Two Novel β-Carboline Compounds from the Maillard Reaction between Xylose and Tryptophan

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INTRODUCTION

The Maillard reaction, also known as nonenzymatic browning reaction, involves the reaction of carbonyl compounds, especially reducing sugars, with compounds possessing a free amino group. Maillard reaction is an important chemical reaction in foods. Apart from the generation of flavor and the formation of color in many foods, it is also responsible for the formation of antimutagenic compounds (Yen, 1992). Some Maillard reaction products also show antioxidant activity in tested food models (Lingnert and Waller, 1983; Yen and Hsieh, 1995; Bedinghaus and Ockerman, 1995). However, due to their complexity and multiplicity, the vast majority of Maillard reaction products, particularly the nonvolatile products, still remain uncharacterized. Recently, some attempts have been made to study nonvolatile Maillard reaction products. One study compared reverse-phase HPLC, ion-exchange HPLC, isoelectric focusing, and capillary zone electrophoresis for the separation of methanol-extractable nonvolatile Maillard products of a model extrusion-cooked cereal product (Ames et al., 1997). Other researchers have dealt with isolation and structural elucidation of nonvolatile compounds from model systems such as xylose and lysine, xylose and glycine, furan-2-carboxaldehyde and proline, and 3-deoxy-d-hexos-2-ulose and arginine systems; a few novel compounds have been characterized from those studies (Hofmann, 1998; Arnoldi et al., 1997; Hayase, 1997).

To our knowledge, nonvolatile Maillard reaction products from tryptophan and xylose models have not been studied. In this paper, we report the isolation and structural elucidation of two novel nonvolatile β-carboline alkaloids from this model system.

MATERIALS AND METHODS

General Procedures. 1H NMR and 13C NMR spectra were obtained on a Varian Gemini-200 instrument at 200 and 50 MHz, respectively. CH3OH-d4 was used as a solvent, and chemical shifts were expressed in parts per million (δ). 13C NMR multiplicity was determined by APT experiment. Desorption chemical ionization mass spectra were measured on a Finnigan MAT-90 spectrometer, using CH4 as a reactant gas.

