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A study of the IR spectra of the copigments of malvin chloride with organic acids

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The infrared spectra of the copigments of malvin with several organic acids: caffeic, ferulic, sinapic, chlorogenic, and tannic, were analyzed in order to elucidate the bonding of the molecules in the copigments. It was established that copigmentation is realized through hydrogen bonding between malvin molecules and the acids under study. The infrared spectra reveal that two groups of hydrogen bonds are formed, which include interactions of different molecular structures: hydroxy groups (bands around 3500 cm^{-1}) and oxonium ions of the molecules (bands below 3000 cm^{-1}). The formed hydrogen bonds were found to be of different strengths. The strengths of the hydrogen bonds were tentatively correlated with thermodynamic properties of the corresponding copigmentation reactions.

Keywords: malvin, organic acids, copigmentation, IR spectra.

INTRODUCTION

Flavonoids are the main pigments in the plant world, besides chlorophyll and carotenoids. Anthocyanidines and their glycosidized forms anthocyanins, responsible for the color of flowers and fruits, belong to one of the most widespread and most intensively colored pigment groups of the class of flavonoids.[1,2] Their structure *in vivo* is very complex, and depends on the heterogeneous composition of the plant tissues in which they exist. The stability of the structure of these molecules, *i.e.*, the stability of their color, depends on the possibility of complex formation, copigmentation, association, and autoassociation.[3,4]

Copigmentation is believed[5,6] to be one of the significant factors of stabilization of the flavylium structure *in vivo*. The structure of the copigments formed in the process has not been elucidated completely, but it is presumed[7–9] that one of the ways of molecular bonding is hydrogen bond formation. This situation has prompted investigations of the copigmentation of anthocyans.

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The present paper presents the results of a study of copigments of malvin with several organic acids: caffeic, ferulic, sinapic, chlorogenic, and tannic. The acids were chosen in agreement with the available literature data,[10,11] according to which the cinnamic acids mentioned, together with tannic acid, are part of plant tissue, in which they have a significant metabolic role. The fact that anthocyans, including malvin, are part of plant tissue, indicated the possibility that these molecules form copigments, which was spectroabsorptiometrically confirmed.[12,13]

The objective of the present study was to use the IR spectra of the copigments of malvin with the mentioned organic acids in an attempt to elucidate the nature of copigment formation, and to correlate the results obtained with the thermodynamic properties of the reactions established earlier.[12,13]

EXPERIMENTAL

Materials

The following substances were used in the experiments: malvin chloride (malvin, in the subsequent text) (97 %, Aldrich Chem. Co), caffeic acid (ICN Biochemicals), ferulic acid (ICN Biochemicals), sinapic acid (Merck), tannic acid (95 %, Aldrich Chem. Co), chlorogenic acid (Aldrich Chem. Co), sodium acetate (p.a., Merck), phosphoric acid (85 %, BDH Poole-England), methanol (Uvasol, min. 99 %, Merck), ethanol (Uvasol, min 95 %, Merck), sodium chloride (p.a., Merck), hydrochloric acid (Merck) and potassium biphthalate (p.a., Merck).

Solutions

The copigmentation reaction was conducted in buffer solutions of pH 2.50 and pH 3.65, which were chosen on the basis of earlier studies.[14] The buffer solutions of constant ionic strength (0.02 mol dm^{-3}) were obtained by mixing sodium acetate (0.02 mol dm^{-3}) with phosphoric acid (0.06 mol dm^{-3}). The pH values of these solutions were controlled using a pH-meter each time after mixing the components. The ionic strength (0.02 mol dm^{-3}) was controlled by the addition of sodium chloride. A stock solution of malvidin 3,5-diglucoside of $c = 2 \times 10^{-3}$ mol dm^{-3} was prepared in methanol, with addition of two drops of 0.1 % HCl (two drops from a 0.1 cm^3 pipette), and left to equilibrate in the dark for 1 h. Stock solutions of the organic acids ($c = 2 \times 10^{-3}$ mol dm^{-3}) were prepared in ethanol. These solutions were diluted to the required concentration (1×10^{-4} mol dm^{-3} for malvin, 6×10^{-3} mol dm^{-3} for cinnamic acids and chlorogenic acid and 1.5×10^{-3} mol dm^{-3} for tannic acid) by addition of the required buffer solution, either of pH 2.50 or pH 3.65. The mole ratio of the components in the copigment solutions was 1:60 (malvin: organic cinnamic acids and malvin:chlorogenic acid) and 1:15 (malvin:tannic acid).

