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THE STRUCTURE OF A NEW AMINO ACID FROM FAGOPYRUM ESCULENTUM MOENCH

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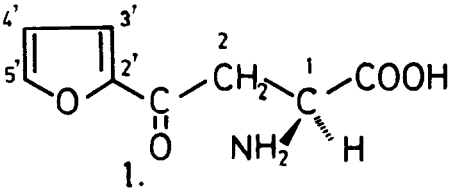
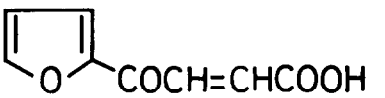
Recently the isolation and characterization of a number of amino acids and amines from Fagopyrum esculentum Moench (buckwheat seeds) have been described[3,4]. In this communication we would like to report the isolation and structural determination of a new amino acid, L-2-(2'-furoyl) alanine 1 from neutral amino acid fraction of the extracts of the seeds.



1.



2.

Neutral amino acids[4] from the solvent extract were fractionated on a Dowex 50(W) X 4 [Pyridium$^+$] column using pyridine buffer as an eluent. Fractions which have yellow color for ninhydrin reagent were further separated on a cellulose column and eluted with n-BuOH:AcOH:H_2O (4 : 1 : 5 upper layer) solvent system to give a crystalline material, m.p. 148~149°C, $C_8H_9O_4N\cdot H_2O$; ν_{max}^{KBr} 3300~3100, 2600~2300, 1570~1540 cm^{-1}(-NH_3^+), 1660 cm^{-1}(conjugated ketone), 1610 cm^{-1}(COO^-), 1035, 880, 780~770 cm^{-1}(furan ring); τ D_2O 6.42 (2H, d J=7 Hz, -CH_2CO-), 5.82 (1H, t J=7 Hz, -CH_2-$\underline{CH}$(NH_2)-CO_2H), 3.30 (1H, q $J_{4',5'}$=1.5 Hz, $J_{3',4'}$=3.5 Hz, 4'-H), 2.48 (1H, d $J_{3',4'}$=3.5 Hz, 3'-H) and 2.17 (1H, d $J_{4',5'}$=1.5 Hz, 5'-H). The maximum UV absorp-

tion at 278 nm (ε 13100) is similar to that of methyl 2-furoate. These spectroscopic data indicate that the amino acid has a structure 1. Further an intense furoyl peak at m/e 95 (base peak) together with other fragment ions, m/e 166 ($M - NH_3$), 110 ($M - \overset{\overset{NH}{\|}}{CH}\text{-}COOH$) is observed in the mass spectrum, which is compatible with the structure 1.

The stereochemistry of the amino acid was determined as follows. Exhaustive ozonolysis of the amino acid in 0.5 N-hydrochloric acid and subsequent decomposition of the ozonide with hydrogen peroxide resulted to afford an aspartic acid[5]. Since the aspartic acid was converted with glutamate oxaloacetate transaminase (GOT) in phosphoric acid buffer of pH 7.5 at 37°C to L-glutamic acid in 80% yield, the aspartic acid must have L-configuration and the amino acid should be depicted as 1.

The structure 1 was confirmed by the synthesis. Condensation of 2-acetylfuran[6] with glyoxylic acid with sodium hydroxide in 66% aqueous ethanol gave an α,β-unsaturated acid 2. The α,β-unsaturated acid 2, was treated with 15% aqueous ammonia[7] at room temperature for 2 days to give a product which was fractionated to give DL-2-(2'-furoyl)-alanine as a crystalline compound, m.p. 149 ~ 150°C. The synthetic specimen is identical with natural one in NMR spectrum and behavior on paper chromatography and amino acid analyzer.

References and Footnotes

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