

# New Polyphenolic Compounds with Xanthylium Skeletons Formed through Reaction between (+)-Catechin and Glyoxylic Acid

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The reaction between (+)-catechin and glyoxylic acid was studied in a model solution system. The major (+)-catechin carboxymethine-linked dimer was isolated and shown to proceed to new polyphenolic compounds exhibiting absorption maxima around 440 and 460 nm. Three yellow pigments were obtained by incubation of the 8–8 colorless isomer. One was the previously reported xanthylium compound NJ2 with a maximum at 440 nm. The other two, showing absorption maxima at 460 nm, were obtained separately by incubation of the colorless dimer in hydroethanolic or methanolic medium. Structural elucidation of these two new yellow pigments was achieved by means of MS and 1D and 2D NMR techniques and showed that they were, respectively, ethyl and methyl esters of NJ2. The fact that these compounds were not obtained when NJ2 was incubated in hydromethanolic or ethanolic medium showed that esterification took place before the formation of the xanthylium chromophores. The detection of the esterified colorless compounds and the corresponding xanthene intermediates confirmed the postulated mechanism. New pigments exhibiting a strong absorption at 560 nm were also observed.

**Keywords:** (+)-Catechin; glyoxylic acid; yellow pigments; red pigments; xanthylium; xanthene; aging; model solutions

## INTRODUCTION

During conservation of grape-derived foods, phenolic compounds usually undergo progressive changes that affect sensorial properties such as color, taste, and colloidal stability (Somers, 1971; Haslam, 1980). This results in the appearance of new polymeric compounds arising from reactions between different groups of polyphenols. In particular, oxidation of polyphenols, which may be either catalyzed by specific enzymes or due to autooxidation, leads to colored quinonoid derivatives that then take part in secondary reactions bringing about the formation of more intensely colored compounds (Pierpoint, 1966; Simpson, 1982; Singleton et al., 1987; Gunata et al., 1987; Cheynier et al., 1989, 1990, 1995).

In addition, two nonenzymatic processes have been proposed to explain the color changes generally observed during the storage of red wine and studied in model solution systems. The first one is a direct condensation between flavanols and anthocyanins giving rise to yellow xanthylium compounds (Jurd, 1967; Jurd and Somers, 1970; Liao et al., 1992). The second process involves reaction mediated by acetaldehyde with the formation of violet pigments (Timberlake and Bridle, 1976; Baranowski and Nagel, 1983; Roggero et al., 1987; Bakker et al., 1993; Rivas-Gonzalo et al., 1995; Escribano-Bailon et al., 1996; Francia-Aricha et al., 1997; Es-Safi et al., 1999a).

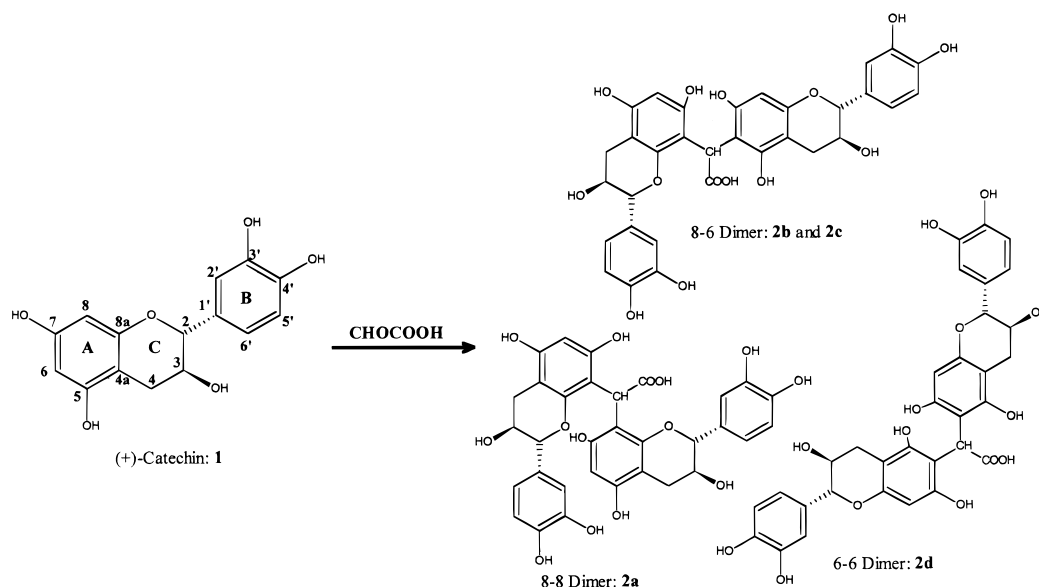
Although the process involving anthocyanins and flavanols mediated by acetaldehyde is well documented,

little is known about the formation of xanthylium salts. However, it has been suggested that xanthylium nuclei might occur in condensed tannins (flavanol polymers) and that such chromophores may contribute to the high absorbance of wine pigments in the 400–500 nm region (Jurd, 1969; Jurd and Somers, 1970; Hrazdina and Borzell, 1971; Somers, 1971; Liao et al., 1992). Up to now, few data have been reported concerning the structures of xanthylium derivatives and their incorporation in plant-derived food constituents (Jurd and Somers, 1970; Hrazdina and Borzell, 1971).

