Intensity of the Long-Wavelength UV Transition of Vitamin E

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The intensity of the long-wavelength UV transition of tocopherols is investigated using the interaction vector model. Intensity of α-tocopherol is the lowest of the series because it is the molecule which allows the most efficiently the effects of the alkyl groups to oppose the effects on intensity of the two alkoxy-like groups (a hydroxy group and a fused trimethyleneoxy moiety). Intensity of η-tocopherol is the highest because the only methyl substituent cannot attenuate the effects of the alkoxy-like groups.

Vitamin E (mainly α-tocopherol, but not exclusively, Fig. 1) is of major importance in food science and dietetics, since its deficiency could lead to strong diseases. Although many questions should receive answers to be sure of the extent of the role of this vitamin in human nutrition, it has been known for a long time that vitamin E is a powerful antioxidant and certainly assumes such a role in human metabolism, preventing, for example, from oxidative destruction of carotene and vitamin A. Vitamin E favours the absorption of iron, with positive incidence on the stability of biological membranes. Its interest can be evaluated by the fact that in the whole fields of scientific research four hundred research papers have been published during the last two years. As concerns the aims of our laboratory, the interest of these papers ranges from meat science [1] to the influence of cooking on the content of α-tocopherol in dry vegetables [2], the microwave roasting effects on the composition of tocopherols in a soya bean [3], the improvement of the yield of α-tocopherol from natural sources [4], medicine [5], *etc.* Surprisingly, although its role on human longevity has been underlined, vitamin E has never been thoroughly studied from the UV spectroscopic point of view. Particularly, little is known about the intensity of the near UV long-wavelength transition of tocopherols, transition which arises from the benzene chromophore (Fig. 2). The aim of this paper is only to reach some understanding of a basic behaviour which has been neglected till now, that is to say the origin of the intensity of the long-wavelength UV transition, and the intensity differences when considering the various types of tocopherols. For example, a question to which one should bring an answer is: why the intensity of α-tocopherol (ε_{sm} = 3180) is the lowest of the series, and on the contrary, why that of η-tocopherol is the highest one (ε_{sm} = 4190)?

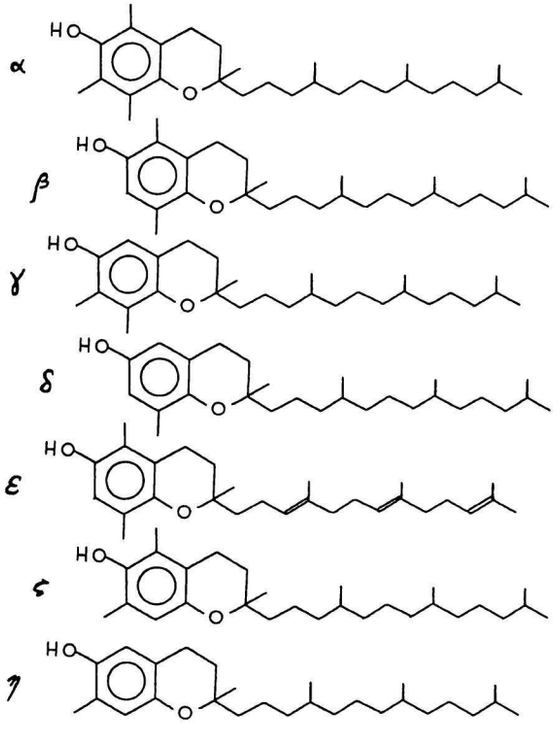

Fig. 1. Tocopherols.

THE SECONDARY TRANSITION AND THE INTERACTION VECTOR MODEL (IVM)

The Secondary Transition of the Benzene Chromophore

The intensity of the secondary transition (towards 255 nm for the benzene molecule itself) obeys a complex scheme. It is a forbidden transition because of

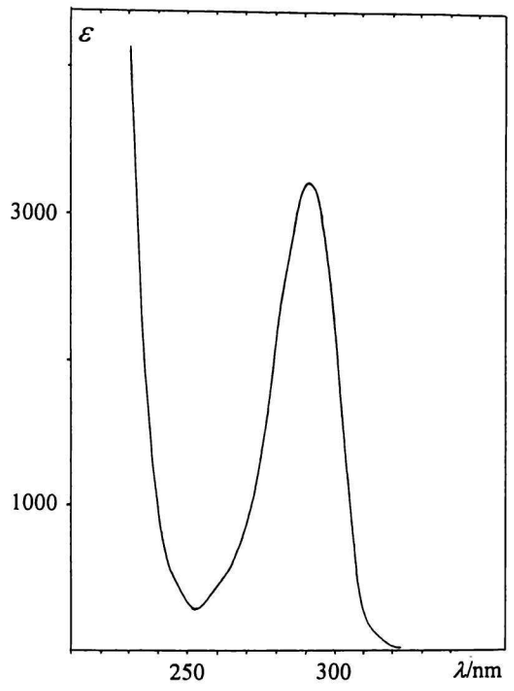

Fig. 2. The near UV spectrum of the secondary transition of the benzene chromophore of α-tocopherol. Medium ethanol + H_2SO_4 (6.20×10^{-2} mol dm^{-3}). A basic medium would produce the enolate form the intensity of which is stronger owing to a greater perturbation imposed on the symmetry of the π system by the charge on the oxygen atom.

