**Note**

**Absolute Structure of N-p-Coumaroyloctopamine in Elicitor-treated Potato Tuber Tissue**

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Treatment of potato tuber tissue with β-1,3-oligoglucosaccharide causes an accumulation of N-p-coumaroyloctopamine (1). In order to determine the absolute structure of 1 in potato, optically active 1 was synthesized from (R)-octopamine which had been obtained from the racemic mixture by the fractional crystallization. By comparing the chromatographic behavior of synthetic and naturally-occurring samples with a chiral HPLC analysis, the absolute configuration of 1 in potato was determined to be S. This indicates that the absolute configuration of the octopamine moiety of 1 is opposite to that of octopamine formed in animal tissues.

**Key words:** Solanum tuberosum; octopamine; N-p-coumaroyloctopamine

Hydroxycinnamic acid conjugates of various aliphatic and aromatic amines have been found in plants as the stress metabolites which were induced by wounding, pathogen infection, and elicitor-treatment.1-4 It has been proposed that these amide compounds are incorporated into the cell wall to make a polymeric compound which acts as a physical barrier against pathogen infection in the plant defence response.5-6 We have recently found that an octopamine (2) amide with p-coumaric acid (N-p-coumaroyloctopamine, 1) was copiously accumulated in the tuber tissue of potato (Solanum tuberosum) that had been treated with oligosaccharide elicitors,6 although the stereochemistry of 1 remained unknown. In this paper, we report the absolute structure of 1 accumulated in potato tuber tissue after the elicitor treatment. The absolute structure of 1 was determined by comparing the chromatographic behavior of synthetic and naturally-occurring samples with chiral HPLC, because 1 was readily isomerized during the isolation procedure.

The R-form of compound 1 was synthesized by the condensation of p-coumaric acid and (−)-(R)-2 (about 40% ee, [α]D20 = −13.1 (c 1.05, H2O)) in the presence of N,N′-dicyclohexylcarbodiimide. Optically active (−)-(R)-2 was obtained from the racemic mixture by the fractional crystallization as described by Kappe et al.7 Obtained 1 showed a positive optical rotation ([α]D20 + 17.4 (c 1.0, H2O)), and the ee value of the (+)-isomer was about 40% on the basis of an HPLC analysis with a chiral column (Shiseido Ceramospher Chiral RU-1 (4.6 × 250 mm)), using a mobile phase of methanol (0.2 ml/min) and detecting at UV 310 nm.

Compound 1 produced in the potato tuber tissue was analyzed by HPLC with a chiral column under the same conditions as those just described. Under these conditions, racemic 1 could be separated to give two peaks at 24.9 and 26.6 min (Fig. 1-A), which were respectively assigned to those of (S)- and (R)-1 on the basis of the chromatographic behavior of the synthetic sample of (+)-(R)-1 (Fig. 1-B).

Compound 1 from potato was eluted as a single peak which was identified as (S)-1 (Fig. 1-C) by the method of co-chromatography (Fig. 1-D, E). It was thus concluded that 1 had been produced in the elicitor-treated potato tuber tissue in a stereoselective manner to give a configuration of S.

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Abbreviations: ee, enantiomeric excess; HPLC, high-performance liquid chromatography
Compound 1 in potato is proposed to be synthesized from p-coumaroyl CoA and octopamine by the catalytic action of an enzyme named hydroxycinnamoyl-CoA:tyramine N-(hydroxycinnamoyl)transferase (THT). Octopamine (2-hydroxy-2-(4-hydroxyphenyl)ethylamine, 2) is well known as a neuroactive substance in invertebrates and mammals, functioning in some cases as the transmitter in nerve systems. It has been shown that 2 is formed in invertebrates by a pathway involving tyrosine and tyramine, and that the (-)-isomer with the absolute configuration of R is responsible for the neuroactivity. Octopamine has been found in such species of plants as Coryphantha macromeiris var. runyonii, Capiscum frutescens, Citrus spp., Cypres rotundus, and Cypers papyrus. However, neither the biosynthetic pathway nor the absolute structure is clear for octopamine in plants. Moreover, although such structurally-related beta-hydroxysphenethylamines as macromerin, halostachine, synephrine, and norepinephrine have also been described as plant constituents, it has been shown that these four amines have the absolute configuration of R and no S isomer has so far been reported. These findings are in contrast to the case of 1 in potato, the octopamine moiety of which has the S configuration. From this point of view, the biosynthesis of 1 in potato is of interest, and work is now in progress to achieve this.

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References