In a previous work, incubation of (+)-catechin in a white wine-like model solution system containing tartaric acid, ethanol, and catalytic amounts of iron was shown to produce both colorless and yellowish compounds, with the latter exhibiting maxima at 440 and 460 nm (Oszmianski et al., 1996). The major colorless compound has been later identified as a catechin dimer with a carboxymethine bridge resulting from reaction between (+)-catechin and glyoxylic acid, which arises from the oxidation of tartaric acid (Fulcrand et al., 1997). Recently, one yellow compound exhibiting absorption maximum at 440 nm was isolated from a model solution system containing (+)-catechin and glyoxylic acid (Es-Safi et al., 1999b). Its xanthylium-based structure was elucidated by means of spectroscopic techniques, and the mechanism of its formation from (+)-catechin was postulated.

The present work deals with the synthesis and isolation of new yellow xanthylium compounds, formed by reaction between (+)-catechin and glyoxylic acid, and their full characterization by means of mass and two-

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**Figure 1.** Synthesis scheme formation and structures of colorless dimers **2a**, **2b**, **2c**, and **2d**.

dimensional NMR spectroscopy. This paper also offers new information concerning the mechanism of their formation.

#### MATERIALS AND METHODS

**Reagents.** Deionized water was purified with a Milli-Q water system prior to use. Acetonitrile was purchased from BDH. Methanol, formic acid, and acetic acid were obtained from Prolabo (Fontenay S/Bois, France). (+)-Catechin was purchased from Sigma. Glyoxylic acid was from Aldrich and sodium tetraborohydride from Interchim.

**Reactions.** Reaction of (+)-catechin **1** in aqueous potassium hydrogen tartrate solution or with glyoxylic acid was achieved as described elsewhere (Oszmianski et al., 1996; Fulcrand et al., 1997). The colorless dimers **2a–2d** were obtained by incubation of (+)-catechin (11.9 mg) with glyoxylic acid (19.0 mg) in H<sub>2</sub>O/EtOH (9:1, v/v). After 2.5 h of incubation at 40 °C, they were purified by semipreparative HPLC as described below.

Evolution of the colorless compound was monitored in pH 3.5 aqueous solution or hydromethanolic (ethanolic) solutions at 39 °C. The mixtures were monitored by analytical HPLC, and the new yellow compounds formed (**8–10**) were isolated by semipreparative HPLC as described below.

Reduction of compound **10** (10 mg) was performed with a large excess of sodium borohydride (20 mg) in ethanol (5 mL). The reaction mixture was then hydrolyzed by 50 mL of acetic acid aqueous solution (2 M) and extracted with diethyl ether (4 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and evaporated. The purity of the obtained xanthene compound **7** was monitored by analytical HPLC prior to NMR analysis.

**Analytical HPLC/DAD Analyses.** HPLC/DAD analyses were performed by means of a Waters 2690 separation module system including a solvent and a sample management system, a Waters 996 photodiode array detector, and Millennium 32 chromatography manager software. UV–visible spectra were recorded from 250 to 600 nm. The column was a reversed-phase Lichrospher 100-RP18 (5 μm packing, 250 × 4 mm i.d.) protected with a guard column of the same material. Elution conditions were as follows: 1 mL/min flow rate; temperature, 30 °C; solvent A, water/formic acid (98:2, v/v); solvent B, acetonitrile/water/formic acid (80:18:2, v/v); elution from 5 to 30% B in 40 min, from 30 to 40% B in 10 min, and from 40 to 100% B in 5 min, followed by washing and re-equilibrating the column.

