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# Aromatization of betanin promoted by trimethylsilyldiazomethane

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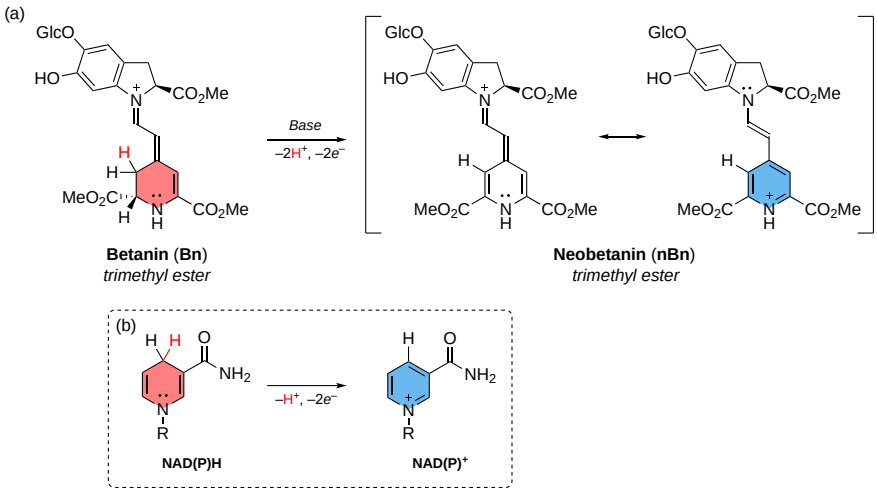
## ABSTRACT

Betanin (betanidin 5-*O*-glucoside, E162) is a natural pigment found in beetroots, used as a food dye.[1] In the late 1960s, Dreiding and coauthors used diazomethane to produce the methyl ester of betanin but obtained the methyl ester of neobetanin, its pyridinic analogue.[2] The oxidation mechanism was not further investigated, likely due to diazomethane's high toxicity and explosion hazards. We confirmed that oxidizing betanin with diazomethane produces di- and trimethylated neobetanin. We also show that trimethylsilyldiazomethane,[3] a safer methylating agent, esterifies and oxidizes betanin as effectively. Both methods indicate the $2H^+/2e^-$ oxidation and esterification by a color change from magenta to yellow. Purification via C18-reversed phase flash chromatography yielded a mixture of di- and tri-methylated neobetanin, up to 30%. The reaction likely proceeds with betanin methyl ester acting as a hydride shuttle, similar to biomolecules like NADH (Scheme 1).[4] This showcases a bio-based system for stabilizing betalain dyes as neobetalain derivatives.




**Scheme 1.** Oxidation of betanin and NAD(P)H. (a) For betanin, either $CH_2N_2$ or $Me_3SiCHN_2$ promote aromatization via $2H^+/2e^-$-oxidation. (b) Oxidation of nicotinamide adenine dinucleotide (phosphate) [NAD(P)]. In this case, $H^+/2e^-$ are usually abstracted as hydride by nicotinamide-dependent enzymes.

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