its D_{6h} symmetry, thus, its intensity is very low (benzene: $\varepsilon_{max} = 220$, $\varepsilon_{sm} = 110$, $\lambda_{max} = 255$ nm). The intensity of the transition increases all the more as the chromophore is distorted towards a new symmetry, provided this new symmetry allows the transition [6—10]. Long ago, *Sklar* [11] proposed a simple vector scheme (Fig. 3A*a*) to obtain a rough evaluation of intensity. The transition moment was assumed to be the vector addition of the individual contributions of the substituents. This evaluation was far too much qualitative to be efficient. So, intensity has been a puzzling challenge during many years for the experimentalist, unless he could use sophisticated quantum approaches, unfitted to his needs. The chemist involved in natural products, or food science studies needs to evaluate intensities on a practical basis, with only a light theoretical background. It has been shown, using a simple vector scheme within the *interaction vector model* [12, 13] (IVM), that it is possible. This model has been used in this work. Experiment is given as ε_{sm}, the maximum of the smoothed absorption curve (*Ballester* and *Riera* [14] (calculated value: $\varepsilon_{sm,c}$)).

The Interaction Vector Model [12, 13]

The π effects of a substituent change the interactions of the others with the π system of the chromophore and their influences on intensity. Within the IVM [12, 13] the new concept of *interaction vector* (Fig. 3A*b*) has been introduced, which takes into account the interaction of two given substituents. Actually, many natural products display a benzene chromophore with simple π-donating substituents (alkyl, —OR, or $—NH_2$ ...) and sometimes these molecules bear rings fused to the benzene one. The strain imposed by these rings induces specific behaviours [8, 9]. Thus, the concept of *strain vector* (Fig. 3) has been introduced, which takes into account the fact that a ring fused to the chromophore imposes a strain distorting the symmetry.

The vector moduli n of the basis vectors $\boldsymbol{n}$ for the substituents are

	$—CH_3$ (homo)	—OR (homo)	—OR ↔ $—CH_3$ (hetero)
basis vector	$n_C = 0.0980$	$n_O = 0.3900$	
ortho interaction vector	$n_{C,o} = 0.0060$	$n_{O,o} = 0.1330$	$n_{OC,o} = 0.0520$
meta interaction vector	$n_{C,m} = 0.0060$	$n_{O,m} = 0.0450$	$n_{OC,m} = 0.0240$
para interaction vector	$n_{C,p} = 0.0120$	$n_{O,p} = 0.1800$	$n_{OC,p} = 0.0630$

$—CH_2—CH_2—$ is considered as being a $—CH_3$.

An interaction vector lies on the line bisecting the angle of the two basis vectors involved in the interaction. Their directions are given in Fig. 3A*b*. Note the direction of the *para* interaction vector, opposed to the direction of the basis vectors.

n_C is the number of alkyl groups on the chromophore, and n_O the number of —OR groups. V is a vibrational component of intensity [14]. S and σ ($\sigma = S^{1/2}$) are increasing functions of the number of substituents. They are related to a sort of *photonic cross-section*. As much the π system is increased through conjugation, hyperconjugation, or coupling, as much the probability for the molecule and a photon to interact increases

$$V = 0.0180 + 0.0390\ K + 0.0030(n_C + n_O)$$
$$\text{if } n_O = 0\ K = 0;\ \text{if } n_O \neq 0\ K = 1$$

$$S = [5n_O/(4.8 + 0.2n_O^2)] + n_C/(4.8 + 0.2n_C^{(2+0.5n_O)})$$

The corresponding vector $\boldsymbol{S}$ displays the same direction as $\boldsymbol{n}$. a is defined as $a = n^{1.5}\sigma^{0.5}$, and b as $b = n(n + \sigma)/2$. Then $p = (a + kb)/(1 + k)$, with $k = d^6$, and $d = |n - \sigma|$.

When the pure electronic evaluation of the electronic transition moment is near to $n = 0$, there is still a weak absorption to take into account. It has been evaluated as $q = 0.006^{1+10n}$.

$\boldsymbol{R}$ is related to the fused ring effect. The calculation is done for the corresponding parent molecule with $—CH_3$ and —OR, and no fused ring. This leads to S,