**Semipreparative HPLC Purification.** HPLC separations at the semipreparative scale were performed by means of a

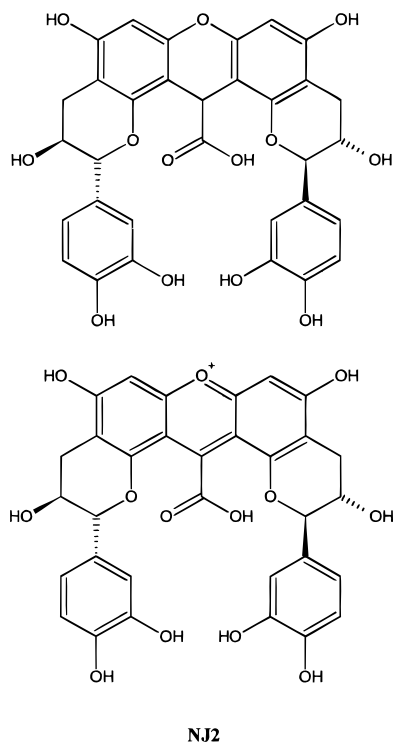
Gilson system including a 305 master and a 306 slave pump, an 806 manometric module, an 811 dynamic mixer, a 2 mL Rheodyne 7161 valve injector, and an 875 UV–visible Jasco detector set at 280 nm. The column was a reversed-phase Microsorb C18 (5 μm packing, 125 × 22 mm i.d.). Isolation of compounds **2a–2d** was achieved using the following elution conditions: 7 mL/min flow rate; solvent A, water/acetic acid (99:1, v/v); solvent B, methanol–solvent A (80:20, v/v); elution from 5 to 30% B in 28 min, from 30 to 50% B in 2 min, isocratic 50% B in 3 min, and from 50 to 100% B in 5 min, followed by washing and re-equilibrating the column. Isolation of compounds **8–10** was done using the same A and B solvents with a flow rate of 7 mL/min and the following elution gradient: from 15 to 60% B in 10 min and from 60 to 90% B in 15 min, followed by washing and re-equilibrating the column.

**MS Apparatus and LC/MS Analyses.** MS measurements were performed on a Sciex API I Plus single-quadrupole mass spectrometer with a mass range of 2400 amu, equipped with an electrospray ionization source. The mass spectrometer was operated in positive- and negative-ion modes. Ion spray voltage was selected at −4 kV and orifice voltage at −60 or +60 V in negative or positive mode, respectively.

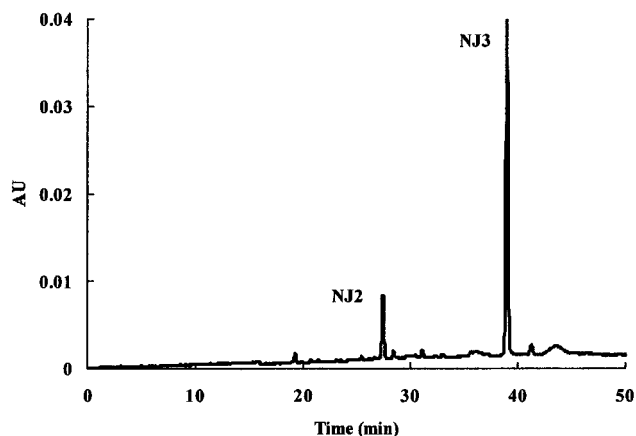
HPLC separations were carried out on a narrow-bore reversed-phase column with an ABI 140 B solvent delivery system (Applied Biosystems, Weiterstadt, Germany). The column was connected with the ion spray interface via a fused-silica capillary (length = 100 cm, 100 μm i.d.). The reaction mixture was injected with a rotary valve (Rheodyne Model 8125) fitted with a 20 μL sample loop. The separation was achieved on a Lichrospher 100-RP18 column (5 μm packing, 250 × 4 mm i.d., Merck, Darmstadt, Germany), with a flow rate of 280 μL/min. The elution was done with solvents A and B used in HPLC/DAD analysis, and the conditions adapted were as follows: isocratic 10% B for 4 min, linear gradient from 10 to 15% B in 11 min, from 15 to 50% B in 25 min, and from 50 to 100% B in 5 min, followed by washing and reconditioning of the column. The absorbance at 280 nm was monitored by an ABI 785A programmable absorbance detector and by a Waters 990 diode array detector linked to 990 system manager software.

**Absorption Spectra.** UV–visible spectra were recorded with a Kontron Uvikon 930 spectrophotometer fitted with a quartz cell.

**NMR Analysis.** NMR spectra of samples (~6 mg) in [2H<sub>6</sub>]-DMSO/TFA (9:1 v/v) (250 μL) were acquired on a Varian UNITY INOVA 500 spectrometer equipped with a 3 mm indirect detection probe operating at 500 MHz for <sup>1</sup>H and at 125.7 MHz for <sup>13</sup>C and processed using FELIX (Biosym Technologies) on a Silicon Graphics workstation. The temper-



**Figure 2.** Structures of the xanthene (top) and the xanthylium salt NJ2 (bottom), previously identified (Es-Safi et al., 1999).