IR spectra

IR spectra were recorded on a Perkin Elmer 983 G IR spectrophotometer. The samples of pure components were recorded using the KBr technique with a ratio of 1 mg: 150 mg (sample: KBr). The pure buffer solutions as well as the buffer solutions containing the copigments were lyophilized by a standard procedure.[15] The volume of all the lyophilized solutions was 1.5 cm^3. The IR spectra of the obtained solids were recorded using the KBr technique, as in the case of the pure substances.

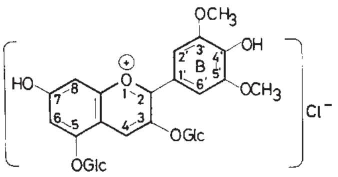
The spectra were recorded under conditions generally applied in quantitative work. IR spectra were recorded in the region from 4000–250 cm^{-1}, but the bands in the region 4000–2000 cm^{-1} were analyzed in detail, since they are characteristic of OH groups of various protonic species that undergo hydrogen bonding interaction. Another region of interest was the region from 1800–1600 cm^{-1}, characteristic of the bending vibrations of the same group. Since the bands in this region are wide and complex, they were resolved using Lorentz-Gauss band shapes.

pH Measurements

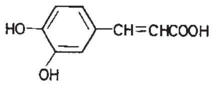
The pH of the solutions was measured by an Iskra MA 5730 pH meter with a combined electrode. The standard buffer solution of potassium biphthalate was used for calibration of the pH meter.

RESULTS AND DISCUSSION

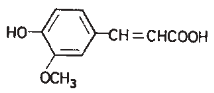
As the copigmentation reaction of malvin with the organic acids under study (see the structures in Scheme I) has been spectroabsorptiometrically confirmed,[12,13] the IR spectra of these systems were analyzed in this study. The IR spectra of the pure components were analyzed first, followed by the spectra of the lyophilized buffer solutions, lyophilized malvin solutions at pH 2.50 and pH 3.65, and the spectra of the lyophilized copigment solutions at those pH values. The pH values were chosen on account of our earlier investigations,[14] as well as available literature data,[8,16,17] according to which the process of copigmentation *in vivo* occurs in acidic and moderately acidic environments, which was the reason for investigating the copigments at pH values close to the ones of natural plant juices.



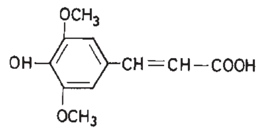
Malvin (Glc-glucose)



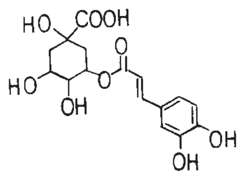
Caffeic acid



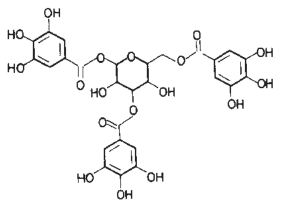
Ferulic acid



Sinapic acid



Chlorogenic acid



Tannic acid

Scheme I. Structural formulae of the compounds.