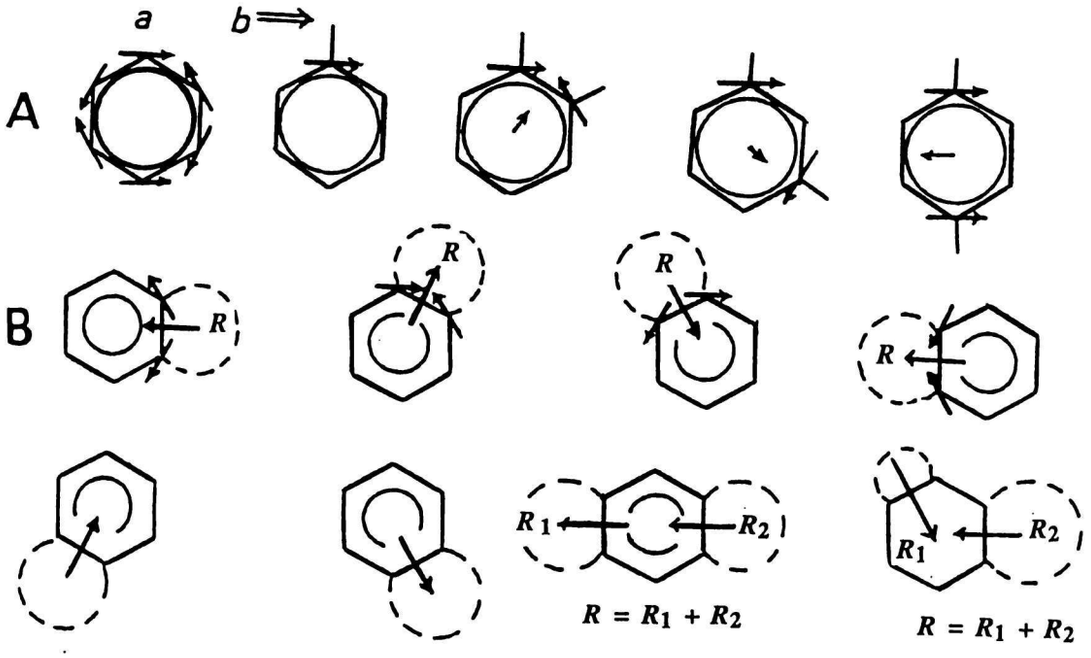

Fig. 3. A. *a*) Direction of the basis vectors. First drawing: the Sklar's basis virtual vectors pattern. Other drawings: *b*) the basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. **B.** Strain vectors corresponding to the fused ring. The basis vectors at the positions of substitutions have also been drawn, since the direction of a given strain vector depends on the direction chosen for the basis vector pattern.

σ, n, p, q, V. Then, the strain is taken into account as a vector $\boldsymbol{R}$ added to the vector $\boldsymbol{S}$: $\boldsymbol{S'} = \boldsymbol{S} + \boldsymbol{R}$. $\boldsymbol{R}$ is the sum of all the individual $\boldsymbol{R}_i$. The direction of $\boldsymbol{R}_i$ proceeds from the Sklar's vector pattern (Fig. 3B). R is given the next values in the IVM: +1.92 for an aliphatic five-membered fused ring, +0.55 for an aliphatic six-membered one, +0.55 for a benzodioxole-type one (methylenedioxy fused rings), and −0.1 for a benzodioxane-type one. When there is no fused ring $S' = S$ and $S'/S = 1$. A general relationship has been obtained

$$\varepsilon_{\mathrm{sm,c}} = 4905[1.025p(S'/S) + q + V]$$

and it has been useful on a wide range of molecules [12, 13, 15, 16].

IVM CALCULATIONS FOR VITAMIN E

Natural vitamin E is composed of several tocopherols, the proportions of which depend on the source. These molecules display an oxygen in the fused ring (Fig. 1), imposing a weak strain on the chromophore. Several methyl possible substitutions are observed. Two alkoxy-like substituents (a hydroxy group and a fused trimethyleneoxy moiety) lie in *para* positions. This allows to predict high values of intensity for the forbidden secondary transition, since the basis vectors of the two alkoxy groups add pointing to the same direction [12].

a) α-Tocopherol

The two alkoxy-like basis vectors ($n_{\mathrm{O}} = 0.3900$) (the hydroxy group and the fused trimethyleneoxy moiety) point to the same direction (Fig. 4). The alkyl substituents display a contribution which opposes to the alkoxy-like one. The resultant of the basis vectors is 0.5840. This value is decreased to 0.5440 when taking into account the interaction vectors (not forgetting that the *para* interaction vectors point to the direction opposed to the direction of the corresponding basis vectors), using the value $n_{\mathrm{O},p} = 0.1800$. As there are two alkoxy-like substituents, and four alkyl ones: $S = 2.0130$, $\sigma = 1.4188$, and $V = 0.075$. Calculations lead to $a = 0.4780$, $b = 0.5339$, $d^6 = 0.4481$, $p = 0.4953$.

As concerns the fused ring strain: $R = 0.225$. It has been shown in a preceding work [13] that R can be taken as the average of the effect of a tetraline-like six-membered fused ring (with no conjugated oxygen atoms) and a benzodioxane one (which displays two conjugated oxygen atoms). $\boldsymbol{R}$ and $\boldsymbol{S}$ display a 60° angle. Vector addition leads to $S' = 2.1344$. The ratio $S'/S = 1.0568$ shows that strain has little influence on intensity:

$$\varepsilon_{\mathrm{sm,c}} = 4905[1.025 \times 0.4953 \times 1.0568 + 0 + 0.075] = 3000$$

Calculation leads to a value already obtained [12] for the *para*-disubstituted OR molecule without other