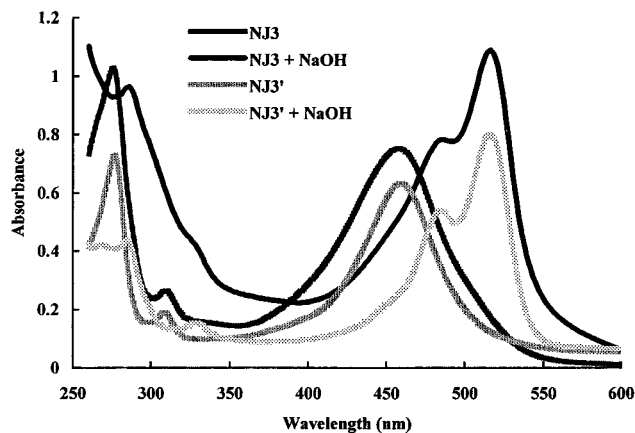
**Figure 3.** Chromatographic profile at 440 nm showing the two yellow compounds NJ2 and NJ3 formed by incubation of the colorless dimer **2a**.

ature was maintained at 297 K. Chemical shifts ( $\delta$ ) are given in parts per million and coupling constant  $J$  values are given in hertz. The central solvent signals of DMSO were used as internal reference ( $^1\text{H}$ ,  $\delta$  2.5 ppm;  $^{13}\text{C}$ ,  $\delta$  39.5 ppm relative to TMS).

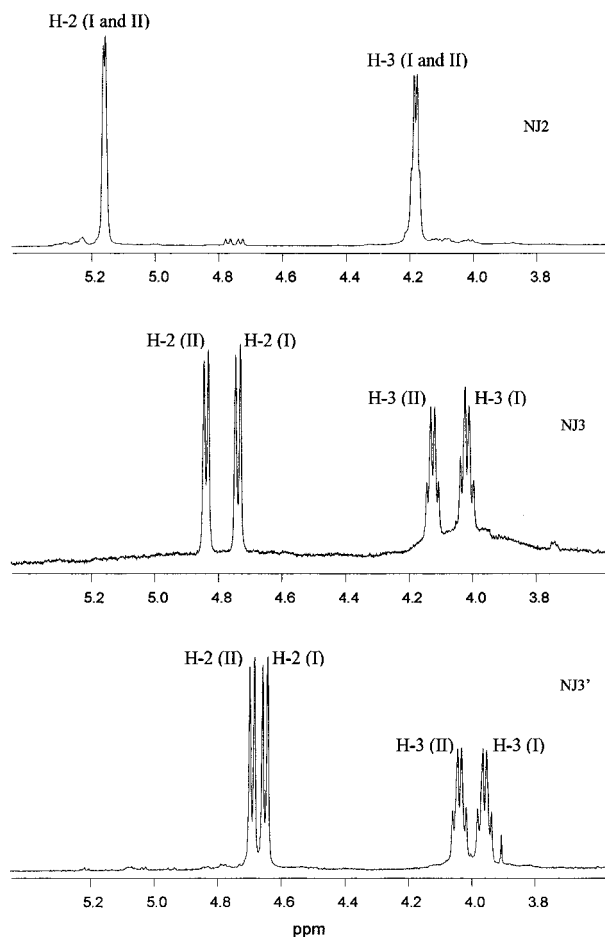
## RESULTS AND DISCUSSION

To study the structure of the yellowish products formed through chemical reaction of flavan-3-ols in wine, (+)-catechin **1** was incubated with glyoxylic acid in hydroethanolic medium and the reaction was monitored by LC/DAD and LC/MS analyses.

LC/MS analysis of the incubated solution, conducted in the negative-ion mode, showed an  $m/z$  signal at 635 ( $M_r = 636$ ) for the four major compounds **2a–2d**, indicating that they consisted of two (+)-catechin units bridged by a carboxymethine group, as previously reported (Fulcrand et al., 1997) (Figure 1). These



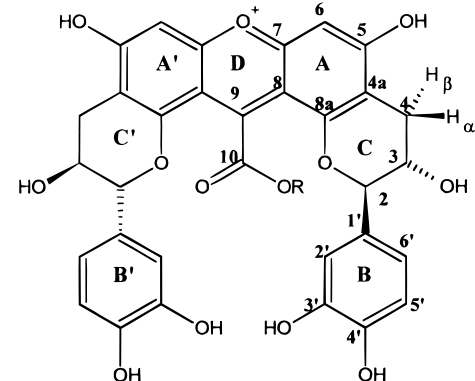
**Figure 4.** UV-visible spectra of compounds NJ3 and NJ3' in acidic and alkaline media.



**Figure 5.** Part of the  $^1\text{H}$  NMR spectra corresponding to the region H-2, H-3 proton signals of compounds NJ2, NJ3, and NJ3'.

products arise from a polycondensation mechanism of glyoxylic acid with (+)-catechin, analogous to that reported for acetaldehyde (Timberlake and Bridle, 1976; Fulcrand et al., 1996).