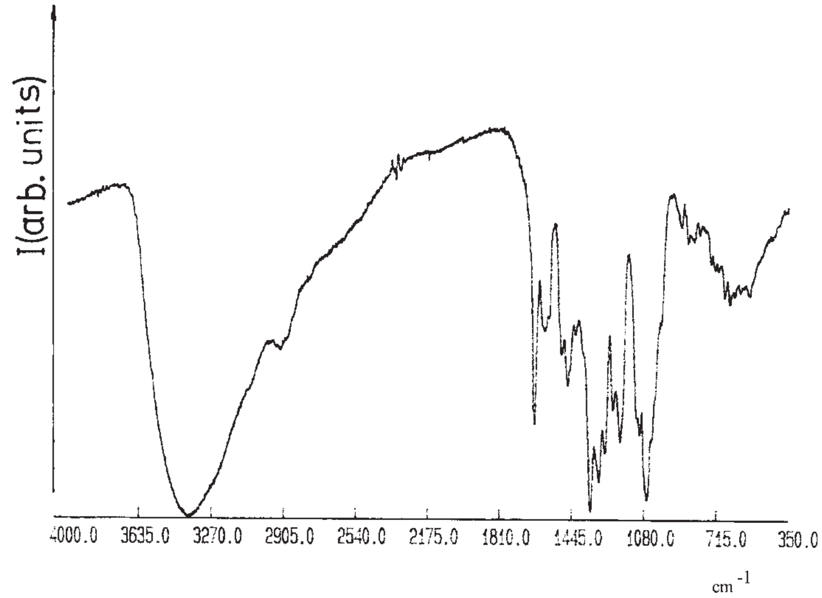


Fig. 1. IR spectrum of pure malvin.

Analysis of the spectra shows that hydrogen bonding is present even in the malvin molecule itself (Fig. 1). The IR spectrum of pure malvin features a broad intensive band at 3388 cm^{-1}, which is characteristic of the hydrogen bond, according to its position and structure. The spectra of the lyophilized solutions of acetate buffer at pH 2.50 and pH 3.65 are presented in Fig. 2. The appearance of the spectrum between 4000 cm^{-1} and 1600 cm^{-1} does not change significantly regarding the number and positions of the bands. The spectrum of the lyophilized solution of acetate pH 2.50 buffer features a sharp, and relatively intensive, band at 1640 cm^{-1} which corresponds to the bending

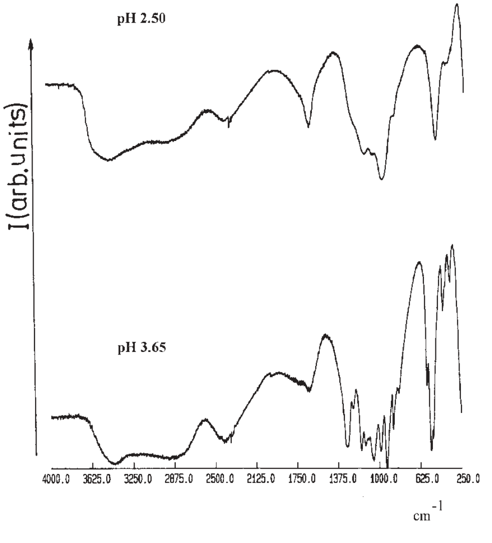


Fig. 2. IR spectra of the pure buffers at pH 2.50 and pH 3.65.

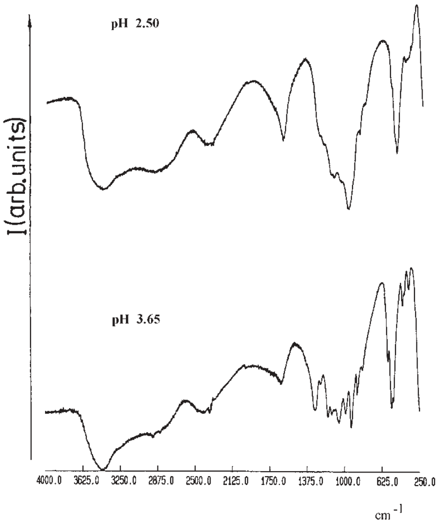


Fig. 3. IR spectra of malvin in the buffers at pH 2.50 and pH 3.65.

vibrations of the OH group. In the spectrum of the lyophilized pH 3.65 buffer solution the same band is of lower intensity and is shifted towards somewhat higher wavenumbers.

