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2,4-Alkadienal trapping by phenolics

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ABSTRACT

Phenolics can trap lipid-derived reactive carbonyls as a protective function that diminishes the broadcasting of the lipid oxidative damage to food macromolecules. In an attempt to clarify the trapping of 2,4-alkadienals by phenolics, this study analyzes the reactions of 2,4-hexadienal, 2,4-heptadienal, and 2,4-decadienal with 2-methylresorcinol. These reactions produced (*E*)-4-(alk-1-en-1-yl)-8-methyl-2,7-bis(prop-1-en-2-yloxy)chromanes, which were isolated and characterized by 1D and 2D NMR and MS. Carbonyl-phenol adduct formation was favored at pH > 7 and moderate temperatures (25–80 °C). Adducts were quantified and shown to be produced as a mixture of diastereomers. Diastereomers 2*R*,4*S* plus 2*S*,4*R* were formed to a higher extent than diastereomers 2*R*,4*R* plus 2*S*,4*S* under the different conditions assayed, although activation energies (E_a) for the formation of all of them was mostly the same (~62 kJ·mol^{-1}). These results show that phenolics can trap 2,4-alkadienals and provide the basis for the later detection of the formed adducts in food pro[ducts.

1. Introduction

Lipid oxidation is a common source of reactive carbonyls in foods (Bastos, Costa, & Pereira, 2017; Concepcion et al., 2018). Once formed, these compounds have a great relevance in food quality and safety because of their sensory properties (Rendon, Salva, & Bragagnolo, 2014), their ability to modify food macromolecules (Lorenzo, Pateiro, Fontan, & Carballo, 2014), and their tendency to produce nonenzymatic browning (Potes, Kerry, & Roos, 2013). Because they are electrophiles, these carbonyls react easily with the nucleophiles present in foods. Among them, a common sink for the most reactive lipid-derived reactive carbonyls is their reaction with amine compounds, including amines, amino acids, aminophospholipids, and proteins (Zamora & Hidalgo, 2005). In addition, phenolics have also been shown to exhibit enough nucleophilicity to act as an alternative sink for lipid-derived reactive carbonyls (Zamora & Hidalgo, 2016). This reaction produces many different carbonyl-phenol adducts, whose structures are related to the structures of the lipid-derived reactive carbonyls involved. At present, the carbonyl-phenol adducts formed in the reaction of phenolics with alkanals (Hidalgo, Aguilar, & Zamora, 2017), 2-alkenals (Hidalgo & Zamora, 2014), 4-oxo-2-alkenals (Hidalgo, Aguilar, & Zamora, 2018), and 4,5-epoxy-2-alkenals (Zamora, Aguilar, & Hidalgo, 2017) have been isolated and characterized. Furthermore, some of these adducts have been detected in food products (Zamora, Aguilar, Granvogl, & Hidalgo, 2016).

In addition to these compounds, 2,4-alkadienals are also major lipid-derived reactive carbonyls produced as a consequence of the lipid oxidation process (Chen et al., 2017). Moreover, they have been shown to be involved in the formation of both foodborne toxicants and food flavors. Among foodborne toxicants, their contribution to the formation of acrylamide (Hidalgo, Delgado, & Zamora, 2009), biogenic amines (Hidalgo, Navarro, Delgado, & Zamora, 2013), and heterocyclic aromatic amines (Zamora, Alcon, & Hidalgo, 2012) has been described. In addition, they contribute to the formation of Strecker aldehydes among other food flavors (Zamora, Gallardo, & Hidalgo, 2007; Zamora, Navarro, Aguilar, & Hidalgo, 2015).

In an attempt to determine the ability of phenolics to trap 2,4-alkadienals, to identify the structures of the produced adducts, and to study the reaction conditions that favor carbonyl-phenol adduct formation, this manuscript describes the reaction of 2,4-alkadienals (2,4-hexadienal, 2,4-heptadienal, and 2,4-decadienal) with 2-methylresorcinol. 2-Methylresorcinol was employed as a model phenolic compound because of its small molecular weight, which facilitates the characterization of the produced adducts, and its high carbonyl trapping potential (Hidalgo, Navarro, & Zamora, 2018; Salazar, Arambula-Villa, Hidalgo, & Zamora, 2014).