In addition to these four colorless compounds, yellowish pigments with maxima in the region of 440–460 nm were also observed, as reported earlier (Oszmianski et al., 1996; Fulcrand et al., 1997; Es-Safi et al., 1998). Their formation was related to the disappearance of the colorless ones, indicating that they were probably formed by evolution and further rearrangement of the

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  Assignments of Compounds NJ3 and NJ3' in TFA/DMSO- $d_6$  (1:9)


position	compound NJ3 (R = Et)				compound NJ3' (R = Me)			
	system I		system II		system I		system II	
	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$
2	4.84 d (6.7)	83.4	4.74 d (7.6)	84.0	4.68 d (7.9)	83.8	4.72 d (7.7)	84.2
3	4.13 m	63.7	4.03 m	64.4	3.99 m	64.7	4.07 m	64.1
4 $\alpha$	2.59 m	26.4	2.86 m	27.4	2.54 dd (16.8; 9.1)	27.6	2.57 dd (16.8; 9.1)	28.3
4 $\beta$	2.78	26.4	2.78 m	27.4	2.87 dd (16.9; 8.7)	27.6	2.87 dd (16.9; 8.7)	28.3
5		171.0		171.0		170.5		171.0
6	6.89 s	95.8	6.89 s	95.8	6.83 s	96.0	6.83 s	96.0
7		156.3		156.3		156.4		156.4
8		104.8		104.8		105.0		105.0
1'		127.6		127.9		128.0		128.0
2'	6.69 bs	114.9	6.69 bs	114.9	6.71	115.4	6.73	115.6
3'		145.0		145.0		145.4		145.4
4'		145.5		145.5		146.0		146.0
5'	6.71 bd (8.1)	115.3	6.71 bd (8.1)	115.3	6.72	115.5	6.74	115.5
6'	6.59 d (8.1)	118.8	6.59 d (8.1)	118.8	6.58	119.0	6.61	119.5
4a		109.1		109.5		109.4		109.2
8a		154.3		154.0		154.6		154.5
9		146.6				146.4		
10		163.8				164.5		
CH <sub>2</sub> -1	2.82 m	61.4						
CH <sub>2</sub> -2	2.95 m	61.4						
CH <sub>3</sub>	0.69 t (7.2)	13.0			2.52 s	51.1		

latter. This prompted us to prepare them from individually isolated colorless products.

The major colorless dimer **2a** was isolated by HPLC on a semipreparative scale. This compound had been previously identified as the 8–8 isomer (Fulcrand et al., 1997). Conversion to yellow pigments, concomitant with the disappearance of the colorless ones, was confirmed by individual incubation of the dimer **2a** in hydroethanolic model solution system. The formed yellow compounds exhibited absorption maxima at 440 and 460 nm. Their spectra were similar to those previously reported in solution containing (+)-catechin, tartaric acid, and iron ions (Oszmianski et al., 1996).

In our previous works (Es-Safi et al., 1998; Fulcrand et al., 1998), we showed by LC/MS analysis that one of the yellow pigments obtained was formed from the carboxymethine dimer **2a** by loss of a water molecule (dehydration), yielding a lactonized molecule, which was then oxidized. We proposed thus a lactonized methylene quinone structure for such yellow pigments. The lactonized structure indicated above obtained by dehydration of the colorless dimer **2a** was also suggested recently by Francia-Aricha et al. (1998), although the proposed structure did not show conjugation between the two catechin systems.