The IR spectra of the lyophilized solutions of malvin in buffers at pH 2.50 and pH 3.65 are presented in Fig. 3. The appearance of the spectra is significantly different from the spectrum of pure malvin (Fig. 1). Bands characteristic of hydrogen bonds by their position and intensity appear in the 4000 cm^{-1} to 2000 cm^{-1} region. As all spectra were recorded with the corresponding buffer as reference, and the experiments were carried out under the conditions for quantitative work, the bands observed in the spectra of malvin in lyophilized buffer solutions can be attributed to hydrogen bonds between the buffer and malvin. The spectra of lyophilized solutions of both pH values show bands in the 4000 cm^{-1} –1600 cm^{-1} region at approximately the same positions, with a somewhat greater width and intensity of the bands in spectrum of the pH 2.50 buffer. The appearance of the spectrum of the lyophilized solutions of malvin in the buffers used can be accounted for both by the concentration relationship of the buffer components (which were present in excess) and malvin itself. These systems serve as references for comparison with the spectra of the lyophilized solutions of the copigments formed at both pH values.

The spectra of the pure acids are given in Fig. 4 and Fig. 5. The difference between the spectra of the cinnamic acids (caffeic, ferulic, and sinapic, Fig. 4a–4c) and chlorogenic and tannic acids (Fig. 5a–5b) is evident. The spectra of the cinnamic acids feature relatively narrow and intensive bands in the region from 3500 cm^{-1} to 3200 cm^{-1}. These bands appear between 3401 cm^{-1} and 3201 cm^{-1} in the case of caffeic acid (Fig. 4a). A narrow and intensive band at 3434 cm^{-1}, with a shoulder at around 3320 cm^{-1}, appears in the spectrum of ferulic acid (Fig. 4b), whereas such bands appear at 3383 cm^{-1} and 3311 cm^{-1} in the spectrum of sinapic acid (Fig. 4c). This structure of the spectra may indicate the existence of two interaction centers and/or two ways of hydro-

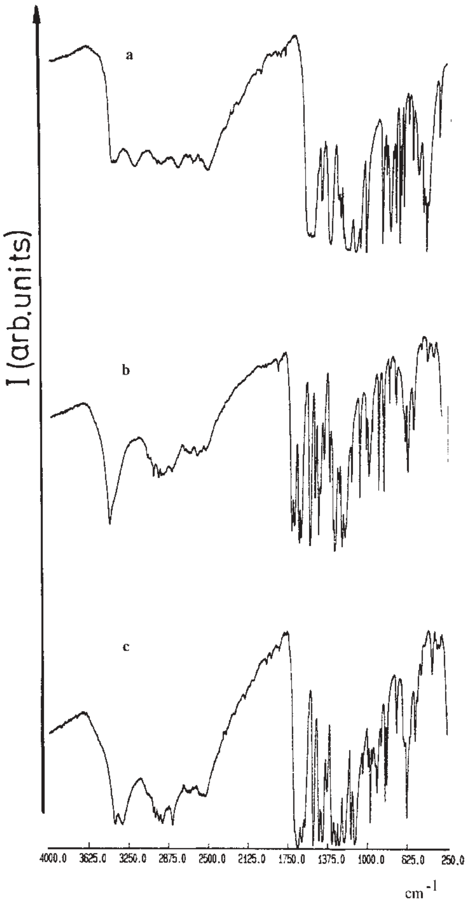


Fig. 4. IR spectra of a) caffeic acid b) ferulic acid c) sinapic acid.

gen bonding between the molecules of the cinnamic acids. Although it was not directly investigated, the formation of intramolecular bonds could be deduced from the structures of the molecules. The characteristic band of the stretching carbonyl group vibration is significantly shifted towards lower wavenumbers (significantly below 1700 cm^{-1}), which may indicate a strong resonance effect in the structure of the carbonyl group. The spectra of chlorogenic (Fig. 5a) and tannic (Fig. 5b) acids feature a broad and intensive band around 3400 cm^{-1}, which can be assigned to the hydrogen bond of the dimeric form of the acids. A weak band around 3500 cm^{-1} also appears in the chlorogenic acid spectrum, which is characteristic to terminal OH groups. This is expectable, given the structure of chlorogenic acid. The band of the carbonyl group stretching vibration appears around 1710 cm^{-1}, characteristic to organic acids which do not have a pronounced bipolar structure of the carbonyl group.