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2. Materials and methods

2.1. Materials

Three 2,4-alkadienals were employed in this study: 2,4-heptadienal, which is the oxidation product of ω3 fatty acyl chains; 2,4-decadienal, which is the oxidation product of ω6 fatty acyl chains; and 2,4-hexadienal, which has a small side chain and helped in the characterization of the structures of the obtained adducts. These compounds, as well as other chemicals employed in these studies, were purchased from Sigma-Aldrich (St. Louis, MO), Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland), and were of the highest available grade.

2.2. Formation of carbonyl-phenol adducts in the reaction of alkadienals and phenolic compounds

For analytical purposes, mixtures containing the alkadienal and 2-methylresorcinol (30 μmol of each in 500 μL of 0.3 M buffer) were heated at 60 °C for up to 24 h under nitrogen. The employed buffers were: sodium phosphate, pH 6–8, and sodium borate, pH 8–10. At the end of the heating, reactions were stopped by cooling at room temperature for 10 min and removing the unreacted aldehyde by evaporation of the reaction to dryness using a flow of nitrogen. This evaporation was facilitated by addition of 1.2 mL of ethanol. Dried samples were then treated with 30 μL of internal standard (a solution of 36.64 mg of *cis*-3-nonen-1-ol in 5 mL of anhydrous pyridine), and acetylated with 1 mL of anhydrous pyridine and 0.5 mL of acetic anhydride. After 20 h at room temperature (22 °C), 2 mL of dichloromethane and 2 mL of water were added. Layers were separated and the organic layer was washed successively with 2 mL of 5% hydrochloric acid (four times), and 2 mL of water. After centrifugation, the organic layer was studied by gas chromatography coupled to mass spectrometry (GC–MS).

For preparative purposes, the reaction was carried out analogously but mixtures containing 2.5 mmol of each reactant were heated in 4 mL of 0.3 M sodium phosphate buffer, pH 8. Acetylation was carried out with 80 mL of anhydrous pyridine and 40 mL of acetic anhydride under the same reaction conditions described above. Acetylated reaction mixtures were fractionated by column chromatography on silica gel 60 using hexane:diethyl ether mixtures as eluent. Separation was controlled by GC–MS. The structures of the adducts isolated and characterized in the assayed reactions are collected in Fig. 1.

2.2.1. Compounds isolated and characterized in the reaction of 2,4-heptadienal and 2-methylresorcinol

Reactions were carried out in phosphate buffer, pH 8. As observed in the total ion chromatogram of the reaction mixture (Fig. 1), two main adducts (**1**,**2**) were formed, which were isolated and characterized. Both compounds were identified as two isomers of (*E*)-4-(but-1-en-1-yl)-8-methyl-2,7-bis(prop-1-en-2-yloxy)chromane.

*2.2.1.1. Spectroscopic and spectrometric data of compound **1**.* ^{1}H NMR ($CDCl_3$): δ 1.06t (3H, J = 7.5 Hz, H4′), 1.91 ddd (1H, J = 2.6 Hz, J = 12.1 Hz, J = 13.9 Hz, H3a), 2.02s (3H, CH_3C8), 2.11s (3H, CH_3CO), 2.11m (3H, H3′ and H3b), 2.33s (3H, CH_3CO), 3.59 ddd (1H, J = 5.7 Hz, J = 8.9 Hz, J = 12.1 Hz, H4), 5.34 ddt (1H, J = 1.5 Hz, J = 8.9 Hz, J = 15.2 Hz, H1′), 5.77 dt (1H, J = 6.4 Hz, J = 15.2 Hz, H2′), 6.57t (1H, J = 2.6 Hz, H2), 6.65d (1H, J = 8.4 Hz, H6), and 7.05d (1H, J = 8.4 Hz, H5). ^{13}C NMR ($CDCl_3$): δ 9.21 ($\underline{C}H_3C8$), 13.80 (C4′), 20.80 ($\underline{C}H_3CO$), 21.29 ($\underline{C}H_3CO$), 25.50 (C3′), 32.08 (C3), 33.68 (C4), 89.90 (C2), 114.50 (C6), 118.66 (C8), 121.99 (C4a), 125.88 (C5), 129.81 (C1′), 135.73 (C2′), 148.53 (C7), 149.71 (C8a), 169.41 (CO), and 169.73 (CO). MS, *m/z* (%, ion structure): 318 (0.2, M^+), 276 (0.2, $M^+ - CH_2CO$), 258 (39, $M^+ - CH_3COOH$), 234 (5, 276 – CH_2CO), 229 (26, 258 – CH_3CH_2), 216 (65, 258 – CH_2CO), 205 (15, 234 – CHO), 191 (51, 234 – CH_2CHO), 187 (100, 216 – CH_3CH_2), and 161 (37, 216 – $CH_3CH_2CH{=}CH$).