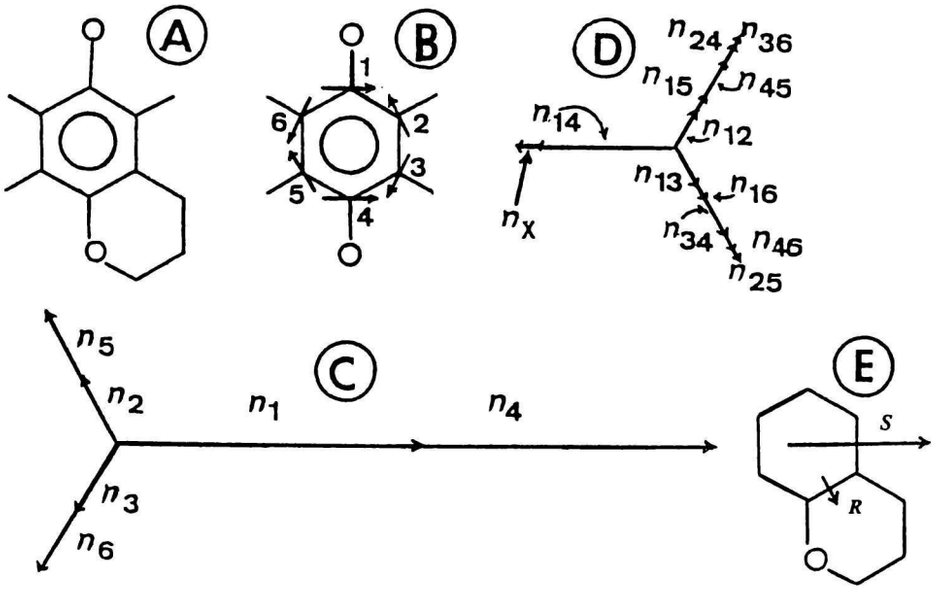

Fig. 4. **A.** The chromophore of α-tocopherol. **B.** The parent unstrained molecule of α-tocopherol. Directions of the basis vectors (only directions are shown; lengths are not proportional to the actual lengths). **C.** Basis vectors pattern: $n_1 = 0.39$, $n_2 = 0.098$, $n_3 = 0.098$, $n_4 = 0.39$, $n_5 = 0.098$, $n_6 = 0.098$. **D.** Interaction vectors pattern: $n_{12} = 0.052$, $n_{13} = 0.052$, $n_{15} = 0.024$, $n_{16} = 0.024$, $n_{34} = 0.052$, $n_{45} = 0.052$, $n_{24} = 0.024$, $n_{46} = 0.024$, $n_{14} = 0.18$, $n_{25} = 0.012$, $n_{36} = 0.012$. $n_x = n_{26} + n_{23} + n_{35} + n_{56}$: $n_x = 0.024$. Thus: $n = 0.544$. **E.** $S = 2.0130$, $R = 0.225$. Resultant: $S' = S + R$, thus $S' = 2.1344$.

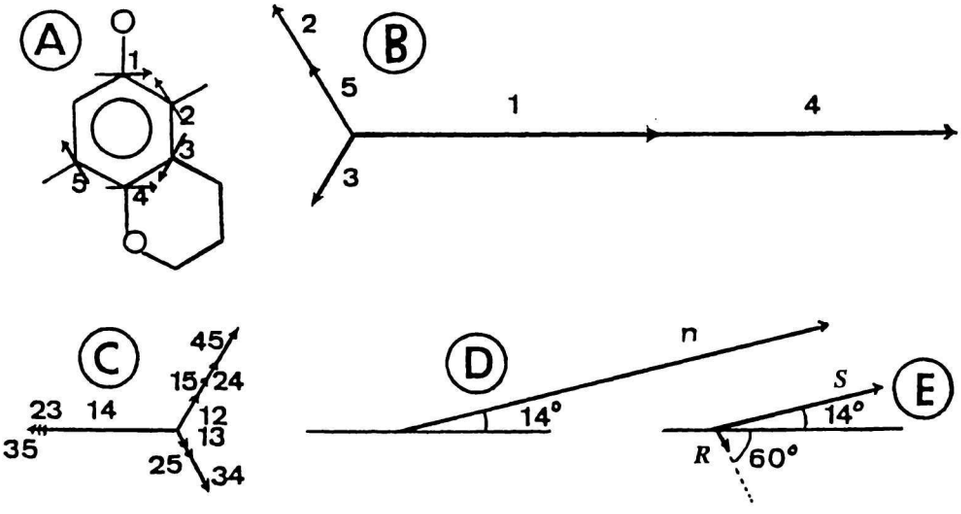

Fig. 5. **A.** The chromophore of β-tocopherol. Directions of the basis vectors for the unstrained parent molecule are shown (only directions are shown; lengths are not proportional to the actual lengths). **B.** Basis vectors pattern: $n_1 = 0.39$, $n_2 = 0.098$, $n_3 = 0.098$, $n_4 = 0.39$, $n_5 = 0.098$. Only indices are written in the graph, not the letters n. **C.** Interaction vectors pattern: $n_{12} = 0.052$, $n_{13} = 0.024$, $n_{15} = 0.024$, $n_{34} = 0.052$, $n_{45} = 0.052$, $n_{24} = 0.024$, $n_{14} = 0.18$, $n_{25} = 0.012$, $n_{23} = 0.006$, $n_{35} = 0.006$. **D.** $n = 0.5783$. **E.** $S = 2.0798$, $R = 0.225$. Resultant: $S' = 2.1526$.

substituents. The reason for such a behaviour, although in α-tocopherol the chromophore is crowded by substituents, which would lead to an increase of intensity through V and S, lies in the fact that the interaction vectors cancel each others because, precisely, of such a crowding. Furthermore, the contribution of the methyl basis vectors points in a direction opposed to the direction of the sum of the alkoxy basis vectors. Again, the methyl substituents are small enough not to introduce strong steric effects able to distort the symmetry (apart from the strain of the ring). The strain imposed by the fused ring is weak, thus the strain vector is short. Furthermore it displays a 60° angle with $\boldsymbol{S}$, which is far from colinearity, the best position to ensure a maximum increase of intensity.