The spectra of the lyophilized solutions of the copigments differ significantly from the spectra of the pure components. In the region from 4000 cm^{-1} to 2000 cm^{-1}

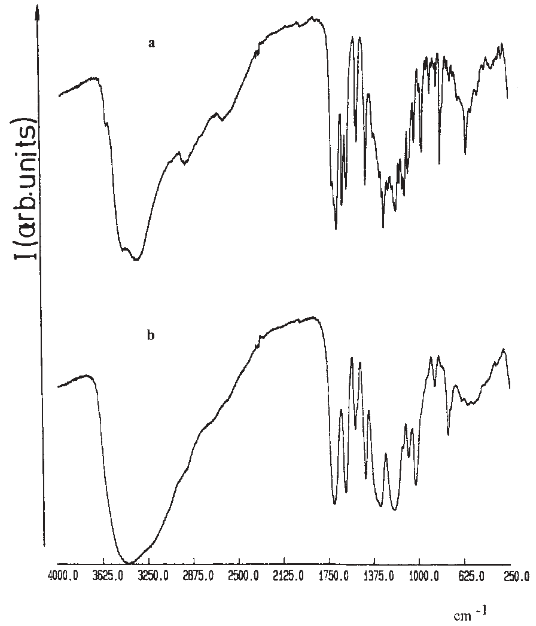


Fig. 5. IR spectra of a) chlorogenic acid b) tannic acid.

the number of bands decreases and in all spectra the band of the carbonyl group stretching vibration is significantly shifted towards lower wavenumbers, and overlaps with the band of the OH bending vibration that appears around 1640 cm^{-1}. The spectra of some of the lyophilized solutions of the copigments are given in Fig. 6.

Since the broad complex bands that appear in the spectra of the lyophilized malvin solutions, as well as in the spectra of the lyophilized copigments solutions, indicate the

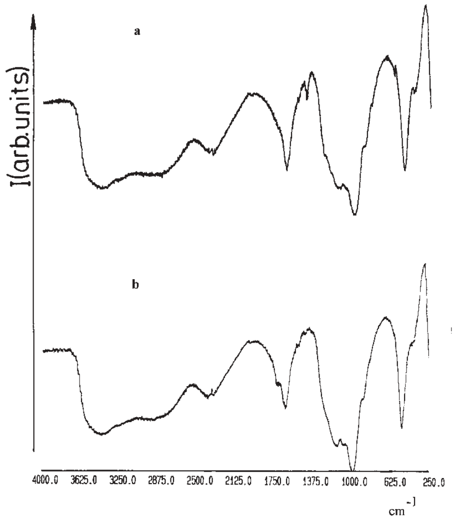


Fig. 6. IR spectra of the copigments formed at pH 2.50 a) malvin-caffeic acid b) malvin-chlorogenic acid.

presence of more than one hydrogen bond, the spectra in the 4000 cm^{-1} to 2000 cm^{-1} region were deconvoluted. This was undertaken in order to determine the exact positions of the individual bands, v, and their characteristic parameters ($R_{O\cdots O}$ distances[18]). The values of these parameters are presented in Tables I and II, for both pH values.

The deconvoluted spectra reveal the existence of two groups of bands, at both pH values, which are significant for the structures of the interacting molecules, malvin and the organic acids. The bands in the region around 3500 cm^{-1} are characteristic of hydrogen bond formation *via* terminal OH groups (H–O--- H bonds), or *via* the carboxyl group in the dimeric form of the acids. The bands that appear below 3000 cm^{-1} are characteristic of the oxonium structure of the molecule. As the formation of the hydrogen bonds causes a shift in the wavenumber of the stretching vibration of the corresponding groups in the molecule towards lower values, the criterion for the strength of the hydrogen bonds in the copigments was associated only with the bands that had the greatest shift towards lower wavenumbers compared to the reference systems. Such shifts of the individual bands can indicate the strengthening of the hydrogen bonds with respect to the ones in the reference systems (see Tables I and II).