*2.2.1.2. Spectroscopic and spectrometric data of compound **2**.* ^{1}H NMR ($CDCl_3$): δ 1.04t (3H, J = 7.5 Hz, H4′), 2.02m (1H, H3b), 2.03s (3H, CH_3C8), 2.11m (2H, H3′), 2.13s (3H, CH_3CO), 2.27 ddd (1H, J = 2.9 Hz, J = 6.4 Hz, J = 13.7 Hz, H3a), 2.33s (3H, CH_3CO), 3.50 q,br (1H, J = 7.0 Hz, H4), 5.55 ddt (1H, J = 1.4 Hz, J = 8.7 Hz, J = 15.2 Hz, H1′), 5.69 dt (1H, J = 6.2 Hz, J = 15.2 Hz, H2′), 6.49dd (1H, J = 2.9 Hz, J = 6.1 Hz, H2), 6.65d (1H, J = 8.4 Hz, H6), and 6.99d (1H, J = 8.4 Hz, H5). ^{13}C NMR ($CDCl_3$): δ 9.17 ($\underline{C}H_3C8$), 13.67 (C4′), 20.80 ($\underline{C}H_3CO$), 21.22 ($\underline{C}H_3CO$), 25.35 (C3′), 32.58 (C3), 36.61 (C4), 91.43 (C2), 114.66 (C6), 118.82 (C8), 121.77 (C4a), 126.53 (C5), 131.29 (C1′), 133.78 (C2′), 148.50 (C7), 150.31 (C8a), 169.36 (CO), and 169.52 (CO). MS, *m/z* (%, ion structure): 318 (32, M^+), 276 (312, $M^+ - CH_2CO$), 258 (3, $M^+ - CH_3COOH$), 234 (20, 276 – CH_2CO), 229 (13, 258 – CH_3CH_2), 216 (56, 258 – CH_2CO), 205 (28, 234 – CHO), 191 (89, 234 – CH_2CHO), 187 (100, 216 – CH_3CH_2), and 161 (55, 216 – $CH_3CH_2CH{=}CH$).

2.2.2. Compounds isolated and characterized in the reaction of 2,4-decadienal and 2-methylresorcinol

Reactions were carried out in phosphate buffer, pH 8, and the total ion chromatogram of the reaction mixture (data not shown) also showed two main adducts (**3**,**4**). These compounds were isolated and characterized as two isomers of (*E*)-4-(hept-1-en-1-yl)-8-methyl-2,7-bis (prop-1-en-2-yloxy)chromane.