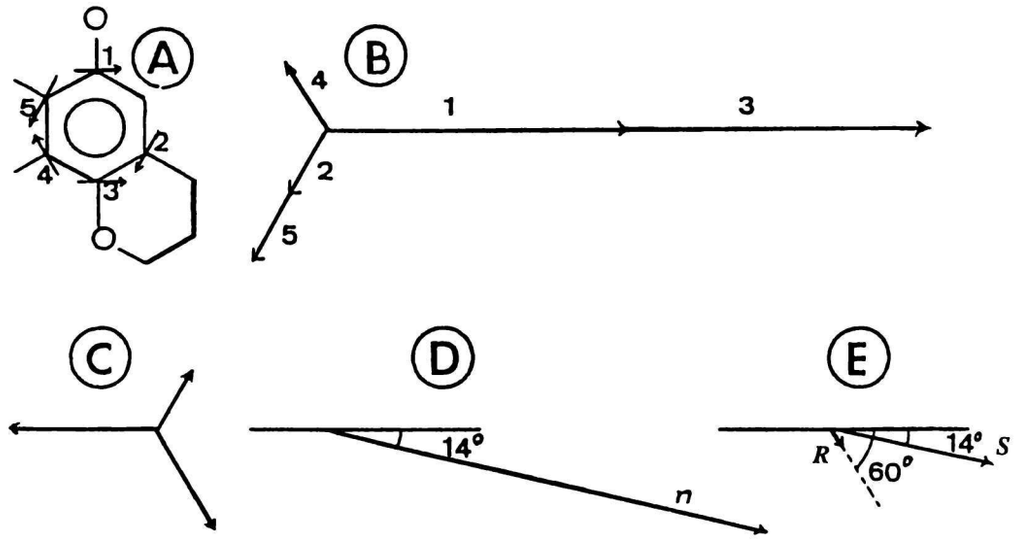

Fig. 6. A. The chromophore of γ-tocopherol. Directions of the basis vectors for the unstrained parent molecule are shown (only directions are shown; lengths are not proportional to the actual lengths). **B.** Basis vectors pattern: $n_1 = 0.39$, $n_2 = 0.098$, $n_3 = 0.39$, $n_4 = 0.098$, $n_5 = 0.098$. Only indices are written in the graph, not the letters n. One sees that this is a pattern symmetric to that of Fig. 5. **C.** Interaction vectors pattern. This pattern is symmetric to that of Fig. 5C. **D.** $n = 0.5783$. n is the same as in Fig. 5D but the orientation of $\boldsymbol{n}$ is different. **E.** $S = 2.0798$, $R = 0.225$. Resultant: $S' = 2.2421$.

b) β-Tocopherol

This molecule differs from the preceding one in displaying a vacant site in *ortho* position to the OH group (Figs. 1 and 5). The vector addition leads to $n = 0.5783$. $S = 2.0798$, $\sigma = 1.4422$, $V = 0.072 \rightarrow a = 0.5281$, $b = 0.5842$, $d^6 = 0.4157$, $p = 0.5446$. $\boldsymbol{S}$ and $\boldsymbol{R}$ display a 74.04° angle, as shown in Fig. 5. Thus $S' = 2.1526$, and $S'/S = 1.0350$.

$$\varepsilon_{\mathrm{sm,c}} = 4905[1.025 \times 0.5446 \times 1.0350 + 0 + 0.072] = 3187$$

The basis vector of the methyl in position *ortho* to the OH group in α-tocopherol imposes a vector contribution which opposes to the contribution of the alkoxy groups. When removing this methyl, as in β-tocopherol, intensity increases.

c) γ-Tocopherol

This molecule displays a vacant site which is in the *ortho* position to the OH group and in the *ortho* position to the aliphatic part of the fused ring (Fig. 6). The vector addition leads to a value $n = 0.5783$ which is the same as in β-tocopherol (using $n_{\mathrm{O},p} = 0.1800$ as above). The number, the nature of the substituents, and the relative orientations of their basis vectors are the same, too, as in β-tocopherol. Thus $S = 2.0798$, $\sigma = 1.4422$, $V = 0.072$ as above, and $p = 0.5446$. $\boldsymbol{S}$ and $\boldsymbol{R}$ display a 60 + 14.04° = 74.04° angle in β-tocopherol, now in γ-tocopherol this angle is 60 − 14.04° = 45.96°. This smaller value will change the vector addition $\boldsymbol{S'} = \boldsymbol{S} + \boldsymbol{R}$, which leads to $S' = 2.24207$, and $S'/S = 1.0780$. The ratio is higher than the preceding one. Thus, although n, p, V, R, and S are the same, the direction of $\boldsymbol{S}$ being changed, the intensity of γ-tocopherol should be higher than the intensity of β-tocopherol.

$$\varepsilon_{\mathrm{sm,c}} = 4905[1.025 \times 0.5446 \times 1.0780 + 0 + 0.072] = 3305$$

d) δ-Tocopherol

This molecule cumulates the vacant sites of the two preceding molecules (Fig. 7). $n = 0.572$, $V = 0.069$, $S = 2.0982$, and $\sigma = 1.4485$. Thus $a = 0.5206$, $b = 0.5779$, $d^6 = 0.4534$, and $p = 0.5385$. $S' = 2.2193 \rightarrow S'/S = 1.0577$.