The first analysis of the IR spectra of the lyophilized copigment solutions after deconvolution, for the case of the pH 2.50 buffer, shows similar behavior of the band around 3500 cm^{-1} in the spectra of the following copigments: malvin-chlorogenic acid, malvin-ferulic acid, and malvin-tannic acid. In the deconvoluted spectra of these copigments this band undergoes a shift towards lower wavenumbers, indicating a strengthening of the hydrogen bond with respect to the reference, according to the sequence malvin-tannic acid > malvin-ferulic acid > malvin-chlorogenic acid (Table I). In the spectra of the copigments malvin-caffeic acid and malvin-sinapic acid, the same band shifts towards higher wavenumbers, that is the formed hydrogen bond weakens, and it can be said that the structures of the molecules associated with the bands in this region are not crucial for copigment formation. The values obtained for the $R_{O\cdots O}$ distances of the band at around 3500 cm^{-1} are, in the spectra of all copigments, greater than 2.9 Å, which, according to Novak, characterizes them as weak bonds.[18] The band at around 3400 cm^{-1} shifts towards higher wavenumbers only in the spectra of the malvin-sinapic acid copigment. In the deconvoluted spectra of other copigments the same band shifts towards lower wavenumbers, *i.e.,* the formed hydrogen bond strengthens according to the sequence: malvin-chlorogenic acid > malvin-ferulic acid > malvin-caffeic acid (Table I). The calculated $R_{O\cdots O}$ distances of this band are greater than 2.8 Å in all copigments (weak bands[18]).

Differences in the behavior of the deconvoluted bands below 3000 cm^{-1} can also be observed. In the deconvoluted spectra of the malvin-chlorogenic acid copigment, the band at around 2800 cm^{-1} shifts significantly towards lower wavenumbers ($\Delta v = -86.4$ cm^{-1}), whereas the same band has a smaller shift in the spectra of the malvin-caffeic acid copigment ($\Delta v = -18.5$ cm^{-1}, Table I). In these copigments the oxonium structure of the molecules associated with this band can be considered significant for their formation. In the deconvoluted spectra of other copigments the same band undergoes a positive shift. The calculated $R_{O...O}$ distances are found to be in the interval 2.6 Å < $R_{O\cdots O}$ < 2.7 Å. Such hy-

TABLE I. Parameters of the most intense bands in the spectra obtained after deconvolution (pH 2.50)

	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$
Malvin+Buffer	3556.4	> 2.9	/	3437.1	> 2.8	/	2899.5	> 2.6	/	2401.3	< 2.6	/
Malvin+Chlorog.a.	3558.7	> 2.9	– 2.3	3410.0	> 2.8	– 27.1	2813.1	> 2.6	– 86.4	2404.2	< 2.6	2.9
Malvin+Caff.a	3560.4	> 2.9	4.0	3433.0	> 2.8	– 4.1	2881.0	> 2.6	– 18.5	2390.9	< 2.6	– 10.4
Malvin+Fer.a.	3548.3	> 2.9	– 8.1	3430.9	> 2.8	– 6.2	2921.7	> 2.6	22.2	2375.0	< 2.6	– 26.3
Malvin+Sinap.a.	3557.3	> 2.9	0.9	3439.0	> 2.8	1.9	2920.0	> 2.6	20.5	2380.0	< 2.6	– 21.3
Malvin+Tann.a.	3545.8	> 2.9	– 10.6	3430.9	> 2.8	– 6.2	2953.9	> 2.6	54.4	2395.3	< 2.6	– 6.0

TABLE II. Parameters of the most intense bands in the spectra obtained after deconvolution (pH 3.65)

