highest pigment content, O1 and O4, were also the most stable. It is not difficult to conclude that oleoresins O1 and O4 were extracted from fruits which, besides high pigmentation levels, include antioxidants that protect against pigment destruction, or that the extraction treatment was exhaustive but not

Table 3. Kinetic Constants[a] for the Degradation of the Yellow Fraction of Carotenoid Pigments in Paprika Oleoresins Subjected to Four Temperatures

sample	slope (k_v)	ordinate (ln C_0)	R^2
Temperature = 40 °C			
oleoresin 1	−0.004 ± 0.000	3.561 ± 0.024	97.25
oleoresin 2	−0.004 ± 0.000	2.920 ± 0.015	98.93
oleoresin 3	−0.010 ± 0.000	2.586 ± 0.048	98.16
oleoresin 4	−0.003 ± 0.000	3.357 ± 0.023	94.66
Temperature = 60 °C			
oleoresin 1	−0.006 ± 0.000	3.582 ± 0.011	97.39
oleoresin 2	−0.012 ± 0.000	2.938 ± 0.019	97.94
oleoresin 3	−0.014 ± 0.000	2.553 ± 0.027	97.22
oleoresin 4	−0.005 ± 0.000	3.396 ± 0.008	98.21
Temperature = 80 °C			
oleoresin 1	−0.028 ± 0.000	3.570 ± 0.024	97.03
oleoresin 2	−0.026 ± 0.001	2.825 ± 0.032	94.31
oleoresin 3	−0.061 ± 0.003	2.597 ± 0.077	91.32
oleoresin 4	−0.016 ± 0.001	3.307 ± 0.033	86.64
Temperature = 100 °C			
oleoresin 1	−0.045 ± 0.00	3.471 ± 0.022	93.81
oleoresin 2	−0.096 ± 0.005	2.933 ± 0.052	92.70
oleoresin 3	−0.071 ± 0.003	2.378 ± 0.033	94.31
oleoresin 4	−0.028 ± 0.003	3.211 ± 0.033	74.43

[a] Integrated equation for first-order kinetics of degradation: $C = C_0 \exp(k_v t)$ (C is pigment concentration in g/kg; t is time in days).

Table 4. Kinetic Constants[a] for the Degradation of the Red Fraction of Carotenoid Pigments in Paprika Oleoresins Subjected to Four Temperatures

sample	slope (k_v)	ordinate (ln C_0)	R^2
Temperature = 40 °C			
oleoresin 1	−0.003 ± 0.000	3.907 ± 0.017	97.42
oleoresin 2	−0.003 ± 0.000	3.327 ± 0.032	92.10
oleoresin 3	−0.007 ± 0.000	3.203 ± 0.043	97.60
oleoresin 4	−0.002 ± 0.000	4.061 ± 0.042	76.66
Temperature = 60 °C			
oleoresin 1	−0.006 ± 0.000	3.930 ± 0.011	97.63
oleoresin 2	−0.010 ± 0.000	3.343 ± 0.013	98.78
oleoresin 3	−0.013 ± 0.000	3.184 ± 0.020	98.08
oleoresin 4	−0.005 ± 0.000	4.027 ± 0.012	95.30
Temperature = 80 °C			
oleoresin 1	−0.037 ± 0.001	3.749 ± 0.033	96.93
oleoresin 2	−0.038 ± 0.001	3.107 ± 0.048	94.19
oleoresin 3	−0.068 ± 0.003	3.087 ± 0.068	94.33
oleoresin 4	−0.027 ± 0.001	3.821 ± 0.040	92.28
Temperature = 100 °C			
oleoresin 1	−0.100 ± 0.003	3.693 ± 0.034	96.95
oleoresin 2	−0.152 ± 0.005	3.222 ± 0.059	96.16
oleoresin 3	−0.122 ± 0.003	2.895 ± 0.036	97.70
oleoresin 4	−0.086 ± 0.004	3.750 ± 0.044	93.33

[a] Integrated equation for first-order kinetics of degradation: $C = C_0 \exp(k_v t)$. (C is pigment concentration in g/kg; t is time in days).

very drastic, thereby achieving a high yield without destroying the antioxidants present.

Kinetics of Degradation of the Isochromatic Fractions of Carotenoid Pigments. Tables 3 and 4 show the rate constants of degradation for the yellow and red fractions of carotenoid pigments in the oleoresin. Considering each fraction individually, the differences found in the rate constants with temperature were similar to those for the total carotenoid pigments. However, at 40 °C, the rate of degradation of yellow pigments was greater than that of red pigments in the four oleoresins. The yellow pigment fraction is therefore the more unstable. It can be concluded that storing the oleoresins at this temperature will result in a predominance of red pigments, although it must be remembered that there will inevitably be a loss of intensity in total color, as all the pigments are degraded.

