CHEMISTRY LETTERS, pp. 771-772, 1986.

OXYSOLAVETIVONE. A NEW BIOSYNTHETIC PRECURSOR OF LUBIMIN IN POTATO[1)]

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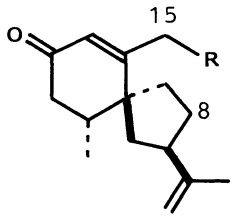
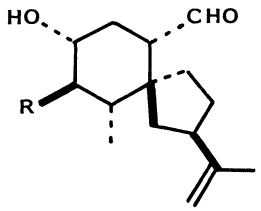
The title compound, isolated newly as a metabolite from solavetivone, was converted into lubimin in potato.

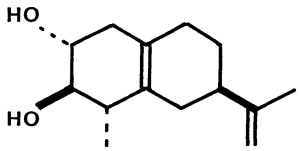
We[2)] recently demonstrated that solavetivone (1) is metabolized into lubimin (2), oxylubimin (3), and then rishitin (4), representative phytoalexins of the genus Solanum, in aged potato (Rishiri, Solanum tuberosum × S. demissum). In this pathway, the metabolic mode of 1 to 2 has not been clarified yet. A reduction in time on feeding of 1 in potato led to isolation of a new metabolite (5), designated as oxysolavetivone. We describe herein that the compound (5) is one of biosynthetic intermediates between 1 and 2 in potato.



1 R=H, 5 R=OH



2 R=H, 3 R=OH



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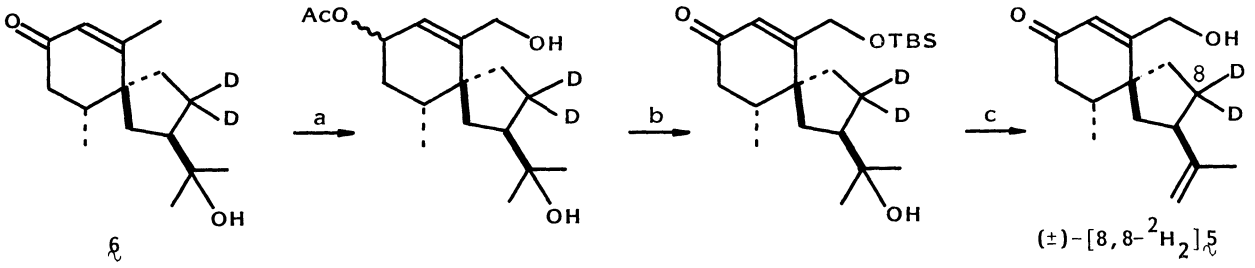
Thin slices of aged potato (Rishiri) were incubated with natural (-)-1 at 23 °C for 2 h and extracted with methanol-chloroform (1:1). The chloroform extracts were purified successively by column and preparative thin-layer chromatography, resulting in isolation of (+)-2 and a new compound (5) in 6 and 18% yields, respectively: 5, oil; $[\alpha]_D^{21}$ -91.6° (c 1.00, EtOH); EI-MS, m/z 234 (M^+) and 216; IR (film), 3420, 3080, 1660, 1650, and 880 cm^{-1}; ^1H NMR, δ ($CDCl_3$) 1.00 (3H, d, J=6 Hz), 1.72 (3H, s), 4.34 and 4.71 (each 2H, s), and 6.10 (1H, s). The structure of 5 was identified as 15-hydroxysolavetivone on the basis of these spectral data.

The deuterated solavetivone, (±)-[8,8-$^2H_2$]1[2,3)] ([$^2H_2$]-content, ca. 100%), was then incorporated into potato slices (Rishiri) at 23 °C for 2 h under the same conditions, giving (-)-[8,8-$^2H_2$]5 ([$^2H_2$]-content, 82.1%),[4)] $[\alpha]_D^{22}$ -5.9° (c 0.58, EtOH) in 17% yield. The result indicates that the compound (5) was metabolized from 1 in vivo.[5)] The corresponding racemic sample of [8,8-$^2H_2$]5 was prepared from the known spirovetivane[2,3)] (6) ([$^2H_2$]-content, ca. 100%) as depicted in Scheme 1 and showed spectra which differed markedly from those of natural 5 only



6 (±)-[8,8-$^2H_2$]5

a) $LiAlH_4$, ether, 0 °C, 30 min; Ac_2O, Py, 20 °C, 16 h; SeO_2, THF, reflux, 2 h, 79%: b) TBSCl, imidazole, DMF, 50 °C, 22 h; K_2CO_3, aq MeOH, 20 °C, 3 h; Jones oxid., 69%: c) Al_2O_3-Py, 215 °C, 5 min; aq HF, MeCN, 20 °C, 3 h, 18%.

Scheme 1. Preparation of (±)-[8,8-$^2H_2$]5.

in the following: EI-MS, m/z 236 (M^+, 100%) and 234 (M^+-2, 0%) ([$^2H_2$]-content, ca. 100%); IR ($CHCl_3$), 2190 and 2100 cm^{-1}. Incorporation of the synthetic (±)-[$^2H_2$]5 in potato slices (Rishiri) at 23 °C for 6 h afforded (+)-[8,8-$^2H_2$]2 ([$^2H_2$]-content, 97.6%), $[\alpha]_D^{25}$ +29° (c 0.13, EtOH) [natural-2,[6] +36°], and unreacted (+)-5 ([$^2H_2$]-content, 99.4%), $[\alpha]_D^{25}$ +27° (c 0.41, EtOH) in 7.3 and 24.1% yields, respectively. The result clearly indicates that only the natural form of 5 was transformed into 2 in vivo. In view of coexistence of various spirovetivane phytoalexins related structurally to 2 in diseased potato,[7] the role of the compound (5) would be significant as a biosynthetic key intermediate leading to their production.

References

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4) The deuterium content in the respective compounds was estimated from their EI-MS spectra.

5) Since the $[\alpha]_D$ value of metabolized 5 decreased intensely in comparison with that of cold sample, we examined the metabolism (23 °C, 6 h) of optically pure samples of natural (-)- and unnatural (+)-1[2] into 5 in potato. Incorporation of the former gave rise to 5, 2, and recovered 1 in 3.7, 24.9, and 14.5% yields, respectively, while that of the latter provided 5 and unreacted 1 in 7.9 and 20% yields, respectively, the compound (2) being not detected.

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(Received February 24, 1986)