	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$	ν/cm^{-1}	$R_{\mathrm{O\text{-}O}}/\mathrm{Å}$	$\Delta\nu/\mathrm{cm}^{-1}$
Malvin+Buffer	3525.0	> 2.9	/	3421.6	> 2.8	/	2916.5	> 2.6	/	2407.0	< 2.6	/
Malvin+Chlorog.a.	3546.0	> 2.9	21.0	3429.7	> 2.8	8.1	2854.8	> 2.6	– 61.7	2426.9	< 2.6	19.9
Malvin+Caff.a.	3535.4	> 2.9	10.4	3417.0	> 2.8	– 4.6	2953.9	> 2.6	37.4	2411.0	< 2.6	4.0
Malvin+Fer.a.	3522.4	> 2.9	– 2.6	3430.0	> 2.8	8.4	2923.1	> 2.6	6.6	2415.5	< 2.6	8.5
Malvin+Sinap.a.	3516.9	> 2.9	– 8.1	3418.2	> 2.8	– 3.4	2928.9	> 2.6	12.4	2417.9	< 2.6	10.9
Malvin+Tann.a.	3520.2	> 2.9	– 4.8	3421.2	> 2.8	– 0.4	2941.2	> 2.6	24.7	2402.7	< 2.6	– 4.3

drogen bonds are of medium strength.[18] The band around 2400 cm^{-1}, also characteristic of the oxonium structure of the molecules, shows a negative shift in the spectra of the copigments in the following order: malvin-ferulic acid > malvin-sinapic acid > malvin-caffeic acid > malvin-tannic acid. The same band undergoes only a small positive shift in the spectra of the malvin-chlorogenic acid copigment (see Table I).

The parameters obtained from the deconvoluted spectra indicate that hydrogen bonds are formed in the copigmentation processes at pH 2.50, and that there are probably more than one kind of such bonds present in the systems. These bonds can be formed via free terminal OH groups (corresponding to the bands around 3500 cm^{-1} and/or 3400 cm^{-1}, and/or *via* the oxonium ions of the molecules (corresponding to the bands at around 2800 cm^{-1} and/or 2400 cm^{-1}) (see Table I). At pH 2.50 the greatest negative shift, with respect to the reference, is associated with the bands that appear in the deconvoluted spectra of the malvin-chlorogenic acid copigment (bands at 3410 cm^{-1} and 2813.5 cm^{-1}). This indicates the formation of strong hydrogen bonds, *i.e.*, a great affinity of the reactants in this copigment, which is in agreement with the large enthalpy change in the reaction ($\Delta H = -$ 118.8 kJ/mol). In the deconvoluted spectra of the other copigments, the shifts of the relevant bands are smaller, and the formed hydrogen bonds are weaker, probably as a consequence of the lower affinity of the reactants, which is also in agreement with the values of the enthalpy of these reactions.[12,13]

The behavior of the bands in the deconvoluted IR spectra of the lyophilized copigment solutions at pH 3.65 (see parameters in Table II) is different from the behavior of the bands in the deconvoluted spectra of the lyophilized copigment solutions at pH 2.50. The band around 3500 cm^{-1} in the deconvoluted spectra of the malvin-sinapic acid, malvin-tannic acid, and malvin-ferulic acid copigments has a relatively small negative shift with respect to the reference (deconvoluted spectra of the lyophilized solution of malvin in the pH 3.65 buffer) ($\Delta\nu = -$ 8.1 cm^{-1}, – 4.8 cm^{-1} and – 2.6 cm^{-1}, respectively, Table II). The same band undergoes a positive shift in the deconvoluted spectra of malvin-chlorogenic acid and malvin-caffeic acid copigments. The band at around 3400 cm^{-1} shows a small negative shift in the deconvoluted spectra of malvin-caffeic acid, malvin-sinapic acid, and malvin-tannic acid copigments ($\Delta\nu$ = –4.6 cm^{-1}, –3.4 cm^{-1} and –0.4 cm^{-1}, respectively, Table II). In the spectra of malvin-chlorogenic acid and malvin-ferulic acid copigments, the same band shifts towards higher wavenumbers, the hydrogen bonds weaken with respect to the reference. The values of the $R_{O\cdots O}$ distances of the bands at around 3500 cm^{-1} and 3400 cm^{-1} are greater than 2.9 Å and 2.8 Å, respectively, which indicates weaker hydrogen bonds, according to the criterion adopted.[18]