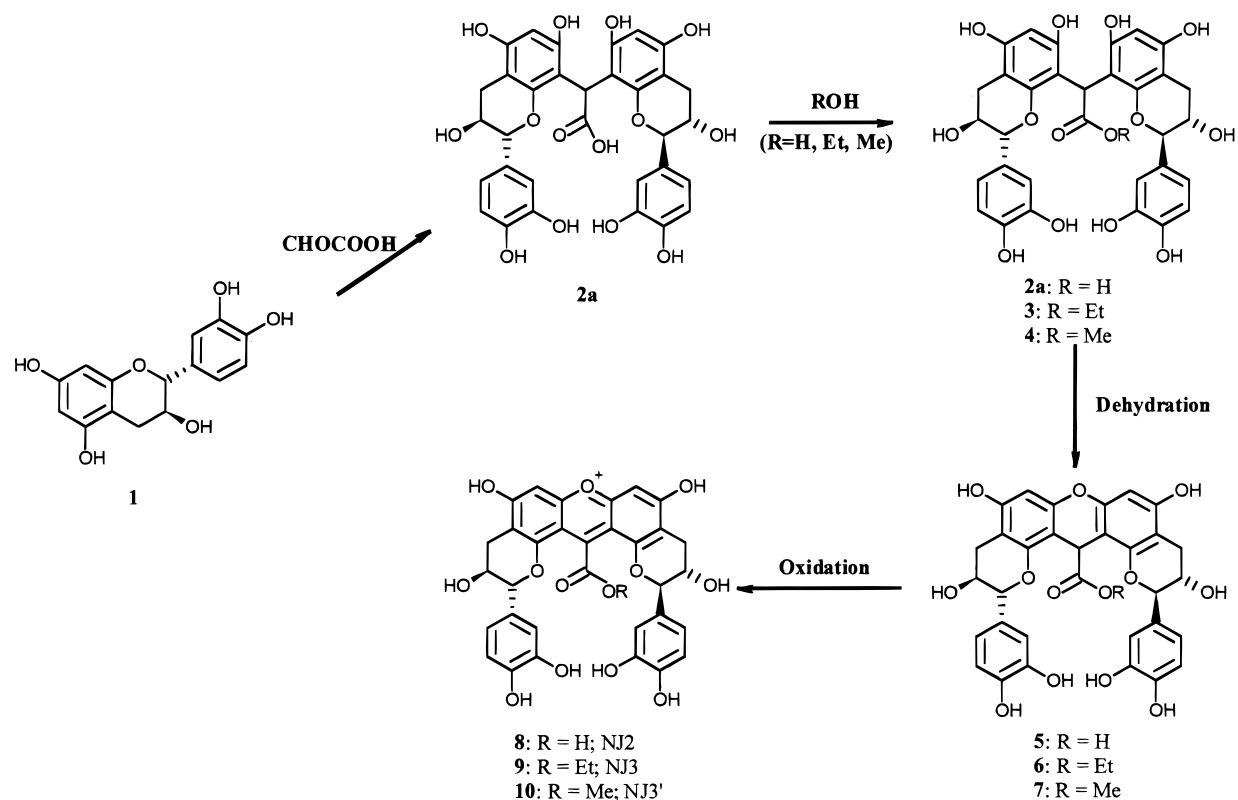
However, our recent investigations (Es-Safi et al., 1999b) indicated that this compound showed properties similar to those of xanthylum salts. Spectroscopic analysis using MS, UV–visible, and NMR spectroscopy allowed the full characterization of the major yellow

compound (NJ2) as the xanthylum salt shown in Figure 2. The mechanism of its formation was proposed to be a dehydration of the colorless compound **2a** giving a xanthene compound (Figure 2, top), followed by an oxidation step yielding the xanthylum salt. Moreover, the detection of the xanthene compound in the reaction medium and its synthesis by reduction of the xanthylum salt followed by its full characterization by NMR tools confirmed the proposed mechanism.

In addition to the identified xanthylum salt NJ2, the chromatographic profile of a solution containing the colorless compound **2a** incubated at 40 °C in hydroethanolic solution showed the presence of another yellow compound named NJ3 (Figure 3). This new compound was isolated by semipreparative HPLC and showed UV–visible absorption characteristics similar to those of NJ2. Thus, when exposed to ammonia vapor, a yellow spot of acidic NJ3 solution took instantaneously an orange color. The UV–visible spectrum of NJ3 showed two maxima, at 276 and 457 nm, in addition to a shoulder at 309 nm. With the addition of NaOH, these maxima were bathochromically shifted to 516, 327, and 286 nm and a new maximum at 485 nm was observed (Figure 4). These properties are similar to those reported earlier for xanthylum salts (Jurd and Somers, 1970; Hrazdina and Borzell, 1971; Dangles and Brouillard, 1994).

Electrospray mass spectrometry of compound NJ3 conducted in the negative-ion mode indicated an  $m/z$  value at 643. The 28 mass unit difference between





**Figure 6.** Mechanism of the xanthylium salt **8–10** formation from the colorless dimer **2a** via the xanthene derivatives **5–7**.

compounds NJ2 ( $m/z$  615 in negative ion mode) and NJ3 suggests that compound NJ3 might be formed by ethylation of compound NJ2. This hypothesis was supported by the fact that when incubation was conducted in hydromethanolic medium, NJ2 yielded another yellowish compound (NJ3') slightly more polar, showing UV–visible characteristics similar to those of NJ3 with absorption maxima at 277, 459, and 308 nm in acidic pH medium and at 516, 485, 327, and 285 nm in alkaline pH medium (Figure 4) but giving by LC-ESI-MS analysis an  $m/z$  value at 629, indicating an NJ2 methylated structure. This hypothetical assumption was further confirmed by 1D and 2D NMR spectroscopy.