*2.2.2.1. Spectroscopic and spectrometric data of compound **3**.* ^{1}H NMR ($CDCl_3$): δ 0.93t (3H, J = 7.0 Hz, H7′), 1.28m (4H, H4′ and H6′), 1.35m (2H, H5′), 1.43m (2H, H3′), 1.91 ddd (1H, J = 2.5 Hz, J = 12.1 Hz, J = 13.9 Hz, H3a), 2.03s (3H, CH_3C8), 2.11s (3H, CH_3CO), 2.11m (1H, H3b), 2.33s (3H, CH_3CO), 3.59 ddd (1H, J = 5.5 Hz, J = 8.8 Hz, J = 12.1 Hz, H4), 5.34 ddt (1H, J = 1.4 Hz, J = 8.8 Hz, J = 15.2 Hz, H1′), 5.72 dt (1H, J = 6.9 Hz, J = 15.2 Hz, H2′), 6.57t (1H, J = 2.5 Hz, H2), 6.65d (1H, J = 8.4 Hz, H6), and 7.04d (1H, J = 8.4 Hz, H5). ^{13}C NMR ($CDCl_3$): δ 9.21 ($\underline{C}H_3C8$), 14.07 (C7′), 20.79 ($\underline{C}H_3CO$), 21.28 ($\underline{C}H_3CO$), 22.51 (C6′), 29.07 (C3′), 29.72 (C4′), 31.40 (C5′), 32.11 (C3), 33.77 (C4), 89.90 (C2), 114.50 (C6), 118.66 (C8), 121.98 (C4a), 125.90 (C5), 130.75 (C1′), 134.28 (C2′), 148.53 (C7), 149.70 (C8a), 169.41 (CO), and 169.72 (CO). MS, *m/z* (%, ion structure): 360 (0.4, M^+), 318 (1, $M^+ - CH_2CO$), 300 (28, $M^+ - CH_3COOH$), 276 (2, 318 – CH_2CO), 258 (37, 300 – CH_2CO), 233 (18, 276 – CH_2CHO), 229 (42, 258 – CH_3CH_2), 187 (100, 258 – $CH_3CH_2CH_2CH_2CH_2$), and 161 (57, 258 – $CH_3CH_2CH_2CH_2CH_2CH{=}CH$).

*2.2.2.2. Spectroscopic and spectrometric data of compound **4**.* ^{1}H NMR ($CDCl_3$): δ 0.92t (3H, J = 6.9 Hz, H7′), 1.28m (4H, H4′ and H6′), 1.33m (2H, H5′), 1.43qu (2H, J = 7.2 Hz, H3′), 2.02m (1H, H3b), 2.02s (3H, CH_3C8), 2.13s (3H, CH_3CO), 2.27 ddd (1H, J = 3.0 Hz, J = 6.4 Hz, J = 13.7 Hz, H3a), 2.33s (3H, CH_3CO), 3.52 q,br (1H, J = 7.0 Hz, H4), 5.54 ddt (1H, J = 1.2 Hz, J = 8.6 Hz, J = 15.2 Hz, H1′), 5.64 dt (1H, J = 6.6 Hz, J = 15.2 Hz, H2′), 6.48dd (1H, J = 3.0 Hz, J = 6.3 Hz, H2), 6.65d (1H, J = 8.4 Hz, H6), and 6.98d (1H, J = 8.4 Hz, H5). ^{13}C NMR ($CDCl_3$): δ 9.17 ($\underline{C}H_3C8$), 14.06 (C7′), 20.79 ($\underline{C}H_3CO$), 21.23 ($\underline{C}H_3CO$), 22.51 (C6′), 29.02 (C3′), 29.70 (C4′), 31.41 (C5′), 32.68 (C3), 36.76 (C4), 91.45 (C2), 114.66 (C6), 118.81 (C8), 121.80 (C4a), 126.49 (C5), 132.18 (C1′), 132.44 (C2′), 148.50 (C7), 150.33 (C8a), 169.37 (CO), and 169.53 (CO). MS, *m/z* (%, ion structure): 360 (12, M^+), 318 (12, $M^+ - CH_2CO$), 300 (11, $M^+ - CH_3COOH$), 276 (5, 318 – CH_2CO), 258 (24, 300 – CH_2CO), 233 (20, 276 – CH_2CHO), 229 (31, 258 – CH_3CH_2), 215 (27, 258 – $CH_3CH_2CH_2$), 201 (22, 258 – $CH_3CH_2CH_2CH_2$), 187 (100, 258 – $CH_3CH_2CH_2CH_2CH_2$), and 161 (58, 258 – $CH_3CH_2CH_2CH_2CH_2CH{=}CH$).

2.2.3. Compounds isolated and characterized in the reaction of 2,4-hexadienal and 2-methylresorcinol

Reactions were carried out, analogously to previous assays, in phosphate buffer, pH 8, and the total ion chromatogram of the reaction

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