The large negative shift of the band at around 2800 cm^{-1} in the deconvoluted spectra of the malvin-chlorogenic acid copigment indicates a strong hydrogen bond. The oxonium structure that produces this band can be considered responsible for the formation of this copigment. In the deconvoluted spectra of the other copigments this band shows a positive shift. The calculated $R_{O\cdots O}$ distances for this band are, in all copigments, greater than 2.6 Å, which classifies them as medium strength bonds. The band at around 2400 cm^{-1} undergoes a small negative shift ($\Delta\nu = -$ 4.3 cm^{-1}) only in the spectra of malvin-tannic acid copigment, whereas in the spectra of the other copigments it shifts towards higher wavenumbers. The values of the $R_{O\cdots O}$ distances for this band are smaller than 2.6 Å, indicating strong bonds.

On the basis of the parameter values obtained from the deconvoluted spectra, it can be concluded that in the copigments formed at pH 3.65 there is also a possibility that more than one hydrogen bond is formed. The bonds could be formed by participation of the oxonium structure of the molecules (copigment malvin-chlorogenic acid), or by participation of only the free hydroxyl groups (copigment malvin-caffeic acid and malvin-ferulic acid), or by the simultaneous participation of these structures (malvin-tannic acid). From the magnitudes of the shifts of the relevant bands, it can be concluded that, at this pH value too, a strong hydrogen bond is formed in the copigment malvin-chlorogenic acid, which is in agreement with the enthalpy of the copigmentation reaction of these molecules (unpublished data). In the deconvoluted spectra of other copigments, the band shifts are significantly smaller than in the case of the pH 2.50 buffer, which indicates weaker hydrogen bond formation in the buffer of lower acidity. As the high enthalpies of the reactions in the pH 3.65 buffer[12,13] are not in agreement with the small shifts of the bands in the IR spectra (the exception being the bands in the spectra of the malvin-chlorogenic acid copigment), it can be concluded that a large contribution to the reaction enthalpies can be ascribed to other possible ways of molecular bonding, other than hydrogen bonding.

CONCLUSION

The presented results confirm the presumption about the existence of hydrogen bonds in the structure of the copigments investigated. The present study has once more confirmed the significant effect of the pH of the medium in which the copigmentation reaction is performed. It has been established that stronger hydrogen bonds are formed in the pH 2.50 buffer solution than in the pH 3.65 buffer solution. It has also been established that the role of the oxonium structure of the molecule in the formation of the copigment is more significant in the pH 2.50 buffer solution, which is probably a consequence of the greater stability of this structure in the more acidic media.

A comparison of the behaviors of the organic acids and flavones[19] as copigmentation molecules in the pH 3.65 buffer shows that weaker hydrogen bonds are formed in the copigments of malvin with organic acids, except for malvin-chlorogenic acid, than in the case of malvin with flavones. Depending on the structure of the acids, the hydrogen bonds in the systems of malvin with the acids under study are formed *via* the oxonium structure of the molecules, but also *via* OH groups, whereas the bonds are formed only *via* the oxonium structure in the copigmentation of malvin with flavones.

ИЗВОД

ПРОУЧАВАЊЕ ИЦ СПЕКТАРА КОПИГМЕНАТА МАЛВИН–ХЛОРИДА И ОРГАНСКИХ КИСЕЛИНА

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У овом раду извршена је анализа ИЦ спектара копигмената малвина и неколико органских киселина: кафеинске, ферулинске, синапинске, хлорогенске и танинске киселине, у циљу разјашњења начина везивања молекула у копигментима. Констатовано је да се копигментација остварује успостављањем водоничних веза између молекула малвина и коришћених киселина. У ИЦ спектрима испитиваних једињења евидентно је постојање две групе водоничних веза које се граде учешћем различитих структура интерагујућих молекула: слободних хидроксилних група (траке на око 3500 cm^{-1}) и оксонијум–јона молекула (траке испод 3000 cm^{-1}). Такође је констатовано да формиране водоничне везе нису равноправне у смислу јачине. Учињен је покушај да се јачина награђених водоничних веза корелира са термодинамичким величинама реакције копигментације испитиваних молекула.

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