$$\varepsilon_{\mathrm{sm,c}} = 4905[1.025 \times 0.5385 \times 1.0780 + 0.069] = 3202$$

e) ε-Tocopherol

As concerns the benzene chromophore this molecule should exhibit ultraviolet spectroscopic results similar to those obtained for β-tocopherol, *i.e.*

$$\varepsilon_{\mathrm{sm,c}} = 3187$$

f) ξ-Tocopherol

Although a methyl neighbours the alkyl part of the ring, the vector scheme leads to the same n as in γ-

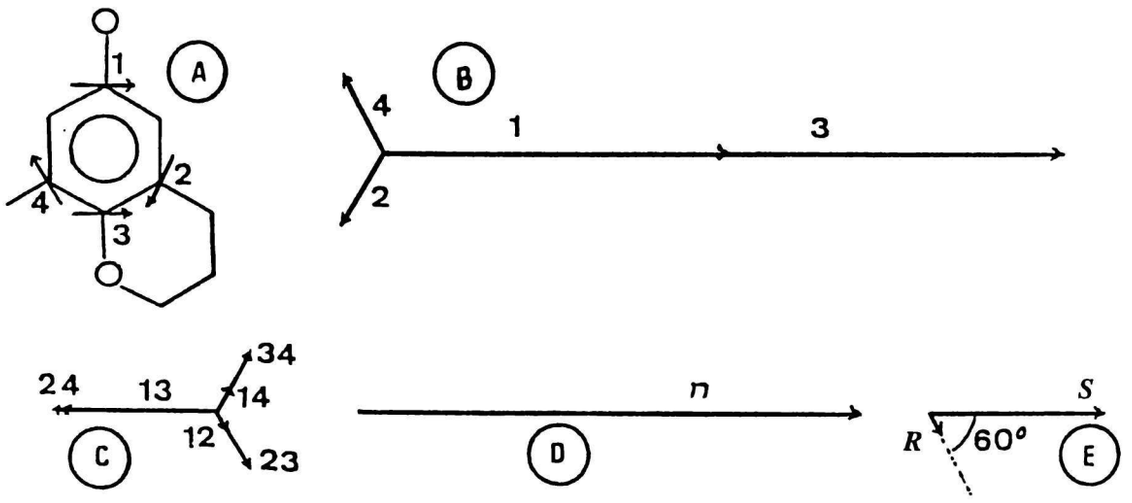

Fig. 7. **A.** The chromophore of δ-tocopherol. Directions of the basis vectors for the unstrained parent molecule are shown (only directions are shown; lengths are not proportional to the actual lengths). **B.** Basis vectors pattern: $n_1 = 0.39$, $n_2 = 0.098$, $n_3 = 0.39$, $n_4 = 0.098$. Only indices are written in the graph, not the letters n. **C.** Interaction vectors pattern: $n_{12} = 0.024$, $n_{13} = 0.18$, $n_{14} = 0.024$, $n_{23} = 0.052$, $n_{34} = 0.052$, $n_{24} = 0.006$. **D.** $n = 0.572$. **E.** $S' = 2.0982$, $R = 0.225$. Resultant: $S' = 2.2193$.

