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

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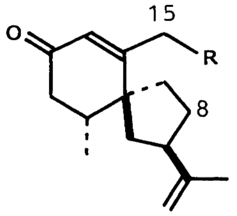
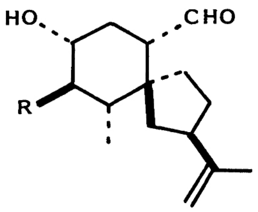
The title compound, isolated newly as a metabolite from solavetivone, was converted into lubimin in potato.

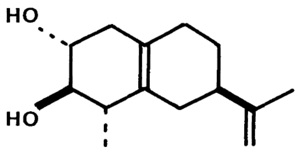
We[2] recently demonstrated that solavetivone (1) is metabolized into lubimin (2), oxylubimin (3), and then rishitin (4), representative phytoalexins of the genus Solanum, in aged potato (Rishiri, Solanum tuberosum × S. demissum). In this pathway, the metabolic mode of 1 to 2 has not been clarified yet. 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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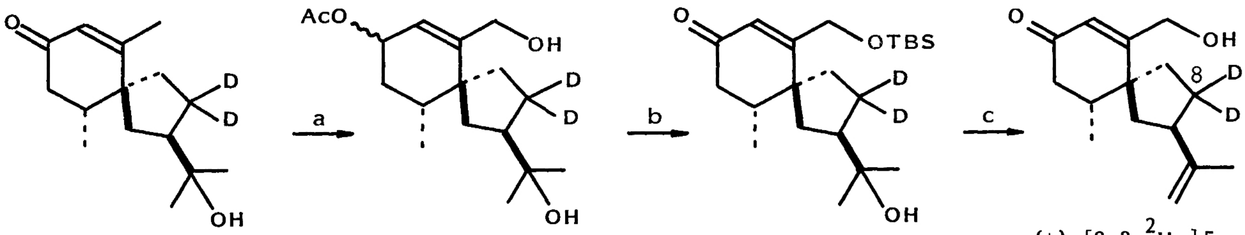
Thin slices of aged potato (Rishiri) were incubated with natural (-)-1 at 23 °C for 2 h and extracted with methanol-chloroform (1:1). The chloroform extracts were purified successively by column and preparative thin-layer chromatography, resulting in isolation of (+)-2 and a new compound (5) in 6 and 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



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(±)-$[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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2) A. Murai, S. Sato, A. Osada, N. Katsui, and T. Masamune, J. Chem. Soc., Chem. Commun., 1982, 32.

3) A. Murai, S. Sato, and T. Masamune, Bull. Chem. Soc. Jpn., 57, 2282 (1984).

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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