When compared to the results obtained with compound NJ2, the presence of an additional ethoxyl and methoxyl group, respectively, for NJ3 and NJ3' was confirmed by NMR analysis. Thus, the  $^1\text{H}$  NMR spectrum of compound NJ3 showed the presence of a triplet integrating three protons located at 0.69 ppm (8.9 Hz) attributed to the methyl radical. The two methylene protons gave multiplets located at 2.82 and 2.95 ppm, which correlated with the methyl group in a  $^1\text{H}$ – $^1\text{H}$  COSY experiment. In HSQC sequence, these groups of protons gave correlations with carbons located at 13.0 and 61.4 ppm corresponding to the carbon chemical shifts of the methyl and methylene groups, respectively.

In the case of compound NJ3', the presence of the methoxyl group was confirmed by the appearance of a singlet integrating three protons at 2.52 ppm and giving in the HSQC experiment a cross-peak with the carbon located at 51.1 ppm corresponding to the methoxy carbon.

In the HMBC sequence, the quaternary carbons were attributed and a correlation between the protons of the methoxyl group and the carbon located at 164.5 ppm corresponding to the carbonyl function was observed in the case of NJ3', showing its ester structure. In the

HMBC spectrum of compound NJ3, correlations were observed between the methylene protons and the methyl carbon and vice versa. A weak correlation was observed between the methylene protons and the carbonyl function through the oxygen atom, in agreement with the ester structure of NJ3. ROESY experiments were also conducted both on NJ3 and on NJ3'. In both cases, cross-peaks were shown between the  $\text{CH}_3$  protons and the H-2' and H-6', showing their geometrical proximity in agreement with the proposed structures. A selective NOESY experiment was conducted on the NJ3 methyl protons, and energetic exchange was shown to occur between them and the two methylene protons in addition to the 2' and 6' aromatic protons. On the basis of these results, the proton and carbon chemical shifts corresponding to the ethylated (NJ3) and methylated (NJ3') xanthylium structures **9** and **10**, respectively, were assigned (Table 1).

The presence of two distinct proton catechin systems was observed in the  $^1\text{H}$  NMR spectra of compounds NJ3 and NJ3'. Figure 5 shows a part of the  $^1\text{H}$  NMR spectra of compounds NJ2, NJ3, and NJ3' corresponding to the protons H-2 and H-3 pyranic ring chemical shifts. Only one broad doublet and one multiplet integrating two protons each and corresponding, respectively, to the H-2 and H-3 protons were observed in the case of NJ2. In the case of NJ3 and NJ3' a splitting of these signals was observed. Thus, two doublets and two multiplets integrating each one proton for NJ3 and NJ3' corresponding to the H-2 and H-3 protons, respectively, were observed. Attribution of each H-2/H-3 system pair was achieved by  $^1\text{H}$ – $^1\text{H}$  COSY experiment.

From a mechanistical point of view, the formation of compounds NJ3 and NJ3' follows the same general mechanism as that of compound NJ2, that is, a cyclization by a dehydration of compound **2a** giving xanthene derivatives as observed for phloroglucinol ethyl-linked

adducts (White and Foo, 1990), followed by an oxidation process yielding finally the xanthylium salt products. The reduction of the xanthylium NJ3' was also achieved using sodium tetraborohydride, and the structure of the obtained compound was elucidated by MS and 1D and 2D NMR spectroscopy, confirming its xanthene-based structure. Compared to the results obtained with the xanthylium NJ3', an additional singlet was observed at 4.81 ppm in the  $^1\text{H}$  NMR spectrum and attributed to the proton H-9. This proton correlated, in the HSQC experiment, with a carbon located at 34.8 ppm, which was then attributed to the C-9. In the HMBC experiment spectrum, correlations with C-7, C-8, and C-10 were observed, confirming the structure of the xanthene compound and thus offering another argument to support the proposed structure **10** for the yellow compound NJ3'.