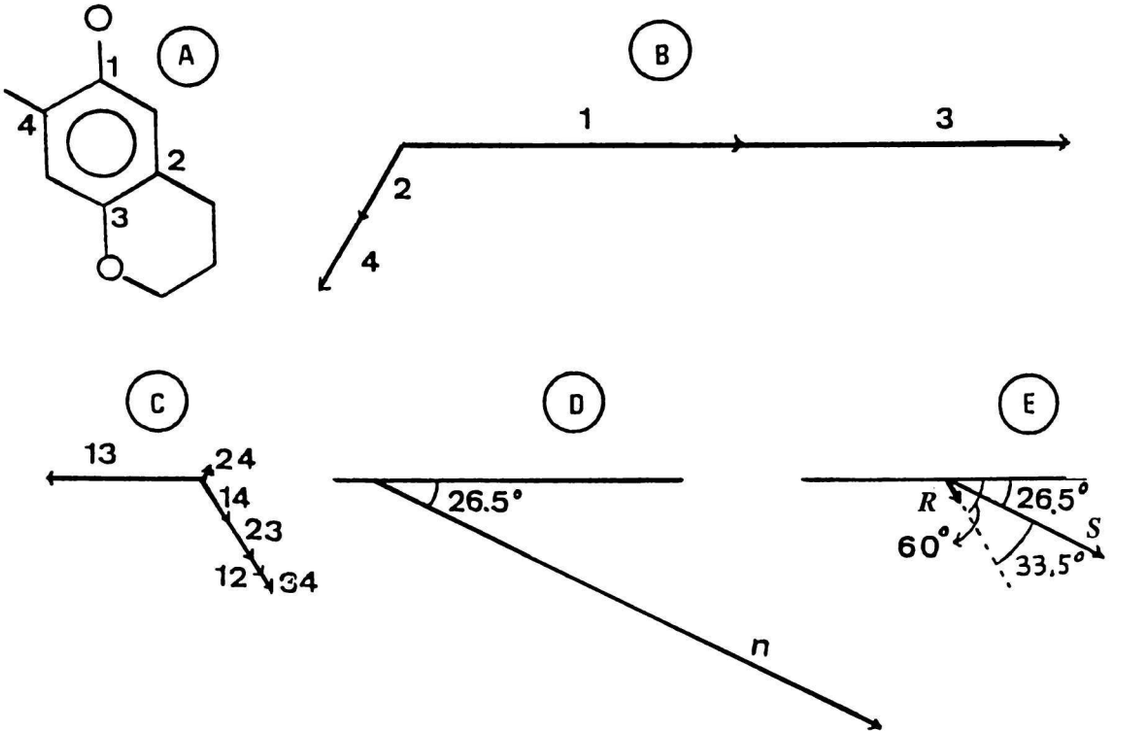

Fig. 8. **A.** The chromophore of η-tocopherol. **B.** Basis vectors pattern: $n_1 = 0.39$, $n_2 = 0.098$, $n_3 = 0.39$, $n_4 = 0.098$. Only indices are written in the graph, not the letters n. **C.** Interaction vectors pattern: $n_{12} = 0.024$, $n_{13} = 0.18$, $n_{14} = 0.052$, $n_{23} = 0.052$, $n_{34} = 0.024$, $n_{24} = 0.012$. **D.** $n = 0.6525$. **E.** $S = 2.0982$, $R = 0.225$. Resultant: $S' = 2.2892$.

tocopherol, the other factors being the same, too.

$$\varepsilon_{\mathrm{sm,c}} = 3305$$

g) η-Tocopherol

This molecule displays two vacant sites in positions where the basis vectors would be colinear (since they

Table 1. Smoothed Intensities of Tocopherols

Tocopherols[a]	IVM(I)[b] $\varepsilon_{sm,c}$	Δ_I/%	IVM(Ibis)	Δ_{Ibis}/%	IVM(II)	Δ_{II}/%	Experiment[c] ε_{sm}
α	3000	−4.2	3280	+3.1	3206	+2.4	3060 [18*a*], 3200 [17] (aver. 3130), 3180 (this paper)
β	3187	−11.5	3485	−3.3	3321	−7.8	3600 [18*b*]
γ	3305	−14.5	3614	−6.5	3553	−8.1	3865 [18*c*]
δ	3202	−12.7	3501	−4.6	3407	−7.7	3670 [18*d*]
ε	3187	−10.7	3485	−2.4	3321	−6.8	3570 [18*e*]
ξ	3305	−4.3	3614	+4.6	3553	+2.8	3455 [18*f*]
η	3875	−7.5	4237	+1.1	4078	−2.7	4190 [18*g*]

a) Only the greek letters have been written. *b*) $\varepsilon_{sm,c}$ (calculations), *c*) ε_{sm} (experiment). Medium for α-tocopherol: ethanol + H^+ (see Fig. 2), for others: ethanol.

are in *para* positions) and would oppose to the OR basis vectors contributions (Fig. 8). Thus this intensity should be higher than any other above intensity: $n = 0.6525$, $V = 0.069$, $S = 2.0982$, $\sigma = 1.4485$, $a = 0.6343$, $b = 0.6855$, $d^6 = 0.2544$, $p = 0.6447$. $\boldsymbol{S}$, as $\boldsymbol{n}$, displays a 33.52° angle with $\boldsymbol{R}$: $S' = 2.2892$ and $S'/S = 1.0910$, and

$$\varepsilon_{sm,c} = 4905[1.025 \times 0.6447 \times 1.0910 + 0.069] = 3875$$

COMPARISON BETWEEN CALCULATIONS AND EXPERIMENT

Literature data are given in Table 1 with the results of the above calculations (IVM(I)). Δ_I is the difference in % of the experiment, between calculation and experiment. Owing to the very solvating medium used (ethanol, or ethanol + H_2SO_4) and to the crowding of the chromophore which imposes many different interactions, there is a smoothing of the vibrational fine structure: $\varepsilon_{sm} \approx \varepsilon_{max}$.

All the calculated values are systematically lower than experimental ones. Four of them lay outside the range of 10 % difference with experiment, range which has been considered as satisfactory in the preceding works. Nevertheless, calculations are not far from experiment, and considerably better than could be obtained using the Sklar's model. We do not know intensities calculations on the secondary transition of tocopherols using sophisticated quantum approaches. In fact, one should put emphasis on the satisfactory fact that the IVM model predicts high values for tocopherols when experimental intensities are high, and low values for molecules displaying low intensities. Furthermore, one sees that using

$$\varepsilon_{sm,c} = 5363[1.025p(S'/S) + q + V] \quad \text{(IVM(Ibis))}$$

that is to say multiplying the theoretical values by an empirical factor 1.0934, would shift the whole values in the good range. This would be an epistemological *ad hoc* behaviour, but this would show the internal consistency of the model, and it is justified by the fact that although it is grounded on numerous experiments the factor 4905 is an empiric one. It is interesting to try to find if modifying some more specific parameter playing a part in all the molecules would allow a better agreement.

The modulus of the strain vector has been taken as $R = 0.225$. It would be necessary to increase this value to at least 0.35—0.40 to reach a much better agreement. This is such a change that it is very difficult to think that R is by itself the origin of discrepancy.