RESULTS AND DISCUSSION

Two major nonvolatile compounds were isolated from the Maillard reaction between xylose and tryptophan. 1 was isolated as a pale yellow powder, and the
The molecular formula C_{15}H_{16}N_{2}O_{2} was deduced from desorption chemical ionization–mass spectrometry (DCI–MS), which showed a [M + 1]^+ at 257 and $^{13}$C NMR spectrum that accounted for a total of 15 carbons. The UV spectrum showed maxima at 223, 263, 295, and 360, the typical absorption of a $\beta$-carboline alkaloid (Gozler et al., 1996; Ohmoto et al., 1981). The $^1$H NMR displayed a total of six protons in aromatic range. Among them, two doublet signals at $\delta$ 8.21 and 7.90 ($J = 5.4$ Hz) clearly belong to H-3 and H-4 of the $\beta$-carboline moiety (Gozler et al., 1996), while four signals at $\delta$ 7.28 (td, $J = 8.0, 1.2$ Hz), 7.55 (td, $J = 8.0, 1.2$ Hz), 7.64 (d, $J = 8.0$), and 8.16 (d, $J = 8.0$ Hz) suggested the nonsubstituted nature of the positions of C-5, -6, -7, and -8. The $^1$H NMR of 1 also gave the signals for a methine proton associated with a secondary alcohol group as a $^1$H triplet at $\delta$ 5.19, terminal methylene protons associated with a primary alcohol as a 2H triplet at $\delta$ 3.59, and two CH$_2$ signals at $\delta$ 2.03 and $\delta$ 1.72 ppm, which suggest a CH(OH)CH$_2$CH$_2$CH$_2$OH moiety in 1. The $^{13}$C NMR of 1 also gave the signals for a methine proton associated with a secondary alcohol group as a 1H triplet at $\delta$ 5.19, terminal methylene protons associated with a primary alcohol as a 2H triplet at $\delta$ 3.59, and two CH$_2$ signals at $\delta$ 2.03 and $\delta$ 1.72 ppm, which suggest a CH(OH)CH$_2$CH$_2$CH$_2$OH moiety in 1. The $^{13}$C NMR of 1 also gave the signals for a methine proton associated with a secondary alcohol group as a 1H triplet at $\delta$ 5.19, terminal methylene protons associated with a primary alcohol as a 2H triplet at $\delta$ 3.59, and two CH$_2$ signals at $\delta$ 2.03 and $\delta$ 1.72 ppm, which suggest a CH(OH)CH$_2$CH$_2$CH$_2$OH moiety in 1. The $^{13}$C NMR of 1 (Table 1) showed signals of typical carboline alkaloids and the signal for a CH(OH)CH$_2$CH$_2$CH$_2$OH moiety ($\delta$ 75.4, 63.2, 30.1, and 34.9 ppm), so compound 1 was elucidated as 1-(1,4-dihydroxybutyl)-$\beta$-carboline.
2 was isolated as a pale yellow powder with the molecular formula C_{15}H_{16}N_{2}O_{3}, which was indicated by its DCI−MS and $^{13}$C NMR. The $^{1}$H NMR of 2 showed similar signals in the aromatic region, $\delta$ 8.22 (1H, d, J = 5.4 Hz, H-3), 8.17 (1H, d, J = 8.0 Hz, H-5), 7.99 (1H, d, J = 5.4 Hz, H-4), 7.64 (1H, d, J = 8.0 Hz, H-8), 7.57 (1H, t, J = 8.0 Hz, H-7), and 7.25 (1H, t, J = 8.0 Hz, H-6), suggesting a 1-substituted $\beta$-carboline moiety in 2. Comparing the molecular weight of 2 with that of 1 suggests one more hydroxyl group in 2, in the $^{13}$C NMR of 2, the 1'-position hydrogen ( $\delta$ 5.40) still remained a triplet, suggesting that this hydroxyl group can only be substituted at the 3'-position, so its structure was elucidated as 1-(1,3,4-trihydroxybutyl)-$\beta$-carboline. Its $^{13}$C NMR (Table 1) were assigned according to literature (Erra-Balsells et al., 1988; Ohmoto and Koike, 1982, 1984).

Alkaloids with $\beta$-carboline structure are widely distributed in nature. Among them, norharman ($\beta$-carboline) and harman (1-methyl-$\beta$-carboline) are well-known compounds of tobacco and cigarette smoke, having been characterized in the 1960s (Poindexter and Carpenter, 1962). 1,2,3,4-Tetrahydro-$\beta$-carboline-3-carboxylic acid and 1-methyl-1,2,3,4-tetrahydro-$\beta$-carboline-3-carboxylic acid have been found in beverages, and 1-methyl-1,2,3,4-tetrahydro-$\beta$-carboline-3-carboxylic acid has been reported as a precursor of mutagenic N-nitroso compounds when tested in Ames tests (Herraiz et al., 1993; WakaBayashi, 1983). Many $\beta$-carboline alkaloids have also been found in plants, and one alkaloid creatine was shown to possess antibacterial activity but no antifungal activity (Mitsunaga et al., 1994; Gozler et al., 1996; Ajayeoba et al., 1995; Liu et al., 1988; Ohmoto and Koike, 1982, 1984; Ohmoto et al., 1981). Some volatile $\beta$-carboline alkaloids were found after the roasting of tryptophan with sugars and sugar degradation products, and the authors proposed the mechanism as intramolecular cyclization of the resulting azomethines and subsequent dehydrogenation producing the thermally stable $\beta$-carboline structures (Knoch and Baltes, 1992).

In this study, $\beta$-carbolines were formed by reacting tryptophan with xylose in an aqueous solution. Only two major caroline alkaloids could be observed on the TLC plates in the ethyl acetate extract. There was no experimental evidence to support any certain mechanism for the formation of these compounds; however, intramolecular cyclization, dehydrogenation, and equilibrium between different tautomeric forms, as depicted in Figure 1, seem reasonable.

LITERATURE CITED


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