Table 5. Kinetic Parameters[a] Determining the Change in the Ratio between the Red and Yellow Fractions of Carotenoid Pigments in Paprika Oleoresins Subjected to Different Temperatures

	constant of change in the parameter R/Y ($k_{vR/Y}$)			
temperature	O1	O2	O3	O4
40	0.001	0.001	0.003	0.001
60	0.000	0.002	0.001	0.000
80	−0.009	−0.012	−0.007	−0.011
100	−0.055	−0.056	−0.051	−0.058

[a] $R/Y_i = R/Y_0 \exp(t k_{vR/Y})$.

When the temperature was increased to 60 °C, in each oleoresin the rate constants of the two fractions were becoming more equal and also similar to their respectives degradation constant of total pigments. No changes were induced in the original pigment profile with treatment time, showing that treatments at this temperature cause quantitative changes but not qualitative ones in the color of the oleoresins.

At higher temperatures, the order of stability shown by the pigment fractions at 40 °C inverted. The yellow fraction became the more stable, and the red lost stability much more markedly with treatment time. This effect was sharper as the temperature increased; the situation can be summed up as that above 60 °C, treatment time causes proportionally greater loss of the red pigment fraction so that the apparent color of the resulting oleoresin becomes more yellow.

The difference in stability in red and yellow fractions of the carotenoid pigments can be due only to the different chemical structure of the two families of compounds. The difference between red and yellow pigments is not exclusively visual. As carotenoids, both families share the basic structure of C40 with 11 conjugated double bonds, and both groups include pigments with hydroxyl groups in their structure. The only differentiating feature is the presence of keto-carotenoids; all the pigments of the red fraction have ketonic groups in their structure, while no yellow pigment has this type of functional group. The presence of this group is probably the cause of the sharper increase in lability with temperature in the red pigments.

Kinetics of Change in the Ratio between Red and Yellow Carotenoid Pigments. The chromatic characteristics of the oleoresins are seen clearly in the study of the ratio of red to yellow (R/Y) pigments in the oleoresins. Each oleoresin has a specific initial value of R/Y depending on the fruit variety and extraction system used. Any later change in R/Y will be due to treatment. An increase in the value of this parameter shows that the yellow pigment fraction is degraded more intensely than the red. Conversely, decreasing values of R/Y show a preferential loss of red carotenoid pigments.

For a dynamic situation, in which the treatment constantly modifies the pigment concentrations over time, the parameter R/Y changes in function of the pigment fraction concentration at each moment. When the dependence between time and concentration of the red and yellow pigment fractions at a particular temperature is known, it is possible to establish the theoretical kinetics of change in R/Y with time and for each treatment temperature. Equation 1 shows the calculation of R/Y from the equations of degradation rate for red and yellow pigments.

$$\left(\frac{\text{red}}{\text{yellow}}\right)_i = \frac{C_{\text{red}}}{C_{\text{yellow}}} = \frac{C_{0\text{red}}\, e^{tk_{\text{vred}}}}{C_{0\text{yellow}}\, e^{tk_{\text{vyellow}}}}$$

$$\left(\frac{\text{red}}{\text{yellow}}\right)_i = \left(\frac{\text{red}}{\text{yellow}}\right)_0 e^{t(k_{\text{vred}} - k_{\text{vyellow}})} = \left(\frac{\text{red}}{\text{yellow}}\right)_0 e^{tk_{vR/Y}} \quad (1)$$

Table 5 shows the calculated values of the term $k_{vR/Y}$ for each oleoresin and treatment temperature. At 40 °C, the calculated value of $k_{vR/Y}$ is in all cases positive, indicating that the parameter R/Y_i increases with time. At 60 °C, the exponent is practically zero, making the parameter R/Y virtually constant. Above this temperature, the exponent is in all cases negative, and increases in absolute value with increasing temperature so that R/Y decreases with time and more quickly the higher the temperature. Using eq 1 and the parameters calculated in Table 5, just introducing the time as variable it is possible to calculate the specific value of R/Y for any treatment time.

From a combination of all the results, it can be concluded that the rate constant of degradation of the total pigments in an oleoresin is a valid parameter for revealing the quantitative changes involved. The quantitative composition of the oleoresin at a given time can be found knowing the rate constant at a given temperature. The qualitative composition, which ultimately decides the tonal quality of the oleoresin, is determined by the kinetic constant of change in R/Y, which reveals the proportion of red and yellow pigments throughout any heat treatment.

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Received for review October 5, 1998. Revised manuscript received June 21, 1999. Accepted June 21, 1999. The authors express their sincere gratitude to CICYT of the Spanish Government for supporting this research under the Project ALI97-0352.

JF981105C