Other parameters have to be investigated: the basis vectors and interaction vectors of the alkoxy groups. Their moduli are very great (0.39 for the basis vector and 0.18 for the *para* interaction one) since such groups interact strongly with the π system. Assuming that these moduli are constant is a simplification. The interactions of a substituent with the others are taken into account by the interaction vectors, but interaction vectors between two given substituents should depend also on the other substituents. In fact, as the alkyl contributions are weaker, it is the inadequacy of the modulus of interaction vector of the alkoxy group, the highest modulus among the whole interaction vectors, which would lead to the more visible discrepancy. A decrease of the *para* alkoxy-like interaction vector from 0.18 to 0.15 would lead to a good fit with experiment (see Table 1, column IVM(II)). This is the same as increasing the basis vector from 0.39 to 0.405 for the —OH and —OR groups. What is a 0.03 decrease for the *para* interaction vector, a 17 % decrease of its modulus, is only a 3 % increase of the two basis vectors. It is difficult to parametrize so tightly, with definitely fixed values, and hope for reaching the same values as experiment on a large range of molecules. The whole effects cannot be perfectly masterized, and one has to accept to agree for smaller range of molecules provided they display the same general features.

CONCLUSION

It is possible now to answer the two questions which have been asked in the beginning of this pa-

per. Why α-tocopherol displays the lowest intensity and η-tocopherol the highest one? The answer lies mainly in the vector addition. First: α-tocopherol displays the lowest intensity because it is substituted in the whole positions of the benzene chromophore. Actually, owing to the positions of the methyl groups and the alkyl part of the ring, each one of the basis vectors of these alkyl groups displays a decreasing effect on the whole basis vector addition when added to the stronger alkoxy basis vectors. More, they display a basis vector sum which directly opposes the contribution of the —OH and the —OR (fused) two alkoxy-like groups. Owing to the number of interaction vectors and their directions, these vectors oppose, and their vector sum is very weak. They cannot change significantly the basis vector sum.

In a rough approach, owing to their possible positions a decreasing number of methyls will impose a decreasing quenching of the intensity of the secondary transition (intensity should increase). Actually, η-tocopherol displays the highest intensity because it has only one methyl substituent. Furthermore, its contribution is not directly opposed to the alkoxy groups, it is 120° to the contribution of these groups. It points in the same direction as the contribution of the alkyl group of the ring. In the δ-tocopherol molecule, too, there is only one methyl on the chromophore. But its vector contribution decreases more the intensity than in η-tocopherol. Actually, in δ-tocopherol the resultant of the interaction vectors opposes directly the contribution of the alkoxy groups when in η-tocopherol it displays only a 120° angle.

The fact that the number of substituents is greater in α-tocopherol than in the other molecules, contributes to increase the intensity through the increase of S (the photonic cross-section increases) and V, but it is a weaker effect than the vector addition effect.

REFERENCES

1. Higgins, F. H., Kerry, J. P., Buckley, D. J., and Morrissey, P. A., *Meat Sci. 50*, 373 (1998).
2. Atienza, J., Sanz, M., Herguedas, A., Alejos, J. A., and Jimenez, J. J., *Food Sci. Technol. Int. 4*, 437 (1998).
3. Takagi, S., Lenaga, H., Tsuchiya, C., and Yoshida, H., *J. Sci. Food Agric. 79*, 1155 (1999).
4. Woggon, W. D., *Angew. Chem., Int. Ed. Engl. 111*, 2881 (1999).
5. Hoffman, R. M. and Garewal, H. C., *Prev. Med. 29*, 112 (1999).
6. Vidal, B., Bastaert, G., and Brocard, J., *Spectrochim. Acta 35A*, 1043 (1979).
7. Denis-Courtois, D. and Vidal, B., *Spectrochim. Acta 39A*, 735 (1983).
8. Vidal, B., Conan, J.-Y., and Lamaty, G., *Aust. J. Chem. 41*, 1107 (1988).
9. Vidal, B., Vardin, J., and Darry-Henaut, A., *Chem. Pap. 44*, 603 (1990).
10. Vardin, J. and Vidal, B., *Chem. Pap. 46*, 301 (1992).
11. Sklar, A. L., *J. Chem. Phys. 10*, 135 (1942); Sklar, A. L., *Rev. Mod. Phys. 14*, 232 (1942); Förster, Th., *Z. Naturforsch. 2a*, 149 (1947); Platt, J. R., *J. Chem. Phys. 19*, 263 (1951); Petruska, J., *J. Chem. Phys. 34*, 1111 (1961); Petruska, J., *J. Chem. Phys. 34*, 1120 (1961); Stevenson, P. E., *J. Chem. Educ. 41*, 234 (1964); Stevenson, P. E., *Ph.D. Thesis*, Part I, University of Chicago, 1964.
12. Vidal, B., *Spectrosc. Lett. 27*, 41 (1994).
13. Vidal, B., *Spectrosc. Lett. 27*, 709 (1994).
14. Ballester, M. and Riera, J., *Tetrahedron 20*, 2217 (1964).
15. Vidal, B. and Wong Pin, F., *Spectrosc. Lett. 30*, 1301 (1997).
16. Vidal, B., *Spectrosc. Lett. 31*, 717 (1998).
17. Perkampus, H. H., *UV Atlas of Organic Compounds.* Spectrum J 6/4. Butterworth, New York, 1992.
18. Budavari, S. (Editor), *The Merck Index.* Rahway, USA, Merck and Co, 12th Edition 1996. *a*) Article 10159, *b*) 9632, *c*) 9633, *d*) 9634, *e*) 9635, *f*) 9636, *g*) 9638.