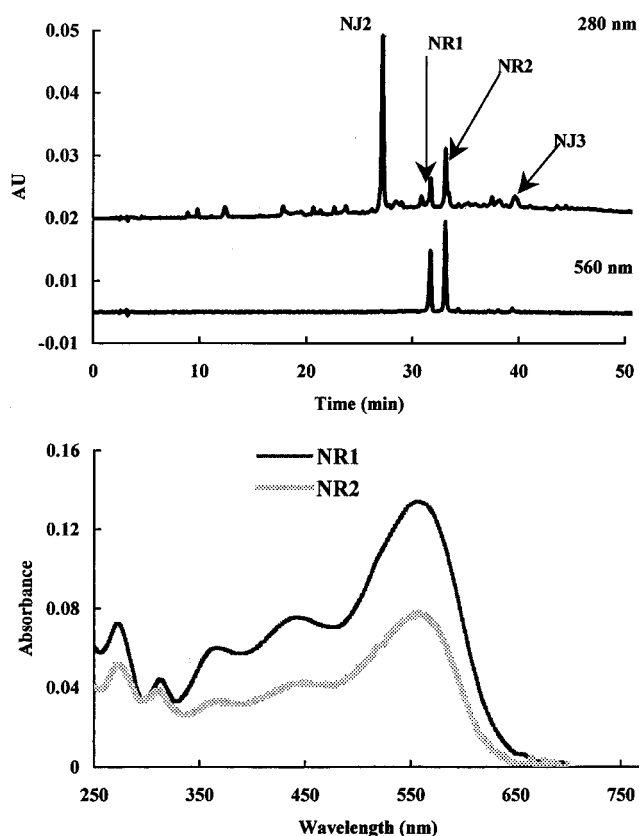
The alkoxy group (methoxyl or ethoxyl) may be fixed by direct esterification of NJ2 or by esterification of the colorless compound **2a**, which by further cyclization can afford the esterified xanthene compounds and by oxidation yield the esterified xanthylium compounds. When incubated in acidic ethanol or methanol medium, compound NJ2 did not give NJ3 or NJ3', excluding thus the first suggestion. In contrast, LC/MS analysis of the methanolic solution of **2a**, conducted in the negative-ion mode, showed the presence of the colorless compound **2a** ( $m/z$  635), the methylated colorless compound ( $m/z$  649), the corresponding xanthene derivative ( $m/z$  631), and the corresponding xanthylium salt derivative NJ3' ( $m/z$  629).

When ethanolic alcohol was substituted for methanol, the corresponding ethylic xanthylium salt NJ3 was obtained ( $m/z$  643) along with the ethylic ester of the colorless compound **2a** ( $m/z$  663) and the corresponding ethylic xanthene derivative ( $m/z$  645). These results showed that esterification was achieved on the colorless compound before cyclization. Figure 6 shows the reaction chains leading to the yellowish pigments **8**, **9**, and **10** from (+)-catechin **1** via their colorless (**2a**, **3**, and **4**) and xanthene compounds (**5**, **6**, and **7**).

In wine-like model solution containing (+)-catechin, tartaric acid, and ethanol, two xanthylium derivatives absorbing at 440 and 460 nm with molecular weights of 617 and 643, with the same chromatographic data as NJ2 and NJ3, were observed. When ethanol was replaced by methanol, the methylic xanthylium salt NJ3' was obtained in addition to compound NJ2. These compounds are obtained by the same reaction involving glyoxylic acid, the latter being formed by oxidation of tartaric acid as described elsewhere (Fulcrand et al., 1997).

The formation of such yellowish compounds in wine-like model solutions suggests their possible contributions in color evolution and browning observed during conservation and aging of grape-derived foods. Moreover, the colorless compounds, the xanthene and the xanthylium derivatives, were detected by LC/ESI-MS analysis in a red wine fraction, indicating that the described mechanism took place in grape-derived foods (Fulcrand et al., 1998).

Although the identified compounds were synthesized in a simplified solution, it is expected that such experiments may at least enable elucidation of the simpler polymeric pigments such as those formed during conservation or maturation. In addition, more polymerized compounds in which xanthene and xanthylium nuclei



**Figure 7.** HPLC chromatograms recorded at 280 and 560 nm showing the formation of the new red pigments NR1 and NR2 and their UV-visible spectra.

are incorporated were also detected in a model solution system containing (+)-catechin and glyoxylic acid, after a 24 h incubation. Thus, LC/ESI-MS analysis conducted in negative-ion mode revealed the presence of signals at  $m/z$  963 and 691 corresponding to dimeric xanthenes linked to another catechin unit through a carboxymethine bridge and to a hydroxyethanoic acid radical, respectively. The corresponding xanthylium derivatives were also detected at  $m/z$  961 and 689, respectively. This shows that xanthylium salts can be involved in glyoxylic acid-induced polymerization in the same way as (+)-catechin and indicates the implication of such derivatives in the polymeric pigments responsible for the high absorption around 450 nm formed during the aging of fruit-derived foods. In addition to these xanthylium derivatives, other adducts exhibiting absorption maxima around 560 nm were also detected (Figure 7). The structure elucidation of these new red pigments is under way and will be published later.

Our results indicate that various reaction pathways contributing to browning compete with polycondensation reactions and offer new information and support to the contribution of xanthylium salts in color evolution and browning in fruit-derived foods. The present work constitutes a new method for xanthylium salt synthesis as up to now only anthocyanin-flavanol rearrangement was described for the obtention of xanthylium salts. They finally open perspectives for further investigations of similar compounds.

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